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WATER MANAGEMENT & TREATMENT

FOR

MINING & METALLURGICAL OPERATIONS

1 JUNE 1985

RANDOL INTERNATIONAL LTD.

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.).....	Milligrams per liter.....	17.12
Milligrams per liter.....	Grains per gallon (U.S.).....	0.05841
Milligrams per liter.....	Tons per acre-foot.....	.001360
Tons per acre.....	Metric tons per hectare.....	2.217
Grams.....	Ounces (avoirdupois).....	.03527
Ounces (avoirdupois).....	Grams.....	28.35
Gallons (Imperial).....	Gallons (U.S.).....	1.2009
Acre-feet.....	Gallons.....	325,851
Acre-feet.....	Cubic feet.....	43,560
Cubic feet.....	Cubic meters.....	.028317
Cubic feet.....	Gallons.....	7.481
Cubic meters.....	U.S. Gallons.....	264.2
Cubic meters.....	Imp. Gallons.....	220.0
1,000 m^3/d.....	I gpm.....	152.8
1,000 m^3/d.....	U.S. gpm.....	183.6
U.S. gallon.....	Cubic meter.....	0.3785

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INTRODUCTION

This investigation has been both frustrating and rewarding. Rewarding because of new insights into some of the many creative possible approaches to water management and their implications for metallurgical operations. Water quality has an impact on metallurgical processes. Some water treatment processes may be integrated into the mine-mill system as metallurgical tools.

The frustrating part has been the often poor quality of available information and understanding of many aspects which are clearly important in optimized mining and metal recovery operations. Another frustrating aspect has been the unwillingness or inability of several companies to cooperate by providing information of interest for this survey. Industry support of this investigation has been disappointing and it has had to be subsidized by RANDOL INTERNATIONAL LTD. to the tune of around $100,000. Sponsors of this study include companies that seem to be the most knowledgable about water management and treatment, and one has to assume that many of the rest do not yet appreciate its significance.

This report is disappointing in that it has not found all the answers that it set out to find. It nonetheless documents the results of two years' intense effort which is more than was promised and should, therefore, be a useful frame of reference or departure point for further work.

It is certainly true that the mining industry, especially in North America, is going through a tough time economically. In fact, in the U.S.A. today, it must be recognized that the industry is still in a depression with retrenchments and mine closures being a common occurrence. It is therefore perhaps not surprising that some mining companies would not now welcome information on new or improved technologies for water treatment or even new water management practices. The installation of new water treatment facilities, however good they may be, means spending money, and right now the mining industry needs to conserve all the cash it can in its effort to stay afloat. Even changing a plant around to implement a new or changed water management plan requires an investment.

Then, there is the struggle with some regulatory agencies who sometimes make seemingly unreasonable demands for expensive water treatment technologies which may put a value on a trout's life at thousands of dollars. The way the regulatory framework in the U.S.A. has developed in this respect is currently counterproductive as will be shown in this report. A point has been reached that when a U.S. mining company does develop an innovative new water treatment process, it is likely to instinctively hide it away so that regulatory agencies do not hear of it. The fear is that if regulators find an improved technology, then they will force all mining and milling operations to use it too. On the other hand, if a U.S. mining company installs a new water treatment process and it fails

to meet the expected performance, then the company will, more likely than not, try to downplay its failure. Even if the regulatory authorities are accommodating, there is always the risk that some private environmental group may learn of the failure. As entitled by present U.S. law, they may demand information from the regulators' files and may also file suit for damages where they find that permit requirements have or are not being met. Consequently, mining companies do not freely admit that a promising process or item of equipment installed to treat water fails to work in their particular conditions. As a result, there is a danger that myths about supposedly effective technology could be perpetuated. Senior management of mining companies seem reluctant to devote adequate funds for R&D to provide technology needed to meet emerging requirements of industry. Mining is a cyclical industry and when it revives the needed technology, may not be ready to meet the emerging regulatory needs which will be stricter than before.

Sponsors are reminded that this report is strictly confidential--particularly information about mining and milling operations which, in most cases, was generously provided by the companies described. Not all the information reported here has been verified, however.

THE NEED FOR INFORMATION ON WATER MANAGEMENT/TREATMENT

There are several compelling reasons for mining companies to become more knowledgable about water management and water treatment technologies. The need depends greatly on geographic location and climate and could be one or more of the following:

- Scarcity of water for a mine or mill may at least partly be overcome by selecting a water-efficient process and creative water recycling and management. Alternative sources of water may be made usable for metallurgical purposes.

- Operations may generate excess water due to a wet climate or mine dewatering. Before discharge of excess water as an effluent, it may have to be treated to comply with regulations.

- Creative water management may make it possible to reduce the amount of effluent that needs treatment before it can be discharged, e.g., through cascaded use and reduction in fresh water intake.

- Knowledge of the impact of water quality on metallurgical process efficiency makes it possible to judge when process water should be treated and when alternative metallurgical processes should rather be selected.

- Even operations that were shut down years ago remain the responsibility of the original operators and owners, and it may be necessary to find cost-effective

remedial steps to restore the area affected and treat drainage water for discharge to receiving waters.

- Acid mine drainage is the most serious environmental problem of mining and milling. There still is no solution to this problem which avoids the need for "perpetual" maintenance of tailings and wasterock disposal sites or the need for water treatment plants to treat AMD from these sites for the next 300-500 years or more. Industry needs more information, firstly to become aware of the problem, secondly to understand its fundamentals, and, finally, as an aid in the search for site specific answers to the problem that are more attractive than the present approaches.

Even though there may appear to have been a "lull" in U.S. regulatory involvement in mine waste and mill tailings disposal at the federal level in the U.S.A., due to the temporary suspension of RCRA (hazardous waste disposal) regulations applicable to the mining and milling industry under the Beville Amendment, the operative word is temporary. The U.S. EPA is regrouping its efforts and reformulating legislation to deal with mining and milling wastes, and protection of surface and groundwater quality is high on their priority list.

At state levels meanwhile, permits are no longer granted or renewed unless the impact of a mine, mill, and all ancillary support facilities on the environment is fully understood in advance and minimized. Since water quality is the most important environmental impact of mining, permit grantors focus attention on the possibility of damage to surface and groundwater and how this will be avoided.

Focus on groundwater protection in mine/mill permitting is relatively new but has already become well entrenched in the trend-setting state of California and others such as Washington, South Dakota, and Wyoming. It is clear that recognition of the need to preserve ground and surface water quality and, hence, the need to protect usable groundwater resources from damage due to seepage from mine/mill wastes is spreading throughout the U.S.A. and to all the major mining centers of the world. Recent amendments to the Water Act in South Africa have been put forward by the Dept. of the Environment (formerly called the Dept. of Water Affairs) which include severe penalties, forfeiture of profits, and liability for damage claims where industrial activities cause damage to surface waters or groundwater beneath these operations. If enforced literally, these new amendments will have a major impact on both existing and future mining operations in South Africa. Brazil and Papua New Guinea are examples of third world countries where regulations are modelled on the U.S.A.

The new consciousness of the potential impact of mining and milling waste on groundwater will have a major impact on how mining wastes and effluents are disposed of. This has already created a growing demand for knowhow and technology for impermeable linings of impoundments for tailings and effluents and, in some cases, also for wasterock piles.

First examples may have erred on the safe side and have possibly been designed to be more expensive than they really need to be. Here is one example where a growing experience factor will make it possible to save on capital costs and still present a margin of safety. Experienced geotechnicians may be able to find a tailings site where natural base materials are such that the need for an impermeable lining can be avoided even within today's permitting framework.

Fortunately, the fact that tailings are to be deposited in a tailings impoundment or an effluent impounded or evaporated does not automatically mean that groundwater will be contaminated or that contamination per se is undesirable. Perhaps the aquifer already contains such poor quality water as to render it unusable in the first place. In such a case, there is little reason to protect it from further contamination. Second, many sites can be shown to be impermeable enough naturally to prevent seepage during the life of a mine and mill. Finally, even where the strata beneath the site are shown not to be impermeable, there are many sites where the natural geochemical nature of these materials is such that they will attenuate contaminants contained in the water that seeps through these layers and, in effect, the natural capacity of the subsurface materials may be adequate to remove all contaminants of concern during the life of the mine and mill thereby avoiding groundwater contamination. With respect to surface water contamination due to runoff, very often diversion ditches can be constructed to reduce the catchment area and, hence, the volume of impacted water. In order to obtain the maximum from the natural advantages of such features, the services of geotechnical engineers, geochemists, and hydrologists with special knowledge of these areas of expertise can be called upon. This is still clearly a developing science, but there have already been several notable successes. This report attempts to identify useful sources of expertise in these areas which form an important part of water management.

There are also significant indirect consequences of the new rules governing groundwater protection. For example, if in order to protect groundwater quality the tailings pond and recycle process water impoundments have to be lined, the water balance of an operation can be significantly altered. More importantly, perhaps, the salt balance of the operation will also be changed with a build-up of dissolved species in solution. Previously, where tailings ponds and impoundments did not need to be lined, very often these offered an effective and convenient bleed of both excess water and contaminants.

Buildup in concentrations of salts in recycled process water due to reagent additions or reactions with the ore itself may reach higher levels now which can have a significant effect on metallurgical recoveries. Industry has limited experience at quantifying this possible problem. To illustrate this point, consider for a moment two uranium mills, both recovering uranium by ion exchange after a sulfuric acid leach and solid/liquid separation. At Rössing Uranium Ltd., described in Appendix I of this report, tailings dam water is recycled as a water conservation measure. Seepage from the rather permeable tailings pond is collected by a series of cutoff trenches around the toe of the

large unlined impoundment and recycled to the process. The quality of this seepage water is significantly better than the tailings pond decant solution as a result of contact with the calcerous substrata which removes many of the undesirable contaminants. Rössing is unquestionably the most water efficient uranium recovery operation in the world and can operate on a zero discharge basis except for a minor seepage loss.

Dawn Mining, Washington, on the other hand, is located in an area with net precipitation. When its tailings dam was lined in 1982, a convenient water and salt bleed from the system was lost. The result was that tailings decant solution had to be used as process water and, during recycle, the TDS increased to the extent that uranium loadings on the ion exchange resins were depressed. Were it not for the timely decision to suspend operations due to poor uranium prices, a way of treating the recycled water would have to have been found if the emerging metallurgical problem was to be solved. This could have been addressed by various water treatment measures, possibly aided by changing the brand of ion exchange resin to select one that was less prone to silica fouling and more selective for uranium. In both cases, the increased use of recycled solutions resulted in the need for measures to overcome the greater corrosivity of recycled solutions.

Rössing Uranium in the Namib Desert and Dawn Mines in Washington state are but two examples of many that illustrate the significance of water management, water quality, and the impact on metallurgical recovery processes.

Despite the difficulties that now prevail in meeting new emerging regulations, new mines and mills are being developed in even the most strict of these locations--e.g., the McLaughlin project of Homestake Mining Company. Much can be learned from these new operations. Now it remains to find environment- and permit-compatible ways of achieving the same but at a more affordable cost.

Throughout this report, the reader should bear in mind the generally easier task as far as water management is concerned of operators in dry net evaporation climates as compared with those in wet net precipitation climates--that is, provided the operator in the dry climate has enough water to meet his needs.

OBJECTIVES OF THIS REPORT

The objectives of this report are to provide an insight into the present and future needs of the mining and metallurgical industry for water management and water treatment technology. The aim is to focus on what can be done rather than what cannot be done, and to lead sponsors to new technology possibilities, i.e., what may become possible with additional development work. The objectives of this report are:

1. To identify and describe useful technology and equipment for effective and economical water treatment--i.e., the state of the art.

2. To identify and describe new water treatment technology frontiers which, after additional development, may be engineered into useful and cost-effective water treatment processes.

3. To investigate and review the philosophy of water management and water treatment technology applications, and to demonstrate how a "systems approach" encompassing the mine, mill, wasterock dumps, tailings, and effluent impoundments may make it possible to achieve better metallurgical results while offering greater environmental protection at a lower overall cost. Such a "systems" approach may even include sewage sludges, treated sewage effluent, and municipal garbage.

4. To find examples of water management successes, failures, and pitfalls in mine-mill environments which provide a useful insight to industry.

5. To identify sources of expertise that can be called upon for help, both from within and outside the mining industry.

THE SYSTEMS APPROACH

Metallurgical plant design should take into account water quality and availability at the mine(s), mill(s), tailings impoundments, wasterock pile, smelter, refinery, effluent treatment plant, concentrate and ore stockpiles, and ore storage areas, etc., all of which should be regarded as one integrated system from a water treatment standpoint.

Gone are the days when miners were responsible only for mining, metallurgical engineers strictly for milling and refining, and environmental engineers for tailings management, water quality monitoring and treatment, if necessary. That kind of company is an endangered species today.

Metallurgical engineers can no longer escape the need for an intimate knowledge of water management and water treatment technology, applicability, and costs in order to select the best overall combination of metallurgical process and water management/treatment for a given situation. Environmental engineers must, on the other hand, learn enough about mineral processing to be able to suggest alternative approaches as well. The difficulty is that this requires multidisciplined experience which is only just starting to come back into style.

There are many examples of where a systems approach makes a major difference to overall cost. Several of these are discussed in the report. For example, the question of

selecting the best flotation arrangement for treatment of complex base metal (Cu, Pb, Zn) sulfides. Effluent discharge restrictions and contaminant limits mean that water should be recycled as much as possible to meet permit requirements as well as to avoid the need to treat more effluent than necessary. Historically, an often used metallurgical recovery approach was to float a Cu-Pb bulk concentrate. This was followed by addition to the bulk Cu-Pb concentrate of sodium dichromate (Cr^{VI}) to depress galena followed by selective flotation of a copper concentrate. Other reagents (e.g., CN^-) were added to depress pyrite, marcasite, and pyrrhotite in the process arrangement.

With the more recent need to recycle water, great care must be taken to seggregate process waters containing dichromate because if this reagent were to find its way with the main process recycle water to the point end of the process, lead recovery in the bulk float would be reduced due to premature depression of galena.

Another example is the question of thiosulfate generation in operations where active sulfide-containing ores are milled at a high pH. Also, thiosalts and thiosulfates are generated when SO_2 is used as a conditioner which is a common practice. Thiosalts can, at times, reach levels that, when discharged in effluents, subsequent natural oxidation results in pH reduction of the receiving waters to levels that are well below permitted limits. A variety of processes have been investigated for thiosalt oxidaton from effluents but with limited success. Possibly, the thiosalt effluent problem will be resolved by achieving almost 100% water recycle and by limiting thiosalt generation in the first place by avoiding or reducing SO_2 addition. Finding the best overall answer to the thiosalt effluent problem requires a <u>systems approach</u>.

An example, albeit an extreme case, was found where water to a mill was provided by the services department which reported to the mining division. Lake water of good quality was treated by lime-soda softening followed by ion exchange to make it suitable as boiler feed. Many years after the mine-mill complex started up, an expansion of the mill was contemplated at which point it was discovered that all process water delivered to the mill was also being treated through the softening/ion exchange plant--a significant unnecessary expense because a systems approach had not been adopted.

In gold and silver recovery operations, if an effluent has to be discharged, it will likely need treatment in North America for metals and cyanide removal if regulations are to be complied with. It costs a lot more to remove a pound of cyanide from solution than it costs to add it in the first place--several times as much, in fact, in most cases. Where "refractory" gold is recovered in a sulfide flotation concentrate, which is roasted and the calcine leached in cyanide, it is possible to reduce the volume of water requiring treatment dramatically by segregating the cyanided calcine leach tails and cyanide containing water from the main flotation tailings and effluent. If the cyanided tails and the main flotation tails are combined, the volume of effluent requiring treatment before discharge as an effluent will be greatly increased. Another advantage of the systems

approach in this case is that calcine leach tailings can be stockpiled for future reprocessing. Also, most gold plant effluents and tailings contain residual values that are worth recovering as an incremental resource. If a "systems approach" is adopted, the metallurgical pros and cons of installing the recovery system before or after cyanide removal are taken into account as well as the merits of treating recycle solutions from the tailings plant for gold recovery before recycling solution to the plant. Normally, recycled gold tailings decant solutions contain valuable residual cyanide and lime values, but in one interesting case, cyanide is removed from recycle solution prior to its return to the plant in order to improve gold recovery.

One operation treats their combined minewater and mill tailings decant and seepage water flow. Another, not far away, uses their metals-contaminated minewater as mill water. The high pH in the mill precipitates undesirable metals and neutralizes the acid thereby consuming some lime at a cost, but at a far lower cost, than the installation and operation of a special treatment facility.

These and many more examples of a "systems approach" are discussed in the report.

DEFINING THE PROBLEM

The mining and metallurgical industry faces many environment-related problems, especially but not only in the U.S.A.

The U.S. regulatory and legal structure relating to environmental protection and permitting of operations is unwieldly and, in many cases, is impractical and counter-productive. It is almost as though the rules were written by lawyers for lawyers with litigation and proliferation of legal work in mind rather than to find suitable ways to protect the environment as well as the mining industry. In the opinion of this author, it will take a major revamping of the whole regulatory system and the regulations themselves to create a meaningful set of site and industry-specific environment protection rules for the mining and metallurgical industry in the U.S.A.

The present regulatory and permitting system as well as the CERCLA (Superfund) rules governing recourse for damage incurred in the past, even before the rules were enacted, is a contributory factor in the current demise of the U.S. exploration and mining industry. At this time, when the strong U.S. dollar discourages foreign investment in mining and exploration in the first place, and commodities are less expensive to import from abroad than to mine in the U.S.A., the additional unwieldy and often unreasonably restrictive permit and regulatory requirements are very discouraging and are part of the cause of the current depression in the U.S. mining industry.

Furthermore, as the federal government increasingly delegates the authority of regulating and policing environmental aspects and permitting of mines and mills to state and local authorities, the requirements vary dramatically from one part of the U.S.A. to another depending on how much local agencies "favor" or "disfavor" mining activities in their midst. The ease of permitting an operation and the time it takes to obtain a permit also tends to increase when the state and local officials have limited experience in dealing with this type of industry--as, for example, when permits were sought for a large new gold mine and mill in the state of Washington or when a major oil company sought to get a permit for a copper-lead-zinc mine and mill in Wisconsin. In these cases, a lengthy education process for the regulators is needed before they are knowledgable enough to be able to formulate regulations. Often, the first drafts of such permits are based on a biased image of the mining industry, and demands are made for the impossible.

This report examines the present regulatory climate and system in several parts of the world. It has not been possible to come up with a formula for instant success in all of them, but some interesting insights and suggestions have been possible.

This investigation has tried to step back and ask the question: What are the real major water-related problems that face the mining and mineral processing industry? Some of the problems as presently perceived seem to be a storm in a teacup. Yet, others do appear to be more serious than is presently realized and will present a major economic burden on much of the industry for centuries to come unless better ways of managing and disposing of tailings and effluents can be developed. This report provides a more global perspective as to where the real needs for new environmental technology lie and why. In this respect, acid mine drainage has been identified as a universal problem requiring more satisfactory technical solutions.

THE CHALLENGE

There are clearly unresolved environmental compatability aspects of mining that have an impact on water management practices and which are affected by water management. These need urgently to be addressed. There are five important challenges that need to be responded to at this time with respect to water management and treatment technology:

Challenge 1

Acid mine drainage is a real problem that needs a technical answer that will not be provided by more regulation or through litigation. Industry needs to find and tackle the root of the problem and not just the symptoms.

Challenge 2

Realistic and practical regulations are needed which protect the environment and water resources while allowing the mining industry to survive. These need to be formulated in a more circumspect way than before. This will require cooperation and perhaps leadership from the mining industry itself and much less involvement by lawyers, particularly those in and around Washington and state capitols who frequently know little about the environment and less about mining and technology for water treatment. All too often, delays in permitting result from inexperienced regulators who first have to become informed. Mining companies can help speed up the permitting process if they themselves are well enough informed to provide guidance that the regulatory agencies often need.

Challenge 3

Improved water management concepts and technology as well as more cost-effective water treatment and safe precipitate sludge disposal methods are needed. Adopting a "systems approach" would fall into this challenge. Another part of this challenge is to adapt technologies to make them compatible with the needs of the mining-metallurgical industry. Remember that though prevention is better than cure, effluents are the symptom, not the cause of the problem.

Challenge 4

This is a philosophical challenge in which the mining industry and regulatory authorities and bureaucracies need to come together to find and apply affordable and practical technologies. As knowhow evolves, there will be a further need for plant-scale experimentation and demonstration of emerging technology. This cannot be done if results must be guaranteed in advance as is required in the present permitting process (with a few notable exceptions). The change in philosophy must be toward cooperation in finding technological answers to practical problems rather than resorting to litigation, confrontation, and mistrust.

Challenge 5

Senior mining company management needs to stop regarding anyone genuinely interested in the environment as an "environmentalist" and, therefore, automatically suspect of being a threat to industry. It is suggested that part of the solution to the "environmentalist" problem is to nurture a breed of "informed environmentalists" who base their opinions on scientific facts and real data as a counter force to the kind that bases its actions on emotional notions or to serve bureaucratic power struggles.

THE OPPORTUNITY

Several opportunities are emerging in connection with water management and treatment at this time. First, the regulatory requirements for environmental protection in opening a new mine or mill are today so complex, particularly in the U.S.A., that fewer companies are equipped to entertain such projects in several parts of the country at the same time. This means that there will be investment opportunities abroad where environmental protection regulations are still more reasonable to fill the supply gap. Within the U.S.A., investment opportunities will be more attractive for those companies that are successful at developing cost-effective water management and treatment technologies.

The level of technology used for water treatment in the mining and metallurgical industry is currently rather basic and rudimentary. There are several opportunities to develop innovative improved water treatment technologies and water management knowhow that can save costs and yield better results. There are numerous R&D frontiers and opportunities to develop patentable, useful technology and devices which will become a profitable endeavor in years to come.

The regulatory framework with respect to mine and mill waste disposal has (in this author's opinion) evolved in the U.S.A. into a counter-productive system that serves neither the environment, the national economy, nor the mining industry. There must eventually be an opportunity for the mining industry to take the lead in formulating a new set of useful rules that serve everyone's interests. First, particularly in the U.S.A., what is needed is much less government.

THE SNAG

Only during the last decade have very powerful new instrumental analytical methods become available which make it possible to measure many contaminants to below 1 ppb. As a result, environmentalists, regulatory experts, and universities are now able to measure the environmental effects of contaminants at various levels down to sub ppb concentrations.

Based on these findings, water quality objectives are being set and effluent limits established.

The snag is that practical technology applicable to the mining and milling of ores in remote locations and often in difficult climates, has not kept pace with the rapidly evolving laboratory work mentioned above. Water treatment processes in use at this time reduce metal contaminants to more like ppm levels than ppb levels.

Based on the legislated need to apply "the best practicable technology" and "the best achievable technology, BAT," there is the distinct danger that every time a university professor announces an apparently improved technology based on laboratory scale tests, that this will be incorporated into BAT regulations as the prescribed effluent treatment process. In field conditions, or for solutions containing other spectra of contaminants, such processes may not be workable. Government needs to provide industry support to develop and test such technologies with participation by everyone involved and to nurture a team spirit. In this respect, an excellent example has been set in South Africa. Pilot testwork and field tests on a full scale to demonstrate new processes are very expensive. Companies must always bear in mind an alternative course of action that they can take if once their new mine/mill has started up, and the prescribed new water treatment process fails to perform in practice as it did in the pilot tests. This adds a new element of risk to mineral processing operations in the U.S.A. and elsewhere.

THE APPROACH

The approach taken in this investigation has been to visit about fifty mine-mill complexes and to describe their water management and water treatment challenges and innovations. These trip reports are documented in Appendix I. Based on these and the gathering of information through literature searches and discussions with numerous technology development organizations, suppliers, and mining companies, the status, needs, and technologies available to deal with water problems are reviewed.

An attempt has been made to find out and document for the reader of this report just what the current state of the art is, what needs for technology are emerging, and where he can go for help.

Other RANDOL multi-client reports have included a list of consultants and engineering contractors serving the industry under investigation. In this case, there are too many facets for such a composite list to be very useful. Consequently, expertise and engineers have been listed in each chapter in the context of their special expertise. Likewise, references are mentioned at the end of each chapter to keep them in context. The last chapter in this report lists what have been concluded to be the most important frontiers for further research and development in this pioneering area of technology.

GUIDING RULES

Three guiding rules have been followed:

1) This report concentrates on <u>what can be done</u> and on identifying technologies of potential value but which may need further development.

2) If a water treatment process is going to be useful in the mining and mineral processing industry work environment, it should be SIMPLE.

3) PREVENTION of water contamination is better than CURE.

WARNING

1. The water management and water treatment science is still at an early point on the learning curve--it is an immature science. Readers are warned that hearsay observations and comments were often the best or only source of information available, and much of it may be unreliable. Information in this report should be used as a guide subject to testing of sponsor's site-specific conditions.

2. This report and its contents are strictly confidential and should not be reproduced or distributed in any way. If serious errors or misinterpretations are identified, these can be rectified by distributing corrections and errata to sponsors.

CHAPTER 1

INFLUENCE OF MINING AND MINERAL PROCESSING ON WATER QUALITY AND THE ENVIRONMENT

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INTRODUCTION

There is no question that unless protective measures are adopted, mining and mineral processing operations will nearly always have an impact on water quality and the environment.

The Kam Kotia abandoned mine and tailings site near Timmins, Ontario, is one example of the type of environmental damage that is caused by a mining operation when an abandoned mine-mill site gets out of control. In this case, the abandoned acidic tailings dam has ruptured, and all vegetation in its path denuded for several miles; tailings have been distributed for miles resulting in further distribution of windblown dust during dry spells. Also, a lake and many miles of river system have become non-viable to all except the coarsest of fish. In addition, the aesthetic impact on this otherwise pleasing landscape has been such that few would wish to see similar events repeated. Fortunately, few have witnessed this sight.

Another famous example is the condition of Whitewood Creek at Lead, South Dakota, before and after environmental controls were employed. Who can deny the remarkable transformation that Homestake Mining Co. and the Lead community have achieved. The creek today supports a trout fishery and, perhaps more importantly, is a pleasant place to be.

The influence of mining and mineral processing on water quality and the environment varies greatly from site to site, and also from one climatic region to another. Whether or not that influence constitutes damage or a nuisance also varies from location to location depending on the nature of the environment to begin with and a host of other factors. For example, a major distinction can be made between locations with a net evaporation and those with net precipitation.

It is beyond the scope of this investigation to probe whether the damage caused by mining and mineral processing is of a greater or a lesser magnitude than the damage to industry and to the national economy of the U.S.A. and, therefore, to the wellbeing of its citizens, of unconstructive, impractical rulemaking and regulation of the industry out of context with the environmental benefits gained. Those who claim that mining and mineral processing damage to the environment is negligible and does not require regulation are as unrealistic as those who believe that profit-motivated free enterprise is wrong, and that the North American mining industry should be inhibited or stopped altogether, if possible, through regulations and permit requirements.

Before discussing a host of new technologies in mining and tailings disposal which have a very positive effect on controlling water pollution and environmental damage from mining and milling operations, it is proper to ask what the nature of the type of damage that can be done by the mining and mineral processing industry to water resources and to the

environment are. An answer to this question is necessary if we are to objectively review what remedial measures are needed. Society as a whole must work toward supporting those protective measures that make real sense while those that serve only the perpetuations of the bureaucracies that create regulations must eventually be abandoned. The difficult part is to have adequate knowledge and data available to be able to distinguish wisely between the two.

An important source of data on the nature of mine and mill wastes and their impact on water quality is the PEDCo (1983) study report which is a primary source of evidence on which the U.S. Congress will formulate federal regulations under the RCCRA laws. PEDCo Environmental, Inc. was commissioned by the EPA to sample a wide variety of tailings, waste rock, sediments in ponds, minewater, mill processing solutions, etc. at several operations in each of the main mining and mineral processing regions of the U.S.A. Leach tests using water and the EP leach test were performed on solid materials and groundwater samples taken.

PEDCO ENVIRONMENTAL, INC.
11499 Chester Road
Cincinnati, OH 45246

Although there are obvious flaws in the PEDCo report, particularly with respect to sampling of groundwater, it is remarkable, in reviewing this data, how little impact the tested cases have had on surface and groundwater quality in their vicinity. The PEDCo study did find several cases where water quality was impacted, but nothing which could not be sorted out through the use of more efficient impoundments. One of the important conclusions that can be drawn from a review of the PEDCo data is that water quality impact by mine and mill waste is very site specific and, even within one branch of the industry, e.g., copper mining, the impact will vary from case to case. Also, natural processes are both useful and powerful in mitigating some of the environmental and water quality impacts of mining. The PEDCo study sampled operating mines.

A second useful source of information are the reviews by such organizations as the U.S. EPA and ONTARIO (1979) which document the rationale for their selection of ambient water quality objectives.

WAYS IN WHICH MINING CAN EFFECT THE ENVIRONMENT

Mining and mineral processing can affect the environment in the following ways:

1) Acid Mine Drainage (Including Non-Acid Mine Drainage)
2) Reagents Used in Mining and Mineral Processing
3) Metallurgical Process Solution Effluents
4) Organics, e.g., Lubricating Oil, Diesel, Grease, Hydraulic Fluids

5) Suspended Solids
6) Temperature
7) Alteration of the Water Table and Local Hydrology

ACID MINE DRAINAGE

Acid mine drainage (AMD) is generated from both open pit and underground mines, wasterock, and tailings where water and air come into contact with sulfide minerals. Acid mine drainage is a universal problem in mining and metallurgical operations and in the estimation of RANDOL INTERNATIONAL LTD., is the most significant cause of water quality and environmental damage. One of the most alarming aspects of AMD is that it will continue to be generated for centuries after the mine-mill operation that generated the tailings has been closed unless site specific better ways of disposing of sulfide-bearing wastes are found.

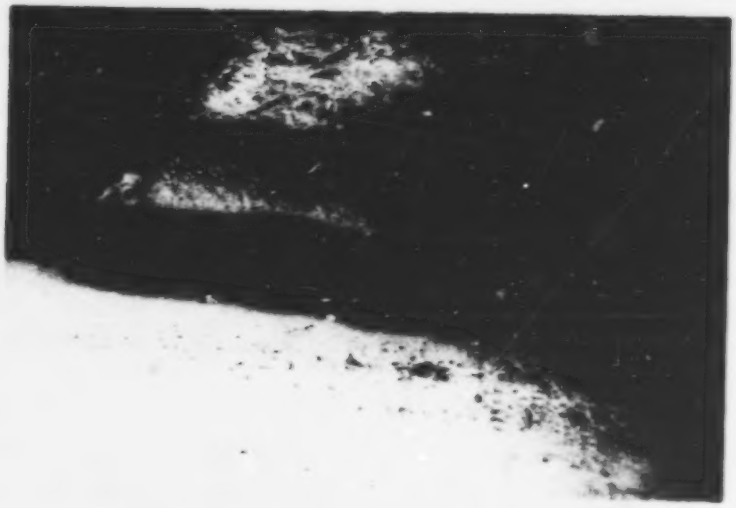
Acid mine drainage occurs in the coal mining industry, uranium mining and milling (e.g., the Witwatersrand and Elliott Lake), gold and silver recovery, the mining and milling of complex and massive sulfide minerals, e.g., copper, lead, and zinc mines on the Canadian Shield, and elsewhere where ores can contain up to 60-75% iron sulfides. Originally, AMD was believed to be a phenomenon associated with only coal mining, but this has turned out to be far from true.

AMD may not be immediately obvious when an operation starts up as it takes up to several years for the accumulating wastes to oxidize before runoff and seepage become noticably acid. Once it becomes acid, the generation of more acid mine drainage seems to accelerate.

AMD is much more of a problem in those parts of the world with a net precipitation, i.e., a wet climate or one with a heavy snowfall. In arid regions where water is scarce, contaminated water can be segregated and evaporated, and tailings disposal methods which encapsulate acid generating species may be developed more easily than in wetter climates. In some such arid environments, for example the Grants Uranium District, there is an excess of minewater that must be pumped from underground, and this water must be treated to remove radium before it is discharged to a "creek" from which it seeps back into the mineworkings.

Where there is a net precipitation, AMD water accumulates in impoundments until a point is reached where it has to be released. In order to treat AMD, usually a lime neutralization and settling plant is needed at the site of such tailings and wasterock piles in perpetuity, which has been calculated to mean for the next 300-500 years. AMD introduces sulfate and hydrogen ions to water that comes into contact with these materials. Heavy metal ions can also dissolve in the AMD which then may become an

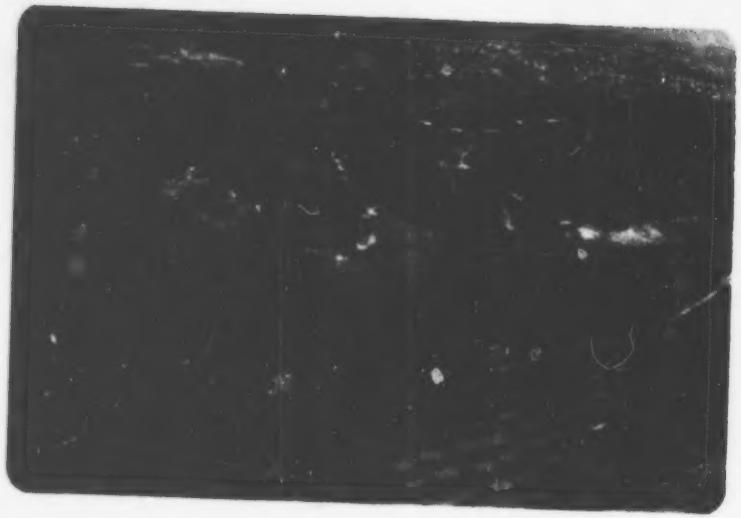
MASSIVE SULFIDE IN ROAD CUT - NATURAL ACID GENERATOR



ACID MINE DRAINAGE FROM TAILINGS

SULFIDIC WASTEROCK ALONGSIDE A CANADIAN LAKE

ACID MINE DRAINAGE GENERATION. TAILINGS AND WASTEROCK INVARIABLY CLOSE TO WATER. NOTE NATURAL MARSH VEGETATION IN LOWER TWO PICTURES.

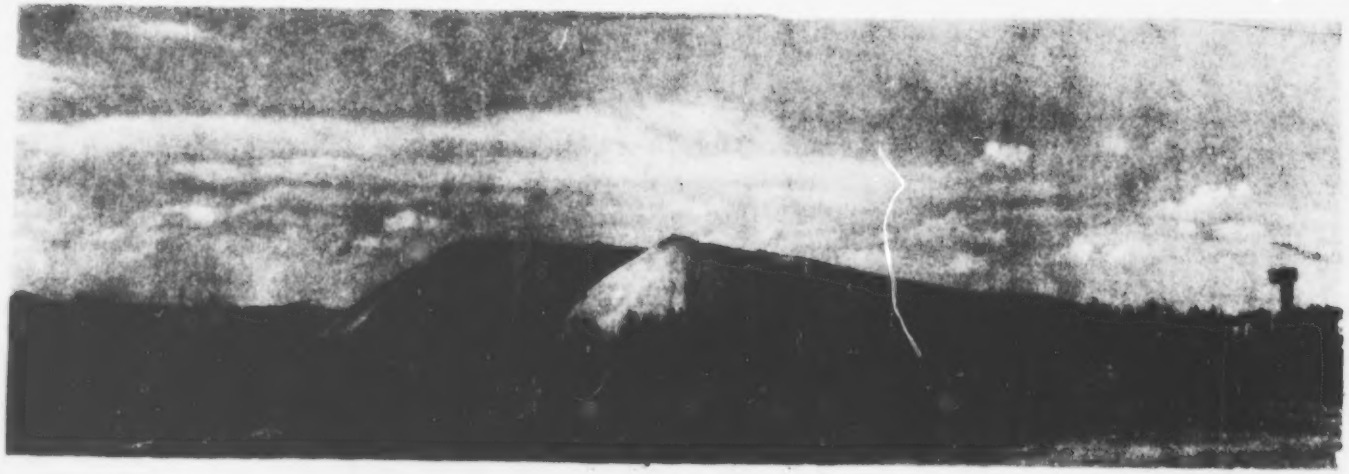


TAILINGS PILES ON THE WITWATERSRAND

Note: 1) Proximity to built up areas.

2) Marsh vegetation adjacent to tailings in all cases despite drought conditions.

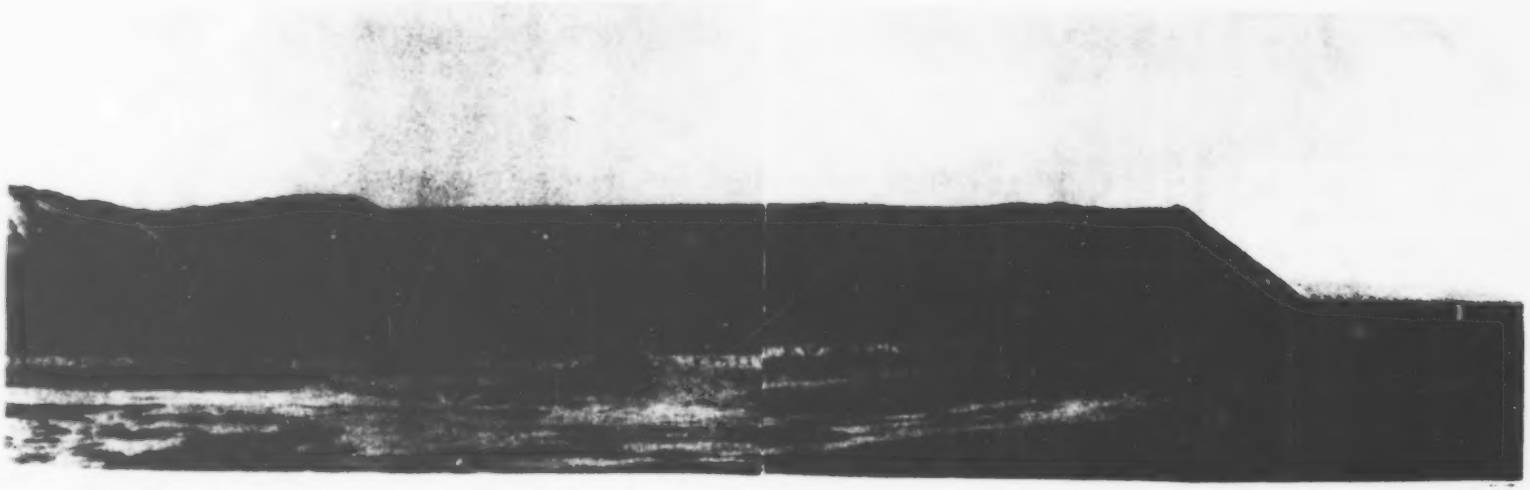
3) Impoundments to catch runoff in some cases have filled with sediment.



WASTEROCK PILE AT WESTERN WITWATERSRAND GOLD-URANIUM MINE

ACID MINE DRAINAGE: WITWATERSRAND SAND TAILINGS PILE

Note: Successful revegetation and marsh environment in foreground.



COAL SPOIL BANK IN THE TRANSVAAL

Note: Pyrophoric nature and measures to control runoff or runon to site by impoundment berm in foreground.

SUPERFUND SITE AT PALMERTON, PENNSYLVANIA, ZINC REFINERY

Note location close to river and vertical retort residues stacked at foot of hill. Also, various piles of waste and raw materials stored openly. Note encouraging revegetation attempts of the vertical retort residues and denuded vegetation on hillside behind.

environmental liability. Another AMD contaminant which can cause severe damage to aquatic ecologies is ammonia which finds its way into minewater through the use of underground explosives and which is very costly to remove or oxidize in large AMD flows. Even if acid mine drainage is treated with lime to neutralize it, there will still be the introduction to the system of calcium sulfate ions and others which may or may not be a problem.

Sometimes the naive argument is raised that in nature, eventually ore deposits containing sulfides will be eroded into by natural forces which will result in their oxidation and the generation of acidic water which will discharge to the environment. This is certainly so, but the time frame over which a sulfide ore deposit will be oxidized in nature will be much longer than when it is mined, and large volumes of wasterock and mill tailings are exposed over a short period of time. This argument could, however, be realistically used in favor of the development of tailings disposal techniques which allow the controlled release of contaminants within the limits that can be tolerated by the receiving waters or the environment generally.

THE WITWATERSRAND - ACID MINE DRAINAGE

In some parts of the world, it is the pH reduction that is considered environmentally undesirable. In others, it is the acidity and also contained base metals such as copper, lead, zinc, etc. Elsewhere, particularly the Witwatersrand area of South Africa, acid mine drainage pumped from deep underground mines contributes high levels of total dissolved solids to the regional water supply in the Vaal Dam. Minewater containing typically 6,800 mg/l TDS before neutralization is neutralized using lime after which its pH is raised to around pH 6.8, and the TDS dropped to 5,000 mg/l. TDS in the point source discharge of minewater pumped from a few large mines contributes about 30% of all TDS from point sources in about 12% of the water volume that flows into the Vaal Dam.

In addition, an as yet unmeasured volume of diffuse source drainage from sand and slimes dumps also drains into the Vaal Dam. The lower level of TDS in this water has been measured at pH 3.1 and 6,200 mg/l TDS, while levels up to 51,000 mg/l tds at pH 2.4 have been reported by KEMPE (1983). BROWN (1981) estimated that the quantity of sand in the top nine-meter layer of just one of the 30 large sand dumps scattered around the Witwatersrand ammounted to 5,705,000 tons from which 57,676 tons of sulfur (at 1.01% sulfur) was available for AMD formation which would yield 176,333 tons of pure sulfuric acid on oxidation. Assuming that this acid was generated over 25 years, this dump was producing about 7,000 tons of pure sulfuric acid per year. KEMPE (1983) estimated that the 30 sand dumps on the Witwatersrand contain up to 26 million tons of sand each.

The sand and slimes dumps on the Witwatersrand cover a total area of about 80 square kilometers. Mines established after about 1918 adopted the all sliming cyanidation method

of gold extraction. This resulted in the elimination of sand dumps and their associated serious water pollution problems. However, sand treatment on established mines continued for many years, and the last one was phased out in the sixties.

Slimes dams, because of the finer division of the tailings contained in them, are very much less porous than sand dumps. Consequently, seepage is also much less. Leaching of pyrite, according to KEMPE (1983) does not appear to penetrate to depths in excess of about 3 meters. Runoff water on top of slimes dams becomes considerable, but it is relatively simple to control and retain it for evaporation. Unfortunately, there was little control of this surface runoff water in earlier days, and it caused serious erosion of slimes dams. On modern operating slimes dams, excess water is drawn off through penstocks and returned for reuse. Trenches are provided to drain any seepage to the penstock pumps.

On the central Witwatersrand area, there today remain three large mines and three smaller concerns. In addition, there are about seven companies that exploit residual gold in surface dumps and slimes dumps. In order to allow underground operations to continue, it is necessary to maintain underground water in the whole Witwatersrand below a critical level. This is achieved by pumping water from the three larger operating mines, Durban Roodepoort Deep, East Rand Proprietary Mines (ERPM), and Grootvlei, the latter pumped via South African Land and Exploration Mine (Sallies) on which the huge East Rand gold and uranium dump reclamation project (ERGO) is situated. All water underground drains to these four points.

Water pumped during the year preceeding August, 1979, contributed 30% of the total 272,000 ton salt load from point sources reaching the Vaal Barrage according to the Water Research Commission (1979). KEMPE (1983) suggested that seepage from the sand dumps and slimes dams no doubt contributes significantly to the 47 percent of the non-point loading and is probably largely responsible for the surge in salt loads experienced at the onset of the rainly season when there appears to be a "flushing out" of salts accumulated during the dry winter months.

According to KEMPE (1983), ERGO's intake water in 1978/79 ammounted to 21.4 million m^3 per annum with a salt load of 38,200 tons which is mostly derived from the Sallies supply of 60% of total and has a TDS content of about 2,000 mg/l. Effluents discharged by ERGO had a salt load of 33,500 tons of TDS to the Barrage in 8.6 million m^3, i.e., a TDS content of 3,895 mg/l which alone constituted 12% of the total salt generation to the Vaal Dam. As described in Appendix I, ERGO is, of course, working on every possible way to reduce this.

The mines referred to by KEMPE (1983) include only the small number of the remaining mines between Roodepoort and Springs, constituting the central and eastern Witwatersrand. About 30-35 additional mines are located in other parts including the west

Rand stretching from Krugersdorp to Klerksdorp and the Orange Free State gold fields. These latter operations do not drain into the Vaal Dam directly although, with the proposed reversal of flow of the Vaal River downstream of the dam back into the dam, drainage from all the mines from Johannesburg to Klerksdorp would in the future possibly drain into the Vaal Dam.

In the area west of Johannesburg, the Witwatersrand ore sequence is overlain by a series of dolomitic sedimentary rock which is porous enough to host a major deep regional aquifer. Mine and mill operations are located on the surface on top of the dolomite formation as well as large slimes dams generated over several years. In recent times, the dolomitic aquifer has been proposed as a location for storage of usable municipal water which could be replenished during years of "plenty" and drawn from during years of drought. Due to the geology and climate of the area, there is a second principal aquifer over much of the area. This is a near-surface, sometimes non-perennial aquifer which is normally in hydraulic continuity with the surface water of the area when present.

The latter aquifer, developed due to the intense weathering of the surficial rocks of the Witwatersrand which were lain down over 2,000 million years ago, is highly permeable and relatively vulnerable to surface pollution. Slow leakage may or may not occur from this near-surface aquifer to the deeper, regional groundwater. The disposal of cyanide-bearing gold tailings can represent, according to SMITH, et al. (1984) a potential pollution threat to both quifer regimes by direct runoff, erosion of tailings, and seepage from the tailings impoundments themselves.

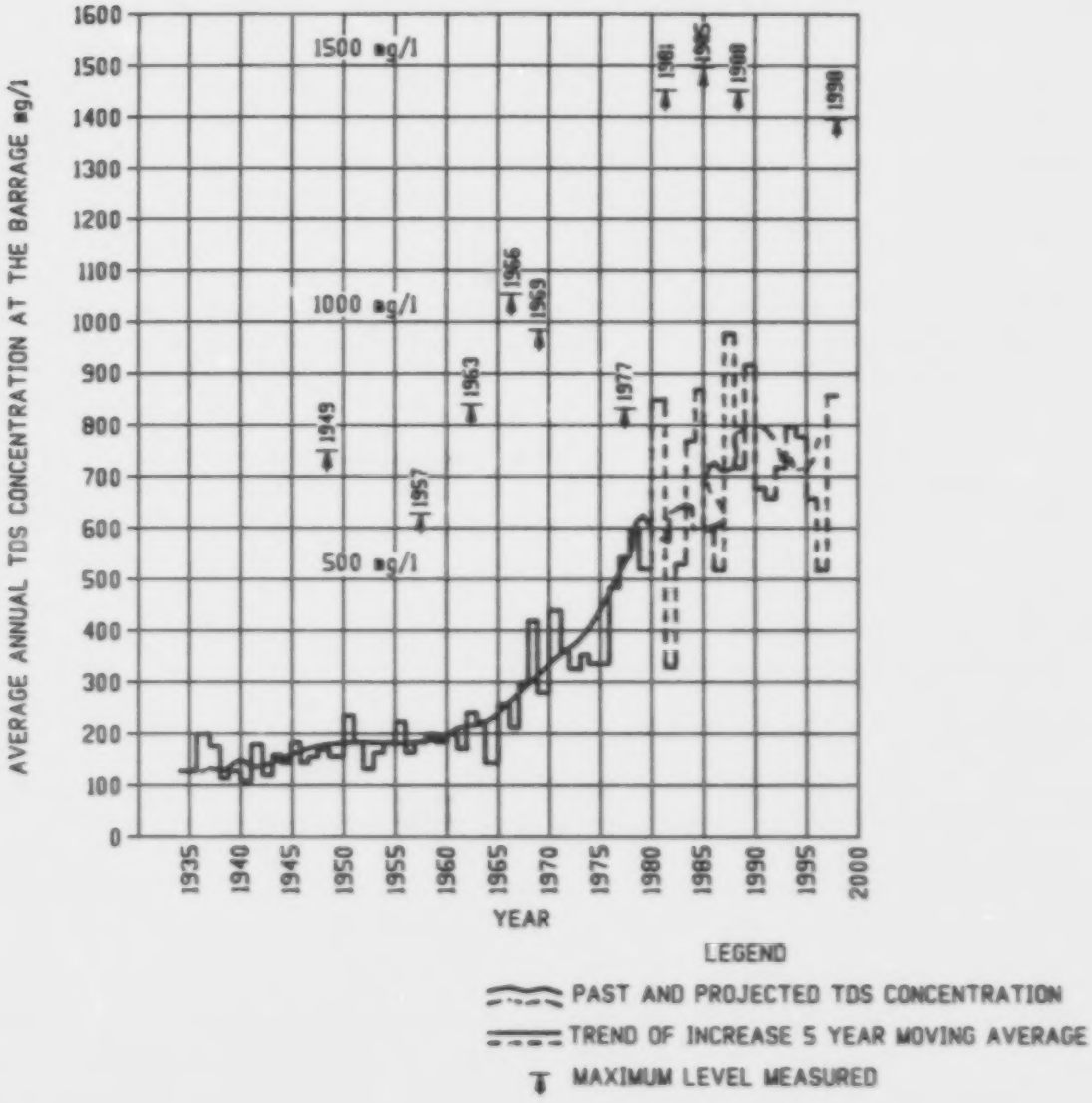
Certainly, where mineshafts and deep drillholes connect the surface with deep underground mineworkings in the area, there may be adequate hydraulic connection between the two aquifers to transport contaminants to the lower dolomitic aquifer.

SMITH, et al. (1984) also compare TDS and sulfate concentrations found in tailings interstitial waters with "background" groundwater levels from several tailings dams as follows:

	TDS	SO_4	Fe	Mn	pH
Dam 1, ±5 Years Old	712	317	0.1	15	6.8
Dam 2, Over 20 Years Old	500	400	34	69	2.9
Dam 3, ±20 Years Old	300	70	4	0.8	5.8
Dam 4, ±10 Years Old	500	-	-	-	7.5
"Background" Water Quality	250	50	0.1	0.1	7.8

Based on their preliminary data, it appears that acid mine drainage in seepage from slimes dams may be less than would be expected, especially where these dams are placed on the naturally occurring, low-permeability clay layer that occurs in much of the area. It has

INCREASING TREND OF TDS CONCENTRATION AT THE RAND WATER BOARD'S VEREENIGING INTAKE



suddenly become important to protect the quality of this aquifer and, for the first time, a real interest is being shown in the impact of mining, milling, and tailings dams in the area on the quality of these dolomitic aquifers.

Surveys are presently being undertaken on behalf of the Water Research Commission by a South African firm of geotechnical engineers to assess the impact of model slimes dams on seepage into this groundwater resource. The survey by Steffen Robertson and Kirsten has yet to be completed, and results have not yet been published. However, SMITH, et al. (1984) reviewed, in general, preliminary results of a survey of cyanide levels in groundwater below gold mill tailings dams including those located over the dolomites and commented on the apparent lack of contamination of the groundwater regime, even in close proximity to the impoundments. They suggested that there are several possible processes which may be responsible for the breakdown and/or fixation of cyanide removed from the aqueous system in the tailings and preventing groundwater contamination:

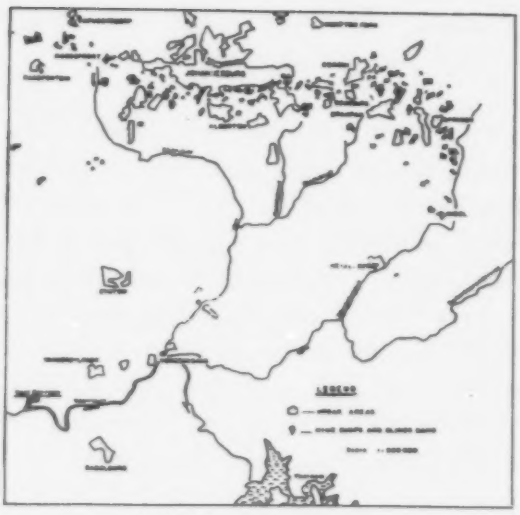
- The method of tailings disposal: the so-called "semi-dry" or "sub-aerial" disposal technique.

- Prevalent climatic conditions.

- The presence of oxidized iron in the tailings and in the highly weathered, semi-lateritic or lateritic near surface aquifer may remove cyanide from solution and serve to co-precipitate several other unwanted metal ions as well.

It is also possible that vertical transport of dissolved salts by capillary action to the surface of slimes dams may result in a perennial contamination of surface runoff water which may be more easily controlled and evaporated than seepage.

As much rainfall runoff as possible is caught in the catchment area of the Vaal Dam and soon, water draining into the Vaal River below the dam will also be used as the main regional water supply serving the growing metropolitan-industrial area around Johannesburg. Vaal Dam water is treated for the removal of impurities, i.e., suspended solids, iron, base metals, etc. These are all relatively easy to remove. The problem lies in the buildup of TDS, mainly of such species as $SO_4^{=}$ and Cl^- which are not removed in standard water treatment processes. Records since 1935 of the average TDS in water at the Vaal Barrage show a steady increase from around 150 mg/l in that year to around 800 mg/l today with peaks close to 1,500 mg/l. Clearly, the drainage system is being overloaded by the impact of industry and the large population. According to HENZON (1983), a recent estimate by the Water Research Commission concluded that the present TDS level in the water supply adds about $680 million annually in cost to society in terms of corrosion, extra detergent needs, and water purification needs. A total of 520,000 tons per year of dissolved solids enters the Vaal Dam from the catchment area of which over 75,000 tons per year came from just three minewater pumping stations.



Sand and slimes dams of the Witwatersrand

TABLE 6. Salt loads generated in Barrage Vaal Catchment: September 1978 to October 1979
(i.e. Difference between intake water and effluent loads)

Source	Flow Volume ($m^3 \times 10^6$)			Annual salt generation (Tons)	Per cent of total
	Intake	Discharge	Net generation		
E.R.P.M.	6,4	13,3	6,9	55 300	
Sallies (excluding supply to ERGO)	0,7	3,1	2,4	7 300	
D.R.D.	4,0	4,5	0,5	12 700	
Grootvlei	1,3	4,4	3,1	7 100	
Sub-Total Mine Pumpage	12,4	25,3	12,9	82 400	30
Sub-Total Six Municipalities	290,7	185,8	-	55 700	20
Sub-Total Industries and Statutory Bodies (includes ERGO) *	73,2	36,9	-	7 700	3
Non-Point Sources (calculated from modelled salt generation rates)				127 000	47
Total				272 800	100

* Details of salt generation by Industry and Local Authorities which includes ERGO, show ERGO to have a small negative quantity.

If it were not for the huge metropolitan center that has grown up around the Witwatersrand mines, the drainage discharge to the Vaal River would not be a problem as the Vaal would serve as a bleed to the ocean. It is only in the context of the whole integrated water system in which the TDS are recycled on macroscale that the salt addition, now seen as an incremental load, becomes critically important. New environmental regulations with respect to water seek to force the mining industry to bear the cost of treating this water.

ELLIOT LAKE URANIUM TAILINGS - ACID MINE DRAINAGE

The Elliot Lake uranium ores consist of quartz pebble conglomerates remarkably similar to the Witwatersrand ores. Elliot Lake ore contains 2-4% sulfide. These ores are typically ground to 50% minus 200 mesh (74 m) which is coarser than the Witwatersrand tailings which are comminuted to 80% minus 200 mesh. Just one of the Elliot Lake Mines, namely Denison Mines Ltd. at Quirke Lake, has already processed 25 million tons of ore, and a further 100 million tons will be mined. This mine-mill alone will yield 125 million tons of tailings containing 2.5-5.0 million tons of oxidizable sulfide. Regulatory limits control radium concentrations and the pH of the final effluent returned to Quirke Lake, but there are no limits on TDS or $SO_4^{=}$.

In this case, the readily oxidizable tailings are disposed of for the most part, above ground level starting off in depressions formed by local lakes and building up in height through the construction of dam walls to contain the slurry.

Acid mine drainage at Elliot Lake tailings impoundments are quite apparent. A steady bleed of sulfuric acid generated by the oxidation of 2-5 million tons of sulfur in these tailings over the next 100-200 years must go somewhere. Vertical migration of salts to the surface of the tailings is one way the dissolving salts are transported. Surface salts are then washed away annually with the spring runoff and dispersed.

The acid mine drainage problem is under intense study by several groups including one established especially for the purpose at Elliott Lake by the Atomic Energy Control Board.

Currently, acid water decanted from the tailings ponds is neutralized using lime, and the decant is discharged to the lake system. However, the prospect of continuing to neutralize acid drainage from these tailings, which are growing larger and larger, "in perpetuity" until all the sulfide has been oxidized is somewhat unrealistic.

Acid mine drainage inhibition and treatment is discussed in a separate chapter. This example serves only to illustrate the scale of the impact of mining this type of ore on the environment. The composition of tailings decant solution after neutralization and $BaCl_2$ treatment for radium removal is reported as follows:

	(mg/l)
pH	8.2
Radium-226	3.3 p Ci/l
NH_3	60
NO_3^-	81
TDS	2,852
$SO_4^=$	1,572
Cu	0.02
Pb	0.11
Zn	0.02
Ni	0.12
Co	LT 0.02
Mn	0.44
Ca	509
K	80
Cl	110
Fe	0.35
Na	87
U_3O_8	0.01

A good additional source of further information on the uranium mill tailings acid mine drainage problem is Gordon Ritcey at CANMET who has been involved for many years in trying to find an improved method for uranium tailings disposal that can avoid the generation of acid on a long-term basis.

CANMET
555 Booth Street
Ottawa, Ontario K1A 0G1
(613) 995-4194
Gordon M. Ritcey

Two leading industry experts in the Elliot Lake region are:

RIO ALGOM LTD.
Post Office Box 1500
Elliot Lake, Ontario
Canada P5A 2K1
(705) 461-2518
Telex: 067-7338
Al J. Vivyurka
Senior Environmental Engineer

DENISON MINES LTD.
Post Office Box B-2600
Elliot Lake, Ontario
Canada P5A 2K2
(705) 848-9111
J. L. Chakravatti
Senior Environmental Engineer

At Elliot Lake uranium tailings areas, a new source of AMD cause was observed. Tailings deposited in above-ground ponds are subject to wind erosion. Sulfide-containing tailings are prone to windblown distribution which results in the distribution of acid-generating tailings over a wider area, perhaps beyond the tailings catchment area within which the acid mine drainage is collected. Establishment of vegetation on the tailings areas would be one way to avoid this problem, but this is not always easy, especially after oxidation and acid generation has started.

BASE METAL AND GOLD MINES, CANADIAN SHIELD AND BRITISH COLUMBIA ACID MINE DRAINAGE

Stretching across the Canadian Shield from Quebec through Ontario and into Manitoba there are numerous gold and base metal mines, most of which are associated with pyrite and other iron sulfide mineralization including pyrrhotite and marcasite. These operations generate wasterock and sulfidic tailings on a large scale which, together with minewater pumped from underground, contribute large quantities of acid drainage. The acid water generated contains several base metal contaminants as well as acid and sulfate ions. HAWLEY (1980) has reviewed the chemical characteristics of the mineral tailings in the province of Ontario.

Eastern Canada has a net precipitation and holds huge amounts of fresh water in a very extensive river and lake system. When maps of Canada in normal atlases are examined, one can see the Great Lakes which hold large volumes of water. It is only when large-scale maps of the individual provinces are examined, however, that one can grasp the large percentage of the surface of Canada covered by fresh water lakes, rivers, and waterlogged muskeg. Canada, in fact, accounts for around 37% of all the fresh water in the world.

Every spring, the snowmelt flushes the whole system, draining to the Great Lakes and untimately down the St. Lawrence River to the Atlantic Ocean. North of the watershed located south of Timmins, Ontario, the whole lake and river system drains to James Bay in the north and, again, the annual spring melt flushes the system out.

On the Canadian Shield, there has been considerable glaciation, and the result is that bedrock is covered by a generally shallow layer of alluvium. Canadian mining people point out that groundwater resources are small compared with surface water and that the groundwater aquifers are localized in bedrock basins which prevent widespread contamination of groundwater.

The nature of the regional hydrology and water use is very important when it comes to discussing or considering the impact of mining and mineral processing and, hence, acid mine drainage on the environment.

In a situation such as in Canada, the huge turnover of water from year to year would likely tolerate a much higher total salt load than, say, the situation in the Witwatersrand where as much runoff as possible is caught for reuse in the regional water supply.

HAWLEY (1979) has discussed the chemistry of acid mine drainage in Ontario. No concise list of AMD-generating operations or surveys of the extent of AMD generation in Canada was found, but in the course of this investigation, several operations in Canada were visited, and the AMD-generating capacity of their tailings and wasterock piles was obvious and awesome.

In British Columbia in the Canadian Rockies, there are numerous copper-molybdenum operations. These are located in areas with rain and snowfall well in excess of evaporation. Because drainage to the ocean is along important salmon fishing rivers, there is a considerable concern about any factors that could possibly affect the river habitat and spawning grounds. At several Cu-Mo operations, the water level constantly rises as precipitation accumulates in these ponds which are AMD generators. One example of such an operation is the Brenda Mine, but there are several others.

The AMD problem of tailings from these operations in British Columbia lends support to the concept of disposing of such tailings in deep lakes or in the ocean deep enough that oxygen levels are depleted to the extent that AMD generation does not occur. There is still debate on the effectiveness of deep lake or submarine tailings disposal as a means of avoiding or minimizing detrimental environmental effects.

AMAX, INC. operates a copper-molybdenum mill in British Columbia which disposes of tailings to the ocean which could possibly now serve as an example for detailed study to determine what, if any, impact on the marine environment there has been.

AMAX ENVIRONMENTAL SERVICES, INC.
1707 Cole Blvd.
Golden, CO 80401
(303) 234-9020
Jim Kerrigan

US BORAX has also extensively evaluated all aspects of submarine tailings disposal which is envisaged in the development of their enormous Quartz Hill molybdenum deposit south of Ketchikan, Alaska. Their operating plans have been under very careful scrutiny as this mine is located in land that was proposed as a wilderness area. Those interested in submarine tailings disposal could expect to find useful information in the Quartz Hill Project Environment Impact Statement which is available from libraries in Alaska--probably at Ketchikan, and also possibly from:

US BORAX AND CHEMICAL CORP.
3075 Wilshire Blvd.
Los Angeles, CA 90010
(213) 381-5311

WESTMIN RESOURCES mines and mills a complex, copper-lead-zinc ore containing gold, silver, and cadmium at a site inside the Strathcona Provincial Park on Vancouver Island. Since 1967, WESTERN MINES has disposed of their tailings to the bottom of Buttle Lake after alkaline chlorination to destroy residual cyanide values. Buttle Lake is the source of the drinking water for the town of Campbell River (ECCLES, 1977). Information on this successful operation and perhaps a reading on the impact on the lake environment as a result of tailings disposal over the last 17 years might be available from the company; alternatively this site might be considered for detailed study of such impact.

WESTMIN RESOURCES LTD.
Campbell River, B.C.
A. G. Eccles
Mill Superintendent

It has been learned that more recently WESTMIN RESOURCES LTD. has stopped deep lake disposal and replaced it with a sub-aerial disposal technique, but no details as to why this change was made were obtained. Mining and milling operations affect the environment in several ways. Examples were encountered where groundwater was contaminated by acid mine drainage at an Ontario base metal recovery operation. The problem was solved by injecting fresh lakewater to the aquifer and removing the source of contamination.

The basic cause of the AMD is a pond in which mill effluents and smelter-scrubber water was contained which allowed sulfide mineral particles to settle. Over the years, the accumulation of sulfide particles in this pond became a source of AMD which contaminated groundwater from which potable water was drawn by a well.

At another location at a railroad loading point, a groundwater well was also contaminated by AMD as a result of seepage from the surface on which, over the years, concentrate had spilled during stockpiling and loading operations. This could have been avoided by preventing the spillages or lining the area, and the problem was solved by picking up the top several inches of soil and processing it through the flotation plant, as well as repairing the leaking railcars.

A major base metal producer in Ontario uses a series of large lakes as their tailings impoundment area and water stabilization and treatment facility. By increasing the volume of water in the impoundment areas, effluent levels of metals have been diluted slightly. An important observation was made between the effluent decant point and the receiving water discharge point. The treated effluent stream flows alongside a half-mile stretch of roadway constructed of wasterock. In this short stretch of stream, the nickel level in the stream increases 10% from 0.9 mg/l to 1.0 mg/l, illustrating the AMD-generating power of wasterock and the need to control the use of wasterock as fill for work areas, roads, and railbeds.

COAL MINING - ACID MINE DRAINAGE

Coal mines all over the world generate large quantities of wasterock or culm which is disposed of in culm banks. Sulfides as pyrite or as organic sulfur compounds occur commonly in coal and coal waste, and acid mine drainage is a very severe problem in both open pit and deep coal mines throughout the world. Measures to inhibit or treat acid mine drainage in coal mines in North America and in South Africa are discussed in chapters 23 and 24.

Because coal mining is such an enormous industry, the impact on the environment has been very serious. There is not much difference in the effect of acid mine drainage from various types of mines--all of it is acid, kills fish and vegetation, and limits the use of the water due to its TDS content.

The coal industry was not surveyed in detail in this investigation as few of the sponsors are interested in coal. Nonetheless, coal mining has had a major impact on the environment. This led to the passage by the U.S. Congress of the Federal Coal Strip Mine Act which centralized the regulation of surface coal mining in Washington, removing authority and power away from state agencies and coal operators, and resulting in the formation of a new agency, the Office of Surface Mining, which was formed to oversee this new regulatory empire.

Certainly, the coal mining industry found itself entangled in a new web of regulatory problems, but this might have been avoidable had the industry been more effective in policing itself and reducing the impact it had on the environment.

In Appendix I, descriptions of Burnside and Northfield Collieries outline some very effective measures that were taken to reduce the environmental impact of abandoned coal mines in Natal, South Africa.

Abandoned coal waste dumps and leaking coal mines generate large quantities of acid mine drainage which, when it drains into creeks and rivers, destroys the benthic environment and renders the water useless for stock grazing and even irrigation.

Historically, coal mine waste usually was deposited in lower-lying ground, invariably alongside a creek or in the path of runoff drainages. The result is that the sides of culm banks would be eroded allowing air and water to penetrate, thereby speeding up the oxidation process.

Areas affected by acid mine drainage were invariably characterized by dead trees and denuded vegetation.

In recent times, since expense and attention has been paid to preventing AMD where possible and treating that which cannot be prevented, there has been a marked improvement in the environment around coal mines and in the quality of streams draining from coal mining districts. AMD remains an expensive problem that needs a less expensive, permanent solution.

ACID MINE DRAINAGE - GOLD AND BASE METAL MINING, COLORADO

There is a highly mineralized belt extending through the Rocky Mountains from Jamestown, Colorado, to Cripple Creek, and on to Telluride. It includes such gold mining districts as Georgetown, Idaho Springs, Central City, Victor, and a host of additional abandoned or forgotten sites.

The famous Argo Tunnel and Yak Tunnels were driven as drainages to allow access to mineral deposits. These tunnels today still serve to drain water from these areas.

Base metal and gold mining of the past has left scattered wasterock piles on the sides of the mountains, mazes of tunnels which serve to collect and drain seepage as well as conduits for air into the mineralized areas, and tailings piles generally on the valley floors, often alongside creeks. The wasterock and tailings clearly are rich in oxidizing sulfides. The abandoned workings and drainage tunnels drain large underground areas which were not regarded as ore, but which nonetheless contain high percentages of acid-generating sulfide minerals.

The ownership and responsibility for these sites has, in most cases, long ago passed from the people who operated these small workings. The responsibility for protecting the environment from damage by these sites now has fallen to the state:

COLORADO DEPT. OF NATURAL
RESOURCES
Mine Land Reclamation Division
1313 Sherman Street
Denver, CO 80202-2273
(303) 866-3567
J. David Holm

HOLM and SIMPSON (1981) reviewed acid mine drainage from the ARGO Mine Tunnel because it is, in their words, one of the most dramatic examples of acid mine drainage in Colorado. The Argo Tunnel drainage is the largest single source of trace elements in the Clear Creek watershed which serves as an important industrial and municipal water supply for the Denver metropolitan area. Their paper is included in the chapter on acid mine drainage treatment.

The mines of Clear Creek and Gilpin were famous, but so were many of the problems in mining these areas. Water seeped into the workings so that pumps worked 24 hours a day. The idea of tunneling into a mountain to reach ore on a slightly inclined plane was applied as a means of draining water and transporting men and equipment at many locations since the 1870's, and the Argo Tunnel was one of the few that succeeded. By 1898, Samuel Newhouse's Argo Tunnel had reached a length of 7,000 feet towards Central City and had intersected 200 mines and over 1,140 veins. By 1904, the tunnel was 12,000 feet long and served many mines producing gold, silver, lead, copper, and iron sulfides. Production of precious metals served by the Argo Tunnel is estimated to have totalled more than $100 million at old values. By 1910, the tunnel was completed at a length of 21,896 feet where it connected to Central City. On January 19, 1943, an underground aquifer was penetrated at one of the workings with the result that the Argo Tunnel was flooded and the tunnel closed.

During the past 25 years, there have been several "blow outs" of toxic mine water. These voluminous releases of polluted water are believed to be caused by roof collapses in the tunnel which prevent water from draining normally. Water backs up behind these dams, and tremendous hydrostatic pressure can develop. On May 21, 1980, a near catastrophic release of toxic water occurred which resulted in the temporary shutdown of five downstream municipal and industrial intakes. Clear Creek water quality was severely impacted throughout the entire downstream reach of 35 miles to the confluence with the South Platte River.

U.S. GEOLOGICAL SURVEY MINE DRAINAGE STUDY (1977)
ARGO MINE DRAINAGE

	Mean Concentration (mg/l)	Proposed Water Quality Standard (mg/l)
TDS	2,925	No Standard
pH	3	5.5-9.0
$SO_4^=$	1,951	250
Arsenic	127	0.05
Cadmium	0.152	0.002
Copper	5.92	0.06
Iron	186.5	1.55 (Total)
Lead	0.14	0.009
Manganese	93.6	1.1 (Total)
Silver	0.028	0.0001
Zinc	46.3	0.55
Nickel	0.39	0.05

The Argo Tunnel water quality reflects one of the impacts of mining on the environment and on water quality.

In the Colorado Rockies, there are numerous larger mines that are still operating and which have a serious impact on water quality. These include the Gilman Mine and Gilman Tailings alongside the Eagle River not far from Vail, Colorado. The Gilman Mine is discussed in a trip report in Appendix I. Gilman tailings, along with the Argo Tunnel, are now designated as Superfund sites under CERCLA regulations as targets for expensive mitigating measures. There are six Superfund sites in Colorado alone, all mining and mineral processing sites which are having an impact on water quality. The others include ASARCO's operations at Leadville which drain into the Leadville tunnel, ASARCO's Globe smelter in Denver, and the COTTER CORPORATION's old uranium millsite at Canon City where contaminated seepage from uranium ore stockpile areas is migrating towards a municipal reservoir. NEWMONT MINING's Idarado mine-mill site is also named as a Superfund site where hexavalent chromium used as a flotation reagent has seeped from tailings into the local aquifer which serves wells in the Telluride, Colorado, area.

At Crested Butte, Colorado, AMAX, INC. has spent $12-14 million on water treatment facilities and site stabilization of the old Keystone Zinc Mine and tailings. Operation of this treatment facility costs around $700,000 per year. The Keystone mine and mill is just one of many in the Colorado Rockies which generates acid mine drainage, but it is one of the few where acid mine drainage is treated. It would be an interesting calculation to determine the DCF ROI over the life of the Keystone Mine if the reclamation and water treatment capital and operating costs were to be included.

In North American operations, chloride may often not be a serious environmental problem, and it is seldom regulated. However, where solutions have to be recycled or where water is used for pressure oxidation or leaching processes in stainless steel vessels, chloride in the water can have expensive consequences. Also, water from the lower reaches of the Colorado River will soon have to be desalinated using an expensive reverse Osmosis process. Discharge of chloride and sulfate-containing effluents into the Colorado River may logically become restricted in the future.

There are also new approaches to hydrometallurgical treatment of ores and concentrates that are under development including ferric chloride leaching processes, ammoniated leaching, and others.

Most recently, hydrometallurgical processing of refractory gold ores, including biological and pressure oxidation of sulfides, are gaining favor over roasting. These hydrometallurgical and biological oxidation processes also generate acid and cause

unwanted metals to dissolve. Recent process arrangements employing pressure oxidation allow the dissolved metals to be separated for simpler treatment before they come into contact with cyanide for gold leaching, which would complicate the metal removal process in effluent treatment. The new McLaughlin project of the HOMESTAKE MINING CO. in California is able to wash most of these nuisance metals from the oxidized ore before cyanidation.

In hydrometallurgical leaching of copper and zinc concentrates (with and without roasting), jarosite salts are generated which must be disposed of. Usually, the jarosites are stored in ponds. Seepage from jarosite ponds is a potential source of contamination and is a recognized environmental challenge. The more expensive "hematite process" has been developed for use in parts of the world where there is inadequate space for jarosite containment ponds around zinc and copper hydrometallurgical refineries.

MINE DRAINAGE - NEVADA

The abandoned mine pit at the famous Getchells Mine in Nevada until recently was partially filled with 400-600 million gallons of water at a pH of over 7. Although this is not an example of acid mine drainage, it is certainly an example of mine drainage. The water contained about 2,000 ppm TDS, mainly $CaSO_4$, which exceeded allowable limits for direct discharge to the natural drainage in Humbolt County, Nevada. This water would, if discharged to the natural drainage, end up in a lake. Deep well injections were examined and estimated to cost around $2.5-3.0 million. A second, probably more practical alternative being explored in 1984 was the possibility of using the water for crop irrigation--e.g., for alfalfa. It is believed that even though the water in the pit was high in TDS and may have also contained some dissolved metals, it probably, in its desert environment, was not causing damage to the environment.

Nevada is a very dry state, and evaporation exceeds precipitation. Consequently, mine-mill operations can almost always operate on a zero discharge basis. A new gold or silver mine in Nevada can invariably design for solution recycle, thereby avoiding the need for effluent discharge. If a barren bleed is necessary, then this can also be achieved without discharge of an effluent by simply evaporating excess water.

Occasionally, the water balance at Nevada operations may be upset by snowmelt or torrential downpours. In such cases, excess solution would unavoidably be released to the environment. Because of large seasonal differences in the precipitation/evaporation ratio, it is important to design solution impoundments in such a way that there is always adequate capacity to store water that can drain from heaps in heap leaching operations.

Nevada is a very dry state, and one would have expected that good quality water would be extremely valuable. Yet, there are mining operations that use huge quantities of

water in gold recovery by CIP on a once through basis with no recycling at all. In one case, water is simply pumped with tailings to the desert floor where it seeps into groundwater. No data was found as to the quality of water in the aquifer that is impacted. This practice does seem to be a waste of water and to have potential for groundwater damage of the kind that is now being scrutinized by regulatory authorities. Fortunately, this approach is not typical in the industry as more companies realize the benefits of being self-policing. It is bad examples such as this, however, that provide fuel to the regulatory agencies, however.

ACID MINE DRAINAGE: ABANDONED MINE SITES IN CALIFORNIA

Sulfur Bank Mine

In California, there are several areas where mining activity of the past is believed to still have an impact on water quality. One such case is the Sulfur Bank Mine.

The Sulfur Bank Mine belongs to the Bradley Mining Company of San Francisco. It is located on the Oaks Arm of Clear Lake in Lake County, California. The water runoff from the abandoned mine area is believed to be the source of mercury which has reached a level of 0.25 ppm Hg in Clear Lake. The mercury level in some fish caught in the lake is well in excess of 1 ppm, and about 75% of the fish in the Lake exceed this level. The larger the bass, the higher their mercury level.

The water discharged from the mine is acid, and discharge is seasonal, reaching a minimum in the summer.

Walker Mine

The Walker Mine in Plumas County, California, is located 150-200 miles north of Sacramento at an altitude of 6,000 AMSL. The nearest towns are Quincy and Portola, California.

The Walker Mine operated since the 1800's and was abandoned in the 1940's. Acid mine drainage at pH 4 containing 18 ppm copper, some zinc, and some sulfate drains from this mine at a rate of 300 U.S. gpm to 2,000 gpm.

At its 6,000 foot altitude, the mine is not accessible in winter because of snowcover. The acid drainage flows yearround into the Grizzly Creek and India Creek on the east branch of the Feather River. The mine is said to involve extensive underground workings into three orebodies. A firm of consultants was hired and, after $260,000 worth of study and pilot testing, they seem to be busy reinventing the wheel.

The minesite also includes a large tailings area, but it is not clear whether these tailings are also generating acid mine drainage.

Possibly, additional information on the site can be obtained through the appropriate California Regional Water Quality Control Board or the consultants:

PEARSON, POTTER AND ASSOCIATES
Richmond, CA

The Penn Mine

The Penn Mine is a third known abandoned copper mine in California that has resulted in AMD discharge over many years. This one is under the jurisdiction of the Bay Area Municipal District, Oakland, California, who would be able to provide details. This mine is located one and one half hours by car southeast of Sacramento in the drainage area serving the Comanche Reservoir. AMD from the site has caused damage to the Mokelumne River and wiped out a trout hatchery. To date, $500,000 has been spent on collecting this drainage and keeping it out of the reservoir.

The perpetual and persistant existence of acid mine drainage pollutants of surface waters from old abandoned mine sites within the areas under their jurisdiction is a motivating force in the critical attitude shown by regulators toward proposed new mining operations in their areas.

ACID MINE DRAINAGE - WISCONSIN ZINC DISTRICT

HOFFMANN (1984) presented an interesting account of the Shuilsburg, Wisconsin, zinc mining district where for many years the Eagle-Picher Mining Company mined zinc ore from mines that were dewatered by pumping. When the mines were worked out, however, and the old workings were allowed to flood, the quality of water in the regional aquifer in the vicinity deteriorated rapidly making it unfit for its traditional applications, namely livestock watering and human consumption. The interesting aspect here is that groundwater quality was impacted only after the mining operations stopped, and the company had moved away. The nature of the contamination was mainly high magnesium and sulfate levels in the water.

REAGENTS USED IN MINING AND MINERAL PROCESSING

A wide range of reagents are used in mineral processing and metallurgical treatment of ores and concentrates. These range from: strong acids for the leaching of ores or elution of ion exchange resins, ammonia, SO_2, and NaOH used in conditioning of pulps prior to flotation; Na_2CO_3 for alkaline leaching of uranium; flotation reagents, including glycols, xanthates, thiophosphates, etc.; organic solvent extraction agents;

hexametaphosphate scale inhibitors; polyelectrolyte surfactants, coagulants, and flocculants; hydraulic fluids; greases; oil; lime, etc. One of the best reviews on the use characteristics and toxicity of mine-mill reagents has been compiled by HAWLEY (1977).

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Head, Mining, Metallurgy and Inorganic
Chemistry Unit
Quality Protection Section
Water Resources Branch
Ontario Ministry of the Environment
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Toronto, Ontario

The toxicity of a wide range of bulk chemicals and acids, frothers, collectors, xanthates, pH modifiers, activating agents, depressing agents, dispersants, flocculants, coagulants, coagulant aids, lubricants, and explosives is discussed in a 250-page document. He also reviews biodegradability of mine-mill reagents and tailings area design and its relationship to the toxicity and biodegradability of mine-mill reagents.

The chemicals themselves tend to be relatively expensive and, as such, the mining industry uses these chemicals with as little waste as possible. However, even a small mining operation may use several hundred pounds of an essential chemical during a normal working day. Residual qualtities of many of these compounds can and do escape in effluents to receiving waters. Also, accidental chemical spills can and do occur. HAWLEY (1977)'s report is the first that deals with the toxicity of these numerous chemicals on aquatic life and on water quality. Numerous references are cited. He emphasized that the reliability of the data is largely questionable, and that it is useful as a guide to the relative toxicities of various mine-mill reagents. The following general conclusions are worthy of note:

1. Mine-mill reagents vary in toxicity. Some are highly toxic while others, considering the circumstances of use, are relatively non-toxic. Some are persistent and hence will escape from a tailings area. Others are unstable and will break down in a tailings area.

   Obviously, when reagents are being chosen for use in a mine-mill circuit, the least toxic compounds available should be chosen. Included in the definition of "least" toxic compounds are those which break down rapidly into innocous substances in a waste stream or those toxic substances which can be removed easily from a waste stream using conventional waste treatment technology.

2. The toxicity of many contaminants under field conditions and in mine/mill effluents, which contain several ionic species, is not wellknown for many contaminants and is often very much different from that determined on simpler systems in the laboratory with unacclimated species.

3. The use of mine-mill reagents that are persistent (that is reagents that do not break down in a natural environment) should be avoided if possible.

4. The use of mine-mill reagents having known or suspected nutrient properties should be avoided if possible.

5. When choosing a reagent for use in a mine-mill circuit or process, the total effect of that particular reagent on the receiving waters should be considered. Reagent characteristics to investigate would generally include chemical oxygen demand, biological oxygen demand, biodegradability, effects on local aquatic life (plant and animal), and the effects on total dissolved solids concentration and the hardness of the receiving stream.

6. The use of mine-mill reagents that consist of or contain water soluble metal salts that are known to cause undesirable environmental effects should be avoided if possible.

In some cases, such as uranium extraction plants in the Elliot Lake region of Ontario, mill capacities range from 3,000 to 6,000 tons of ore per day. About 65-70 pounds of 100% sulfuric acid is used per ton of ore treated. In tests, surprisingly low levels of H_2SO_4 were found to be toxic to fish. For example, BELDING (1927) reported that only 6.25 mg/l H_2SO_4 is toxic to trout in 24 hours. However, it is noted that a dose that would be lethal in distilled or soft water might be harmless in a highly buffered water.

Surprisingly, just 92 mg/l lime in water was reported by MEINCK, et al. (1956) to be toxic to trout after 26 minutes of exposure.

Ammonia is used in large quantities as a pH modifier and also for precipitation of uranium. HAWLEY (1977) reports that nearly all mine-mill operations in the province of Ontario utilize ammonium-based compounds for one reason or another, including ammonium-based explosives. The toxicity of ammonia and ammonium salts to aquatic animals is directly related to the amount of undissociated ammonium hydroxide in solution which, in turn, is a function of pH. A high ammonia level at a low pH may not be toxic but if the pH is raised, toxicity is also increased. The toxicity of a given concentration of ammonium toward fish was found to increase by 200 percent between pH 7.4 and 8.0. Carbon dioxide at 15-60 mg/l appears to reduce the toxicity of ammonia in water by reducing the pH.

Hexavalent chromium has traditionally been employed as a galena depressant in the separation of copper-lead sulfide flotation concentrates. Hexavalent chromium remains soluble in water over a wide range of pH unless it is converted to trivalent chromium in which case, it precipitates above pH 5. Hexavalent chromium is very toxic and also is undesirable in domestic water supplies. This is the subject of a Superfund site at the Idarado Mine near Telluride, Colorado, where hexavalent chromium was used as a flotation

reagent for a short period. The state of Colorado and others are preparing to sue the mine owners under the CERCLA (Superfund) regulations for many tens of millions of dollars in compensatory and reparation damages, even though no specific incidences of actual damage to life or property have been reported.

The occurrence of hexavalent chromium in groundwater near Telluride was identified and described by the U.S. Geological Survey and reported by GROVE, et al. (1979) and STOLLENWERK and GROVE (1979).

METALLURGICAL PROCESS SOLUTION EFFLUENTS

Hydrometallurgy

Hydrometallurgical processes employ corrosive reagents as lixiviants and oxidants to leach metal values from ores. For example, sulfuric acid is commonly used to leach uranium, copper, and zinc from oxide ores and from roasted copper concentrate calcines as well as zinc concentrate calcines.

Cyanide solutions at pH 10-10.5 are used to leach gold and silver from ores. In hydrometallurgical processes, metals other than those which are to be recovered as products and by-products can also be leached. For example, in leaching Witwatersrand gold ores, small amounts of cobalt, nickel, copper, and others are also dissolved. In North American gold hydrometallurgy, small amounts of arsenic, copper, lead, zinc, nickel, antimony, mercury, thallium, and others may be leached depending on the ore being treated.

In the hydrometallurgical processing of ores and concentrates, the environmental effects of the lixiviants used and also contaminants leached from the ore in the process need to be taken into account. In gold and silver leaching, cyanide solutions are recycled until such impurities build up to such levels that they interfere with the process. To keep the process working, a barren bleed is necessary. This bleed contains cyanide complexes of a wide variety of metals.

In leaching uranium ores, oxidants such as manganese dioxide and sodium chlorate are routinely used to make the reaction work. These add manganese and chloride to the pulp solution.

Flotation

In flotation processes, a whole range of reagents are used for adjustment of pH and conditioning of mineral surfaces, collectors, frothers, depressants, activators, etc. These reagents may react with mineral species in the ore or with eachother. For

example, SO_2 used to condition complex ores in an alkaline medium generates thiosalts. Thiosulfate is also generated when some sulfide ores are milled in an alkaline medium. Oxidation of sulfides during milling and, commonly, dissolution of metal values from oxidized fragments of ore can result in metal buildup in recirculated flotation mill solutions.

At the PALABORA MINING COMPANY, South Africa, flotation plant solutions build up calcium and magnesium from the carbonatite ore. These species interfere with the process and must be counteracted by gangue depressent addition. After recovery of copper from the ore at PMC, their tailings are pumped across the fence to Foskor for phosphate mineral recovery. The quality of entrained water in the tailings contains several dissolved species as a result of contact with the ore, including relatively high levels of fluoride.

Several organic reagents may be added as reagents in flotation recovery operations. Organic species in mining and metallurgical effluents are not generally regulated (except visible oil and grease). WIXSON (1977) described a multi-disciplinary intensive study of environmental pollution at the New Lead Belt of southeastern Missouri and found considerable amounts of organic contaminants in the tailings decant effluents from both mine-mill operations in the area.

Pyrometallurgical Processes

Pyrometallurgical processes employ roasting and smelting as a means of extracting, separating, and refining metals. These originally were dry processes until the need to prevent air pollution arose. Since then, water has been used to scrub SO_2 from roaster gases, generally producing sulfuric acid, and in smelter and refinery operations to remove airborne particulates. Ambient air in lead refineries is extracted and cleaned to provide hygienic working conditions. The scrubber sludges produced can build up large amounts of metal values, typically containing arsenic, lead, copper, cadmium, zinc, nickel, cobalt, etc.

Cleaning roaster gases and smelter off gases prevents the distribution of metal-bearing particles to the environment around the metallurgical complex environment. This results in a much reduced water quality control problem since less soluble metals are now distributed and not as fallout where they can come into contact with plant runoff water or across the general environment.

EFFLUENTS

Consequently, just about every metallurgical process yields a solution containing reagents, metal contaminants, or process-generated chemicals. In many cases, these solutions can be treated and recycled resulting in a zero discharge operation. In others, this is not possible and a bleed is necessary, or it is necessary to discharge an effluent to maintain a water balance in the plant.

In some cases, a zero discharge mill operation may be feasible, but mine drainage water containing contaminants is used in the mill as a way of treating it. This additional water imput to the mill requires that water be discharged as an effluent from the mill tailings system even in areas where there is net evaporation.

Comprehensive information surveys on the toxicity effects of a huge list of contaminant species that can be found in metallurgical process effluents have been compiled by several organizations including ONTARIO (1979), U.S. EPA (1972, 1976,), and Environment Canada Reviews of Water Quality Criteria for many contaminant species, e.g., arsenic, lead, and copper which are referenced in the sections of this report that deal with the individual contaminants.

ORGANICS - LUBRICATING OIL, DIESEL, GREASE, HYDRAULIC FLUID

Mining operations consume significant amounts of lubricating oil, diesel fuel, grease, and hydraulic fluids.

Available information, according to ONTARIO (1979) on occupational health and industrial hygiene, indicates that tolerable health concentrations for petroleum-derived substances far exceeds the limits of taste and odor. Hazards to humans from drinking oil-polluted water will not arise because such substances become objectionable at concentrations far below their chronic toxicity levels. Oils of animal or vegetable origins are usually non-toxic to humans and aquatic life.

The amount of oil that produces a visible oil slick varies depending on the type of oil and weather conditions. The American Petroleum Institute estimates that the first trace of irridescence or color is formed when about 15 ml of oil is spread over 100 m^2, i.e., 100 U.S. gallons per square mile (0.15 microns thick), (NAS/NAE, 1974).

ONTARIO (1979) lists four objectives for oil and petrochemicals in water.

Oil or petrochemicals should not be present in concentrations that:

- Can be detected as a visible film or surface discoloration.

- Can be detected by odor.
- Can cause tainting of edible aquatic organisms.
- Can form deposits on shorelines or bottom sediments.

Surface slicks must be prevented to protect water birds and aquatic animals. Even less obvious but long sustained small slicks such as from sewered oil will have debilitating effects on resident water birds in the end. Heavy oil contamination causes rapid death.

In general, oil and other petrochemical contamination of water by mine-mill operations is a lesser evil than AMD. Once a mining operations ceases, the source of these materials to the environment ceases, and the problem will be solved. Oils and petrochemical products can cause problems in metallurgical processes when contaminated water is recycled.

The introduction of this type of material into mine/mill effluents from operating mines is much more widespread than is generally realized and has a lot to do with underground housekeeping practices and on whether the local garage owner has access to the dump as a location at which to dump waste crankcase oil.

In the water treatment plant at AMAX's Mount Emmons project, operations underground invariably introduce hydraulic oil into the system. This oil must be removed from the surface to avoid coating the pH meter bulb and causing an erroneous reading which would also cause inaccurate activation of the automated reagent adjustment in the pH control system.

ONTARIO (1979) applied an application factor of 0.09 to the average lethal concentrations of oils for freshwater fish and concluded that the following are "safe" levels for fish:

Bunker Oil	180 ml/l
Used Crankcase Oil	120 ml/l
Crude Oil Slicks	45 ml/l
Jet Aviation Fuel	45 ml/l
Diesel Fuel	15 ml/l
Automobile Diesel	9 ml/l

SUSPENDED SOLIDS

Fisheries, particularly salmon spawning grounds, are particularly sensitive to suspended solids. In Idaho at the headwaters of the Salmon River, a famous sport fishing ground and tourist attraction, the Stibnite Mine heap leaching operation is located right on the banks of a creek. Although the Forest Service is concerned about the possibility of cyanide release into this creek, they are even more concerned about suspended solids

from the mining/extraction operation washing into this salmon spawning ground at the wrong time of the year.

A nearby small placer operation, the Golden Reef Mine, incurred a small spill containing suspended solids which involved a stream in the Payette National Forest on Thunder Mountain. This resulted in a settlement with the Idaho Dept. of Health and Welfare and the Idaho Dept. of Lands in which the company was fined $5,000 and $20,000 for damage to the streams. This led to a congressional inquiry in the U.S. Congress led by Representative John Sieberling, D-Ohio, into the incident and involvement by the Idaho Conservation League. Clearly, effluents containing suspended solids are harmful to both fish, regulators, and the emotional wellbeing of certain congressmen, as well as being inflamatory to environmental groups.

ONTARIO (1979) found that suspended solids should not be added to surface water in concentrations that will change the natural Secchi disk reading by more than ten percent. The turbidity of water can have a great effect on the types and quantities of algae that grow in lakes by altering the quantity and quality of light available for photosynthesis as shown by BRYLINSKY and MANN (1973) and several other authors.

CHANDLER (1940, 1945) showed that the algal productivity is high in the Great Lakes when turbidity is low and vice versa. His studies also show that the composition, size, duration, and emergence of phytoplankton pulses in the Great Lakes are influenced by turbidity (CHANDLER, 1942a, 1942b, 1944, 1945).

The U.S. EPA in a report published in 1975 adopted recommendations of the NAS/NAE (1974):

"Aquatic communities should be protected if the following maximum concentrations of suspended solids exist:

High Level of Protection	25 mg/l
Moderate Protection	80 mg/l
Low Level of Protection	400 mg/l
Very Low Level of Protection	+400 mg/l

EIFAC (1966) identified four categories of concern in the effect of suspended solids on fish, namely:

1) Direct action on fish either killing them or reducing their growth rate, resistance to disease, etc.

2) Preventing successful development of fish eggs and larvae.

3) Modification of natural movements and migrations of fish.

4) Reducing the abundance of food available to fish.

This investigation concludes that turbidity and suspended solids content of water are not synonymous. Suspended solids load can change the productivity and behavoir of fish in a lake and/or creek and certainly will activate the behavioral instincts of private environmental groups, regulators, and congressmen, mainly because of the aesthetic obviousness of this type of pollution.

TEMPERATURE

Trout, one of the symbols of a clean environment, for example, do not survive in streams or lakes where the water temperature exceeds a certain maximum. That is why trout occur in mountain streams rather than subtropical ponds.

At ST. JOE MINERALS CORP.'s operation at Pierrepont, New York, for example, the company has installed an innovative meander system in which plant and algal growth is encouraged as a means of enhancing natural biological water purification processes. In order to provide a viable environment for marsh plants, these ponds can be no deeper than about three feet. While the marsh was establishing itself, an unexpected problem arose. During summer days, the temperature of water in the effluent from the meander system (before the marsh vegetation was fully established) exceeded that of the minewater entering the pond and also exceeded limits considered safe for the survival of trout in the small receiving stream. Presumably, trout would migrate downstream and upstream of the discharge point temporarily during the days when they find the temperature unpleasant.

Minewater from some mines is likely to be warm or even quite hot, and the temperature effect on receiving streams should be taken into account when considering the environmental impact of minewater discharge.

SOME TECHNOLOGIES THAT REDUCE WATER CONTAMINATION

MINING METHODS AND BACKFILL TECHNOLOGY

Mining methods have evolved within recent years which will have a beneficial impact on the environment and greatly reduce the impact on water quality as well as long-term control requirements after the mine-mill complex has shut down. A very important part of this is the development of mine backfill technology.

Mine backfill technology, as well as mining methods which depend on backfill for their success, are already well developed in Canada, particularly in the exploitation of massive sulfide deposits.

Waste rock and/or tailings are returned underground to fill the voids left by mining. From a water quality point of view, this achieves two important objectives. First, the cavity is filled thereby eliminating space for minewater to accumulate or circulate as well as for air to circulate in the old stopes. Second, the volume of tailings and wasterock left above ground is reduced correspondingly, thereby leaving less above ground as a potential AMD generator.

There are limitations to backfill application, however. First, due to the expansion factor when rock is crushed and milled, not all the material can be replaced back in the mine. At least 40% would still have to be disposed of in the conventional way. Second, very high sulfide tailings are pyrophoric and cannot be used as backfill as this results in a fire hazard underground. Hence, that fraction of the tailings which are the cause of the greatest environmental concern cannot be disposed of in this way.

On the Witwatersrand, underground disposal of tailings is already practiced on a growing scale at this time by some of the companies. It is believed that the ANGLO AMERICAN CORPORATION of South Africa may be taking a lead.

KIDD CREEK MINES primarily employs sublevel blasthole stoping for underground mining operations. During pillar recovery in the No. 1 Mine and panel mining in the No. 2 mine, the free-standing fill exposures may reach a height of 100 m or more. Consequently, a competent consolidated rockfill has been required to fill the mine openings. The successful technique of backfilling these stopes that has been developed for KIDD CREEK MINES has been described by YU and COUNTER (1983). More information could be requested from:

KIDD CREEK MINES LTD.
B-2002
Timmins, Ontario P4N 7K1
(705) 267-2161
T. R. Yu, Ph.D.
Chief Engineer, Rock Mechanics

TAILINGS DISPOSAL TECHNOLOGY

New technology for tailings disposal can dramatically reduce their impact on the environment and reduce concerns about their long-term stability. Two important aspects are of particular interest here. First is the "sub-aerial" tailings disposal method first used in South Africa which, depending on the nature of the tailings material, can make such an impermeable tailing that it acts to effectively encapsulate contaminants. Second

is the "controlled release" tailings dam design in which dewatering trenches are constructed inside the tailings pond to remove liquids from the impoundment. This lowers the phreatic pressure on the dam wall thereby rendering it safer and more stable. It also allows seepage from the tailings dam to be directed to one outlet from where it can be monitored, discharged, treated, recycled to the plant, or returned to the dam. In both cases, the major benefit of the new technologies is improved positive control of the way the tailings impact the environment.

An important example of sub-aerial tailings disposal which allows stabilization by encapsulation of a water treatment sludge that would otherwise be toxic is THE KEY LAKE MINING operation in Saskatchewan. This approach is also applied on numerous Witwatersrand slimes dams.

The Climax Molybdenum Division of AMAX operation at Climax, Colorado, is the classic application of the controlled release technique of tailings disposal using underdrains. AMAX staff, in fact, refer to this as the "Climax System" which they developed.

An engineer who was involved in the development and implementation of the controlled release tailings system at Climax and who new offers an independent consulting service is:

JOHN D. WELSH
John D. Welsh and Associates
247 Freeport Blvd.
Sparks, NV 89431
(702) 358-2992

Expertise in the "sub-aerial" or "dry" tailings disposal technique is available in North America from:

KNIGHT AND PIESOLD
409 Granville
Vancouver, B.C.
Canada V6C 1T2
(604) 685-0543
R. Bruce Knight

STEFFEN ROBERTSON AND KIRSTEN
1030 West Georgia
Vancouver, B.C.
Canada V6E 2Y3
(604) 681-4196
Telex: 04-352578
Andrew McG. Robertson

TAILINGS RETREATMENT

On the Witwatersrand, the retreatment of sand dumps is undertaken on a massive scale by several companies. This has several beneficial effects on the environment, particularly on runoff and groundwater quality.

1) The removal of pyrite from the tailings by flotation reduces the acid generating capacity of the tailings.

2) Recovery of soluble uranium by acid digestion removes uranium values that may already have been solubilized in the heaps due to the action of acid generated by pyrite oxidation in situ.

3) Fine grinding of tailings for retreatment is not often practiced because the grade is too low to justify the expense. Some operations apply a sand/slime split. The slime fraction can now be disposed of using the less permeable "semi-dry" tailings disposal technique referred to above which makes a less permeable tailing.

4) The new tailings can be designed using the latest, more environmentally conscious designs and can sometimes also be moved to a less sensitive location. For example, the Simmergo tailings, after reprocessing, are being pumped 38 km to the new ERGO/E. Daggafontein tailings pond south of Brakpan.

IMPOUNDMENT TECHNOLOGY

Impoundment technology has advanced significantly in the last few years. Not only have a host of new, improved synthetic membranes come onto the market, but the knowledge of how to apply them has advanced to a point where the risk of failure can be significantly reduced. As importantly, geotechnology has developed to a point where it is possible often to find a site where a liner is not needed at all.

Building a pond which is lined with a synthetic membrane is not nearly as easy as it looks, and there have been numerous failures, even of those ponds designed by large, stable, high-profile companies.

New bentonite-stabilized sand lining technology appears to be particularly effective and in some locations, potentially economical as applied at the GETTY MERCUR Mine at Toelle, Utah, and as a safety measure beneath a synthetic membrane at the KEY LAKE MINES operation in Saskatchewan.

In South Africa a treated bentonite lining, in which the clay is spread out as a layer without being mixed into the soil, is finding numerous applications.

WATER TREATMENT

Effluent treatment encompassing a huge spectrum of applications and technologies is increasingly required to meet effluent discharge permit requirements. Several of these technologies are described and discussed in chapters 12-53. It is always advisable to try and find a way through creative water management to prevent or to solve a water quality problem without the need for a water treatment plant.

WATER MANAGEMENT ADVANCES

Water management advances make it possible to use less water and, through appropriate and informed recycling, to reduce the volume of water that is impacted by the operation and the process.

A very important aspect of areas where there is a net precipitation is to design an operational area that reduces, as much as possible, the catchment area that will collect precipitation. Once water drains into this catchment area and comingles with other contaminated waters draining from the plantsite or tailings area, it will all need to be treated. Keeping the catchment area as small as possible by building interceptor trenches, berms, etc. reduces the size of this catchment area and can, therefore, result in the need for a much smaller water treatment plant or evaporation pond.

Examples of operations where water management has included the use of measures to reduce the catchment area of runoff water are many and include the following:

AMAX: Mount Emmons Water Treatment Project
AMAX: Climax, Colorado, Tailings
HOMESTAKE McLaughlin Project, Knoxville, California
NORANDA Grey Eagle Gold Operation, Happy Camp, California

The first three of these operations are described in trip reports in Appendix I.

CONCLUSIONS

1) It is concluded that the impact of mining and metallurgical operations on the environment and on water quality may be blatant and severe, or it may be subtle and gentle.

2) At the Friedensville Mine in Pennsylvania, a case was found where minewater was so clean and contained so little nutrient value that it could not support a lively aquatic

ecology (e.g., trout) until the mining company (THE NEW JERSEY ZINC COMPANY) added nutrients to the minewater discharge (BAKER, 1984).

3) Some environmental impacts of mining are temporary and persist only as long as the mine is in operation--typical mine life is 10-20 years before reserves are depleted. Examples of such temporary impact would be the impact of reagents which are added only during the life of the operations.

4) Some environmental impacts of mining may persist for several centuries after a mine shuts down. Examples are acid mine drainage from inclined drainage tunnels and sulfide tailings oxidation from a wide variety of mining categores.

5) Some environmental impacts are readily remediable, e.g., pH adjust, while others are not. Right now, there is no known way to dispose of highly sulfidic mine-mill tailings and wasterock at mines located far from the coast or deep lakes in net precipitation climates that avoids the need for perpetual AMD treatment and tailings management.

6) In arid climatic regions where effluent can be impounded and evaporated and where there is less likely to be valuable fishery resources and aquatic ecologies to protect, the impact of intelligently designed mining and milling operations on the environment is much easier to control than in areas where there is a net precipitation, and discharge of effluents cannot be avoided.

7) In considering the environmental impact of mining and milling operations, there are three phases to be aware of:

   - During construction and startup and early operation of the mine/mill.

   - Mature operation impact, i.e., after the tailings in the pond and wasterock have a chance to oxidize.

   - After mine/mill closure.

8) The impact on the environment of historical mining operations is not a perfect model of what to expect from current and future operations. The modern mines tend to be larger and to disturb more rock and land. Because of recent environmental awareness and pressures and changes in design and philosophy, mining and milling operation designs now take water quality and the environment into account. Much more emphasis is placed on water conservation and recycling and on advance planning for ultimate mine-mill closure.

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CHAPTER 2

OBJECTIVES AND SCOPE OF WATER MANAGEMENT

Focus on the need for environmental and water quality protection that emerged in the U.S.A. and which is spreading to other industry centers such as South Africa and Australia and now to the third world make it imperative, or at least very desirable in most cases, to develop a quantitative water management plan before a mine/mill operation is started and also to have an active water management program.

The cost of impoundments is high and by managing an operations water balance, it is usually possible to reduce the size of impoundments needed to take care of an operation's fresh water requirements, recycle solution inventory, and effluent control. It may however be better to spend more up front to save bigger problems after mine closure. Remember to manage the root of the problem, not just the symptoms.

OBJECTIVES OF WATER MANAGEMENT

1. To insure adequate water to meet the operation's needs during the dry season.

2. To avoid or minimize the volume of effluent that must be discharged or treated.

3. To avoid accidential spills due to impoundment failure and/or overflow, particularly during the months of spring runoff and/or highest precipitation.

4. To optimize water utilization to achieve the most cost effective combination of water treatment facilities, water recycling and reuse, and evaporation and effluent discharge within the constraint of minimized negative impact on metallurgical recovery efficiency.

5. To manage the seggregation of water and process solutions in various parts of an operation as needed for process and/or environmental reasons.

6. Because acid mine drainage is such an important problem, an objective of water management must be to resolve the problem of acid mine drainage in mines and tailings disposal sites.

WATER MANAGEMENT - A SYSTEMS APPROACH

This section of the report may not provide details of as many technologies as some of the other chapters, but it contains the most important message. A few companies already use

a systems approach to water management and treatment, and these include some of the sponsors of this study. Many mining companies are structured in such a way that implementing a systems approach is not easy. The systems approach has already proven very successful in cutting water consumption in more than one drought-stricken mining center, and in capital cost savings in new mine-mill complexes in wet areas.

WHAT IS A SYSTEMS APPROACH?

The systems approach examines every aspect of the mine-mill-tailings-wasterock system to design an optimized use and management of water within the framework of the overall economics of the operation.

Because water is used and affected by each unit operation and even by the nature of the climate, topography, soil and rock type, and vegetation as well, it is necessary to take the complete picture into account. This systems approach to water management is best applied before the mine or mine-mill system is installed. However, because it is a relatively new concept as far as water management is concerned, there are many more cases of significant cost savings through the application of a systems approach to existing installations.

The aims of a systems approach are:

1) To use one water problem to solve another through synergisms to achieve the best overall cost benefit.

2) To use the assets of the operation to advantage, e.g., large tailings pond or bog.

3) To avoid the need for costly treatment where possible--prevention is better than cure.

4) To take long-term costs into account; final reclamation should be included in the original plan, including consideration of long-term acid mine drainage inhibition or control.

5) To integrate incremental metal recovery or reduced metallurgical efficiency into water management considerations.

6) These days, public relations aspects may also be included.

HOW TO APPLY A SYSTEMS APPROACH

In many of the larger mining companies, water management is the responsibility of the mechanical and engineering department which reflects the days when pipes and pumps were the main concern about water.

Implementation of a systems approach in water management whatever the prime goal, be it conserving water or meeting effluent discharge regulations in the most cost effective way, requires that all the specialized disciplines and expertise on a mine-mill complex be taken into account. In several cases, local municipal effluents and wastes have been incorporated into the system or synergisms found between two or more adjoining mining operations. These disciplines include:

Geology	
Mining Engineer	- Design of a Mine
Mining People	- Mining Operation
Metallurgical Engineer	- Design of Mill and Process
Mill Operating People	- Mill Operation
Environmental Engineer	- Tailings Disposal
	- Effluent Treatment Facilities
	- Monitoring
Biologist-Botanist	- Passive Water Treatment
	- Design and Management Revegetation Program
Rock Mechanics	-
Soil Mechanics	-
Chemist	- Water Chemistry Specialist
Service Engineer	- Provision of Power, Steam, Heat, and Water
Civil Engineer	- Layout of Surface Facilities, Roads, Rail, Etc.
Human Resources Management	- Providing a Work Environment that Attracts a Good Workforce and Encourages Quality Performance
Townsite Managers	- Domestic Water Supply
	- Sewage and Garbage Disposal
Legal Department	- Interpretation of Regulations
Public Relations Dept.	- Enhancing the Corporate Image

The Systems Approach must taken into account water use requirements, water quality effects on the performance and the nature of effluents, as well as the availability and cost of alternatives at each unit operation, considering at least the following:

Ore Type
Gangue Characteristics
Quality, Cost, and Availability of All Available Water Supplies and Requirements
Mining Operating

Underground Dewatering
Mill
Metallurgical Process Alternatives
Nature of Wasterock
Wasterock Disposal or Use
Tailings Disposal and Management
Water Treatment Plant
Soil Characteristics
Subsurface Geotechnics
Climate
Vegetation
Topography
Location
Relative Reagent Costs
Regulations
Other Uses for Water Downstream and Sensitivities
Nearby Cities and Townsites
Sewage Plants at Mine and Nearby Urban Areas
Garbage Disposal
Location of Power Plant Flyash Availability

During the last several decades, society has become technology-oriented and increasingly specialized. To apply the systems approach, what is needed is a multi-disciplined coordinator with a strong technical background, operating experience, proven ability to weigh cost benefits, and management clout.

The main aim of a mining company is to make as good a profit as possible as well as long-term survival and growth. The water management focus should never lost site of this and should, therefore, be heavy on operating experience.

To make the systems approach work, it needs the dedication of all departments--each one must be aware of its role and potential roles. Usually, more information and education is needed than is currently available. To keep all the diverse interests working in the same direction, the water management staff must have the support of top management. The General Manager needs to be knowledgeable about water management and for this, he needs good staff support.

WATER MANAGEMENT AND METALLURGICAL ENGINEERING

BAKER and BHAPPU (Undated) concluded an excellent review on the effects of mineral processing on water with the following statement:

"NEED FOR ENVIRONMENTAL AWARENESS AND TRAINING

It is obvious that the mineral process engineer of today and the future has to play a dual role, that of a metallurgist as well as environmentalist. Traditionally, he is trained in the basic sciences and engineering common to both fields. What is needed is a keen awareness and concern to fulfill the dual responsibility that our mineral-based society has imposed on him.

This awareness and technical competence can only be developed through a realistic and well-balanced engineering curriculum. It is not necessary that the undergraduate engineer be required to take a specific course or courses in environmental science and engineering. However, it is essential that the student be made aware of the similarities in the two fields throughout all the engineering courses. With proper orientation and a minimum of deviation an instructor can do an adequate job of training the mineral process engineer so that he will be in a position to solve the environmental problems facing him in his professional career."

BAKER and BHAPPU (?) examined the problem mainly from the standpoint of mineral flotation processes in southwestern Arizona from porphyry deposits and their statement implies that environment related aspects be integrated into university training.

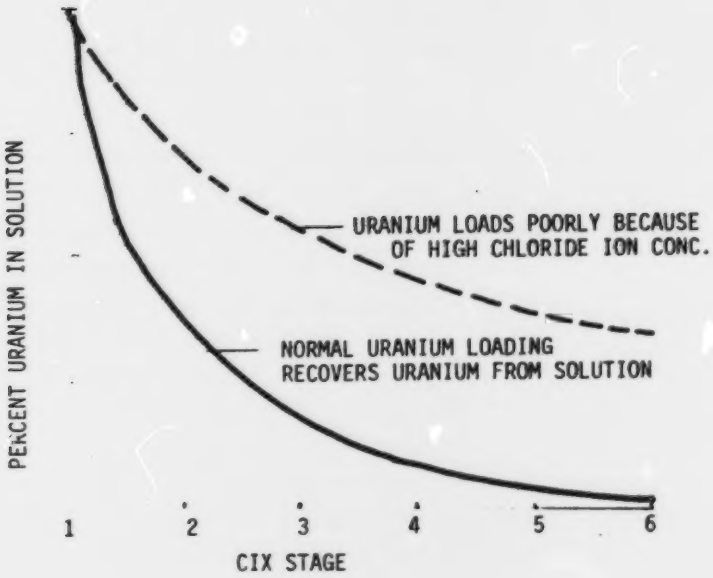
This report concludes that metallurgical and mineral processing engineers require specific formal education and practical training in water chemistry and water treatment technologies with a bias toward the needs of mineral processing facilities and also, education on the environmental aspects of metal and reagent impact and behavior. Without this type of background, it will be that much longer before a really appropriate systems approach to water management can evolve. Cross-breeding of disciplines usually yields valuable results. The biggest environmental problem of mining and milling is acid mine drainage, and this will not be resolved without understanding the fundamentals of the problem and adopting a systems approach.

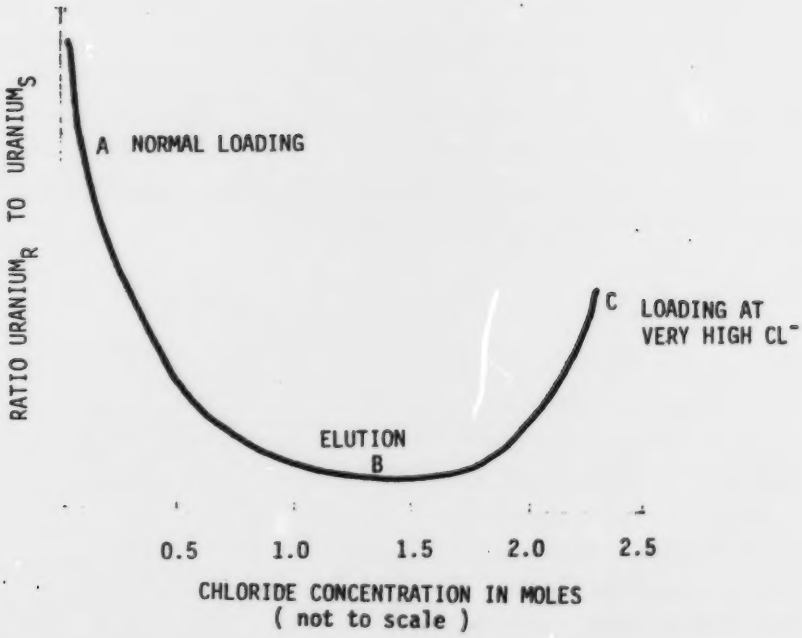
The Real Cost of Water

Cost of New Water
Cost of Delivery System
Cost of Distribution System
Cost of Treatment to Discharge Effluent
Cost of Storage, Monitoring
Cost of Sludge, Concentrate Disposal
Cost of Filing Reports
(Incremental Resource Recovered)

HONEYMOON URANIUM PROJECT

24,000 PPM TDS, 10,800 PPM Cl^-





The Cost of Recycling Water

Corrosion Damage to Pipes and Equipment
Corrosion Control Measures
Scale Control
Effects of Scale (Reduced Throughput, Higher HP)
Energy Consumption Increase Due to Scale on Heat Exchange
Metallurgical Efficiency Cost
Water Reclamation Cost of Pumps, Pipes
Pumping Costs
Cost of In-Plant Water Treatment
Extra Reagent Consumption Due to Recycled Water Quality
(Reagent Recovery Cost)
(Energy Recovery Cost in Recycling Warm Solutions)
(Metallurgical Performance Improvements Using Recycle Water)

EXAMPLES

HONEYMOON PROJECT, AUSTRALIA

The Honeymoon project was uranium resource in the Australia outback. It was clearly an attractive in situ leach target. The problem was that there was no fresh water available for many tens of miles.

The local aquifer contains brackish water with a very TDS level (30,000 ppm), including a high chloride level. If conventional uranium recovery by ion exchange resins were to be used, recoveries would be so poor as to be unworkable at the high Cl^- levels in solution.

An example of overlap between metallurgical process selection and development and water management in terms of the systems approach that this report promotes is the discovery that by adding more salt to the available water to reach very high chloride concentrations, a point on the equilibrium curve for ion exchange adsorption can be reached where uranyl chloride loads to a reasonable level. In this case, uranium would be eluted from the loaded resin by a more dilute solution. Instead of working in the range A-B of the curve for adsorption/elution, it would be possible to work in the range C-B for uranium recovery using the existing poor-quality water. This would surely be much less expensive than desalinating the water and applying the conventional process.

A CANADIAN URANIUM MILL: NO SYSTEMS APPROACH

A large uranium mine-mill complex on the edge of a lake practiced macro recycling of water. Treated tailings decant water is discharged to the lake system. Lake water is used in the mine and mill.

The mill put in a request to the utilities department of the structured large organization for an additional 3,000-4,000 gpm water for use in the mill. They were advised that this would not be possible for six months. Reason: It would take that long to expand the water treatment plant which was operating at capacity.

Utilities water was being treated by IX for use in the boilers to make steam for uranium leaching which requires a heated pulp. Somehow, the total water needs of the mill were being supplied from this plant, including that used in the grinding circuit. Only after more water was not available was an investigation started which asked the question as to whether lakewater could be directly used in the mill. This is an extreme case of not using a systems approach to water management.

SYSTEMS APPROACH - SELECTING A WATER TREATMENT PROCESS

Many factors must be taken into account when selecting a water treatment process. To illustrate the systems approach idea, consider the case where several reagents are considered for base metal removal from effluents. In the first case, hydroxides precipitation may not get solubilities down quite as far as needed. Sulfide precipitation may achieve the low solubility but has the disadvantage of being more difficult to remove the suspended precipitate and uncertainty about stability of sludge disposal and toxicity if excess reagent is used. A combination of sulfide and lime can possibly solve all the problems:

- It reduces the metal levels in solution to that of sulfide precipitation.
- Lime-sulfide precipitates settle faster than lime precipitates and yielding lower S/S than for sulfide precipitate settling.
- Only a small fraction of the quantity of sulfide reagent is required compared with straight sulfide precipitation.

This is an example of how a systems approach can help solve problems.

THE OVERALL WATER COST FOR TWO GOLD RECOVERY OPERATIONS

Generalized costs for mining and milling at a large Witwatersrand gold-uranium mine and at a Nevada heap leaching operation are compared below along with a total overall water and water quality related cost guestimate. This shows that, depending on circumstances, water quality control and modification can justify significant attention and investment in the ore case, very much less in the second case. Some heap leaching operations, however, will not be feasible at all without appropriate water quality modification.

	RSA Au-U $/t Ore	Nevada HL $/t Ore
Removal of Overburden	--	4t @ $4.00/t - $4.00
Ore Mining	$45.00/t	$1.00/t - 1.00
Total Mining Cost	$45.00/t	$5.00/t
Metallurgical Cost	3.50/t	2.00/t
	$58.50/t	$7.00/t

Water Cost

Pipes, Pumps, Valves, Say 8% of Overall Cost in RSA	$4.85	±$0.50/t
Water Consumption	1.0 m^3/t	0.2 m^3/t
	0.17/m^3 water	0.17/m^3 Water
	$0.17/t Ore	$ 0.03/t Ore
"Total" Water Cost	$5.02/t Ore	$ 0.53/t Ore

SCOPE OF WATER MANAGEMENT

The scope of water management in a mining operation should enable a "systems approach" to be adoped which includes the mine, mine services, mill, tailings, wasterock, catchment area, smelter, refinery, water impoundment, water source(s), and water treatment as well as environmental monitoring program. By applying a systems approach, the water cost savings by recycling more water and possible resulting effluent treatment cost savings can be weighed against the "cost" of metallurgical inefficiencies resulting from higher incremental salt buildup and possible increased corrosion or scale control costs.

The scope of water management should, therefore, encompass all facets of the operation. For example, if it costs more to dispose of a precipitate formed in the water treatment plant in a landfill than the penalties incurred by shipping it to a smelter blended into a concentrate, then this could conceivably also be the business of the water manager.

Scope of water management can include:

- Water Balance Design and Control
- Salt Balance Design and Control
- Input at Plant Design Stage
- Matching Metallurgical Processes with Available Water Qualities
- Meeting Regulations and Permit Reporting Requirements
- Problem Solving when Permit Conditions Threaten to be or are Exceeded
- Negotiating New Permits or Renewals
- Negotiating Less Costly or Simplification of Permit Compliance
- Corrosion Protection or Avoidance
- Scale Inhibition Measures
- Water Conservation Measures
- Negotiation of Improved Water Prices
- Preservation of Water Quality
- Seeking Synergisms to Save Pumping/Water Costs
- Resource Recovery from Water
- Cost Reduction Through Innovation
- Public Relations
- Development of Management Support

Water and salt balance computation in mine-mill complexes is in itself an emerging science which has been greatly furthered by the now general availability of cost-effective desk top computers and software.

In applying for permits for new operations, it is now nearly always necessary to project the water balance for the operation in advance. This means that in addition to predicting the water balance, the salt balance must also be known so that the impact of recycled solutions on the metallurgical processes can be predicted, and the extent of salt bleed determined as well as the size and type of water treatment facility.

Expertise in this area is relatively limited, but the following companies are known to be developing computer models for water and salt balance modelling:

CH2M HILL, INC.
Post Office Box 91500
Bellevue, WA 98009-2050
(206) 453-5002
James D. Mavis, Jr.
Terry Chatwin

EXXON MINERALS COMPANY
Post Office Box 4508
Houston, TX 77210
(713) 895-1110
Crandon Project Manager

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Thomas Wolf

NORANDA RESEARCH CENTRE
240 Boulevard Hymus
Pointe-Claire, Quebec H9R 1G5
(514) 697-6640
Dr. Joe Bayah

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Don't get just an equipment supplier. Think of RCC's systems engineering approach.

There are dozens of suppliers offering equipment for an individual element of water and wastewater treatment. RCC gives you a single-source solution for water and wastewater control. You'll be assured of getting the most advanced technology and the best equipment to fit your need, from simple end-of-pipe treatment to an integrated plant water system. And after startup, we'll still be there providing continued service for data monitoring, operator training, or critical parts handling.

RCC is experienced in applying systems analysis to the design and retrofit of water systems in all phases of industry. Our clients include chemical processing plants, mining companies, pulp and paper mills, oil refineries, synthetic fuel producers, distilleries, electric utilities, and government agencies.

RCC's engineering services

Laboratory and pilot plant testing
Systems analysis and conceptual design
Detailed design and procurement
Installation and construction management
Project management and control
Startup and checkout
Operator training
Continued customer support

Resources Conservation Co.

P.O. Box 3766
Seattle, WA 98124
206-828-2400

Resources Conservation Co.

Water Management Systems

RCC assumes single-source responsibility for industrial water systems

Our technology delivers cost-effective solutions

The water that powers industry, irrigates the land, and quenches our thirst is a finite resource.

If the historic trend continues, clean water will become a diminishing resource in this decade. Industrial growth is placing extraordinary demands on water supplies. Regulations for disposal of wastewater are becoming ever more complex.

Critical point analysis has been overlooked when it comes to water management.

In nearly every industrial facility, a "systems approach is used to develop the primary process or manufacture the product. Many economic, technical, and regulatory factors are carefully analyzed and integrated into a system solution. This same logical approach is seldom applied to the supply, use, reuse, and disposal of water. Yet, water systems analysis and good water management can save industry millions of dollars and can significantly reduce regulatory burdens.

The quality and composition of wastewater streams affect economics.

To minimize the influence of these factors, RCC's systems engineering approach considers the total water system from supply through disposal. The objective is to design a water system to maximize water recycle and reuse, reduce waste streams to meet discharge requirements, and recover valuable resources from the streams. Consistently, our integrated system design offers a life cycle cost less than end-of-pipe treatment alternatives.

An integrated systems approach is more than a discrete product or process.

It is a logical step-by-step understanding of all aspects of a water problem and its relation to plant operation. The economic and risk alternatives to maximize reuse and minimize discharge are given careful systematic attention to produce effective long-term solutions.

Just treating and discharging water is spending a lot of money to throw something away.

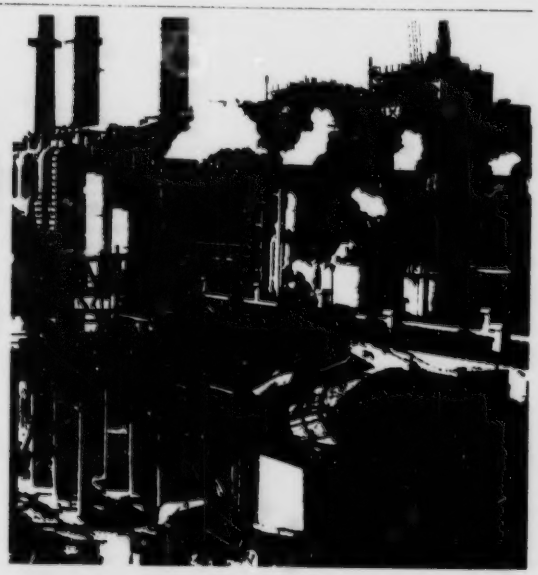
We offer more cost-effective solutions. An RCC water management system reduces intake requirements, cascading the effluent of one process to another process or operation. Treatment of each effluent can be tailored to its contaminants and its next use. This integrated systems approach affords the most economical solution to the problem.

We realize your waste and recycle requirements are special.

Every operation has a set of unique water considerations. RCC is a water management company that can identify and understand your requirements. We can act as your engineer to analyze your objectives and assess your alternatives. We can design the optimum system to solve your specific water recovery problem. We will even procure the equipment, install and test the system, and train your operators. Our customers call RCC the best turnkey service in the business.

3.8-million-gal/day wastewater treatment facility

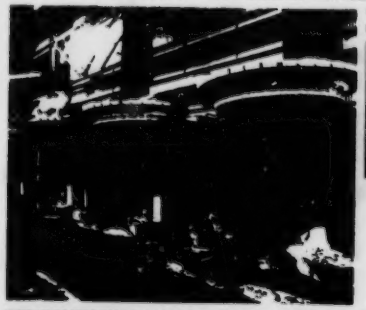
Total zero liquid discharge by 1985 was a goal set for this 1,700-MW coal-fired power station. After thorough engineering study and careful analysis of environmental regulations, an optimum wastewater treatment system was integrated into plant operations. The technology employed included neutralization and clarification, demineralization, sludge dewatering, reverse osmosis, and brine concentration. The human elements of plant operation were also addressed and a water conservation training program was developed to strengthen work functions.

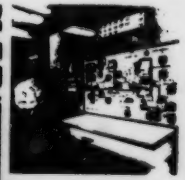


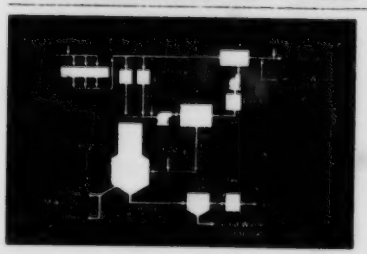
Water use cut 55%—zero liquid discharge protected

A Washington industrial plant's water inflow consistently exceeded its evaporating capacity. The company asked RCC to evaluate its process waters to develop treatment alternatives and to select the most cost-effective method to correct the problem and remain at zero discharge.

Our solution uses a crucible wash water reuse process to minimize contamination of storm lake water and a Brine Concentrator process to evaporate 80 gal/min of the plant's surplus water. Much of the plant's internal water was cascaded or placed on closed or recirculating loops. Zero liquid discharge was maintained and the company's water consumption has been reduced from about 300,000 gal/day to less than 70,000 gal/day.







Wastewater inventory reduced by 50%

A significant and unexpected growth of wastewater was about to cause major problems at a southeastern utility's 900-MW coal-fired station. RCC moved onsite, analyzed all major streams and produced a near-term solution to intercept and divert rainwater and reroute some existing wastewater. Simultaneously, we developed long-term alternatives to better manage the internal streams. Now operating, our water management system has not only reduced actual wastewater outflows, but also allowed zero liquid discharge.

CHAPTER 3

REVIEW OF WATER USE, AVAILABILITY AND COST AT MINES AND MILLS

The purpose of this part of the investigation was to determine answers to some of the following questions:

- How much net new water is required by different types of mineral processing and metallurgical operations.
- What quantity of water is recycled in the operation.
- What are the limitations on water recycling in the plant.
- What factors influence the specific fresh water consumption requirements.
- If there are more than one metallurgical process that can be used to recover a mineral or metal, is one more water efficient than the other. Does one avoid environmentally sensitive reagents needed by the other or reagents that cause problems in recycled solutions.
- What is the range in cost of water at metallurgical operations, and what factors influence the cost, i.e., are there ways for an existing operation to save water costs.
- What is the structure of water costs? If costs are all in a fixed overhead cost to be distributed over the amount of water used, with a negligible amount for water itself, then little will be saved by conserving water.
- Is the process adaptable to use alternate water sources, e.g., seawater, high TDS groundwater, or treated sewage water.

These questions and more were asked at each of the operations visited. Although many operations do compile water balances defining how water is used in their mine-mill complexes, very often these are not very definitive. Only some milling operations meter flows to different sections of their plant.

It was remarkable how many mine-mill complexes were visited and, despite the willingness of the staff involved, the visit was concluded without adequate data to obtain a clear picture of how water is used in the operation. Historically, mill operators were not concerned about the amount of water that they consumed, nor how much is discharged, or what became of the rest as long as there was enough water available. This was

particularly true in locations where there is no limit to the amount of water available and no restriction on the volume of effluent. The answer to pollution was, more often than not, dilution. Since effluents were also usually discharged without treatment, there was little or nothing to be saved in recycling more water. If treatment is needed before effluent can be discharged, then the mill operator may not be concerned because that is taken care of by the environmental control department, and they have their own budget.

Other operators will proudly advise that they now use, for example, 75% recycle water in their mill. Defining water use in this way is meaningless though. For example, if one operator uses 1 m^3 of water per ton of ore treated of which none is recycled, and another uses 4 tons of water per ton ore of which 75% is recycled, they both have a net use of 1 m^3 water per ton ore. One recycles 0% while the other recycles 75%, yet in terms of net water consumption and net discharge of water per ton ore treated, both situations are identical.

At any particular operation, the mill superintendent looking after the mill more often than not was not involved in its design and erection; he inherited that. He is bent on optimizing the primary functions of the mill--namely the recovery and grade of concentrate or product. To achieve this, he knows that he needs a certain pulp density, i.e., volume of water per ton solids treated. Once he has optimized these parameters, if he has extra time and energy, he may next work on using more recycle water if pressure is put on him by the services department, the environmental department, or by management to do so. If the driving force requiring recycling is a shortage in water supply, then he is likely to think in terms of the net volume of fresh water per ton used per ton of ore treated. If his motivation is to reduce the amount of effluent, then he will think in those terms. He may step by step introduce recycled water to each part of his circuit, one at a time, carefully exsmining the results each time to see whether grade or recovery has been affected. As he does so, he is likely to think in terms of percentage of his total water use that is fresh water as he competes with himself to make progress. If he wants to appear to be responding to outside pressures but is concerned about the effect of using more recycle water in his plant from the grade/recovery standpoint, he could also use more recycle water but also add more fresh water to offset its effects, and he may actually be recycling a bigger percentage of water but still be using more fresh water per ton ore treated.

It was clear at virtually every operation visited that attempts were being made to reduce the net fresh water intake. In Canada, the motivation was in reducing the volume of effluent to be treated. In South Africa and South West Africa/Namibia, the motivation lay in conserving water supply at a time of drought. In some parts of the world, there is no fresh water, and the operations have had to be based on the poor quality water available at site or even seawater.

The volume of water used in a variety of operations per ton ore is summarized in the table below. So is the cost of water used overall and per ton ore. It is noteworthy how many mill operators do not know the cost of their water unless they are located in a part of the world where water is particularly scarce or expensive.

Another factor that makes it difficult sometimes to compare operations in terms of net water consumption is the amount of water that must be removed by pumping from underground mines. This minewater may be used in the mill, thereby replacing fresh water needs. If an operation is located in a very arid climate, it does not necessarily mean that it will be short of water. RØSSING URANIUM LTD. in one of the world's driest climates has reduced their water consumption dramatically through a wide range of conservation measures because water in the Namib Desert location is scarce. At Grants, New Mexico, the Quivira Uranium Mine could be expected to be short of water, but so much groundwater needs to be pumped from the mines that most of it has to be discarded to a "creek." Near Yuma, Arizona, the Chemgold heap leaching operation is located in a country as dry as the Namib Desert, yet they have as much water as they can possibly need from the Colorado River through a deeded right.

In mine-mill operations, water of different qualities can be suitable for one part of the process but not another. For example, in complex sulfide flotation plants, recycle water is usable just about everywhere in the process except, it is found, in the Pb-Cu separation circuit. It is not known what causes the separation efficiency to suffer when recycle water is used at that point.

Several conclusions were possible based on the still rather limited spectrum of data available on water use:

- The amount of water that is needed for metallurgical operations is directly proportional to the amount available.

- The cost of water per se, although it can be a substantial amount of money, is generally a negligible factor in the overall operating cost structure of a mine-mill complex.

- The "total" cost of water used in a mine-mill complex can be much more than the cost of the water per se, when the cost of effluent treatment, scale inhibition, corrosion, and impact of water quality on metallurgical recovery are factored in.

- Some processes are very much more water efficient than others for recovery of the same metals, i.e., heap leaching vs. conventional agitation leaching.

- One of the problems in using the data gathered during this investigation for comparisons of the amount of water consumed for a given type of process is that it

has not been possible to avoid "comparing apples with oranges." For example, at one mine-mill complex, the housing for employees will be included in the water consumption data but not at another. Elsewhere, although water for housing amounts to as much as for mineral processing and is not figured into the mill fresh water needs, treated sewage is blended with recycle water, is a large factor in overall water supply, but is not shown in the net fresh water consumption figure. In some cases, water consumed in the refinery is also lumped into the water consumption data. For example, at INCO's Ontario Division, the mine-mill-smelter-refinery complex water use was given as follows:

Fresh Water Use:	
Mills, Smelter, and Refinery	53,418 m^3/d
Townsites	59,072 m^3/d
Mines	18,479 m^3/d
Reclaimed Water:	
Mill Water Recycling	98,795 m^3/d
Smelters	26,473 m^3/d
Mines	48,000 m^3/d

It is interesting to note that the domestic fresh water needs of the townsite exceed that needed for the mills, smelter, and refinery. The same applies at Vaal Reefs in South Africa. Water is used in so many different integrated operations at Copper Cliff that is was not possible to reduce it to a usable basis for comparison with, for example. the mills and smelter-refinery at Timmins.

- In some cases, the catchment area of the tailings disposal may be very large, and large quantities of water may be accumulated which augment tailings recycle water.

- Elsewhere, there may be a net evaporation loss from the tailings area, but large quantities of available minewater.

- Another factor that complicates the comparison of water recycling between one operation and another is that some mill circuits recycle more solution internally whereas others depend more on external recycle.

For example, many gold mining operations keep cyanide out of their milling circuits by milling in fresh water which is mostly recovered by a thickener installed to thicken the cyclone overflow in the classification circuit following the grind. The thickener overflow is recirculated to the front of the milling circuit whereas the thickener underflow is repulped with barren solution which contains cyanide and lime. This mill circuit has two internal water recycle loops. Yet another is the

tailings repulping step which is likely to use tailings decant solution. Internal recycle of solutions is not observed in summary tables.

- When water is expensive as for example at the Black Mountain Mine/Mill at Aggeneys, South Africa, (R1.20/m^3), there is often not much advantage to using less water as the price charged is based mainly on an overhead levy to recover the capital investment in the pipeline and the pumps and not so much for the water actually consumed. If water consumption is cut back, then the unit price simply goes up.

- In computing water needs for an operation, it can be misleading to simply look at the water requirements for a mill. Consider the following water consumption at the Black Mountain Mineral Development operation in the Northern Cape Province of South Africa where rainfall averages 4" per year, and evaporation is 65" per year:

Metallurgical Plant	4,000 m^3/d
Township	4,000 m^3/d
Road Maintenance	500 m^3/d
For Mine Backfill	1,200 m^3/d
To Shaft	800 m^3/d
Cooling, Compressors, Etc.	500 m^3/d
Annual Average	11,000 m^3/d
Summer	14,500 m^3/d

Water for metallurgical purposes in this case account for only 29-36% of the total water needs of the operations.

- Water Use in mining and milling is clearly site specific, and generalization are not appropriate.

USE OF WATER IN MINES AND MILLS

Mines

1. Potable Water Operations
2. Boiler Feedwater
3. Backfill Transport of Tailings
   Backfill Moisture Content in Place
4. Dust Control in Mine Workings and Roadways
5. Cooling Underground, Compressors
6. Dust Control at Working Faces
7. Hydraulic Power for Underground Tools
8. Underground Hydropower Generation

Mills

1. Potable Water
2. Boiler Feedwater
3. To Grinding Circuit
4. To Flotation Circuit
5. Filtration or CCD Plant Washwater
6. Tailings Repulp Water

Smelter/Refinery

1. Potable Water
2. Process Water
3. Cooling Water
4. Scrubber Water
5. Acid Plant

Townsite

1. Potable Water

ANNUAL COST OF WATER FOR MINE-MILL OPERATIONS

How much does water cost for mine-mill operations? This varies considerably from site to site obviously, and the results of a survey are summarized in the following table. Water ranges in price from "free," i.e., the cost of pumping it, to A\$1.00/m^3 or U.S.\$0.65 in Western Australia around the Kalgoorlie area where it has to be pumped about 600 Km from the nearest source. In the survey, one small operation in the California desert reported a water cost of \$3.97/m^3 reflecting the cost of hauling water.

Overall cost of water for an operation ranges from "free" to \$1.62 million/year. Although in this case the largest water bill went to the largest mine, the size of an operation has little to do with its water bill.

ANNUAL COST OF 'NEW' WATER INTAKE AT MINE-MILL OPERATIONS

Operation	Location	Facility	Volume Used m^3/Year	Unit Cost $/$m^3$	Total Cost (Annual)
Black Mountain	South Africa	Mill	1.46mm	$0.30	$ 450,000
	(Desert)	Township	1.46mm	$0.30	$ 450,000
		Mine	0.91mm	$0.30	$ 275,000
		Roads	0.20mm	$0.30	$ 60,000
		Total	4.0mm	$0.30	$1,235,000
Cortez Gold Mines	Nevada	Mill/HL	-	-	$ 5,000
Foskor	South Africa	Mill	10.2mm	$0.035	$ 255,000
Freeport Gold Co.	Nevada	Mill	2.3mm	$0.09	$ 200,000
Getty Mercur	Nevada	Mill	1.25mm	$0.20	$ 250,000
Giant Yellowknife	NW Territories	Mill	1.25mm	Free	$ 70
Hayden Hill	California	HL	0.5mm	$3.97	$ 15,000
OFS Gold-Uranium	South Africa	Mill	2.4mm	$Free	-0-
Uranium Mill	Namibia/OFS	Mill	5.5mm	$0.27	$1,485,000
East Witwatersrand	South Africa	Mill	1.26mm	$0.12 x 60%	$ 82,000
Au-U		Mine	1.52mm	$0.12 x 20%	$ 35,000
		Total	2.78mm		$ 117,000
Vaal Reefs	South Africa	Mills	10.7mm	$0.05 Ave.	$ 510,000
		Mines/Hostels	13.8mm	$0.08 Ave.	$1,100,000
		Total	24.5mm		$1,610,000
Western Mining	Kambalda, WA	Mill	1.00mm	$0.65	$ 650,000
Whim Creek	W. Australia	Mill/HL	0.39mm	$0.25	$ 100,000

SUMMARY: WATER CONSUMPTION IN MINERAL PROCESSING

Operation	Type	Location	Average Plant Capacity mtpd Ore	Gross Water Use m^3/d	Net Fresh Water Consumption m^3/d	% Recycle Water	Specific Net Fresh Water Consumption m^3/mt	Cost of Water $\$/m^3$	Cost of Water $/mt Ore	Volume of Water Discharged As Effluent m^3/d
Denison Mines Ltd.	Uranium, Acid Leach	Elliot Lake, Ontario	5,400	N/A	12,800 Mines 14,000 Mill	Macro Recycle	2.4 m^3/t Mines 2.7 m^3/t Mill 5.1 m^3/t Total	Pumping Costs	N/A	Tailings Decant n/d Discharges to Lake
Cotter Corp. Mine	Uranium Mine	Golden, CO	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2,750 m^3/d Minewater
Key Lake Mining Corp.	Uranium Mill/ Mine	Saskatchewan	720	1,500	1,440	N/A	2.0	N/A	0	50,000 m^3/d Minewater
Quivira Mining Co.	Uranium Mine/ Mill	Grants, NM	5,600 (Design)	10,700	8,244	24%	1.5	N/A	N/A	8,400 m^3/d To Tailings and Large Volume Minewater
Rossing Uranium Ltd.	Uranium Acid Leach	Swakopmund, SWA	38,000	15,500*	15,000	81%	0.39	N/A	N/A	*Excludes Townshites; Zero Discharge and Seepage
Homestake Mining-McLaughlin	Gold Leach	Knoxville, CA	3,600	N/A	N/A	N/A	N/A	N/A	N/A	Zero Discharge
Homestake Mining-Lead, SD	Gold Leach	Lead, SD	6,000	N/A	N/A	N/A	N/A	N/A	N/A	21,000 m^3/d Combined Mine/Millwater
Cominco Ltd, Con Mine	Gold Leach	Yellowknife, NWT	650	4,383	1,180	0	1.8	Pump Costs	Low	1,380 m^3/d and Catchment
Stibnite Mine	Gold Heap Leach	Yellowpine, ID	1,600 (In Season)	N/A	N/A	High	N/A	N/A	N/A	N/A
Giant Yellowknife Mines	Gold Float/Roast/ Leach	Yellowknife, NWT	810	N/A	N/A	0	N/A	Pump Costs	Low	5,000 m^3/d In Summer
Phosphate Development Corporation	Phoskorite Flotation	Phalaborwa, South Africa	50,000	85,300	50,000	41%	1.0	N/A	N/A	39,800

SUMMARY: WATER CONSUMPTION IN MINERAL PROCESSING

Operation	Type	Location	Average Plant Capacity mtpd Ore	Gross Water Use m^3/d	Net Fresh Water Consumption m^3/d	% Recycle Water	Specific Net Fresh Water Consumption m^3/mt	Cost of Water $/$m^3$	Cost of Water $/mt Ore	Volume of Water Discharged As Effluent m^3/d
Falconbridge, Strathcona Mill	Cu,Ni Flotation	Onaping, Ontario	6,500	22,000	22,000	N/A	2,90	Pump Costs	N/A	9,692 m^3 To Tails
Kidd Creek Mines Ltd.	Cu,Pb,Zn Mine	Timmins, Ontario	17,100	Potable 55 Equipt 3300 Total 3850	Potable 550	N/A	N/A	N/A	N/A	16,000 m^3/d Minewater (Includes Surface Drainage)
Kidd Creek Mill/ Smelter	Cu,Pb,Zn Mill	Timmins, Ontario	11,800	100,800	51,800	49%	4.4	Pump Cost	Low	43,560 m^3/d
Mine-Mill G Canada	Cu,Pb,Zn Flotation	Ontario	3,850	N/A	1,420 Potable 11,000 Process	88%	3.2	Pump Cost	Low	9,000 m^3/d
Mine-Mill B Canada	Cu,Pb,Zn Flotation	Eastern Canada	10,000		15,000 Subject to Change	Aiming for 100%	1.5	Pump Cost	Low	1,584 m^3/d Minewater
Mine-Mill M Canada	Cu,Pb,Zn Flotation	Ontario	2,500	8,475	2,000	76.4%	0.80	Pump Cost	Low	N/A
Black Mountain	Cu,Pb,Zn Flotation	Aggeneys, South Africa	3,300		4,000 Met. 2,000 Mine	Grind 40% Float 65%	1,21	R0.60/m^3 $0.30/$m^3$	$1.09 (Overall) $0.36 (Met.)	Zero Discharge (Evaporation Pond)
Waite-Amulet Tailings	Effluent Treatment Plant	Noranda, Quebec	--	--	329 m^3/d	N/A	--	--	--	4,320 m^3/d
Brunswick Smelting	Lead Smelter	Belledune, N.B.	65,000 TPA Lead	--	15,552	N/A	N/A	Pump Cost	Low	4,000 m^3/d
St. Joe Minerals	Zinc Pyro Refinery	Monaca, PA	N/A	N/A	6,600	Internal Recycle	N/A	Own Wells	N/A	32,700 m^3/d
Zincor SA Pty Ltd.	Zinc Electrolytic Refinery	Springs, South Africa	96,000 TPA Zinc Slab	N/A	4,000	N/A	15 m^3/t Slab	R0.23/m^3 $0.12/$m^3$	R3.34 $1.77/t	Exclusive of Mining & Township Needs
Kidd Creek Mines	Cu,Pb,Zn Mill, Smelter and Refinery	Timmins, Ontario	11,800	100,800	51,800	49%	4.4	Pump Cost	Low	43,560 m^3/d

SUMMARY: WATER CONSUMPTION IN MINERAL PROCESSING

Operation	Type	Location	Average Plant Capacity mtpd Ore	Gross Water Use m^3/d	Net Fresh Water Consumption m^3/d	% Recycle Water	Specific Net Fresh Water Consumption m^3/mt	Cost of Water $\$/m^3$	Cost of Water $/mt Ore	Volume of Water Discharged As Effluent m^3/d
INCO Ltd. Copper Cliff	Ni-Cu Mill, Smelter and Refinery	Sudbury, Ontario	100,000 TPA Nickel	226,686	53,418*	76.5%	193 m^3/t*	N/A	N/A	*Excludes Town-site Needs 59,000 m^3/d
Rustenburg Refinery	Cu,Ni,PGM Refinery	Rustenburg, Transvaal	N/A		See Below: PGM Plant - 5-60 m^3/d Base Metal Plant - 5-600 m^3/d Steam Condensate - 100 m^3/d Demin. Water - 100 m^3/d Total - 900 m^3/d	N/A	N/A	N/A	N/A	Zero Discharge
Rustenburg Platinum Mine Hostels	PGM,Cu,Ni	Rustenburg Transvaal	N/A	"	2,000 m^3/d	N/A	N/A	N/A	N/A	Sewage Effluent
ERGO	Gold, Uranium, Acid from Tails	Brakpan Transvaal	66,000	124,700	Rand Water Board 13,500 Underground H_2O 36,408	N/A N/A	0.75 m^3/t	N/A	N/A	Tailings Discharge 16,728 m^3/d Complex Discharge 12,960 m^3/d Total Effluent 29,688 m^3/d
Kloof Gold Mining Co. Ltd.	Gold-Uranium Leach	Witwatersrand	6,666	"	"	"	"	R0.23/m^3 $0.12/$m^3$	"	"
Kloof Gold Mining Co. Ltd.	Mine Hostel	Witwatersrand	"	"	0.4-0.8 m^3/min./day					
Rand Mines Milling and Mining Co.	Tailings Treatment, Au,U,Pyrite	Johannesburg	15,500	"	N/A	N/A	N/A	N/A	N/A	Zero Discharge
Vaal Reefs Expl. and Mining Co.	Gold/Uranium Leach, Pyrite Flotation	Witwatersrand	31,000	"	33,480 m^3/d	High	1.08 m^3/t	R0.12/m^3 $0.06/$m^3$	R0.109/t $0.05/t	Zero Discharge

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	Campbell Red Lake	Giant Yellowknife Mines Ltd.	Lac Minerals Doyon	Lac Minerals Macassa	Lac Minerals LTA
Climate: Rainfall (cm)	38	150	70	65	71
Snow (cm)	89	135	32	30	32
Evaporation (cm)	127	40%	29	25	39
Tons of Ore Processed: mt/d	1,000 tpd (M-C)	1,135	1,500 (M-C)	500 (M-C)	1,550 (M-C)
mt/yr	-	273,000 (CIP,VL,CIL)	-	-	-
Ave. Net New Water Intake	500 gpm	3,450 m^3/Day	91 m^3/Hr.	135 gpm	150 gpm
Net Water/Ton of Ore Processed m/t	303	3.0 m^3/t	1.5 m^3/t	1.5	0.53
Source of New Water	Stream/Lake	Stream/Lake	Minewater/Precip.	Minewater/City Water	Stream/Lake
Cost: $/Unit	-	-	-	C$.36/1,000 Gal.	-
$/Year	-	C$70/Yr.	-	-	-
Distance of Water from Plant (Km)	.5	3	2	-	3
Treatment Required	No	No	No	No	No
Quality Problem	No	No	Minor Sediment	No	No
Tailing Used for Backfill	Yes	Until '76, None Now	No	No	No
Backfill: Cement Used	Yes	Until '76, None Now	No	No	No
Water Used	-	N/A	-	-	-
Tons Tailings Solids to Backfill	280 TPD, 26% Solids	12.6% Solids	-	-	-
Tailings Pumped to Tailings Dam	660 TPD	276,000 Tons/Yr.	1,360 tpd, 50% Solids	450 tpd, 50% Solids	1,550 tpd, 50% Solids
Volume Barren Bleed Discarded	70%	181 TPD	300 m^3/Day	None	90 tpd
Contaminants in Barren	CN,Fe,Ni,Cu,Zn	As,CN,Cu,SO_4	Cu,CN,Zn,Fe	CN,Cu,Zn,Fe	Cu,CN,Zn,Fe
Barren Sent to Tailings	Yes	Yes	Yes	Yes	Yes
Calcine Washwater to Tailings	Yes	Yes	No	-	-
Decant Water from Tailings Recycled to Plant	None	None	None	None	250 gpm
Process Constraints on Tailings Water	Yes	No	No	No	Not Suitable for Reagent Make-Up
Main Contaminants in Effluent/Tailings	CN 6.136mg/l,Cu Pb 3.57mg/l,Zn 24.5mg/l	All ppm: CN 0.2,Cu 0.6 Pb .065,Zn .05,Ni .11 As .14,NH_3 6.5,S/S 1.2	CN 100ppm,Cu 5 ppm Pb 0.5ppm,Zn 12 ppm	CN 200ppm,Cu 0.5ppm Pb 0.1ppm,Cn 0.5ppm	CN 150ppm,Cu 10 ppm Pb 1ppm,Zn 5 ppm
Treatment Applied to Effluent	Carbon Columns	Settling Pool	Natural Degradation	Acidification/Aeration	Natural Degradation
Treatment of Pulp or Solution	Solution	Solution	Solution	Solution	Solution
Treatment Plant Installed	Yes	Yes	No	No	No
Fate of Treated Effluent	Stream/Lake	Stream/Lake	Stream/Lake	Stream/Lake	Stream/Lake
Volume of Effluent	-	319 Gal.(1983),303 Gal.(1984)	-	-	-
Amount of Reagent in Treated Effluent	-	Lime 520T,Ferric Sulphate 667T Cl_2 174T,Percol 35 3.1T	-	-	-
$/Unit of Reagent	-	-	-	-	-
Ratio of Cl_2/CN (ppm) for CN Destruction	-	13.5	-	-	-
Composition of Treated Effluent	CN,Cu,Pb,Zn,Hg,Ni,As,SO_4,Fe	-	ppm:CN 5,Cu 3,Zn 1,Pb 0.2	ppm:Zn 0.1,Pb 0.1,CN 10,Cu 0.1	ppm:CN 2,Cu 5,Pb 0.5,Zn 1.0
Regulatory Authority with Jurisdiction Over Effluent	Ministry of Environment	NW Territories Water Board	Ministry of Environment	Ministry of Environment	Ministry of Environment
Permit for Discharge	No	Yes	Yes	Yes	Yes
Capital Cost of Treatment Plant	C$400,000	C$2,000,000	-	-	-
Annual Operating Cost of Treatment Plant	C$60,000	C$700,000	-	-	-
When Plant Installed	1983	1980	-	-	-
Does Plant Operate Yearround	-	184 Days/Yr.	-	-	-
Does Plant Achieve Zero Discharge	No	No	No	No	No
Volume of Minewater Discharge	-	128 Million Gal. (1983)	-	-	-
Lime or NaOH for pH Control	Yes	Yes	Lime	Lime	Lime
Anti-Scaling Measures in Plant	Alchem Balls	Alchem Balls	Yes	Yes	Yes
Supplier of Anti-Scale Reagent	Alchem	Alchem	Alchem	Alchem	Alchem
Where Anti-Scale Reagent Applied	Clarifier	Clarifier	Thickener Overflow	Thickener Overflow	Thickener Overflow
Name of Anti-Scale Reagent	-	-	Alchem 961	Alchem 961	Alchem 961
Dosage	6,250 Kg/Yr.	.05 Kg/Ton	.02 Kg/Ton	.02 Kg/Ton	.04 Kg/Ton

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	Freeport Gold Company Nevada	Cortez Gold Mine Nevada	Hecla Knob Hill Mine Washington	Candelaria Mine Nerco Minerals Hawthorne, Nevada	Hayden Hill California
Climate: Rainfall (cm)	30	12.7	61	25	10.6
Snow (cm)	-	23.0	91	Minimal	33
Evaporation (cm)	40	152.0	N/A	-	153
Tons of Ore Processed: mt/d	3,200 (CIP)	1,800 (CIL)	227 (VL)	7,545 (HL)	28,000 on Heap (HL)
mt/yr	1,200,000	360,000 (HL), 1,017,000 (Total)	-	-	91,000
Ave. Net New Water Intake	-	120 gpm	86,000 gpd	200 gpm (1,090 m^3/d)	1.25 mm gpy
Net Water/Ton of Ore Processed m/t	-	0.23 m^3/t (Ave.)	1.43	0.14	0.05
Source of New Water	Wells	Wells	Wells	Wells	Precip./Stream & Lake
Cost: $/Unit	US$.40/1,000 Gal.	-	-	-	US$15/830 Gal.
$/Year	US$180,000-$200,000	U.S. $5,000	-	-	US$15,000
Distance of Water from Plant (Km)	3.2	On Site	5.6	7.2	8
Treatment Required	No	No	No	No	N/A
Quality Problem	No	No	No	Some Carbonates	N/A
Tailing Used for Backfill	No	No	Yes	N/A	N/A
Backfill: Cement Used	No	No	No	N/A	N/A
Water Used	No	N/A	Drains Off	N/A	N/A
Tons Tailings Solids to Backfill	None	N/A	40-60% Solids 55%	N/A	N/A
Tailings Pumped to Tailings Dam	100%, 45% Solids	Yes, 40% Solids	Yes, 15% Solids	N/A	N/A
Volume Barren Bleed Discarded	7,500 gpd (5 Day/Week)	Intermittent	LT 1%	N/A	N/A
Contaminants in Barren	CN, Zn, Free Ammonia	No	CN, Zn, Lime	N/A	N/A
Barren Sent to Tailings	No, to CIL	Yes	Sometimes	N/A	N/A
Calcine Washwater to Tailings	None	No	No	N/A	N/A
Decant Water from Tailings Recycled to Plant	None To Plant, Sent to Carbon Columns	416 gpm	50% for 7 Mo./Yr. (Until Dam Freezes)	N/A	N/A
Process Constraints on Tailings Water	None	No	No	N/A	N/A
Main Contaminants in Effluent/ Tailings	CN 0.01 g/l Cu 2ppm Zn 5ppm Hg 5ppm	CN, Cu, Zn, Hg, S/S	CN - 150 ppm (Winter) 5-7 ppm (Summer)	-	-
Treatment Applied to Effluent	None	No Effluent	Spray into Air	N/A	N/A
Treatment of Pulp or Solution	-	Solution	No	N/A	N/A
Treatment Plant Installed	None, Zero Disch. Dam	No	No	No	N/A
Fate of Treated Effluent	Tailings Dam	Recycle	Evaporation Pond	-	-
Volume of Effluent	333 Million Gal./Yr.	None	None	N/A	Evaporation Pond
Amount of Reagent in Treated Effluent	None	None	None	N/A	N/A
$/Unit of Reagent	-	U.S. $.78/Gal. $NaClO_6$	-	N/A	N/A
Ratio of Cl_2/CN (ppm) for CN Destruction	-	1.5 x Stiochiometric	-	N/A	1.1
Composition of Treated Effluent	-	1-2 ppm CN	-	-	-
Regulatory Authority with Jurisdiction Over Effluent	Nevada Dept. of Env. Protection	Nevada Dept. of Env. Protection	E.P.A.	Nevada Dept. of Env. Protection	Calif. Reg. Water Quality Board
Permit for Discharge	Yes	Zero Discharge Permit	Yes	Yes	Yes
Capital Cost of Treatment Plant	N/A	N/A	-	-	-
Annual Operating Cost of Treatment Plant	N/A	U.S. $.10-.12/Ton	-	N/A	N/A
When Plant Installed	N/A	N/A	N/A	N/A	N/A
Does Plant Operate Yearround	N/A	N/A	N/A	N/A	N/A
Does Plant Achieve Zero Discharge	Yes (1982-84)	Yes	-	Yes	Yes
Volume of Minewater Discharge	None	None	-	None	None
Lime or NaOH for pH Control	No	Both	No	Yes	-
Anti-Scaling Measures in Plant	None	In Strip Circuit	No	Yes	No
Supplier of Anti-Scale Reagent	N/A	Drew Chemical	-	Drew Chemical	N/A
Where Anti-Scale Reagent Applied	N/A	Strip Circuit	-	Barren Pond	-
Name of Anti-Scale Reagent	N/A	Millisperse 802	-	Millisperse 802	N/A
Dosage	-	2-5 ppm	-	50 cc/Min.	-

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	Elandsrand Gold Mining Company	Consolidated Modderfontein Mines, Ltd.	African Mining Corp. Fumani/Louis Moore Mines Gazankulu	Bracken Gold Mine Gencor Group	Leslie Gold Mine Gencor Group
Climate: Rainfall (cm)	-	60	59	60	60
Snow (cm)	-	Nil	-	-	-
Evaporation (cm)	-	-	178	High	High
Tons of Ore Processed: mt/d	7,000 (M-C)	1,333 (CIP)	160	3,300 (Gravity & M-C)	4,300 (Gravity & M-C)
mt/yr	2,100,000	480,000	48,000 CIP	996,000	1,300,000
Ave. Net New Water Intake	300 m^3/Mo. Potable	1,500 KL/Day	200 m^3/d to Mill, 1,400 m^3/d Tails	105,000 t/Mo.	127,00 t/Mo.
Net Water/Ton of Ore Processed m/t	-	1.1	1.25	1.26 m^3/t	1.17
Source of New Water	Wells	Stream/Lake	Minewater	Minewater 40%-Water Bd. 60%	Minewater 80%-Water Bd. 20%
Cost: $/Unit	-	-	-	-	-
$/Year	R24,000	-	-	R174,000	R7,000
Distance of Water from Plant (Km)	60	3	1	On Site	On Site
Treatment Required	No	Nil	No	No	No
Quality Problem	No	Nil	No	No	No
Tailing Used for Backfill	No	No	No	No	No
Backfill: Cement Used	No	No	N/A	No	No
Water Used	N/A	Nil	N/A	N/A	N/A
Tons Tailings Solids to Backfill	N/A	Nil	N/A	N/A	N/A
Tailings Pumped to Tailings Dam	10,200 t/Day, 59% Solid	51%	Yes, 10-20% Solids	56,000 t/Mo.	116,000 t/Mo.
Volume Barren Bleed Discarded	5,000 KL/Day	N/A	No	Nil	Nil
Contaminants in Barren	CN 0.015%, CAO 0.01%	N/A	N/A	N/A	N/A
Barren Sent to Tailings	No	N/A	N/A	N/A	N/A
Calcine Washwater to Tailings	No	N/A	Yes	No	N/A
Decant Water from Tailings Recycled to Plant	All	10,000 KL/M	100-300 t/Day	24,000 t/Mo.	-
Process Constraints on Tailings Water	N/A	No	No	No	No
Main Contaminants in Effluent/ Tailings	Cu, CN, Zn, SO_4 Ca, S/S	CN 0.02%, Ca 0.015%	N/A	CN 160ppm Ca 160ppm Na 120ppm S/S 20ppm SO_4 50ppm	CN 150ppm Ca 120ppm Na 140ppm S/S 20ppm SO_4 50ppm
Treatment Applied to Effluent	None	N/A	N/A	None	None
Treatment of Pulp or Solution	N/A	N/A	None	N/A	N/A
Treatment Plant Installed	N/A	No	No	No	No
Fate of Treated Effluent	No	N/A	Tailings Dam	N/A	N/A
Volume of Effluent	Tailings Dam	N/A	N/A	N/A	N/A
Amount of Reagent in Treated Effluent	N/A	N/A	N/A	N/A	N/A
$/Unit of Reagent	N/A	N/A	N/A	N/A	N/A
Ratio of Cl_2/CN (ppm) for CN Destruction	N/A	N/A	-	-	-
Composition of Treated Effluent	N/A	N/A	N/A	N/A	N/A
Regulatory Authority with Jurisdiction Over Effluent	N/A	Dept. of Env. Control Insp. of Mine	N/A	Dept. of Env. Affairs (S.A. Gov't)	Dept. of Env. Affairs
Permit for Discharge	No	-	N/A	Only for Excess Mine H_2O	For Excess Mine H_2O
Capital Cost of Treatment Plant	-	Yes	N/A	N/A	N/A
Annual Operating Cost of Treatment Plant	N/A	N/A	N/A	N/A	N/A
When Plant Installed	-	-	N/A	N/A	N/A
Does Plant Operate Yearround	N/A	N/A	-	N/A	N/A
Does Plant Achieve Zero Discharge	No	Yes	-	No	No
Volume of Minewater Discharge	-	Nil	-	Nil	Nil
Lime or NaOH for pH Control	CaO	Lime	Lime	Lime	Lime
Anti-Scaling Measures in Plant	No	Nil	No	Acid Treatment/Water Blast	Acid Treatment/Water Blast
Supplier of Anti-Scale Reagent	N/A	N/A	N/A	S.A. Explosives	S.A. Explosives
Where Anti-Scale Reagent Applied	N/A	N/A	N/A	Pump Gland/Service Water	Pump Gland/Services Water
Name of Anti-Scale Reagent	N/A	N/A	N/A	Triple Polyphosphate	Triple Polyphosphate
Dosage	-	-	-	10 Kg/Day	10 Kg/Day

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	South Roodepoort Main Reef Areas Ltd.	Western Deep Levels Gold Plant	Major Gold Plant A Witwatersrand	Major Gold Plant B Witwatersrand	Major Gold Plant C Witwatersrand
Climate: Rainfall (cm)	60	60	50	53	45
Snow (cm)	Nil	Nil	Nil	-	-
Evaporation (cm)	-	N/A	-	14	5mm Day (Summer)
Tons of Ore Processed: mt/d	1,100	12,000 (Conventional	-	-	53,000
mt/yr	312,000 (M-C)	3,600,000	9,200,000(Grav,Conv,HL,Under Const.)	3,400,000 (Grav.& M-C)	7,600,000 (CIP, M-C)
Ave. Net New Water Intake	21,000 m^3/Mo.	200,030 m^3/Mo.	9.9 Million m^3/Yr & Sewage Effl.	43,700 KL/Yr. Potable	-
Net Water/Ton of Ore Processed m/t	0.81 m^3/t	0.67 m^3/t	1.07	-	-
Source of New Water	Minewater	-	River and Well	River	Well, Minewater
Cost: $/Unit	Nil	Minewater	R0.10/m^3 Ave.	-	Water Authority
$/Year	.5	Free	-	R17,300 (Potable)	-
Distance of Water from Plant (Km)	N/A	2	4 River, 5 Well	70	-
Treatment Required	Nil	No	No	Nil	Lime
Quality Problem	No	No	No	No	Acidity, Precipitates
Tailing Used for Backfill	No	No	No	No	Yes
Backfill: Cement Used	No	No	No	-	Yes
Water Used	Nil	N/A	N/A	-	-
Tons Tailings Solids to Backfill	Nil	N/A	N/A	-	-
Tailings Pumped to Tailings Dam	26,000t/Mo,55% Solids	300,000t/Mo,50% Solids	9,300,000 t/Yr., 25-30% Solid	50% Solids	45% Solids
Volume Barren Bleed Discarded	21,300 m^3/Mo.	Nil	-	-	-
Contaminants in Barren	Cn,CaO	N/A	-	CN - Recirculated in Bleed	-
Barren Sent to Tailings	Yes	Yes	Yes	Yes	Yes
Calcine Washwater to Tailings	No	N/A	No	No	No
Decant Water from Tailings Recycled to Plant	100 KL/Mo.	100,000 m^3/Mo.	-	Yes, 30%	Yes, 20%
Process Constraints on Tailings Water	No	No	Yes, Solids and Organics	No	Yes
Main Contaminants in Effluent/ Tailings	CN 0.016% Ca 0.015%	CN 0.006% CAO 0.002%	CN,Cu,Pb,Zn,Mg,Mn As,Bi,NH_3	CN 1 ppm	Cn
Treatment Applied to Effluent	Nil	None	Yes, pH Adjusted to 9.5	Nil	None
Treatment of Pulp or Solution	N/A	N/A	Pulp	No	Pulp
Treatment Plant Installed	No	N/A	Yes	No	Yes
Fate of Treated Effluent	-	Tailings Dam	Tailing Dam	-	Tailings Dam
Volume of Effluent	N/A	N/A	Nil	Nil	Nil
Amount of Reagent in Treated Effluent	N/A	N/A	10-20 kg/CaO/ Ton of Slime	Nil	17 Kg Lime/Ton of Residue
$/Unit of Reagent	N/A	N/A	R80/Ton of CaO	N/A	R70/Ton
Ratio of Cl_2/CN (ppm) for CN Destruction	-	-	-	-	-
Composition of Treated Effluent	-	N/A	N/A	N/A	N/A
Regulatory Authority with Jurisdiction Over Effluent	Dept. of Env. Control, Insp. of Mine	Dept. of Water Affairs	Dept. of Env. Control	Min. of Environmental Affairs and Fisheries	Dept. of Env. Control
Permit for Discharge	N/A	No	Yes	Yes	Yes
Capital Cost of Treatment Plant	N/A	N/A	-	N/A	-
Annual Operating Cost of Treatment Plant	N/A	N/A	-	N/A	-
When Plant Installed	-	N/A	-	N/A	-
Does Plant Operate Yearround	-	N/A	-	N/A	-
Does Plant Achieve Zero Discharge	Yes	Yes	No	Yes	Yes
Volume of Minewater Discharge	-	5,000 l/Day	-	Nil	Nil
Lime or NaOH for pH Control	Lime	Yes	Lime	Lime	Yes
Anti-Scaling Measures in Plant	No	Physical Descaling	No	No	Yes
Supplier of Anti-Scale Reagent	N/A	N/A	N/A	N/A	-
Where Anti-Scale Reagent Applied	N/A	N/A	N/A	N/A	Boiler Feed
Name of Anti-Scale Reagent	N/A	N/A	N/A	N/A	N/A
Dosage	-	-	-	-	-

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	Kiena Gold Mine	Lac Minerals East Malactic	Noranda Hemlo Canada	FMC Paradise Peak (Design)	Mercur Gold Mine Nevada
Climate: Rainfall (cm)	89	70	-	-	18-24
Snow (cm)	-	-	-	28	80-380
Evaporation (cm)	-	39	-	120	-
Tons of Ore Processed: mt/d	-	1,700 (M-C)	2,275, (3,635 After Expansion)(CIP)	3,000	3,000 tpd (CIL)
mt/yr	400,000 (CIP)	-	-	1,000,000	-
Ave. Net New Water Intake	29 m^3/Hr.	450 U.S. gpm	21g(330)Overall,185(296)m^3/h to Mill	500 gpm	500 gpm, 330 gpm (Mill)
Net Water/Ton of Ore Processed m/t	0.64	1.44 m^3/t	1.95 (1.95)	0.91 m^3/t	0.6 m^3/t (Mill)
Source of New Water	Stream/Lake	Stream/Lake	Stream	Wells	Wells (2)
Cost: $/Unit	-	-	-	$0.33/1,000 Gal.	US$.92/1,000 Gal.
$/Year	-	-	-	$90,000/Year	US$250,000/Yr.
Distance of Water from Plant (Km)	.15	3	-	5	13
Treatment Required	No	No	No	No	None
Quality Problem	Suspended Solids	Untreated Sewage	No	No	No
Tailing Used for Backfill	Yes	No	Yes	No	N/A
Backfill: Cement Used	Yes	No	Yes	N/A	N/A
Water Used	No	No	-	N/A	N/A
Tons Tailings Solids to Backfill	45% of Feed, 70% Solids	None	-	N/A	N/A
Tailings Pumped to Tailings Dam	55% of Feed, 70% Solids	1,560, 50% Solids	-	Yes, 50%	38-40% Solid
Volume Barren Bleed Discarded	13 m^3/Hr.	270 tpd	-	No	No
Contaminants in Barren	N/A	CN, Cu, Zn, Fe	-	N/A	N/A
Barren Sent to Tailings	To CN Destruction	Yes	-	-	N/A
Calcine Washwater to Tailings	No	No	N/A	-	N/A
Decant Water from Tailings Recycled to Plant	Nil	None	None	100-200 gpm	330 gpm
Process Constraints on Tailings Water	No	No	-	No	Pump Capacity
Main Contaminants in Effluent/ Tailings	-	CN 50ppm Cu 30ppm Pb 0.3ppm Zn 10 ppm	CN,Ag,As,Sb	0.7 gpl Cn, 2 mg/l Cu 5 mg/l Zn, 5 m/l Hg	CN 0.5lb./Ton,TL 45ppm Hg 15ppm,As 0.5%
Treatment Applied to Effluent	SO_2 Condition Prior to Flotation	Natural Degradation	-	No	None
Treatment of Pulp or Solution	Pulp	Solution	Solution	-	N/A
Treatment Plant Installed	N/A	No	No	N/A	No
Fate of Treated Effluent	Stream/Lake	Stream/Lake	Stream/Lake	-	Tailing Dam
Volume of Effluent	-	-		-	---
Amount of Reagent in Treated Effluent	N/A	-	-	-	N/A
$/Unit of Reagent	-	-	-	-	-
Ratio of Cl_2/CN (ppm) for CN Destruction	N/A	-	-	-	-
Composition of Treated Effluent	-	CN 5ppm Cl 3ppm Zn 1ppm	-	-	-
Regulatory Authority with Jurisdiction Over Effluent	Ministry of the Environment	Ministry of Env.	-	Nevada State and EPA	-
Permit for Discharge	Yes	Yes	-	Yes	Board
Capital Cost of Treatment Plant	C$600,000	-	-	None	Zero Discharge
Annual Operating Cost of Treatment Plant	-	-	-	-	-
When Plant Installed	1984	-	-	-	-
Does Plant Operate Yearround	Yes	-	N/A	-	N/A
Does Plant Achieve Zero Discharge	No	No	No	Yes	Yes
Volume of Minewater Discharge	100 gpm	-	-	-	-
Lime or NaOH for pH Control	-	Lime	-	Lime	Yes
Anti-Scaling Measures in Plant	-	Yes	-	Baroid S-35	Yes
Supplier of Anti-Scale Reagent	-	Alchem	-	NL Baroid	Nalco Chemical
Where Anti-Scale Reagent Applied	-	Thickener Overflow	-	Barrens and Leach	CIL Plant
Name of Anti-Scale Reagent	-	Alchem 961	-	Barochem S-35	Nalco 8830
Dosage	-	.04 Kg/Ton	-	To 0.05 lb./t	27 Kg/Ton

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	Black Mountain Mineral Development (Pty) Ltd.	Western Mining Corp. Kambalda Nickel Operation Australia	Gimlet South Project Australia	Gold Mine A Zimbabwe	Gold Mine B Zimbabwe
Climate: Rainfall (cm)	10	16	-	110	90
Snow (cm)	-	-	-	-	Nil
Evaporation (cm)	280	Extreme	-	150	150
Tons of Ore Processed: mt/d	-	-	-	320 (CIP)	550 (Gravity & Conv.)
mt/yr	1,125,000 (Flotation)	2.5 Million	100,000 (CIL)	100,000	165,000
Ave. Net New Water Intake	4,300 m^3/d	3,400 m^3/d	323 m^3/d	-	-
Net Water/Ton of Ore Processed m.	1.4 m^3/t	1.0 m^3/t	1.2 m^3/t	-	-
Source of New Water	River	Precip.80%,Reclaimed Sewage 20%	96% Groundwater,4% Fresh	Wells,Steam,Minewater	Stream
Cost: $/Unit	R60/m^3	A$1.00/$m^3$	A$.25/Litre	-	-
$/Year	R900,000	-	A$27,000	-	-
Distance of Water from Plant (Km)	60	600	15	-	1
Treatment Required	Yes, Flocculation & Clarification	No	No	3-4	No
Quality Problem	Nil	Cl^-+500ppm tds	Saline,Mg,Si	No	No
Tailing Used for Backfill	Yes	Yes	-	N/A	No
Backfill: Cement Used	Yes	No	-	N/A	Nil
Water Used	25-80% by Wt.	Mixed at Site	-	N/A	Nil
Tons Tailings Solids to Backfill	10,000-25,000/Mo., 70-75% Solids	300,000 t/Yr.	-	-	Nil
Tailings Pumped to Tailings Dam	50,000-70,000t/Mo,40-45% Solids	80% Solids	164,000 m^3/Yr.	5,000 t/Mo.,50% Solids	13,750 t/Mo., 50% Solids
Volume Barren Bleed Discarded	N/A	1.9 t/Yr.,53% Solids	-	-	7,000 t/Mo.
Contaminants in Barren	N/A	Nil	-	-	-
Barren Sent to Tailings	N/A	N/A	-	Yes	Yes
Calcine Washwater to Tailings	N/A	N/A	-	N/A	N/A
Decant Water from Tailings Recycle to Plant	1,500 m^3/Day	36%	20% Recycle	Nil Due to High Evaporation	Nil
Process Constraints on Tailings Water	Yes, Impairs Flotation Circuits	No	-	N/A	N/A
Main Contaminants in Effluent/ Tailings	CN 15ppm,Cu 30ppm,Pb 20ppm Zn 0.5ppm,SO_4 1,400ppm	Cu,Cn,Ni,Ca,Fe	-	Ni,As,SO_4,Ca	CN,Cu,Pb,Zn,Ni,SO_4,Ca
Treatment Applied to Effluent	Oxidation in Pond	None	-	None	None
Treatment of Pulp or Solution	Solution	No	-	No	No
Treatment Plant Installed	No	No	No	No	No
Fate of Treated Effluent	Tailing Dam	Tailing Dam	-	-	-
Volume of Effluent	Nil	N/A	-	N/A	
Amount of Reagent in Treated Effluent	N/A	N/A	-	N/A	-
$/Unit of Reagent	N/A	N/A	-	-	-
Ratio of Cl_2/CN (ppm) for CN Destruction	-	N/A	-	N/A	-
Composition of Treated Effluent	N/A	-	-	-	-
Regulatory Authority with Jurisdiction Over Effluent	Dept of Water Affairs	Australian Dept. of Mines	Australian Dept. of Mines	Ministry of Mines, Ministry of Health, Nat'l Resources	Ministry of Mines, Ministry of Health, Nat'l Resources
Permit for Discharge	No	Yes	Yes	Yes	Yes
Capital Cost of Treatment Plant	N/A	N/A	-	-	-
Annual Operating Cost of Treatmer Plant	No	N/A	-	-	-
When Plant Installed	-	N/A	-	-	-
Does Plant Operate Yearround	N/A	-	-	N/A	-
Does Plant Achieve Zero Discharge	N/A	No	Maintains Low Circuit pH	-	-
Volume of Minewater Discharge	N/A	N/A	-	Minimal	Minimal
Lime or NaOH for pH Control	Both	Lime	-	Lime	Lime
Anti-Scaling Measures in Plant	N/A	None	-	No	No
Supplier of Anti-Scale Reagent	N/A	N/A	-	N/A	N/A
Where Anti-Scale Reagent Applied	N/A	-	-	N/A	N/A
Name of Anti-Scale Reagent	N/A	-	-	N/A	N/A
Dosage	-	-	-	-	-

SURVEY OF WATER IN GOLD-SILVER RECOVERY OPERATIONS

	XYZ Corp. S.E. Asia	Whim Creek Consolidated NL Australia
Climate: Rainfall (cm)	600	25
Snow (cm)	-	-
Evaporation (cm)	Low	7.6 Meters (25 ft/year)
Tons of Ore Processed: mt/d	-	-
mt/yr	100,000 (M-C)	546,000-50%HL,50%CIP
Ave. Net New Water Intake	100,000 t/Yr.	1,080 m^3/Day
Net Water/Ton of Ore Processed m/t	1.0 m^3/t	0.72
Source of New Water	Stream	Wells
Cost: $/Unit	-	A$.40/$m^3$
$/Year	US$5,000/Yr.	A$157,680/Yr.
Distance of Water from Plant (Km)	.1	19
Treatment Required	No	No
Quality Problem	None	No
Tailing Used for Backfill	No	No
Backfill: Cement Used	No	No
Water Used	N/A	N/A
Tons Tailings Solids to Backfill	N/A	N/A
Tailings Pumped to Tailings Dam	-	50/Hr., 40-50% Solids
Volume Barren Bleed Discarded	100,000 t/Yr.	N/A
Contaminants in Barren	Au,Zn,Fe,Cyanides	N/A
Barren Sent to Tailings	Yes	N/A
Calcine Washwater to Tailings	N/A	N/A
Decant Water from Tailings Recycled to Plant	None	30% Winter 10% Summer
Process Constraints on Tailings Water	No	No
Main Contaminants in Effluent/ Tailings	Cu,Zn,CN,Ca,S/S	CN 0.006%,SO_4 600ppm Ca 500ppm,Na 1,000ppm
Treatment Applied to Effluent	Chlorination	Nil
Treatment of Pulp or Solution	Pulp	N/A
Treatment Plant Installed	Yes	N/A
Fate of Treated Effluent	Tailings Dam	Tailing Dam
Volume of Effluent	140,000 m^3/Yr.	N/A
Amount of Reagent in Treated Effluent	1.5 Kg/t Calcium-Hypochlorite	N/A
$/Unit of Reagent	US$2.00/Kg	N/A
Ratio of Cl_2/CN (ppm) for CN Destruction	-	N/A
Composition of Treated Effluent	-	-
Regulatory Authority with Jurisdiction Over Effluent	Mines Dept.	State Gov't
Permit for Discharge	Yes	Yes
Capital Cost of Treatment Plant	-	-
Annual Operating Cost of Treatment Plant	-	N/A
When Plant Installed	Under Construction	N/A
Does Plant Operate Yearround	Yes	N/A
Does Plant Achieve Zero Discharge	No	No
Volume of Minewater Discharge	70 m^3/Hr.	N/A
Lime or NaOH for pH Control	Yes	Yes
Anti-Scaling Measures in Plant	None	No
Supplier of Anti-Scale Reagent	N/A	-
Where Anti-Scale Reagent Applied	-	-
Name of Anti-Scale Reagent	-	-
Dosage	-	-

CHAPTER 4

REVIEW OF WATER PROBLEMS IN MINES AND MILLS

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INTRODUCTION

All water-related problems in mines and mills stem from three main problems: Too much water; not enough of it; and/or its quality. The greatest need of all is how, at the end of the life of the mine and mill, to restore the site to be able to abandon it without a perpetual maintanance program and water treatment plant.

Mine Dewatering

Both operating mines and abandoned mines may become the subject of dewatering needs. During operations, it may be necessary to keep water out of a mine. BOSMAN (?) has pointed out that if an abandoned mine can be kept dry, then the generation of acid mine drainage may be reduced. Minewater may also be the most available water resource for a mine-mill project. Minewater may or may not be acid or contain species that interfere with metallurgical recovery if it is used as process water, but it nearly always contains species that require removal before it can be discharged without environmental damage.

Scranton Anthracite Coalfields

Water has resulted in the closure of mines in the past. The Scranton anthracite coalfield was a major producer of anthracite coal. Numerous operations worked independently and, collectively, their many pumps kept the water table below a manageable level. Until one of the operators penetrated the bed of a river and within that day, all the operations were flooded.

The Argo Tunnel

In 1943, when a lateral from the Kansas drift struck water in one of the workings served by the 21,000 foot long Argo Tunnel, four miners were drowned, and all the operations served by the tunnel were closed never to open again.

Friedensville Zinc Mine, Pennsylvania

The Friedensville Zinc Mine, Pennsylvania, is a famous wet mine that had been kept dry for many decades by giant pumps--enough to form a picturesque creek in the Saucon Valley. The closure of this mine in 1984 has resulted in the flooding of its workings, and it is highly unlikely that it will ever open again. Water pumped from this mine was so low in nutrients that they had to be added to promote aquatic life in the discharge.

West Driefontein Gold Mine

In the 1970's, one of the world's richest gold mines, West Driefontein, hit a massive underground river which flooded part of its deep underground workings, threatening the whole operation. This was solved by segregating the flooded area and plugging the shaft, allowing the rest of the mine to operate.

ERPM

All present-day operating mines on the central Witwatersrand are connected underground and, in order to keep them from flooding, water is drained from three of the deeper ones into which minewater from surrounding operations drains. The East Rand Proprietary Mines Ltd. (ERPM) is one of these. 64,000 m^3/d of acid mine drainage is first partially neutralized underground and then pumped to the surface where it is treated by HDS neutralization and discharged to the Vaal Dam drainage.

ERGO, at Brakpan on the eastern Witwatersrand, treats 1.6 million tons per month of tailings. It uses water pumped from Durban Deep and from Grootvlei, adjacent underground gold mines. This minewater, although the acidity can be neutralized with lime, contains quantities of dissolved salts which are now a cause of concern because of their contribution to TDS buildup in the Vaal Dam--the regional water supply source

serving 1.6 million inhabitants. Pressure is being exerted on the mining industry to consider desalination of this water to reduce the Vaal Dam TDS load, and an innovative new reverse osmosis process has been tested successfully at this and at the ERPM site. See the trip report in Appendix I on ERPM.

The Dolomites - West Rand

West of Johannesburg on the Witwatersrand, a large area of land is underlain by a dolomitic formation that hosts a very large regional aquifer containing good quality water. Mining operations connect the surface with deep underground gold and uranium ore deposits located in formations deep below the dolomites with the result that water drains from the dolomites into the mineworkings below. The dolomites in the immediate vicinity of the mines are dewatered, and the water is recharged to the aquifer some distance away. Associated with the change in hydrology that this has brought about, numerous large sinkholes have resulted in the dewatered areas. This has resulted in the virtual evacuation of some of the affected areas and several unfortunate sinkhole incidents. It is believed that this is a problem related to mine dewatering.

Getchell Mine, Nevada

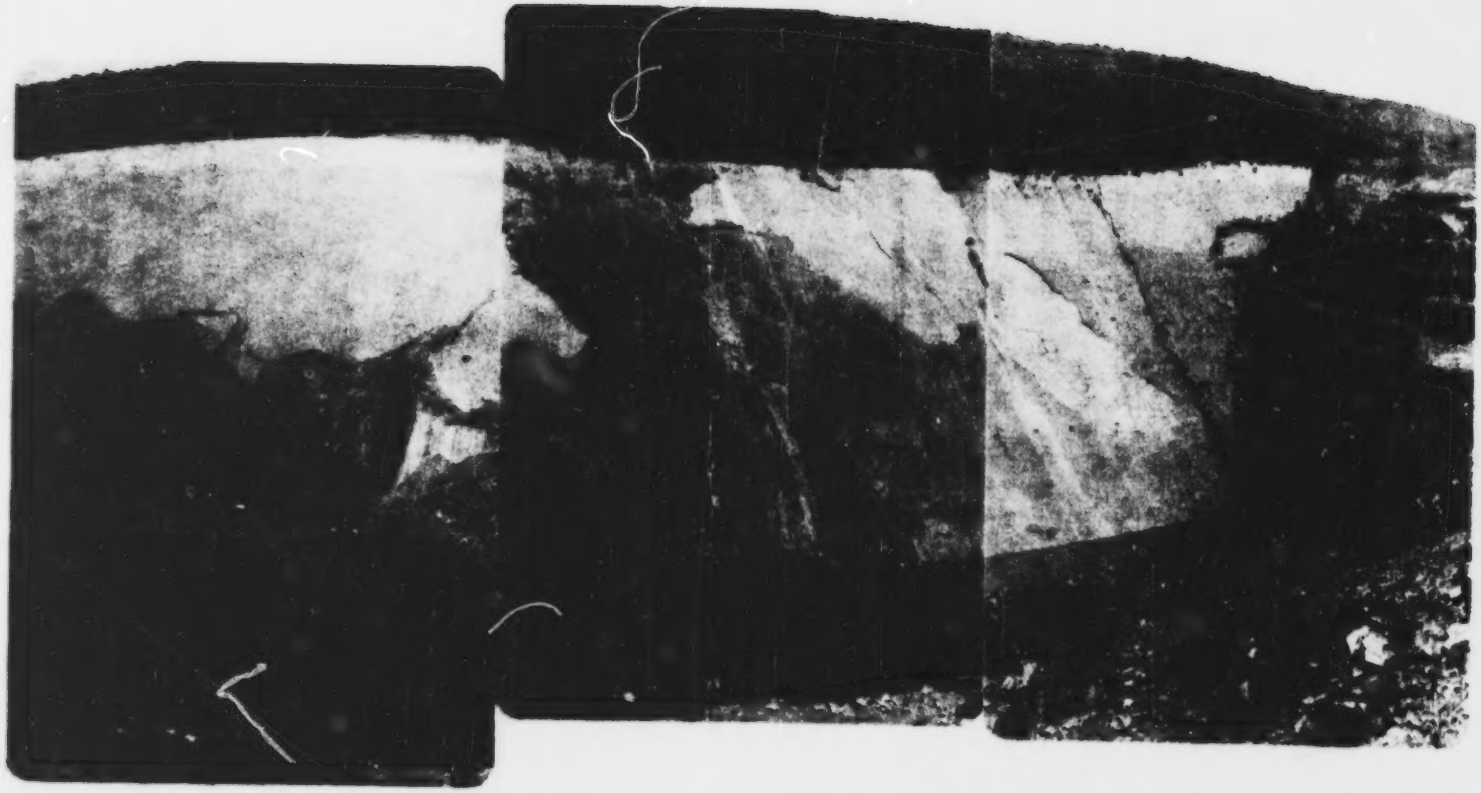
In Nevada, the abandoned open pit at the Getchell Mine near Winnemucca contained 300-400 million gallons of water which needed to be dewatered before work could resume on evaluating resources below the pit. Deep-well injection of this water was estimated to cost $2.5-3.5 million. The quality of this water made it unsuitable for direct discharge to drainage in Humbold County. The answer to this problem appears to have been to get into the agriculture business and to use the water to irrigate crops. More details on this solution might be available from:

FRM MINERALS, INC.
66 South Van Gordon Street
Lakewood, CO 80228
Eric Peterson

Gilman Mine, Colorado

The Gilman Mine in Colorado, which recently shut down after a very long life, is another example which is described in Appendix I. In this case, clean underground minewater has been segregated for direct discharge while acid mine drainage was treated by lime neutralization and settling underground before discharge to the Eagle River.

In the case of Gilman, if the mine is abandoned allowing the water level to reach a critical level, the acid minewater would overflow into the clean water reservoir, and it would all have to be treated before discharge. Also, the pump serving the clean water discharge function, being made of cast iron, would soon be corroded. The water treatment facility



BETHLEHEM MINES CORP.: PANTHER VALLEY ANTHRACITE MINE

does not have the capacity to treat the combined flow, and the owner-operator of the mine was low enough on cash for lime deliveries to have been suspended and the power company to have served notice of its intention to cut power. At the same time, the state of Colorado had named the tailings pond to which the precipitate sludge from the underground sludge is disposed of as a Superfund site.

MR. JACK MERCHANT
(303) 328-6349

Kromdraai Coal Mine

At the worked out Kromdraai Coal Mine in the Transvaal, minewater is pumped to the surface and treated by lime neutralization and HDS settling. The treated water, virtually free of metal cations except calcium, magnesium, and alkali metals, was pumped to a local military base as potable water. It soon had the army on the run. Mine water is often loaded with sulfate which has a cathartic effect.

Schullsburg Zine District

For many years, the Eagle Picher Company mined zinc and lead in Wisconsin. When the ore was depleted and the mines abandoned, the pumps were shut off, and the mines were allowed to flood. Some time later, a regional groundwater quality problem resulted in which extremely high $SO_4^=$ and Mg levels were detected in nearby wellwaters rendering them unsuitable for their traditional uses. Mine dewatering may have an impact on water quality that becomes evident only after the mining operation ceases.

PROFESSOR JAMES I. HOFFMAN
College of Letters and Science
University of Wisconsin
Oshkosh, WI 54901

Panther Valley Division, Bethlehem Mines Corp.

At their Panther Valley Division near Tamaqua, Pennsylvania, the Bethlehem Steel Company mines anthracite coal from a huge steeply dipping seam. The area was originally mined by conventional underground prining, and the workings were dewatered by large pumps installed to depths of 600 feet. The present pit is nearly 600 feet deep and extends well below the original underground workings.

Prior to neutralization of the acidic minewater, it is thoroughly aerated to drive off CO_2 as an effective means of reducing its lime consuming capacity. Minewater environments at stabilized or warm temperatures especially often host bacteria that get their energy from reactions with sulfide minerals and carbon source. These bacteria liberate CO_2 which is kept in solution as HCO_3^-. At depth, the CO_2 solubility is also increased. Consequently, when lime is added to such water, it can exhibit extremely scaling

characteristics generating excessive sludge volumes. By pre-aeration at a near neutral pH, CO_2 is displaced from solution, and both lime consumption and sludge volumes are reduced accordingly. Additional information may be objtained from:

BETHLEHEM INTERNATIONAL ENGINEERING
CORPORATION
Bethlehem, PA 18016
(215) 694-2424
Stewart T. Herman

When using minewater for metallurgical process solutions, caution should be exerted as in some cases its water chemistry may cause interferences.

Falconbridge Onaping Mine

At Falconbridge's Onaping Mine in Ontario, minewater pumped from underground is scaling and every so often, the vertical pipes carrying it must be reamed out with a special tool. Eventually, the pipes were wearing thin, and the operation was faced with a likely need of replacing the pipeline. By connecting this mine with the new adjacent Craig Mine, the new dewatering system in the adjacent shaft was able to do the job for both, thereby avoiding the need to replace the older worn out system in the Onaping shaft.

More information can be requested from:

FALCONBRIDGE ONAPING OPERATIONS
Onaping, Ontario
Canada P0M 2R0
(705) 966-3411
Mark Wiseman

Abandoned Mines

Mining, unlike forestry or agriculture, has to do with a depletable resource. Once the ore has been mined, the site is abandoned. Typical mine life may be two to twenty years, although a few have even celebrated over 100 years of operation.

One major problem facing the industry is the contamination of surface and groundwater caused by abandoned mines. These old workings may fill up with water which then seeps through fissures in the rock to eventually reach an aquifer. Alternatively, the mine may incorporate an inclined shaft which allows mine drainage to flow from a portal.

A major concern to regulators is how existing mines will be closed to prevent this from occurring.

By no means all mines generate acid water. Some are not wet at all. Others involve materials that do not contain sulfides, or the gangue is so basic that any acid generated from sulfide particles is immediately neutralized. Mine drainage can, infact, be at a relatively high alkaline pH, say 8, but this is rare. In one case, mine drainage at a high pH when it flowed into a pond to which nutrients are added in the form of treated sewage effluent from a nearby settlement, resulted in an algal bloom. In some cases, minewater must be acidified to bring down the pH in order to meet ammonia criteria for discharge.

Rooiberg Tin Mine, Transvaal

At one of the Rooiberg tin mines in the Transvaal, minewater has an almost neutral pH, but it contains 5-6 ppm F^- which is in excess of the 1.5 mg/l F limit for potable water. Since this is one of the only sources of water in the area, it has to be treated for fluoride removal before it can be rendered potable.

Copper-Molybdenum Flotation, U.S.A.

The San Manuel copper-molybdenum mine-mill complex is believed to have developed its own flotation technique for copper-molybdenum separation. Eventually, they abandoned this method and changed over to the conventional NaHS depression technique because oils, greases, and hydraulic fluids that contaminated their ore and minewater interferred with the process. Oils and hydraulic fluids in minewater at operating mines can present metallurgical problems when this water is used in the metallurgical operations.

INCO Ltd., Cu-Ni Flotation

At INCO mines and mills at some point in the past, it was found that hydraulic fluid losses underground were excessive, and that these losses resulted in metallurgical impact until the cause of high frequency hydraulic line rupturing was found and rectified.

It is beyond the scope of this report to review the techniques and equipment employed in mine dewatering or constraints on the materials used in dewatering pumps. From a water management and treatment point of view, there are some basic points to bear in mind:

1) The likelihood of corrosive or scaling waters which may require pipes and pumps of special materials.

2) Suspended solids are abrasive to pumps and pipes and are often best removed underground. Special separating thickener-clarifiers are used for this purpose and described in Chapter 12.

3) Prior to pumping acid mine water from underground, its quality may require adjustment, if necessary, to avoid scale or corrosion problems in the pipes.

4) Water pumped from underground is likely to have been in contact with oxidizing mineralized rocks and may contain undesirable contaminants. It may require treatment before it can be discharged to the environment.

5) Bacterial processes can contribute several chemical species to water including native sulfur sulfides, HCO_3, and organic species. Rotting timbers can contribute sulfo lignates, etc.

6) Acid mine drainage abatement or treatment is dealt with a length in other sections of this report.

Tailings and Wasterock Runoff and Seepage

Acid mine drainage has been identified as the greatest water-related problem facing the mining and mineral processing industry. This term includes water that is discharged from mines as well as that which drains from waste materials generated by the mining industry. A large part of this report is dedicated to acid mine drainage prevention and cure. The magnitude of the acid mine drainage problem is greater than expected. Despite the tens of millions of dollars spent on research, an economical way to prevent acid mine drainage from occurring does not seem to have been found yet.

Acid mine drainage is generated by wasterock and tailings from base metal mines, collieries, uranium operations, gold and silver mines, and even at times from rock moved in roadmaking--wherever sulfide-containing ores are mined and milled.

Open pit mine descriptions refer to strip ratios of 2:1, 5:1, 10:1, etc., and sometimes higher. That means that for each ton of ore mined, 2, 5, or 10, etc. tons of waste must be removed. If this waste contains sulfide minerals it is a likely source of acid mine drainage, and there is much more of this waste than ore. Mine waste disposal represents a problem with respect to acid mine drainage inhibition or control that has often been overlooked in the past. For example, mine waste has typically been used to build rail and roadbeds or as fill in building workshop areas and storage yards or tailings dam walls.

Many times this mine waste is ideal for the purpose, but the problem arises when it contains sulfides, possibly sulfides containing base metals. Crushed wasterock piles are a perfect trickle filter, and sulfides will oxidize rapidly yielding acid mine drainage solutions. At the Onaping mine-mill complex in Ontario, a half mile roadway built of crushed wasterock alongside a creek carrying their final tailings effluent results in the

increase of nickel levels from 0.9 to 1.0 ppm which is the permit limit for their discharge. This is only one of numerous examples that could be cited.

Tailings impoundments for modern mines can be very large and represent large catchment areas which collect precipitation. Also, the surface is exposed to the sun and air and during dry spells, it accumulates high concentrations of salts transported from the interior of the tailings by capillary action. Precipitation draining from these areas can carry high levels of dissolved solids. Water draining into the Vaal Dam after extended dry periods followed by a downpour contains a noticably higher dissolved solids content than normal when has been ascribed by KEMPE (1983) to this phenomenon.

One might have expected that as the surface leaches, the concentration of salts in the runoff would diminish with time. The capillary transport phenomenon which continuously replenishes and concentrates salts on the surface of tailings is a more powerful factor than is commonly appreciated. There are effective counter measures that can be applied, but first the problem must be recognized.

ROUSE (1984, personal communication) has observed a location where the pH of tailings remain close to neutral throughout tailings except at the surface. This is interpreted as due to vertical transportation of ferrous sulfate to the surface by capilliary action where it is oxidized to ferric sulfate + acid with a drop in pH only at the surface.

The problem acid mine drainage generation in surface runoff from tailings in South Africa with its net evaporation, generally dry climate does have remedies which are discussed later in this report as long as the problem is recognized and dealt with. In net precipitation areas, this problem is less easy to solve.

Huge wasterock piles have accumulated around the large Witwatersrand gold-uranium mines. These unquestionably are AMD generators, but the extent has still not been quantified. Elsewhere in the world, careful wasterock management, including selecting a site with soil of very low permeability, comingling acid generating waste with highly alkaline calcerous wastes or depositing acid generating waste on top of acid consuming waste, and providing provision for drainage collection can make wasterock AMD generation into a manageable problem. The extent of AMD generation by wasterock piles does not yet seem to be fully appreciated by the mining industry or regulators, although it is certainly being addressed in the revised RCRA (Resources Conservation and Recovery Act) regulations now being formulated by the U.S. Congress.

Acid mine drainage generation from tailings and wasterock can continue for centuries after these materials are lain down. The prospect of "perpetual" management, runoff collection from these sites, and treatment of the collected water certainly compounds the problem.

Quality of Available Water Supply

Mineral deposits are not made to order but are discovered wherever they may be. For a variety of reasons, they are more likely to be discovered in remote arid regions. Mills are, for economic reasons, best located adjacent or close to the ore deposits. Consequently, there is not as much leeway in the site selection of mines and mills as there might be for an oil refinery, chemical plant, or other types of industry.

Generally, it is after the mining plan has been devised, the mill and mineral process selected and pilot tested, and the decision made to go ahead that the project managers set off to find a water source. Of course, if it is known in advance that water is likely to be a limiting factor, then water supply factors are addressed early.

Apart from availability of water which is a prime concern, the quality of the available water can be a major problem.

A classic case is the western Australia gold fields around Kalgoorlie where locally available water is highly saline. Fresh water is pumped in over a distance of 600 kilometers from near Perth at a price of A$1.00/m^3.

Purchased Water

Most regional water supplies are good quality, and no problems were identified in their use when available.

River Water

The quality of river water varies greatly from river to river and from season to season.

Vaal Reefs Exploration and Mining Company uses water from the Vaal River to supplement the regional supply. This water is attractively priced. River water may carry a high suspended solids load which should be settled for application in some sections of the metallurgical process. However, it is unlikely that river water containing sediment would be a problem if used in the grinding circuit, for example. Where river water has a high suspended solids load, one way to avoid this problem is to draw from wells in alluvia and sand alongside the river which provides a means of drawing filtered water. In some parts of the world, vegetation growing along rivers can break loose, and the vegetable matter floating in the river water can present a problem at certain times of the year.

Elsewhere, river flow can fluctuate significantly between dry and wet seasons. Flash flooding can threaten water quality and pump stations. Generally, river water quality is satisfactory for metallurgical use and usually, after settling, filtration, and disinfection, also for potable use.

Rand Mines Milling and Mining Co. Ltd., in treating tailings on the outskirts of the city of Johannesburg, uses creekwater from a nearby stream. Metallurgical problems have been partially ascribed to the poor quality of this water which is impacted upstream by other industries including an abattoir. The species that cause the problem have not been identified, but the presence of an abattoir upstream implies that oxygen depletion (BOD) and fulvic acids could be investigated as a problem.

Humic acis and sulfo lignates can be generated by vegetation, timbers, and wood left to rot in water. These species can cause metallurgical problems if present.

High levels of calcium and magnesium in river water are possible, and this can result in the need for larger doses of reagents when used in flotation circuits.

Groundwater

Water quality varies dramatically from aquifer to aquifer. Some aquifers contain extremely pure water; others are so high in dissolved salts or toxic contaminants that the water is unusable for most applications.

In California, several heap leaching operations have shut down in the Mojave Desert because the only water available has such a high TDS level that it interferes with just about every phase of the recovery process, i.e., the heap permeability is reduced, sprinkler heads and pipelines scale up, activated carbon or filterpresses scale up, etc.

One operator in the Mojave successfully uses groundwater saturated with magnesium chloride for heap leaching followed by carbon adsorption of gold.

In Australia, particularly western Australia, groundwater can contain up to 100,000 mg/l TDS which, surprisingly, is used satisfactorily in some CIP operations. The salts consist largely of NaCl, and there is even an indication that gold leaching may be enhanced by the presence of chlorides at this level, but it has not been confirmed. Certainly the ore leaches extremely rapidly.

Wellwater used in conjunction with certain types of ore and reagents in some Nevada heap leaching operations has resulted in severe scaling problems. Under pressure (i.e., at depth in a well), water can dissolve very much more CO_2 than at ambient conditions. When the pH is adjusted with lime or calcium is added to solution through contact with the ore, this is likely to precipitate $CaCO_3$ as scale. This phenomenon, which is related to the wellknown carbonate-bicarbonate equilibrium which is often overlooked in the field, is a common factor in heap leaching.

Many aquifers yield very hard water, and many metallurgical operations require steam. This means that boiler feed water must be demineralized which is expensive. Scale impairs heat exchanger surfaces and must be dealt with.

High TDS groundwater may also be very corrosive, which can present an operating expense problem.

Treated Sewage Water

In some parts of the world where water is in short supply, sewage plant treated effluent has been considered as a supplementary source of water. It is believed that Chuquiquamata Division of CODELCO is one operation which is forced to use recycled sewage water in their copper recovery operation. No information is available on the impact of using this water on metallurgical recovery.

At the Climax Molybdenum Mine, a relatively small volume of sewage was discharged to the tailings pond from which water was decanted for reuse in the mill. Based on laboratory tests, sewage addition to tailings would have a deleterious effect on flotation recoveries if it were not for the addition of activated charcoal with the tailings. As long as sewage was added to the tailings impoundment at Climax, activated carbon was added. Both practices stopped at Climax when the mining camp moved to Leadville some years ago, and the present staff do not have details available.

Extensive testwork at Anglo American Research Laboratories showed that when sewage plant effluents are mixed with tailings pond decant water for use in flotation plants recovering pyrite and gold from Witwatersrand-type tailings, sometimes does and sometimes does not have an effect on recovery. Could this have something to do with sporadic bacterial or algal blooms or detergents?

Operators at the President Brand Gold Mining Company, Welkom OFS are convinced that the addition of sewage reclaim water to their flotation circuits results in deterioration in recovery sometimes, but not always. They believe that if the affected water is first used in the Peabody scrubbers to cool roaster gases and remove particulates, then it can safely be used in the flotation process. President Brand floats tailings at an acid pH.

At Vaal Reefs Exploration and Mining Co. Ltd., one of the largest gold mining complexes in the world, mine hostel sewage water after biofiltration is mixed with tailings and decanted. Use of this water in the gold and uranium leach circuits has not been found to have an impact on recovery.

Anglo Transvaal Research Laboratories in the outskirts of Johannesburg has conducted laboratory flotation tests to recover pyrite and gold using high pH flotation such as they employ at their Hartebeestfontein Gold Mining Co. and Lorraine operations. They tested

treated sewage water from two sewage plants at Stilfontein, and their preliminary results showed that the old sewage plant effluent, which employs a biofilter, did result in a serious negative impact on flotation recovery. However, effluent from the new plant, which uses an activated sludge process, does not. Quality of effluent from small town sewage treatment plants varies from day to day, and it is not at all clear yet under what conditions the sewage plant effluent will or will not interfere with flotation results. The tests, however, are highly significant in that they indicate that depending on how it is treated, sewage effluent interference in flotation of sulfide minerals and gold may be avoidable.

Witwatersrand mines and mills are labor intensive operations employing many thousands of workers. Sewage plant effluents amount to very large volume of water, typically 2,000 m^3/d from just one hostel. This water represents an attractive supplementary water resource.

In the deep Witwatersrand mines, underground cooling also consumes large quantities of water. It would be economically attractive to use sewage plant treated effluent as cooling water underground. This, in practice, presents two major problems. First, ammonia in the sewage water attacked the copper-nickel refrigeration coils. This problem can be solved by the addition of certain inhibitors to the water or by changing the coil material. Second, all water used underground in South African mines must be disinfected and rendered potable as mineworkers are accustomed to drinking it where they find it.

This is usually achieved by subjecting water to breakpoint chlorination prior to use in the mines. However, because of the ammonia content in reclaimed sewage water, chlorine consumption at 10 Cl_2:1NH_3 would be excessive. The possibility of partial chlorination as a disinfecting method and the health effects of chloramine are now being evaluated.

It is not known what species in recycled sewage water cause metallurgical problems in flotation plants. One theory is that detergents may be the cause; another is that polyelectrolytes used in the sewage treatment process are responsible.

Gencor Ltd. metallurgists refuse to consider the use of recycled sewage water anywhere near uranium operations that use solvent extraction for uranium recovery because they believe organic species in the water would interfere with SX recoveries.

In the desert southwest of the U.S.A., most copper-molybdenum operations also avoid the use of reclaimed sewage water in their metallurgical operations in nearly all cases in the belief that it interfers with recoveries in the flotation circuit.

Most operator prejudice toward the use of reclaimed sewage water is based on empirical observations. Very little information is available on what species cause the problems and what can be done to correct the problem. New sewage treatment processes are described

which certainly can reduce ammonia and phosphate to levels below which they are a problem.

Tailings Return Water

Water used in metallurgical processes or to repulp tailings can be partially recovered from tailings ponds by decantation and returned to the operaton as process water. As water is recycled in this way, dissolved salts concentrations will build up until, ultimately, they result in metallurgical interference or other problems such as scale or corrosion.

Specific metallurgical problems are discussed separately--for example, depressed loading of uranium on IX resins due to competition for loading sites with other species in the recycled water, and the use of recycled water in flotation circuits which were the two main problem areas identified.

Some operators are very successful at cleaning up their tailings water, rendering it suitable for recycle in various ways.

Typical species that build up in recycled tailings water and which interfere with metallurgical processes are:

$CaSO_4$, $CaCO_3$:	Scale.
Bacteria:	Corrosion.
Cl^-:	Corosion, especially in acid pressure reactors at elevated temperature.
$SO_4^=$, Cl^-:	Competition with uranium for IX adsorption sites.
SiO_2:	Silica fouling of filter media; fouling of IX resins; possible enhanced crud formation in SX plants.
Base Metals, Arsenic:	Interference with Merrill-Crowe precipitation of gold and silver unless purged in "barren bleed." Increased cyanide consumption. Chromate and copper in recycle solution to complex sulfide flotation ruins selectivity.
Thiosalts:	Above a certain level in effluent, these oxidise with resultant pH drop in the receiving waters; may generate S^0 in suspension which fouls IX resins and carbon pores.

Magnesium:	Believed to modify the adsorption characteristics of gold onto carbon in CIP. Forms insoluble Ca-oleate with some flotation reagents resulting in higher reagent consumption needs.
Bismuth:	Believed to affect gold loading onto carbon in CIP.
Ferrous Ions:	Interferes with gold desorption from carbon when present in solution at the time gold is adsorbed.
Oil and Grease:	Problems in gold adsorption on carbon and flotation.
Cyanide:	Problems with preg robbing in grind in some gold mill water recycle and reduced pyrite-gold recovery in some flotation circuits.

WATER PROBLEMS IN MINES

Cooling and Ventilation

Very large quantities of water are used in cooling deep Witwatersrand gold and uranium mines. The prospect of using treated sewage reclaim water for this purpose as a supplemental water source was discussed above. The main problems seem to be the ammonia content which corrodes cooling coils made of copper-nickel and the heavy demand for Cl_2 if it is used to disinfect the water prior to its use as a coolant.

This has resulted in several innovative R&D projects in South Africa.

According to the Calgon Corp., the corrosion of Cu-Ni cooling coils can be corrected by treating the coils with one of their products:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Dr. Bennett Boffardi
Russ Kirwin

Disinfection of the treated sewage water usually requires treatment with chlorine to breakpoint. However, each 1 ppm NH_3 in the water consumes at least 10 mg/l CL_2 to achieve this. Several alternatives are possible to solve this problem which is mainly one of expense and the continuous addition of chlorides to the reacted water:

1) Remove the ammonia first through a more effective biological tertiary sewage treatment process, e.g., activated sludge, Badenpho process.

2) Remove ammonia by adsorption on clinoptilolite clay as descrived in Chapter 27 on ammonia removal.

3) Determine whether partial chlorination yielding chloramines would be an effective bactericide and whether the chloramines are themselves safe contaminants.

4) Use chlorine dioxide for sterilization of the water in lieu of chlorine. ClO_2 can be generated on site using equipment provided by:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Dr. Bennett Boffardi
Russ Kirwin

FLOCCATAN (PTY) LTD.
Box 52662
Saxonwold 2132
South Africa
(011) 442-9001
Andrew Wilkinson

5) The use of silver-impregnated activated carbon is used to sterilize water in hospitals. It is not known whether the same approach could be developed for sterilization of sewage plant effluent water to render it suitable in underground cooling systems.

6) Treated sewage water might be used in a closed loop refrigeration system that does not allow it to be released underground, thereby avoiding the need for disinfection.

7) Alternative underground cooling systems such as the use of liquified or chilled compressed air might be investigated.

8) Hydraulically powered tools have been developed that are powered by the hydrostatic head from the underground workings to the surface using water as opposed to oil as the hydraulic fluid. There is the opportunity to use this also as a supplementary cooling system, and special water management and treatment measures will be needed to implement this.

Ventilation

Ventilation deals with air distribution, but it is rumored that the use of water injection into the inlet airstream is being considered as a secondary cooling method. If treated

sewage water is to be considered for this application, then it will have first to be disinfected and second, be free from detergents or foaming agents. It is not known how far along the evaluation of this concept has come or even whether it is real or not.

Underground Sludges

In underground workings, invariably large quantities of finely divided materials are caught up with water, and it has been found to be more economical to settle out these solids as sludges and to pump the water to the surface separately to reduce abrasion.

Several innovations in sludge separation and handling were encountered in passing which may be of interest.

Various designs of clarifier have been used underground. The main needs of these are that they should be reliable and operator-proof, and compact enough to be installed in confined underground workings where headroom is restricted or expensive to excavate.

The development of an improved cylindro-conical underground settler by the CSIR was sponsored by Anglo American Corporation and Gencor Ltd., the two largest South African mining houses. Subsequently, the Anglo American Corporation introduced additional modifications. The recommended standard design of the improved cylindro-conical settler was described in an internal Anglo American Research Laboratories report by MARSDEN (1980).

In the late 1950's and early 1960's, considerable attention was paid by the South African mining houses to the best and most economical procedures for settling and recovering sludge from underground mine water. Since large volumes of water needed treatment underground, the cost of flocculant was high, and it was concluded that a substantial cost savings could be realized by optimizing the balance between cost of settling the suspended solids and the cost of pumping, i.e., abrasion wear which is enhanced by the presence of solids. Studies by the National Mechanical Engineering Research Institute concluded that pumps handling water with relatively coarse particles were subject to high wear costs. Their report emphasized the advantages of vertical settlers rather than horizontal settlers for particle removal. The costs of excavations, chemical dosing, and labor all favored vertical settlers over horizontal settlers. An overflow turbidity of 340 mg/l was forecast in the "horizontal" settler compared with 25 mg/l for the vertical unit. Not only would pump wear be reduced, but gold losses in the turbidity carried in the overflow would be reduced by 90% using the vertical settler.

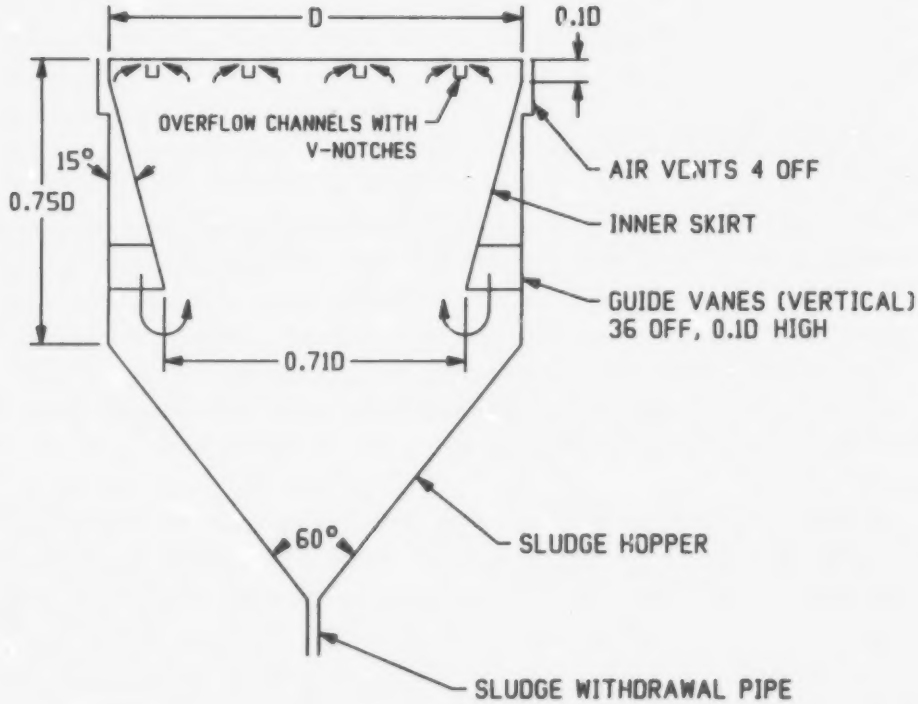
Because suspended particles in underground water are 90% smaller than 5 microns, at 5 microns particles settle at 1.6 mm/min. Settling of particles larger than 5 microns can be achieved in a settler at a rate of 2.2 m^3/m^2/day of surface area. Consequently,

flocculation was clearly essential to increase the settling rate and therefore the volume throughput.

Optimum flocculation is achieved by applying a violent mixing phase for floc formation followed by gentler agitation for floc conditioning to enlarge the floccules and increase their settling rate. There is a further need to withdraw sludge as rapidly as possible before it increases in density as well as to remove the overflow as uniformly as possible. The advocated technique was the vee notched launder developed at the Harmony Gold Mine.

In the cylindro-conical settler design, dirty inflow water enters the settler tangentially near the cylindrical side and outside an inner skirt. The concept of inclining the skirt at 15° and feeding into a small anular space which, as the water spirals downward englarges, is the concept developed by the NEMRI and CSRI. Water enters the settler rapidly and turbulently and gradually slows down with a concurrent reduction of turbulence. This enhances its hydroclynimic performance considerably. Another superior feature is the fact that the cross section of the skirt is exactly 50% of the total (outer) cylindrical cross section, hence there is no change in velocity, and consequently, a minimal increase in turbulence as the downward flow rounds the bottom of the skirt and starts moving upwards inside the skirt. Many tests undertaken on a 1.5 m Ø model at the West Driefontein Gold Mine clearly demonstrated the hydrodynamic advantages gained from maintaining an even flow.

THE AARL-CSIR SETTLER



MARSDEN (1980) recommended further improvements in the standard CSIR cylindro-conical settler design:

1) The mode of entry of the minewater to the settler was changed to minimize air entrainment.

2) Air vent passages diameter was increased to 150 mm to allow entrained air to escape without lifting water.

3) The distance upstream and condition under which flocculants are added is changed. Where a polyacrylamide flocculant, e.g., Separan MG200, is used, the more violent and instantaneous the mixing, the better. The applicable criterion is the total energy input during mixing. A certain energy quotient is required for mixing, and the more rapidly this is applied, the better. Thereafter, for the second agglomeration phase, only relatively gentle but still turbulent flow is required. A 100 meter channel at a slope of 1 in 200 allows adequate agglomeration of the floccules.

5) pH adjustment is recommended. If the discharge water is not limed, the pH value often drops to pH 2.5-3.0. Acid corrosion of pipes and pumps is high. Weld heat affected zone corrosion where pipes are welded along their seams is also likely to occur.

   If water is over limed to a pH of 9.0-10.0, calcium carbonate and/or calcium sulfate sealing of the pipe column occurs, and periodic cleaning using a spiked scouring ball or even by removing the pipes may be necessary.

   If the water pH is adjusted to 7.6-8.0, experience has shown that corrosion, including weld-heat affected corrosion, is minimized while scaling is very slow. The suggested pH is best ascertained by weekly determination of the water analysis and adjusting its Langelier index by lime additions to +0.5.

6) For general design purposes, MARSDEN (1980) recommends using an upflow velocity of 60 mm/minute (1 mm per second) for design purposes. This value can be used to calculate the daily capacity even though during peak periods actual flow velocity can be almost double. The capacities of common diameters of cylindrical settlers is given as follows:

Diameter Area			Settler Flow Rate		
m	Ft	m^2	l/s	m^3/h	Ml/d
6.1	20	29.2	29.2	105	2.52
7.9	26	49.4	49.4	178	4.27
9.1	30	65.7	65.7	237	5.68

Lamella Clarifers

If space underground is a constraint, it is very surprising that lamella clarifiers have not caught on in South African mines for underground sludge separation, provided scale in the plate pack can be controlled, and indications are that it can through optimization of the Langelier index.

Lamella-type clarifiers are offered by:

SERPAC PLATE CLAIRFIERS:

R. J. SPARGO LTD.
Post Office Box 3793
Alrode 1451
South Africa
(011) 864-2744
Telex: 420 365
Jimmy Van Der Bergh

LINATEX CORP. OF AMERICA, INC.
Stafford Spings, CT
(203) 684-2756
Robert E. Ennis
Executive Vice President

A SERPAC plate clarifier was installed on a test basis in 1983 at the Blyvooruitzicht Gold Mine on the Witwatersrand and possibly information on its effectiveness could be requested through:

RAND MINES (MINING AND SERVICES) LTD.
Post Office Box 62370
Marshalltown 2107
(011) 833-0611
Telex: 4-89671
Johann Wagner,
Consulting Civil Engineer

Another wellknown Lamella thickener-clarifier is offered by:

PARKSON CORP.
Box 408399
Fort Lauderdale, FL 33340
(305) 974-6610

Disinfection

Water used on mines as potable water requires disinfection prior to use. The disinfection process employed should destroy coliform bacteria and also viruses.

On mines in North America in which a sparate potable water system is installed, it is adequate to disinfect only the potable water supply. In large labor-intensive mines in developing nations and some developed countries such as South Africa where

labor-intensive mining methods are practiced, all water supplied to underground mines must be disinfected. The reason is that mineworkers tend to drink water wherever they find it.

Chlorination

The conventional method of water disinfection is through breakpoint chlorination as practiced at most municipal water treatment plants. These units are standard equipment supplied by such companies as:

PENNWALT CORP.
Three Parkway
Philadelphia, PA 19102
(215) 587-7183

PENNWALT CORP.
Wallace and Tiernan Div.
925 Warden Avenue
Scarborough, Ontario
Canada M1L 4C5

Small volumes of water can be chlorinated using sodium hypochlorite, but this would be too expensive for large systems.

The chemistry of disinfection is described by CULP, WESNER and CULP (1977). They point out that suspended solids in the water to be treated should be reduced to the lowest possible level prior to chlorination to assure maximum contact between remaining pathogens and the disinfectant.

At Kloof Gold Mining Co. on the Witwatersrand, the cost of chlorination of treated sewage effluent has been reduced by using a sewage treatment process that reduces ammonia levels to less than 0.5 mg/l.

Chlorine Dioxide

Chlorine dioxide is claimed to be an effective disinfectant which is not consumed by ammonia. Chlorine dioxide systems and generators are offered by:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Dr. Bennett P. Boffardi

FLOCCATAN PTY LTD.
Box 52662
Saxonwold 2132
South Africa
(011) 442-9001
Andrew Wilkinson

Iodine can be used to prevent mine absenteeism

A revolutionary water purification system that could help reduce absenteeism will soon be launched in South Africa. The system, based on Iodine disinfection, has proved to be trouble-free, inexpensive and easy to install. Developed in America by Continental Water Conditioning Corp a fully-owned subsidiary of Millipore Intertech Inc.

Miners at stope level are at times in danger of drinking contaminated water, usually resulting in periods of disabilitating sickness. While chlorination systems are the answer in urban areas where vast volume is used, the problem of the smaller consumer locations remains a problem.

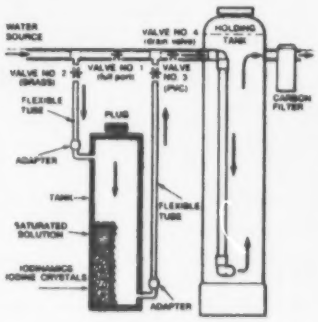
Iodine is more stable chemically than chlorine and other germicides and less affected by sunlight, PH and temperature, giving more lasting protection against micro-organisms. Iodine is less volatile, safer to work with and less noticeable to the taste than chlorine.

By using iodinators a wide spectrum of micro-organisms (see table) is destroyed.

Iodine in a saturated solution of a fixed temperature is always of consistent strength. Through a simple valving system a small portion of the saturated iodine solution is introduced into the main water stream where it is greatly diluted to a range of 0,5 part to 1,0 part per million.

An iodinamics test kit informs the user if the concentration of iodine is right. If not, then feed supply can be quickly adjusted. There are no moving parts, no need for electricity, and, unlike chlorinators, there is no need for venting, wiring or complicated maintenance.

Installation is simple. The iodinator is connected directly into the water system between the pump and storage tank. The low concentration of iodine residual must be retained in a holding tank for a few moments before use so the germicidal affect can take place. The smallest iodinator can treat approximately 730 000 *l* of water (at 0,5 ppm residual feed) before it needs refilling. When the iodinator is empty a cap is unscrewed and crystals are poured in; the whole operation taking moments.



Drawing of Iodinator shows how water moving through the system becomes saturated with iodine and is then mixed in precise quantities with the main water stream to control germs.

A problem that might face mines is dissolved or precipitated iron in the water. Dissolved iron has no effect on the function of effectiveness of the iodinator nor will iodine precipitate the dissolved iron.

If the level of precipitated iron is high enough to be visible, prefiltration is recommended to prevent plugage. If iron bacteria presents a problem then there are no remedies to apply.

Septic tanks too are safe. Bacterial demand is so great that the trace amount of iodine is quickly rendered ineffective as a germicide, leaving no harmful effects.

Hydrogen sulphide problems too can be treated. It takes about 7,4 ppm of iodine residual to offset each part per million of hydrogen sulphide.

There have been extensive tests in America to determine the long term effect on health. No claims have been made that drinking iodinated water has caused any ill effects.

Costing about R250 for the unit and some R100 a year for maintenance the system would appear to be something that the mines will look closely at with regard to their health problems.

To show how effectively iodinators can control organisms a partial list follows — the iodinator controls many other kinds of organisms as well: ■

Approximate contact time in which these potentially dangerous organisms can be controlled with an Iidinamics® Iodinator® (0,5 ppm iodine, pH 7,5, 20°-26°C)

Bacteria	Disease caused	Approximate Contact Time
Escherichia coli	Cystitis of urinary tract	50 seconds*
Salmonella typhosa P-4	Typhoid fever; gastro-enteritis	1 minute**
Salmonella typhosa P-5	Typhoid fever; gastro-enteritis	1 minute**
Salmonella typhosa P-10	Typhoid fever; gastro-enteritis	1 minute**
Salmonella paratyphi P-2	Paratyphoid fever	1 minute**
Salmonella schottmuelleri P-3	Paratyphoid fever	2 minutes**
Salmonella typhimurium P-6	Food poisoning	5 minutes**
Shigella flexneri P-7	Paradysentery	2 minutes**
Shigella dysentariae 11 P-8	Dysentery; intestinal ulcers	2 minutes**
Shigella sonnei P-9	Paradysentery	2 minutes**
Streptococcus fecalis E-40	Can be pathogenic	2 minutes**
Staphylococcus aureus	Septicemia; brain abscess; enteritis	50 seconds +
Staphylococcus epidermidis	Subacute endorcarditis	1 minute +
Virus		
Poliovirus Type 1	Polio	9 minutes*
Cysts at 1 ppm Iodine)		
Entamoeba histalytica	Severe dysentery	30 minutes*

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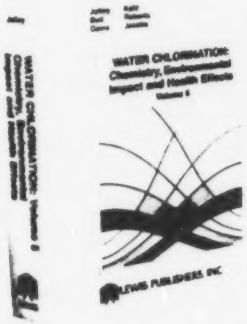
WATER CHLORINATION Vol. 5

Chemistry, Environmental Impact and Health Effects



Robert L. Jolley, Environmental Chemist, Oak Ridge National Laboratory, Oak Ridge Tennessee; **Richard J. Bull**, U.S. EPA, Cincinnati; **William P. Davis**, U.S. EPA, Gulf Breeze, Florida; **Sidney Katz**, ORNL; **Morris H. Roberts, Jr.**, College of William and Mary; and **Vivian A. Jacobs**, ORNL, Editors

NEW 85

- Comprehensive, systematic, holistic
- The significant original contributions of the last 3 years
- International in scope, encyclopedic treatment
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- Up-to-date chlorination research, developments
- Alternatives
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This work will be cited thousands of times in articles, papers, chapters, and books.

OF PRIMARY INTEREST TO: Chemists, public health scientists, water treatment specialists, activated carbon adsorption, regulators, toxicologists, utilities, libraries.

This is a comprehensive examination of the chemistry, environmental impact, and health effects of water chlorination as practiced in the areas of water treatment, wastewater disinfection, and cooling water use. *It is the peer-reviewed proceedings of the Fifth Conference on Water Chlorination held at the College of William and Mary*, Williamsburg, Virginia, June 3-8, 1984.

The volume, however, represents more than the proceedings. Organized in a systematic and holistic fashion, it can be read either as a scientific treatise or selectively as individual research and development papers. The philosophy of organization and presentation makes this work truly unique. Rigorously peer-reviewed, up-to-date research papers represent significant original contributions to research in the areas of chemistry, toxicology, environmental toxicity, and public health. In addition to chlorination, this work also deals with the chemistry and effects of alternatives (e.g., ozone, chlorine dioxide, chloramines).

There is no recent book similar to this one. Includes all the ramifications of water chlorination practice, presents the most significant research and developments that have occurred within the last three years. Also details significant new developments in epidemiology, risk assessment, toxicology, and photochemistry of oxidants.

Unique to this work also are its comprehensive treatment of chemistry, toxicology, health effects, and environmental effects.

BENEFICIAL USERS OF THIS HOLISTIC REFERENCE: People of numerous disciplines and areas of interest will find much valuable information and data in this comprehensive, peer-reviewed book. *Chemists* will especially want the sections dealing with chemistry of water chlorination, chlorine demand reaction, chloramination reaction, photochemistry of oxidants, chemical methods, reaction kinetics, alternatives to chlorination (e.g. O_3, ClO_2). *Public health* people will value *Water Chlorination 5* for risk associated with water chlorination, toxicology, mutagenicity, carcinogenicity, disinfection, water treatment. *Water treatment* people, for process chemistry, chemical effects of drinking water treatment processes. *Activated carbon adsorption*, for disinfection of drinking waters and wastewaters, chloroorganic precursors. *Regulators*, for risk, chemical effects, toxicology, health and environmental effects. *Biologists*, for environmental effects, toxicology, bioassy results, species and community changes associated with chlorinated outfalls. *Toxicologists* will use the information on toxicity, mutagenicity, carcinogenicity, risk, and disinfection. *Utilities* will need sections that cover environmental effects, bioassy results, biofouling studies, modeling, chemistry of cooling waters, chlorine minimization.

July 1985 **1,650 est. pages** **hundreds of figures, tables** **thousands of references** **ISBN 0-87371-005-3** **$69.95**

ORGANIZED IN 16 MAIN SUBJECT AREAS: More complete even than previous editions, *Water Chlorination 5* organizes 116 original chapters into 16 principal categories, as follows:

1. Water Chlorination: Basic Issues
2. Risk: The Bottom Line
3. Epidemiological Considerations
4. Carcinogenic and Mutagenic Effects
5. Toxicology of Disinfectants and Their By-Products
6. Aquatic Models and Tumor Induction
7. Environmental Effects
8. Disinfection
9. Reaction Dynamics
10. Chlorine Demand Reactions
11. Chemistry of Chloramination
12. Photochemistry of Oxidants
13. Chemical Methods
14. Drinking Water Treatment
15. Cooling Water Treatment
16. Wastewater Treatment

LEWIS PUBLISHERS, INC.
121 South Main Street
P.O. Drawer 519
Chelsea, Michigan 48118

It is known that chlorine dioxide was being considered as one possible way to disinfect treated dewage water for reuse underground, but the evaluation seemed in 1984 to be at an early stage.

Ultraviolet Light

Ultraviolet light is used in several non-mining applications as a means of disinfecting water. It is not known whether this treatment is cost-effective or whether it also destroys viruses. U-V disinfection systems are available from:

ULTRA-VIOLET PRODUCTS, INC.
5100 Walnut Grove Avenue
San Gabriel, CA 91778
(213) 285-3123
Telex: 688-461
Laurence G. Trossell
International Sales Manager

Carbon-Silver

Silver impregnated carbon is used to disinfect water used in hospitals. It is not known how effective this method would be on a massive scale for cooling water nor whether viruses would also be destroyed.

SCALE FORMATION

When water from mines and mills is recycled, especially where sulfuric acid leach processes have been employed or where levels of HCO_3^- are present and the solutions/tailings neutralized, then scale is likely to form in pumps, pipes, tanks, etc.

Acid mine drainage on the Witwatersrand is typically at pH 2.5-3.0. Neutralization with lime generates substantial gypsum and other scale-forming species in the water.

Experience has shown that by optimizing the Langelier index at around pH 6.7-7.2, that scale formation in underground pipes can be minimized.

Scale formation is a really serious problem at operations that reclaim Witwatersrand mine-mill dumps. The partially oxidized sulfides in the dump material generates sulfuric acid which reacts with lime added with the dumps when they were laid down. At ERGO, for example, dump materials are reslurried with recycle water and treated by flotation followed by sulfuric acid leaching for uranium. This all adds sulfate to the system. Finally, the tailings pH is raised followed by gold cyanidation. Ultimately, solution is decanted and returned to the plant. Also, sulfate-rich minewater is also used in the operation. The high sulfate levels combined with lime for pH adjustment results in water

with high sulfate levels. Surprisingly, the tailings reclaim water return lines are not very prone to scale formation. However, monitor water used to repulp tailings presents a scale problem; so much so that, on occasion, operators have resorted to the use of explosives to try and fracture scale on the inside of the pipe.

Scale formation is a very serious problem in many different operations. Apart from the one cited above, the following additional examples of scale problems were noted:

1) Numerous heap leaching operations experience scale formation in their pipes and even on activated carbon or in the heap which require counter measures.

2) At Brunswick Mining and at Noranda's Geco Division, acid mine drainage was neutralized with lime and the precipitate settled in a Lamella plate thickener. Although Lamella thickeners are used successfully for AMD precipitate thickening at several other operations, in these cases the system failed due to excessive gypsum scaling.

3) At Noranda Grey Eagle mines in California, gold cyanidation tailings seepage and decant water are treated by alkaline chlorination for cyanide and metals removal. Scaling in the alkaline chlorination reactors and thickener was a problem as was excessive solids formation. It is suspected that some of this might be avoided by vigorous aeration of the solution at a slightly acid pH to drive off CO_2 before lime addition. Much of the precipitate is expected to be due to $CaCO_3$ precipitation as a result of HCO_3 in the water and lime used in gold leaching even though pH control for cyanide destruction uses NaOH.

4) At Delta Manganese where high sulfate solutions are pumped from one part of the plant to another, scale in the pipes results in the need for a seven-man, full-time scale control crew who, armed with sledgehammers, have disfigured several pipes in the plant.

5) In in-situ leaching with high $CO_3^{=}$ solution into which CO_2 is injected as a lixiviant and complexing agent for uranium, the pregnant solutions on reducing the pressure prior to ion exchange become saturated with $CaCO_3$ which is kept in solution as a carbonate complex when excess CO_2 is present under pressure. Consequently, $\underline{CaCO_3}$ scaling occurs and can blind the ion exchange units unless counter measures are taken.

6) In the treatment of acid mine drainage by membrane and evaporative desalination processes, the level of ions increases steadily in the concentrate as water is recovered from the feed solution. Eventually the concentrate becomes supersaturated, and membrane fouling occurs unless counter measures are taken.

This is a limiting factor in the use of conventional membrane processes in desalination unless innovative systems are used which avoid the scale problem.

Typically, sequestering agents are used to inhibit or modify the nature of the scale formed. A typical sequestering agent is sodium hexametaphosphate. Excess sodium hexametaphosphate added converts to orthophosphate which can contribute to phosphate scale formation itself, or which can result in an effluent with a high phosphate content which can exceed effluent discharge limits itself.

Several water treatment companies specialize in scale control, and this aspect is discussed in further detail in a later chapter. Centainly, scale and scale prevention are two expensive problems facing the mining industry.

Among the expert companies that offer a scale prevention or scale control service are:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Bennett P. Boffardi
Frank Daniher

NALCO CHEMICAL COMPANY
2901 Butterfield Road
Oak Brook, IL 60521
(312) 887-7500
Robert E. Finch

DREW CHEMICAL CORP.
Idaho First Plaza
101 South Capitol Blvd.
Suite 1103
Boise, ID 83702
(203) 342-2747
Gary F. Yost

NL INDUSTRIES, INC.
NL Baroid Division
Box 1675
Houston, TX 77251
(713) 527-1100

Corrosion

Corrosion is a major problem in many mine-mill complexes. Sometimes the cost of corrosion to an operation is not well known to the operators.

MOKKEN (1977) has provided a most constructive insight into the cost to the South African mining industry of corrosion. Based on the 1978 figures of R700 million in cost of materials of construction and equipment consumed as an operating cost in 1978 and 78 million tons of ore milled as provided by MOKKEN (1984), it is clear that breakages, abrasion, and corrosion costs the South African mining industry R8.97/t ($4.00/st). Of

this amount, a goodly fraction, speculatively say R2.00-R3.00/t is surely due to corrosion. MOKKEN's 1977 paper is inserted in the chapter on corrosion. Updated information would be available from:

MR. A. H. MOKKEN
Consultant
35 Lakefield Avenue
Lakefield Beroni 1500
South Africa
(011) 542-038

As solutions are recycled to conserve water or minimize the need for effluent treatment or effluent discharge, dissolved solids build up with the result that corrosion effects can be enhanced due to the water chemistry. A prime example of this is the metallurgical plant of RØSSING URANIUM LIMITED which recycles as much water from their tailings pond as possible. The limiting factor is corrosion due to chloride level buildup at low pH.

An interesting corrosion phenomenon has also been found to occur in which bacteria in the recycle solution deposit metal-rich precipitates on the inside surface of steel pipelines carrying this water back to the plant. Galvanic action between the precipitate and the steel of the pipe results in an electron flow which is highly corrosive, and pitting corrosion results. The high TDS of recycled solution acts as an electrolyte.

At Bethlehem Mines Division, Panther Valley Division, Tamaqua, Pennsylvania, acid minewater is pumped from a 600 foot deep anthracite coal pit. Similar bacterically deposited metal precipitate scale was observed on the interior of these pumps and pipes.

At a Witwatersrand gold and uranium mine, corrosion of Cu-Ni cooling coils in a refrigeration plant serving the underground workings was due to the test use of sewage treatment plan effluent containing 10-20 ppm NH_3 which corroded the alloy.

At Rustenburg Refiners, a platinum and base metals refinery near Rustenburg, Transvaal, the regional water supply containing elevated chloride levels was delivered for metallurgical use during the drought years 1982-1983-1984. Chloride levels increased further in process waters due to solution recycling. Eventually, the stainless steel 316L autoclaves used for high temperature and pressure hydrometallurgy were found to be corroding due to the reaction with chloride at the elevated T&P, to the extent that more than one had to be replaced.

At RØSSING URANIUM LTD., when the original plant was started up, the solution distributors in the CIX plant failed because a contractor installed mild steel instead of stainless 316L bolts which were soon corroded in the acid solution.

At the uranium leach circuit in the Western Areas Gold Mining Co. plant, a rubber-lined steel agitator propeller was was installed which , due to an imperfection in the coating, soon was corroded until all that was left of the propeller was two floppy rubber bags.

MOKKEN (1977) and MARSDEN (1980) both refer to the phenomenon of "trainline" corrosion of arc welded pipe seams which manifests itself in the form of longitudinal grooves at the juncture of the weld and parent metal. This type of corrosion has plagued the mining industry for the last 35 years and is attributable to the physical metallurgy of the pipe metal adjacent to the weld. Pipes carrying acid mine drainage are particularly subject to this type of corrosion unless its corrosiveness in counteracted or the pipes treated to avoid the problem.

At the Battle Mountain operation of DUVAL CORP. where water was pumped through a polyethylene pipe, severe corrosion caused failure of a steel section of pipe that was connected to the plastic waterline. The corrosion occurred very close to the juncture of the two pipes. Information on this phenomenon could be requested from:

RICHARD A. SUMIN
General Manager
Battle Mountain Operation
Duval Corporation
Post Office Box 451
Battle Mountain, NV 89820
(702) 635-2465

All of the above are examples of corrosion related to water quality and materials selection in the mine-mill environment. There are solutions to most corrosion problems, some of which are discussed in a separate chapter on corrosion.

At the RANDOL Workshop on Water Management, an illuminating discussion of what causes corrosion and how it can be prevented or minimized was presented by Bennet P. Boffardi of CALGON CORP. whose address is shown above.

Abrasion of Pipelines

The main cause of pipeline abrasion is due to the pumping of water containing mineral particles. Removal of such particles by settling was mentioned above under - "underground sludge." By removing the suspended solids from water, abrasion costs can be dramatically reduced.

include gold price

MINING FEATURE

THE VIABILITY OF THE GOLD MINING INDUSTRY IN RELATION TO THE RATIONAL USE OF MATERIALS OF CONSTRUCTION AND PROTECTION

By A.H. Mokken*

**Consulting Metallurgist, Union Corporation, Limited.*

Introduction

Gold production in South Africa, which has already reached its tenth decade, has depended for its continuity and viability on the contribution of two major resources. These are its human resources, composed of non-whites and whites in the approximate ratio of 9 to 1, with varying degrees of skills, and by its materials resources that have provided the tools, structures and equipment for the mining, transportation and processing of vast tonnages of ore and end products.

Collectively these two facilities, aided by such essential commodities as explosives, electric power, water and processing chemicals have produced in excess of one billion ounces of fine gold, equivalent to 31 104 metric tons, and account for about 80 percent of total operating and capital costs. It is clear, therefore, that the continued viability of the industry under a stable or steadily rising gold price will, essentially, remain a function of the proper control and use of these two major cost elements.

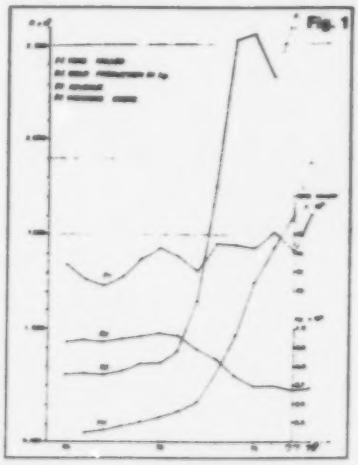
Great strides have been made by the industry in its endeavours to improve the working conditions, quality and effective utilisation of its human resources and research is continuing. However, the same cannot be said of its material resources and it is in this field, therefore, that major opportunities still await exploitation.

For many years the gold mining industry has provided opportunities for experimentation and research, opportunities that, in the field of materials selection and application have not been adequately visualized nor exploited. The main reason for this can be attributed to preoccupation with production and the absence of a facility solely concerned with materials, virtually the parallel of the many and varied facilities that cover the employment and welfare of its human resources.

The absence of such a facility in one of the country's major industries is believed to have had an adverse effect, technically and economically, on the industry as a whole and, in addition, on the productive status of manufacturing industry engaged on mining supplies.

Research, development and control in the field of materials of construction as components of plant and equipment in the mining industry should therefore not only change the direction of the cost trend of this resource, but would also bring with it an imposition of higher standards of production in manufacturing industry.

In a properly motivated environment research and development should thrive under conditions that provide ample and immediate scope for trials and tests and feed back and offer opportunity for technological innovation, a further resource that would not only contribute to the technical and economic health of the mining industry but could add to the country's exports in the form of spares and equipment, expertise and royalties.



Major Trends in the Gold Mining Industry

Figure 1 shows trends of four major elements in the productive and economic sector of the gold mining industry. Ominous signs of a narrowing of the profit gap are apparent. A redeeming feature is the increasing tonnage that is being hoisted and milled (although part of this ore came from surface dumps) and a levelling off in the fall of gold produced. This denotes continuity of operation and employment in a period when other sectors of the economy are on short time and, generally, in a depressed state.

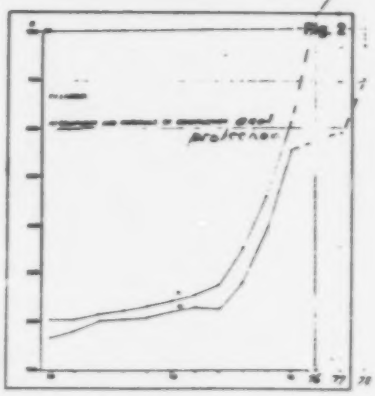
The industry has no control over the selling price of its product and the future trend of the price remains uncertain. However, continuing inflation and political and monetary uncertainties should keep attention focussed on gold and for these reasons the chances of a steady improvement in price is viewed with a measure of controlled optimism. A further favourable factor, but perhaps only to a limited degree, is the magnitude of present world industrial demand which can now absorb South Africa's entire production. United States policy in relation to its vast stock of gold will, however, remain an unpredictable influence.

Costs of the Two Major Resources

Cost trends of the two major resources namely, labour and materials of construction and equipment are depicted graphically in Figure 2. Complete figures for 1976 are not to hand and the graphs therefore cover the eleven year period from 1965 to 1975. It is interesting to note that the amounts spent on these two resources are of much the same order.

Approach to the Problem of Cost Control

In his address to mine managers at the last annual general meeting of the Association of Mine Managers of South Africa, Mr. P.A. von Wielligh, Vice President of the Chamber of Mines, uttered the following pertinent warning:



"We must do everything in our power to ensure that, in the present economic circumstances, we do not add an unnecessary cent to mine working costs."

By stressing that managers should direct their attention at the smallest monetary unit implies that they should look at detail, at the finest, smallest detail of anything that could have a bearing on overall cost. This is good counsel. By interpreting the words "must" and "everything" as an unequivocal directive to industry, let us look at alternative approaches that could be followed towards optimising or rationalising the use of materials and equipment.

A problem would arive in finding an acceptable definition of "unnecessary cent". Putting the question to a number of mine managers could result in as many different interpretations. An inherent danger is that a measure of "price consciousness" rather than "cost consciousness" could arise with possible adverse effects on true costs. For was it not John Ruskin who observed that, whatever the price of an article, there will always be someone who could make it cheaper and of lower quality? Managers' decisions should therefore be made on as broad and as realistic a base as possible and this would apply in particular to marginal mines with large low grade ore reserves.

In the field of materials of construction one could divide the base into two main levels of expertise, the one centred on intelligent observation, rationalisation and standardisation and the other aimed at maintaining a continuous and in-depth scientific and technical investigation into the behaviour, quality and composition of all forms of materials used or proposed for use in the mining industry.

The Starting Point

In attempting to get the best and most out of our spares and equipment a good starting point would be to define, in each and every case and as adequately and as accurately as possible the underlying reasons for discard or failure.

It is admitted that, in some cases, the cause of failure or need for replacement might be fairly obvious. In others a level of technical knowledge and experience would be required whilst in the remainder only careful scientific investigation might or might not reveal the cause. In any case, potential improvements in design or quality that would emerge from such an assessment should be evaluated with the object of possible incorporation in future replacement orders.

By applying this approach even to the most menial of service parts as for example a hose mender and ensuring that the replacement would be an improvement on the original article, even if only to a small degree, repetition of inferior practices would be halted. If, for example, corrosion was the reason for failure of a mild steel hose mender, should the replacement be made in one or other quality of stainless steel and in what gauge or, bearing in mind the pernicious danger of crevice corrosion, would a plastic part be better? In any case the price of the article would be higher but would the cost, on a per ton mined basis and calculated over the life of the article, not be less? A properly controlled test would be needed to give the final answer.

Major Cost Items

Figures 3, 4, 5, 6 and 7 show, in order of decreasing magnitude the five categories that account for the highest expenditure on equipment and spares in the gold mining industry. Total disbursements on these five items amounted to R127 467 479 in 1976 or about 9 percent of total industry working costs.

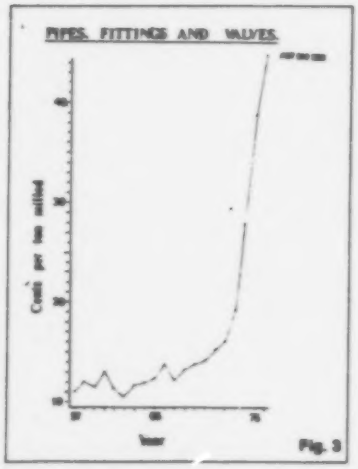


Fig. 3

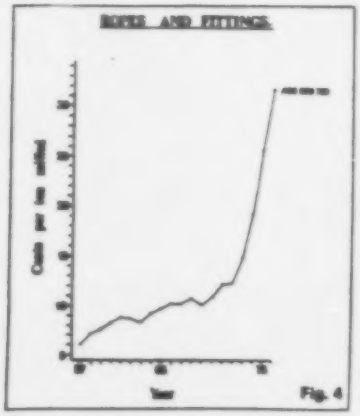
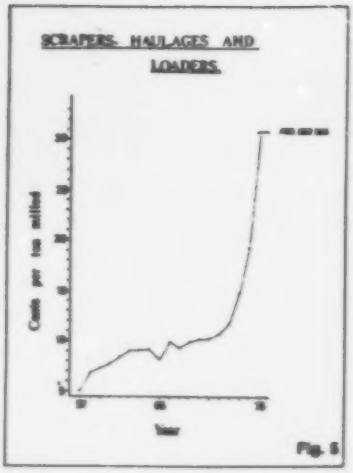


Fig. 4



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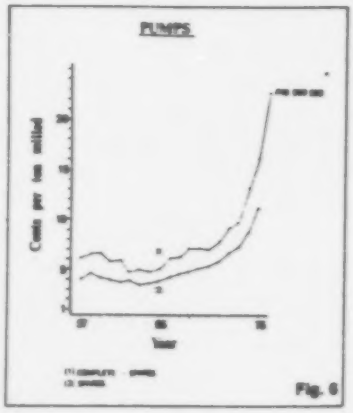

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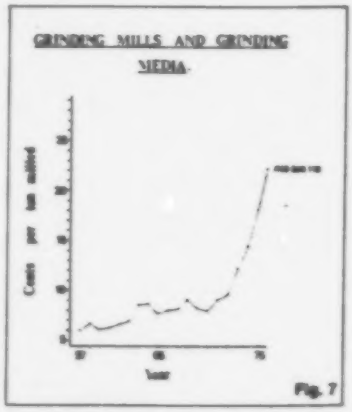

Fig. 7

It should be noted that, as the graphs were prepared for a paper presented in 1984, and date back to 1957, they are still based on short tons.

In view of the marked influence on overall costs in the form of purchases of new material, expenditure on replacement and maintenance labour and loss of production resulting from equipment failure, it is possible that in this region the highest savings could be made by a proper approach. The expertise gained in controlling these costs would naturally rub-off on other items of lesser financial importance but they would nevertheless contribute to the overall objective.

Two complementary approaches present themselves. The first would be concerned with the application of known technology. The second would involve a more fundamental study of design and material usage as, for example, proper assessment of suitability for the specific requirements to which particular materials are subjected, possible improvements in quality and design, acceptability of substitute materials or even the generation of new materials tailored to meet particular needs.

Pipes, Valves and Fittings

The destructive forces that result in the need for replacement of this equipment could be grouped under corrosion, abrasion, erosion and mechanical damage including water hammer and cavitation.

In spite of the availability of known technology developed to protect pipe lines against the above hazards, it is surprising that more use has not been made of these facilities to overcome the problems of deterioration.

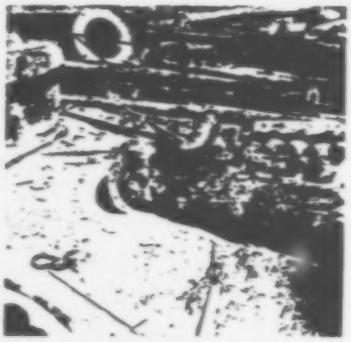

Fig. 8. *Compressed air pipe failure due to crevice corrosion.*

Figure 8 is a photograph of a 300 mm steel pipe that had to be removed from a mine shaft because of a blow-out at a badly corroded area near a flanged end. The pipe carried compressed air to the mine workings. Failure was clearly due to general external corrosion which was intensified at the point of failure by crevice corrosion underneath a pipe clamp. One can safely say that, if this pipe had been suitably protected, it would still have been in service and would have remained so for many years to come.

The cost of galvanizing the pipe would have added about 20 percent to its price, whilst a cold applied tape cover would have accounted for an additional 12 percent. If these considerations had been taken into account at the time of replacement of the corroded pipe, would they have been interpreted as unnecessary cents or as an investment with potential for capital appreciation and elimination of replacement costs?

Another cause of failure of pipe columns carrying mine waters, sometimes with catastrophic effect, is due to the phenomenon of "tramline" corrosion of submerged arc welded pipes, a type that manifests itself in the form of longitudinal grooves at the junction of weld and parent metal. This type of corrosion which has plagued the industry for the past 25 years, at least, is attributable to the physical metallurgy of the pipe metal adjacent to the weld. It was found to be more pronounced in single pass welds than in multi-pass welds which pointed to the beneficial effects of the heat treatment of subsequent passes on the previous run. Experiments have shown that a normalizing treatment

eliminates the problem but the practical difficulties of implementing this procedure on a large scale have hindered its adoption.

A similar phenomenon in the case of resistance welded pipes is manifesting itself in a new form to which the name "monorail" corrosion has been given. It occurs as a single groove in the centre of the fusion zone. Again here a normalizing treatment could be the answer.

A measure of success against corrosion of the outer walls of pipe columns has been achieved by galvanizing and by the application of a cold applied tape cover, whilst in the case of pipes handling abrasive slurries or corrosive liquids, rubber pipes or rubber lined steel pipes have proved very successful.

Attempts have been made to use plastic pipes of various qualities in both underground and surface installations. The measure of success has so far not been of a high order but it still remains an area that deserves closer attention before final unbiased conclusions are reached. Such attention can only be given by a separate facility, divorced from production pressures.

The use of stainless steel as pipe material, properly selected and used, also merits investigation as would the economics of solid drawn piping versus the fabricated form.

In the case of valves on which nearly 8 million Rand were spent in 1975, it is again surprising that in these days cast iron valves with broken wheels and bridges are still seen reaching mine scrap yards for re-conditioning. These practices undoubtedly account for the expenditure of many unnecessary cents in the form of inferior materials with a very uncertain life and augmented by the associated maintenance and replacement labour. It would not require a great deal of imagination to improve the position and, in fact, it could be a very interesting field for research and development aimed at producing an article that would not only meet the material requirements for the particular applications but that could withstand the ravages of indiscriminate operation.

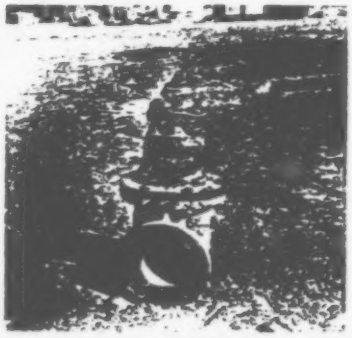

Fig. 9. *Cast iron valve with broken wheel and bridge.*

Figure 9 shows a valve with broken wheel and bridge and Figure 10 shows an inscription that does not really meet the literary standards of many underground users.

Ropes and Fittings

In the interests of safety of men and equipment, close attention is given by the industry to the condition, quality and performance of winding ropes. Ropes are discarded for a number of reasons. These could include a fixed service life, inferior mechanical properties, rope distortion, corrosion, broken wires

Fig. 10. *Inscriptions that do not meet the literary standards of many underground workers.*

due to fatigue or mechanical damage, reduction in length due to the removal of statutory test pieces and accidental overload.

In spite of the high cost of ropes to the industry, but always bearing in mind the need for utmost caution, this would still appear to be an area where scientific research into the many aspects of rope manufacture, supported by comprehensive feed-back from industry, could lead to improvements that would not only benefit the local mining industry but carry its impact far beyond the country's borders.

It is estimated that scraper ropes account for about 60 to 70 percent of total rope costs. These ropes are exposed to extremes of abrasion, corrosion and stress under fatigue loading conditions and the question may well be asked whether protection of the ropes by a wear resistant coating would not merit investigation.

Scrapers, Haulages and Loaders
Grinding Mills and Grinding Media

These two categories are grouped together for the reason that a high percentage of replacement cost is due to the common factor of abrasive wear aided by corrosion.

A number of abrasive resistant alloys are used by the mines normally designated by name only as for example manganese steel, chrome steel, white iron, but never qualified by an exact specification nor controlled by adequate test. It is gratifying to note, however, that the position is changing and that the accent will be placed, increasingly, on material conforming to definite specifications. Only in this manner will it be possible to gather accurate information on the behaviour, performance and true cost of particular qualities of steel and iron alloys. These could then form the basis for comparison with the performance of new alloys under test.

The Republic is not a world leader in the production and supply of abrasion resistant alloys to meet the requirements of the worlds' mining industry. It could well be when viewed against the productive capacity of the country's steel casting industry which is about half that in the United Kingdom and in France, its vast resources of chromium and vanadium, and lesser resources of nickel and zirconium and, above all, a large facility for immediate and continuous testing of new alloys under highly abrasive conditions. The products of such research and development, coupled with sophisticated market research and assisted by generous tax concessions could generate a new resource that would create job opportunities, contribute to the gross domestic product and add to foreign exchange earnings. Quality of product and reliability of delivery would, however, be of paramount importance and would require the necessary supporting facilities.

Pumps

It is interesting to note that the amount spent annually on pumps and spares is a little below that for grinding mills and grinding media. It is true that large quantities of water of varying pH and solids in suspension are pumped daily, the ratio of water pumped to tons milled being of the order of 3 to 1. In addition all ore mined is eventually handled by pumps serving the ore processing stages in reduction plants. Much success has been achieved by the use of rubber in pumps handling ore slurries and favourable reports on the use of stainless steel for multi-stage pumps have been forthcoming. This observation seems to point to other reasons for the high pump costs, and exposes a field that merits closer attention.

It is confidently believed that substantial savings could be effected by research into pump design, materials of construction and standards of operation. Because of the universal need for pumps in a multitude of applications such research could become of great economic value.

Standardisation and Quality Control

The original emphasis on the need for standardisation in industry is attributed to a City of London iron merchant, H.J. Shelton, who wrote to the Times in 1895 complaining that rolled steel girders were being imported into Britain from Belgium and Germany because there was "too much individualism in this country where collective action would be economically advantageous". He stated further: "In this country no two professional men are agreed upon the size and weight of girders to employ for given work and the British Steel manufacturer is everlastingly changing his rolls or appliances at a greatly increased cost of manufacture to meet the irregular and unscientific requirements of professional architects and engineers".

It is interesting to note that, as a result of this complaint, an Engineering Standards Committee was set up in 1902. One of its actions was the reduction in the number of tramway rail sections from 75 to 5.

In South Africa, at about this time and following the discovery of gold, there was an urgent need for mining equipment which was imported from many different sources. The chaos that ensued called for a measure of standardisation and, as a result, the Transvaal Chamber of Mines appointed in 1905 its first Standardisation Committee to consider standardisation of machinery and other materials used by the industry. The committee seemed to have functioned for only a few years and was followed by an organisation known as the Committee for Standardization of Specifications for South African Materials.

It was only in 1946 when, owing to rapid post war industrialisation and a call for more organised testing facilities that the present South African Bureau of Standards came into being. A large piece of polished gold bearing rock, conspicuously placed in the portals of the present new building of the Bureau in Pretoria, symbolizes the fact that the needs of the mining industry have led to the development of standardisation in South Africa.

The Republic's gold mining industry consists at present of 41 producing mines, all still actively engaged on the extraction of gold (and in certain cases uranium) from the

milling and processing of about 76 million tons of ore annually.

In 1975 the industry earned R2 563 497 000, mostly in the form of foreign exchange and paid to the State in tax and lease payments R789 897 000. In addition, its dividend payments amounted to R522 867 200 and disbursements covering its cost of production, R1 243 854 000.

From these figures it is readily seen that the industry is a major pillar in the country's economic structure and therefore its continued existence and viability remain of vital importance. As explained before, the industry has no or very little control over the price of its product but it has a major hold on working costs, a hold which, when properly managed could still exercise a further profound influence on the standards of technology and quality of manufacture in the field of its overall activities.

The Republic's goldfields, as existing in the Transvaal and Orange Free State, are unique and of relatively uniform character. Mines working the deposit are, essentially, all doing the same thing. However, over the years, with advancing knowledge and facilities, systems and standards have changed and the newer mines have been able to incorporate the improved technology in their designs. In spite of this there are still large areas of common interest amongst the older and newer mines and these are therefore areas that could be exploited to common advantage. It should be observed here that, contrary to so many mining and industrial undertakings, the gold mines are not in competition with each other and therefore any technological advancement becomes available to the industry as a whole. In this way new standards are created which, in turn, become the bases for further development.

The mining industry in its present state could still benefit appreciably from the generation and adoption of standards on a group or industry basis. Such rationalisation should lead to lower manufacturing costs and to keener competition amongst suppliers.

It should be emphasized that standards should never be static. During the currency of their application they should be subjected to the closest scrutiny with a view to incorporating any new ideas and improvements when the designs are next reviewed. Economic factors must override resistance to change. To achieve such a condition in the mining industry would require a large measure of open mindedness and enthusiasm, motivated by enlightened leadership.

The development and maintenance of standards can only be successful if adequate facilities for control are established to exercise a continuing monitoring authority. Such a facility is available at the South African Bureau of Standards for articles carrying the Bureau mark. For the remainder the industry should establish its own facilities.

Design of Plant and Equipment

The word "design" as generally understood or used in the mining industry refers to the manifestation of an engineering concept in diagrammatic form. Important features of such a manifestation are shape, dimension, materials of construction and indicated standards of workmanship. The design could be a repetition of an existing facility or item of equipment with perhaps minor modifications or it could represent the embodiment in diagrammatic form of an entirely new concept either in its proto-type or final shape.

Undoubtedly the most important elements in the design are the materials of construction that have been selected to form the basis or framework and the functional parts of the equipment together with the manner of their use. Depending on the technical standards of selection and design the resultant economic and functional performance of the facility could be favourable or it could be unfavourable or even dangerous and remain so, knowingly or sometimes unknowingly, for many years of operation.

To achieve high standards of economic and functional performance requires a wide and thorough knowledge of engineering fundamentals and of the composition and behavioural characteristics of a large number of elemental and composite materials. In the mining industry these include reinforced concrete, ceramics, glasses, rubber, plastics, wood, mild steel, high carbon steel, low alloy steel, high alloy steels, stainless steels, nickel-chrome alloys, copper, brasses, bronzes, titanium, aluminium and various protective and insulating coatings in the form of paints, tapes, metals, and so on.

In the absence of a facility that could provide expert advice on the selection, use and protection of materials of construction, designs which are based on a limited knowledge of these requirements can only be of average standard. In addition to hidden costs, such a limited approach harbours a further danger by allowing the seeds of potential failure and destruction to be implanted in design details, weaknesses that could manifest themselves in breakdown of a minor nature or result in catastrophic failures with high cost to plant, production and human lives.

To quote an example outside the mining industry it will be remembered that the catastrophic failure of two Comet jets was traced back to a design weakness that promoted metal failure.

As a protection against potential break down of operating equipment recourse has been taken to the provision of stand-by equipment. Whilst this is admissible in certain cases of important equipment requiring regular inspection, the provision could be a wasteful expenditure of capital when the cause of such breakdown can be traced to design and materials inadequacies.

Although many examples could be given in support of the above observations, the following single instance should be of interest, as it illustrates the unnecessary expenditure of capital on equipment designed on the basis of an inadequate knowledge of the properties and fabrication of stainless steels.

The example concerns an investigation, presently being conducted, into the design of rotary filters in stainless steel for the filtration of acid slurries. The investigation has revealed that, in one particular instance at least, the design is an exact duplicate of the mild steel counterparts used for the filtration of alkaline gold plant slurries. This approach has ignored the superior qualities of stainless steel and fabricating techniques that promote its adoption.

A redesign of the agitator mechanism which has now been completed and costed has resulted in a technically more sophisticated structure that could be made and supplied at a price about three quarters of that of the old design.

Figure 11 and 12 show one detail of the design in which a costly and vulnerable procedure is replaced by a neatly fabricated shape.

Corrosion

Of all the deleterious influences to which the industry's materials resources are exposed, corrosion is perhaps the most pernicious and the most wide spread. It is a destructive force that manifests itself in a variety of forms with effects either readily noticeable, as for example general superficial corrosion of a metal surface, or completely hidden from sight as, for example, crevice corrosion in which the end result could be sudden or even catastrophic failure.

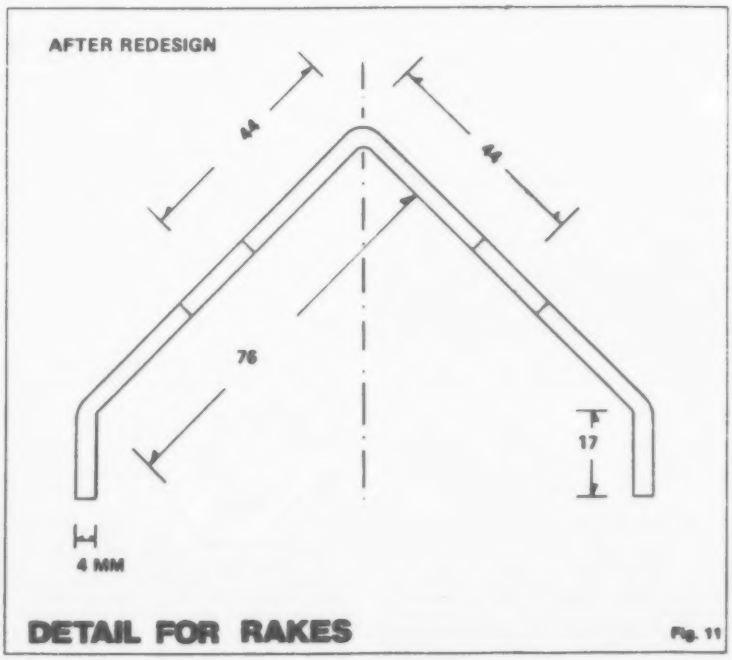

Fig. 11

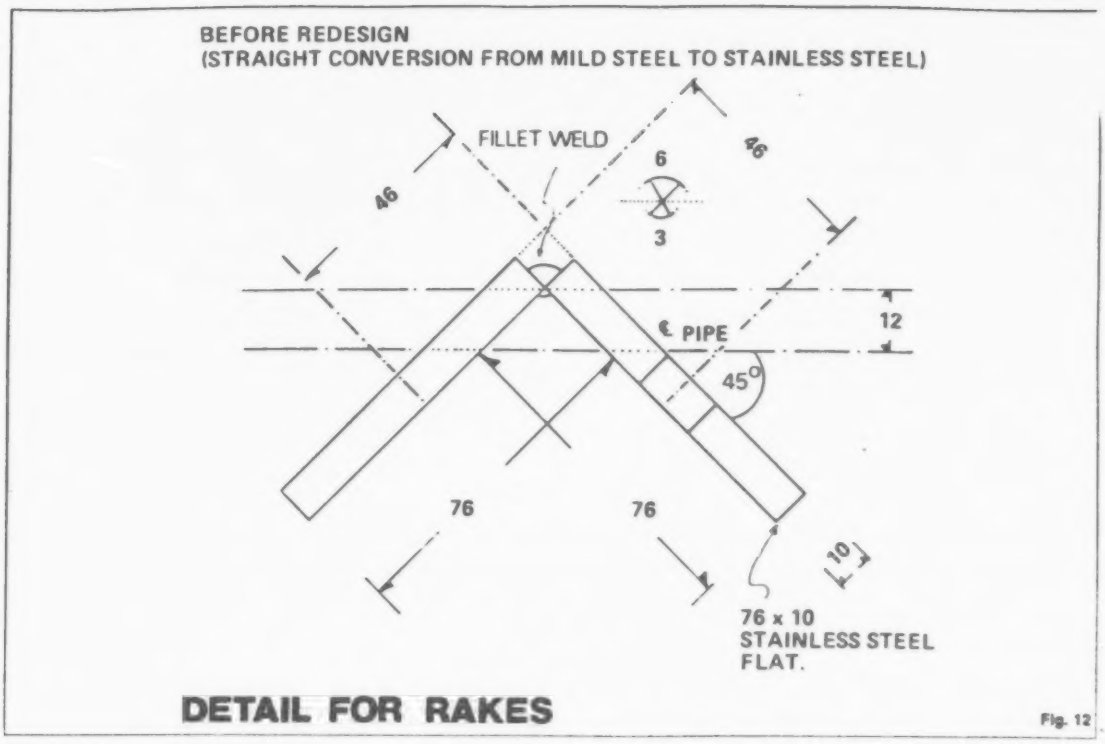

Fig. 12

The scientific basis of corrosion in its various forms is well known and well documented. Its proper understanding, however, calls for an adequate knowledge of physical metallurgy and electrochemistry. For this knowledge to be of practical value in corrosion control, extension into the field of protection of equipment and engineering design would be important and essential prerequisites.

From a fair knowledge of conditions in the mining industry it is believed that many millions of unnecessary cents are still added to costs, annually, as a result of unchecked corrosion. Although, in certain instances, steps have been taken to apply a measure of consultative and supervisory control towards corrosion prevention, the need for a facility within the industry to supplement this service still remains an urgent necessity.

Conclusion

In a matter of only seven years gold production in South Africa will have reached its 100th year. The chances that this will in fact eventuate and, hopefully, extend well into the second century, will depend on the trend of the gold price, the cost structure and the gold, in situ, that will become available in terms of these controlling factors.

Whereas the gold price will remain an unpredictable entity, the success in maintaining the viability of the industry will therefore depend largely on the effective and productive use of its two major operating resources, namely its human and its materials and equipment resources. At present the costs of these resources are of much the same order, each being about R600 million per annum.

It is firmly believed that substantial improvements in costs can still be achieved by sophistication in the choice and utilisation of materials of construction and that, to this end, facilities should be established in parallel with those already in existence for the industry's human resources. From a reasonably fair knowledge of the present status of the industry it is estimated that savings of from 10 to 20 percent could, with time, be effected. In 1976 money terms this would average about R95 million per annum or R1,25 per ton milled. This saving would be exclusive of further savings in the associated maintenance and replacement labour.

By applying the approach of investigating, in each and every case, the reason for failure or discard, major changes in materials use and equipment design are visualized. An excellent example of this approach was the development by the South African Railways of the Scheffel bogie. This achievement, which no doubt will have far-reaching effects, was the result of two objectives, the one aimed at increasing the speed of trains and the other at eliminating the excessive wear on truck wheels that was experienced on iron ore trucks used on the Sishen-Port Elizabeth line.

A further example, but based on slightly different objectives, is what might be described as the down-to-earth spin-off of materials research in the aerospace programme. The need for a certain quality of stainless steel resulted in the development of an alloy with hardness, surface qualities and corrosion resistance that, fortuitously, became ideal for bone implants.

It is not inconceivable that the gold mining industry, bent on similar objectives and provided with a large field for the immediate testing of its innovations, could not come up with improvements that not only would benefit the industry itself but could spill over into mining and industry in general and even augment the country's exports. In this way a diminishing resource could generate a new resource in the form of technological innovation, charged with massive potential.

Greater sophistication in underground mining machinery and the processing of ores, as for example uranium, has called for superior materials and techniques to meet the new and, in certain cases, exacting requirements. It is becoming increasingly realised that no matter the merits of a new concept in the form of a machine or process, its translation into practice could be seriously hampered or even prevented by poor design or choice of materials of construction. In the case of new developments in process technology it is important that these should be supplemented, at laboratory and pilot plant stage, by a materials engineering facility, to take care of materials needs. Failure to do this could lead to costly repairs and replacements with long delays and serious loss of production. Without such a facility the approach to design of plant and equipment can never be regarded as truly professional.

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WATER PROBLEMS IN MINERAL PROCESSING AND EXTRACTIVE METALLURGY

Numerous water-related problems are encountered in mineral processing and extractive metallurgy. Many have good solutions and so probably, "water-related challenges" might possibly be a more appropriate terminology. Several of these have been mentioned already. The most prominent water-related problems are those which result in a reduced recovery or selectivity of recovery due to the presence of contaminants in water. The contaminants may be present in the water supply or get into the process water due to contact with the ore, and in this latter case, may be enhanced due to water recycling.

Mineral Processing

Mineral processing refers to such processes as gravity concentration, flotation, wet magnetic separation, etc., i.e., mainly the physical separation processes.

Examples of water-related problems are:

- Reduced efficiency of flotation recovery of sulfide minerals at Rustenburg area platinum mines reputed to be due to high magnesium and other salts in the process water.

- The need to segregate water from one circuit to another when depressants are used, e.g., hexavalent chromium for galena depression in Pb-Cu separation. If the Cr^{VI} containing water is not segregated and finds it way into water recycled to the primary flotation process, then it will result in recovery losses in the primary bulk float stage.

- Oils, greases, and hydraulic fluids discharged or lost through leaks underground during mining can get into water and interfere in flotation recovery.

- Discharge of tailings from Umgaba sands ilmenite and rutile heavy mineral recovery operation in South Africa in the 1960's resulted in clay mineral pollution of bathing beaches.

- The need for additional gangue depressant doses when Ca and Mg levels in hard water build up as at Palabora Mining Company, Phalaborwa, South Africa, where copper and foskorite minerals are recovered from a carbonatite ore.

- Fluorspar flotation recovery is sensitive to water quality and deteriorates when water is recycled.

- Grinding and flotation circuits can generate thiosalts and thiosulfate which, if present in high enough quantities, makes it almost impossible to meet pH limits in receiving waters.

- When mine backfill using cement is used, calcium and other species in mine drainage can interfere with flotation recovery if used in the process water.

- In gravity concentration of gold (placer mining), recycled water can build up suspended solids levels and root fragments which can interfere with the recovery process.

- Sewage (either treated or untreated), if discharged into mill tailings and recycled with decant water to flotation plants, may or may not cause a recovery problem.

- Recycled water in complex sulfide flotation plants can build up dissolved metal levels due to oxidation of fine fragments of ore in the water or due to the presence of oxide ore in the feed. Dissolved copper in recycle solution cause a loss in selectivity in these circuits.

- Several reagents which, from a metallurgical point of view, are preferred may require special conditions or have to be avoided because of environmental problems when effluents are discharged (e.g., SO_2, NH_4OH, hexavalent chromium), or because of problems related to the emotional type of "environmentalist" (e.g., cyanide).

Extractive Metallurgy

A sampling of water-related challenges encountered in extractive metallurgy include:

- Cyanide-soluble base metals in gold and silver ores build up in recycled solutions until they interfere with the process and must be discharged as a barren bleed. Barren bleed contains a relatively high concentration of metals complexed with cyanide which represents a water loss, a cyanide and lime reagent loss, and presents an effluent treatment problem.

- Extraction of copper or zinc by hydrometallurgy results in jarosite formation which must be impounded to prevent a pollution problem.

- In acid leaching of uranium ores, tailing decant solutions cannot be recycled beyond a certain point because of the buildup of ions such as Cl^- which eventually make the solutions corrosive to stainless 314L steel and interfere with uranium recovery. At that point, discharge of an effluent or evaporation of the solution bleed is unavoidable. Depending on the climate, this may present a serious obstacle.

- When lixiviants are used to leach valuable eomponents from ore, more likely than not, other less than desirable species are leached too. For example, in uranium leaching, radium-226 and thorium, as well as selenium and other metals, are likely to

be leached as well. These present effluent treatment needs which add cost to an operation.

- Choice of lixiviant may be dictated as much by the cost of final effluent treatment as metallurgical process desirability.

- At least one uranium leaching operation is known (Agnew Lake) where the metallurgy would have indicated the use of solvent extraction, but environmental concern that organic solvents might harm a nearby trout steam resulted in the decision to use ion exchange.

- Recycling of solutions in several metallurgical processes results in the buildup of species in solution that one otherwise would not have been aware of, e.g., silica. Silica can cause fouling problems on ion exchange resins, filters, etc.

- The presence of metal cations in solutions can have an impact on recovery by recovery processes. For example, copper and nickel in solution can have a negative impact on gold and silver adsorption on carbon. Magnesium ions in a CIP pulp can affect gold adsorption, and so can bismuth.

- In order to secure a permit for most metal recovery operations, it is necessary to show in advance how damage to the environment will be avoided. To demonstrate that zero discharge can be achieved, a water balance for the total operation is required.

- To determine what, if any, effluent must be discharged, a salt balance may also have to be computed in advance. This presents a problem as metallurgical salt balance modelling skills and experience are still at a low point on the learning curve.

Mill Tailings Disposal

Mill tailings and mine waste containing sulfide minerals are the cause of the most serious environmental problems that face the mining industry and for which no complete answer has yet been demonstrated in practice.

Metallurgical and mineral processing waste disposal is under scrutiny at this time in several parts of the world most notably in Canada but also in the United States where the application of the Resource Conservation and Recovery Act (RCRA) to the mining industry is currently being debated. Although the Beville Amendment to RCRA regulations in the U.S.A. excludes mining and mineral processing wastes from RCRA, this inclusion is only temporary. Solid waste disposal and hazardous waste disposal rules will in one or another form be applied to mining and mineral processing waste in federal regulations which aim to protect surface and groundwater. Meanwhile, at the state level,

regulations very similar to the hazardous waste regulations of RCRA have been passed or are being proposed which will be applicable to mining and mineral processing wastes.

In South Africa, mineral processing wastes, i.e., tailings and wasterock, are being investigated to determine their impact on surface and groundwater and changes to the South African Water Act have been made that, if applied rigidly, could have very expensive consequences for some of the existing mining companies if it can be shown that they cause damage to water on land adjoining or beneath the operations. Although actual fines are not too severe, the law makes provision for compensation to neighbors that suffer damages as a result of water pollution and forfeiture of profits by a company that pollutes water on adjacent property or groundwater beneath the operations.

Mill tailing impoundment designs are evolving along with environmental protection awareness. Some of these, when applied in conjunction with tailings which have certain physical and chemical properties, may result in tailings which have extremely low permeabilities and which, therefore, effectively encapsulate contaminants.

Perhaps the most important of these is the "sub-aerial" or "semi-dry tailings" system of Knight and Piesold, also used in Steffen Robertson & Kirsten-designed impoundments. This method and others are described in a separate chapter later in this report, and are more appropriate in areas with drier climates and net evaporation. CANMET in Canada has conducted experiments which hold promise for prevention of AMD from tailings in wetter climates which rely on special vegetation cover applications.

There are several problems and challenges relating to mill tailings disposal:

1) Mill tailings for modern mine-mill complexes can involve very large tonnages of material. The Witwatersrand and Orange Free State gold and uranium mining industry alone in 1978 disposed of 78 million tons of tailings, almost all to above-ground "slimes dams." These are by no means the only large volume sulfide containing tailings in the world.

2) Often, mill tailings contain unoxidized sulfide minerals, e.g., pyrite, pyrrhotite, and marcasite. These tend to oxidize over a period of time and yield acid mine drainage, probably the most serious problem facing the mining industry today.

3) The prospect of "perpetual" treatment of acid mine drainage collected from tailings disposal areas and the need to manage tailings disposal sites for the next 300-400 years or longer presents a significant problem to the mining and mineral processing industry.

4) Mill tailings are generated at mine-mill locations, and often there are not all that many options for tailing disposal sites at some of them.

5) Mill tailings are prone to dusting, and wind-blown tailings distributed from the site can result in an even widerspread acid mine drainage problem. This means that if water quaiity protection is to be achieved, then especially sulfide-containing tailings must be disposed of in such a way that prevents wind erosion and distribution of the material beyond the managed impoundment area.

6) Some states are calling for double linings of tailings impoundment areas regardless of the cost-benefits of installing them. This presents a cost problem in some cases.

7) Disposal of wet tailings in impoundments ties up a large volume of water.

There are several emerging and improved technologies which avoid or overcome these and other problems which are described in later chapters, but the fundamental mechanisms of generation of AMD in sulfide-bearing tailings and how to avoid it are not yet understood.

Reagent Storage and Spills

Mining, and especially mineral processing operations, employ a long list of reagents, surfactants, and other reactive materials. Some of these are corrosive or toxic; others flamable, while many in small doses are unlikely to harm the environment.

Reagent transportation, storage, and spill control is an area of increasing concern for existing mining and milling operations as well as new ones.

In some parts of the U.S.A., transportation of reagents to a millsite is specifically not permitted during certain times of the year.

Reagent spills must be reported and would be subject in many cases to punitive action in the U.S.A. In new mill designs, chemical storage areas require berms--often lined--to catch any accidental spills.

Hazardous reagents are often used, e.g., chlorine, cyanide, $BaCl_2$, and special safe handling storage procedures and facilities are required.

Reagent transportation, storage, and spill control would seldom be a problem when the operators are properly equipped and trained and when the facilities are intelligently designed to contain such spills.

Recent groundwater quality awareness has brought to the surface the problem of underground storage tank leaks, particularly gasoline and fuel tanks. Underground storage tanks, particularly at older operations, can leak and present a serious contamination problem, but no more so than the neighborhood gas station in most cases.

Boiler Water

Many mineral processing and metallurgical operations employ boilers to generate steam. Boiler feed water used should be soft and as low in TDS as possible to avoid scale formation on the heat exchanger tubes.

This very often requires that demineralized water be used when the local well, stream, or lake water TDS is high.

When boiler feed water must be demineralized, this is generally done by a lime-soda softening process followed by dual-bed ion exchange demineralizers.

Apart from the cost, demineralizer systems produce a concentrated salt solution which must be disposed of.

Potable and Service Water for Mines and Mills

Potable water is required for the mine and mill operators and also at change houses for the maintenance staff as well as at mine housing.

The quality of water available at mines and mills may be poor where a regional water supply is not laid on. Sometimes, this presents a problem which calls for a costly solution.

Examples of this include the Rooiberg Tin Mines operation where the only available water is from one of the mineshafts, and it contains fluoride well in excess of the maximum permissable level for drinking water. The company has had to install two defluoridation plants and a pumping/piping system linking both their mines at a cost in the milling range. This a major expenditure for a small mining company.

All water delivered to underground workings in South African mines must be disinfected to render it drinkable. African mineworkers have a habit of drinking water where they find it regardless of instructions, and the disinfection requirement is a safety measure to prevent virus or bacterial infections.

Disposal of Contaminants

Many mineral processing operations generate contaminated effluents. So would desalination units in effluent treatment plants. All of these must be contained and/or disposed of.

When a large stream of water is treated to remove contaminants, e.g., dissolved metals, a smaller, but appreciable volume of precipitate sludge is generated. Often, a toxic waste is generated from a non-toxic waste, and this can present special disposal problems of its own if the legal requirements are to be met. There are innovative ways to achieve this, but this can also present a problem, see Chapter 21. Sometimes this consideration is the deciding factor in selecting one type of effluent treatment process over another.

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CHAPTER 5

WATER RECYCLING IN METALLURGICAL PLANTS

CONCLUSIONS

1) The incentive to recycle water may be to meet the zero discharge permit requirement or because fresh water is not available in adequate amounts, or only a excessively high cost.

2) The minimum amount of water required in a mineral processing plant seems to be proportional to the amount available.

3) Considerable water savings can be achieved, for example, in acid uranium leaching when there is no alternative, but there are significant costs involved both in measures to counteract corrosion and abrasion, as well as in recovery and plant throughput.

4) Sulfide mineral flotation recovery operations vary from simple straightforward flowsheets to complex sensitive operations with numerous interdependent circuits. Water can be recycled in these but, in several circuits, recovery losses or deterioration in concentrate grades result. To date, the reason for these phenomena are not fully understood, and much more fundamental work will be needed before the mechanisms for these empirically-based phenomena are explained and counter measures found. Some circuits are more sensitive than others and, at one complex sulfide plant, recycled water constitutes 80% of the water used with only 0.55 m^3 fresh water used per ton ore.

5) Research work by Brunswick Mining and Smelting and Lakefield Research is believed to have indicated a process arrangement that uses a higher percentage of recycled water than was possible before.

6) Recycling of water results in changes in water quality as dissolved salts build up in solution. Prediction of these changes for an integrated multi-component plant through water balance and salt balance modelling is, at this stage, an emerging and as yet imprecise skill.

7) Buildup of dissolved salts in recycled solutions result in interferences with processes such as filters and clarifiers for solution polishing, for example, as required ahead of solvent extraction of uranium from acid solutions. Building of dissolved solids in tailings solutions due to water recycling can also introduce problems such as scaling up of tailings pond underdrains. These are problems that will occur more often due

to increasing use of more efficient solution recycling in metallurgical operations and for which better and more routine answers are needed.

The RANDOL investigation asked six questions at every operation that was visited over the last 18 months:

- How much net water does your operation consume?
- What is the quality of your water, and what effect does this have on your process?
- How much water do you recycle, and where in the circuit?
- What effect on water quality and on metallurgical recovery does recycling have?
- How much water can you recycle, if necessary, without running into metallurgical or other problems?
- Is water treatment used or needed to make recycled water more usable?
- Are your tailings pond, water storage impoundments, etc. lined, i.e., are there salt bleeds? Is solution reclaimed from the tailings pond via decantation, underdrains, or seepage cutoff trench collection?

Most often, the RANDOL inquiry was referred to an environmental engineer to answer questions about water. Very seldom were these staff members able to respond to questions about metallurgical effects of recycling. This is an example of the need for a "systems approach" to this important aspect of water management.

HOW WATER IS RECYCLED

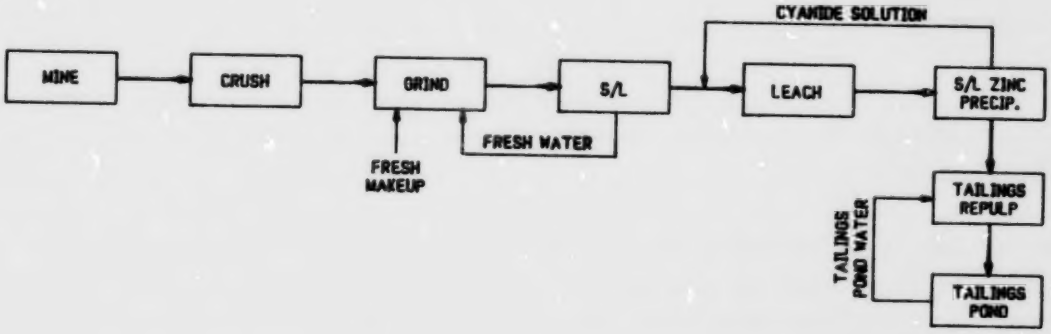
Water can be recycled in several ways. For example, tailings decant solution may be the main water supply to the mill with fresh water added either to the return solution reservoir or directly to specific circuits in the plant.

In some cases, recycle solution is drawn from the tailings pond directly by decantation or through underdrains, or it may be pumped to an ageing pond prior to reuse. There are several possible arrangements in which water can be recycled within a mine-mill complex. These are illustrated schematically below.

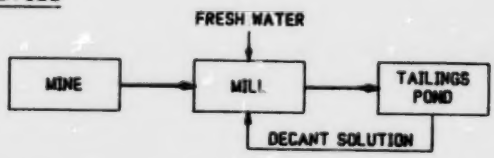
In operations that recycle tailings solution, this can be through decantation directly from the tailings dam or seepage collection via cutoff trenches. When seepage is collected and recycled, its quality may be significantly different to the solution recycled directly from

the pond--very often the seepage will be much lower in TDS as some degree of natural purification often occurs while the seepage is in contact with soil or rocks.

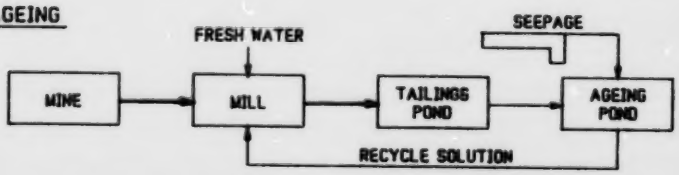
Some metallurgical operations recycle solution internally. For example, consider a conventional Witwatersrand gold mill that segregates fresh mill water, then recycles cyanide-bearing barren solution back to the leaching circuit, and finally recirculates tailings pond water which is used to repulp filtered tailings.



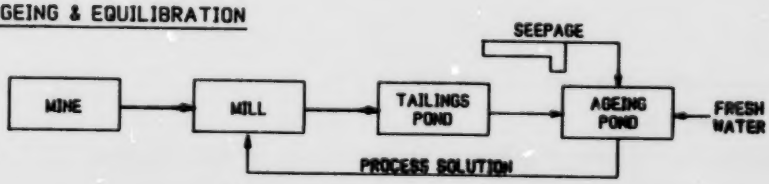
DIRECT RECYCLE



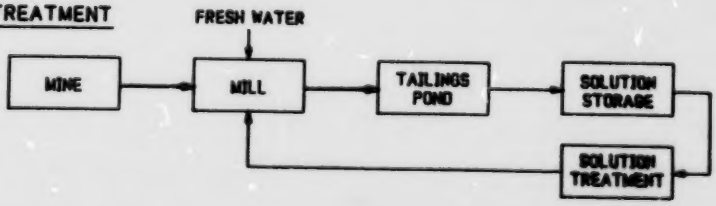
RECYCLE AGEING



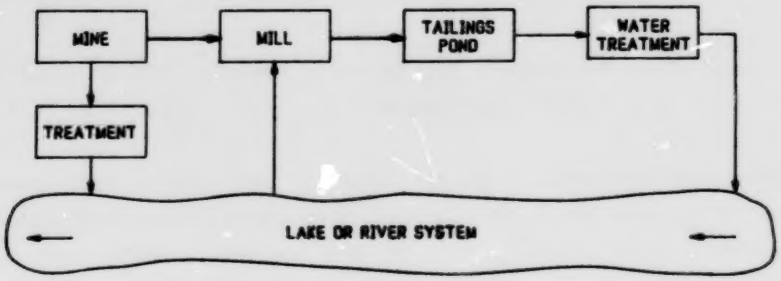
RECYCLE AGEING & EQUILIBRATION



RECYCLE TREATMENT



MACRO-RECYCLE



PERCENT RECYCLE VS. NET WATER CONSUMPTION

It is customary in many metallurgical operations to report the percent water recycle used. It is important to distinguish between percent recycle water used and net water consumption.

For example, in one operation using 1.0 m^3 fresh water per ton ore treated combined with 3.0 m^3 recycled water per ton ore is using 75% recycled water. A second operation consuming 0.8 m^3 net fresh water per ton ore combined with 1.6 m^3 recycled water is using only 66% recycled water, but it is in fact using less fresh water and discharging a smaller volume of effluent.

Percent recycle water used in the operation does not reflect how water efficient an operation is.

INCENTIVE FOR RECYCLING

Most metallurgical operations have set an objective to use as much recycle water as possible. Some do not recycle any water. The incentives of those that do recycle water may be quite different on a case-by-case basis. The most common incentives to recycle water are:

- Water conservaton; to reduce net water use.
- Reagent conservation.
- To minimize the volume of effluent to be treated or discharged.
- To meet zero discharge requirements of the operating permit.

EXAMPLES OF WATER RECYCLING

Rössing Uranium Ltd.

Rössing Uranium Ltd. has reduced their 1984 net water consumption for an acid uranium leach to 0.4 m^3/t ore which is a remarkable achievement, even though their consumption may increase again once the water level in their tailings pond has been lowered to the planned level. By comparison, the QUIVIRA MINING COMPANY at Ambrosia Lake, New Mexico, which also recovered uranium by acid leaching using a similar process, consumed 1.75-2.4 m^3 fresh water per ton ore treated depending on plant throughput which is typical of water consumption by uranium mills that have less need to recycle water.

Rössing Uranium achieves this low water consumption at the expense of metallurgical efficiency in the ion exchange plant, but because so much of their solution is recycled, some of the uranium not recovered the first time around is recovered later as the water recycles. Using water with a much higher TDS including $SO_4^=$ and Cl^- results in competition for adsorption sites on the ion exchange resins employed. There are also enhanced corrosion and scale effects. These are all discussed in the trip report on Rössing Uranium in Appendix I. CIX is employed for primary uranium recovery in both the main plant and at a plant treating reclaimed tailing solution.

Nowhere else in the world has such an immense effort been made to cut down on net water intake at an acid leach uranium mill. The composition of seepage collected below the tailings dam indicates that during seepage, several contaminant levels are significantly reduced. The effect of recycled water quality is discussed in the following correspondence from Rössing Uranium Ltd., and more information may be available from:

RÖSSING URANIUM LTD.
Post Office Box 22391
Windhoek 9000
South West Africa/Namibia
(061) 36760
Peter N. Vernon,
Technical Controler

RÖSSING URANIUM LTD.. reduced their water consumption from 30,000 m^3/d to 14,000 m^3/d. Because RÖSSING uranium ore is relatively low grade, the concentration of uranium in solution is reasonably low, within the realm of applicability of continuous ion exchange recovery as opposed to SX which is more cost-effective for more concentrated solutions. CIX systems are not as vulnerable to suspended solids levels in the pregnant solution as SX, consequently, the need for multi-media filtration to polish pregnant solution ahead of recovery is avoided.

Rössing Uranium Limited
Capital Centre, Kaiser Street, Windhoek
South West Africa/Namibia

Correspondence to
PO Box 22391, Windhoek 9000
South West Africa/Namibia
Telephone (061) 36760 Telex 908-3104 WK

Rössing

TC. 198/84

2nd May 1984

Mr. H. von Michaelis,
Randol International Ltd.,
21578 Mountsfield Drive,
GOLDEN, COLORADO 80401.
U.S.A

Dear Hans,

Sometime ago you asked for information regarding the effect of increased TDS on Ion Exchange performance.

I attach hereto, a copy of a memorandum from Steve Kesler to myself that I think gives you a fair picture of the effect of high TDS water being used in the Metallurgical Plant as a whole.

The only point that I would add myself is that, although we can certainly cope while we are on a slightly reduced production level due to the present state of the Uranium market if we were striving for every ounce throughput, Ion Exchange capacity would in my opinion be a constraint on our performance.

Yours sincerely,

P.N. VERNON
TECHNICAL CONTROLLER

RÖSSING URANIUM : NATURAL ATTENUATION OF CONTAMINANTS

	TAILS DAM EFFLUENT	SEEPAGE
pH	1.8	6.6
TDS (ppm)	33,084 ppm	13,430 ppm
S/S	134	20
Al	625	12
SO_4	20,657	8,102
NH_3	401	172
F^-	98	42
NO_3	160	72
Iron	1,825	0.1
Mn	1,925	1,100
K	260	76
Silica	320	27
Uranium	17	0.5
Ra-220 (PiC/l)	243 PiC/l	21 PiC/l

Memorandum

Rössing

To
Technical Controller

From
Metallurgical Manager

Ext
298

Date
5th April 1984

Copies to
f-CIX

Ref SBK/lvl/1035

CIX info for Randol

At present we are recycling about 60% RDS and 25% seepage into the rodmills. The recycle water has a TDS of about 50 000ppm with 30 000ppm sulphate and 1 300ppm chloride. This compares to the analysis of fresh water at 900ppm TDS, 35ppm sulphate and 280ppm chloride. It is obvious therefore that with this rate of water recycle there will be a build up of TDS in the pregnant solution circuit.

At present the sulphate concentrate in pregnant solution to CIX is 35 000ppm whilst chlorides are about 1 300ppm. These figures compare to sulphate levels of 25 000ppm and chloride levels of 600ppm prior to water recycling.

Considerable test work has been carried out in the laboratories to determine the effect of increased levels of sulphate and chloride on the ion exchange plant performance. Both sulphate and chloride are competitive ions to uranium for exchange sites on the resin. Test work has indicated that a 10 000ppm increase in sulphate level would increase the CIX barrens by about 4ppm. Similarly a 1 000ppm increase in chloride concentration would increase barrens by about 1,5ppm. However, in practice on the plant we have not had an increase in barrens due to water recycling because of modifications made to the elution sequence. In order to overcome the deleterious effect of water recycling, the resin transfer rate has been increased by increasing the elution frequency from 30 elutions per day to 35 elutions per day.

A computer model of the plant indicates that eventually an equilibrium situation will exist whereby sulphate levels and chloride elvels in the pregnant solution will stabilise at about 40 000ppm and 1 600ppm respectively.

Before the recycle programme commenced, the ion exchange plant capacity was increased somewhat by the addition of an extra absorption stage to each CIX line.

The other major deleterious effect of the water recycling programme has been the increased incidence of precipitation of scale in the plant. This is particularly noticed at solution/air interfaces and the scale has been identified as predominantly jarosite but with appreciable calcium sulphate. There are indications that the precipitation of jarosite has also been associated with the introduction of a ferric leach plant and due to some microbiological activity. The scale results in some plant nuisance and of course increased operator activity. The formation of a rough jarosite scale

within the barren pipeline has been the most problematical scale to remove. However, tests had been undertaken with polypropylene pigs which appear to remove the scale satisfactorily in about three passes. It is planned to purchase these pigs and to run them through the barren line during normal operations on a regular basis.

Within the reduction plant extensive use is made of 316L stainless steel, i.e. for thickener rakes. With increased water recycle we have encountered formation of jarosite on the rakes and beneath the jarosite the onset of pitting corrosion. Crevice corrosion has also been noted behind nuts etc. After some experimentation four thickeners have now been coated with polyurethane after sandblasting to obtain a satisfactory surface for bonding. To date our experience leads us to think that urethane coating will be a satisfactory solution for corrosion protection of these rakes. Although water recycling is not without its problems, the benefits far outweigh the problems which are not insurmountable.

S B KESLER

New Mexico Uranium Operations

The uranium operations in New Mexico are also located in a very arid climate around Grants, New Mexico. It was expected that these would also have to recycle a lot of water because of limited supply. This is not the case. At QUIVIRA MINING, excess minewater is treated to remove uranium by ion exchange and radium by $BaCl_2$ addition and settling before being discharged to the desert.

Of about 3,500 m^3/d water that goes to the tailings pond daily with tailings, only 1,022 m^3/d is returned for recycle and, indeed, the only reason and need to recycle solutions is to avoid having to construct additional costly lined evaporation ponds. Composition of process water at this Ambrosia Lake operation is as follows:

TDS	2,286 ppm
Hardness	900
Ca	200
Mg	80
Na	300
SO_4	1,300
Cl	113
U_3O_8	2.3
Se	0.2
Mo	.75
Si	Less than 10

The QUIVIRA MINING CORP. would like to recycle more water from the tailings plant to reduce the amount to be evaporated still further, but the limiting factors are lower recovery by SX and the enhanced corrosion of the CCD thickener parts made of stainless steel which would not stand up to the 1,300 ppm Cl^- level at pH 1.2 of pregnant solution. If water was a real economic factor, however, it would be possible to coat the stainless steel with polyurethane as has been done at Rössing. Another factor to consider if more water were to be recycled is the buildup of TDS which could also result in cementing of media in the multimedia polishing filters ahead of the SX plant which would be more prone to scaling up.

MACRO RECYCLE AND EFFECTS

Because of widespread seepage of high TDS tailings solutions into underground working, there has been a steady change in the quality of underground water pumped from the Ambrosia Lake mines amounting to the effects of a macor recirculation of water from underground. The minewater delivered to the CIX plant near the mill now contains 2,800 ppm TDS, including 1,600 ppm $SO_4^=$ and 150 ppm Cl^-. Under these conditions, uranium

which is present at 10-12 ppm loads onto resin at only 0.6 lb/ft^2 (10 g/l) before breakthrough occurs compared with a loading of 2 lbs. U_3O_8/ft^3 at the second CIX plant serving mines 35 and 36 further away from the tailings where TDS in minewater is lower.

The result of the change in water quality and increase in competing ion concentration in the CIX process has been to require an increase in elution cycles from 16 per month to over 100. Resin inventory has had to be increased as well to keep the U_3O_8 level in the CIX treated water at below 2 ppm U_3O_8 for discharge. This has required a much greater load on the elution plant and a correspondingly greater cost of reagents consumed with no increase in uranium recovery.

IN SITU LEACH

The very nature of in-situ leaching implies striving for optimal recovery and recycling of solutions and lixiviant values. Reagents are added to solutions which are pumped underground under pressure where uranium is leached, and uranium values are then recovered, usually by CIX from the pregnant solutions.

Recycling of solutions is likely to build up competing ions as well, but it is not know what specific effects these have on the metallurgical process.

Certainly, great care must be taken to avoid the use of Na salts in the reagents where there are smectite clays in the leachfield. Replacement of calcium by sodium in clays causes them to swell resulting in a marked decrease in porosity. If, through recirculation of solutions, Na could be replaced by calcium on the other hand, then there would be the possibility of improving the porosity of the leachfield.

WATER RECYCLING IN BASE METAL FLOTATION PLANTS

There is a wide discrepancy in the amount of water that can be recycled from one base metal flotation plant to another. Factors that influence water quality effects on flotation chemistry are not quantitatively known. Whether or not a mill superintendent will use a particular stream of recycled water in a particular circuit often depends on the way he feels about rather than on hard fact. Even when a water stream has been found to result in a reduction in metallurgical efficiency, the reasons are seldom known but gives rise to guessing. The result is a dearth of knowledge of what steps could be taken to correct the problem and make the water usable. This is an area that was recently being examined in some detail by NORANDA MINES LTD. Some comments and characteristics of water recycling and recycling effects at base metal flotation plants are listed below.

Cu-Pb-Zn Mill G, Ontario

This 3,850 stpd mine recovers a copper, lead-silver, and zinc-silver concentrate from a massive sulfide orebody. The tailings contain an average of 20% pyrite. Ammonia is used for pH adjustment in the plant because of the ease of handling and because after addition of freight costs, it is the most economical reagent. Lime is used in the effluent treatment plant.

Of all the flotation plants visited, this operation recycles a greater percent of its total water needs from tailings amounting to 80%. This mill has been working on improving its water recycling program since 1972. Their objective is to achieve 85% recycle.

Water to the mill concentrator plant is made up as follows:

Fresh Lake Water	184.51 mm I gal/yr	1,929 m^3/d	0.55 $m/^3t$
Water in Ore Feed	7.30 mm I gal/yr	77 m^3/d	
Lake Potable H_2O	1.92 mm I gal/yr	22 m^3/d	
Recycle Water	594.6 mm I gal/yr	6,210 m^3/d	1.77 m^3/t
TOTAL	788.33 mm I gal/yr	8,244 m^3/d	

0.6 m^3 new water per ton ore feed is used, excluding potable water and water contained in ore feed. Overall water used is 2.55 m^3/mt including potable and fire fighting service needs.

- When recycled tailings water which is saturated with $SO_4^=$ was used for reagent mining, it was observed that when ammonia and cyanide reagents were used in the plant, that severe scaling resulted in the reagent system, and reagent feed control was impossible. As a result, the mill switched to fresh lake water for this function.

- SO_2 and ammonia are mixed to form $(NH_4)_2\ SO_3$ before addition to the rod mill to depress zinc in the bulk Cu-Pb-Ag flotation step.

- Recycle water, even though ore is milled in an alkaline pH, contains only about 100 ppm thiosulfate which is lower than in some other operations. This is ascribed to lower reactivity of the sulfides in the ore.

- Cemented tailing backfill is employed underground. Sometimes cemented backfill fragments get into the ore, and this appears to result in a reduction of selectivity in the copper rougher circuit. Tests in the lab confirmed that when cured backfill gets into the ore, both copper recovery and selectivity are affected, i.e., zinc appears in the copper concentrate. Copper concentrate grade can drop.

- Attempts to correlate calcium in the rod mill discharge with Cu recovery and grade were inconclusive.

- At times of selectivity problems in the plant, it was found that soluble copper concentrations in the process solutions had increased from 6 ppm to 11 ppm which might be significant and realted to water recycling.

- Fresh water is used in pump glands and for the Cu-Pb separation step. Separation is impaired when recycle water is used as launder water for the Pb-Cu concentrate and onwards. Operators are not certain what species present in the recycle water affects the Cu-Pb separation.

  With fresh water, a lead concentrate of 65-70% can be achieved by depressing Cu with cyanide. With recycled water, the lead concentrate grade reaches 50% with difficulty. It is possible that sulfate or something else in the recycle water affects lead concentrate flotation performance.

- Tailings pond rec'aim water at this operation is found to be too scaling for a lamella thickener to be used after treatment by lime addition. A convntional thickener is used.

Cu-Pb-Zn-Ag Mill M, Ontario

This mill in Ontario was designed to treat 3,000 stpd. A high pyrite variable underground massive sulfide orebody with up to 40% sulfide is mined at one site. The second open pit ore contains 25-30% pyrite.

Cu, Pb, Zn, and Ag are recovered in three concentrates by floating a copper-lead-silver concentrate first. This is then separated to make a copper concentrate by depressing lead with quar gum and SO_2, and whatever zinc may have carried over with the Cu-Pb. SO_2 helps Cu to float. Zinc is floated from the primary flotation tails.

Soda ash is used for the Cu-Pb bulk flotation circuit which is operated at pH 9-9.5. Sometimes, some SO_2 is used in the rod mill when the ore is not "clean." The zinc can be quite oxidized in some of the ore feed.

As in the previous case, recycle water is found to result in a lower grade concentrate if it is used in the Cu-Pb separation step. Fresh water is used for flotation of a copper concentrate from the Cu-Pb concentrate.

At the time of the Randol visit, fresh water was added to the rod mill with Na_2CO_3 and SO_2 reagent and to the ball mill. Recycle water, if used in the ball mill, results in a

higher zinc content in the Cu-Pb bulk concentrate. This might be due to activation of sphalerite by low levels of dissolved copper in the recycle water.

Recycle water is used without problems for zinc flotation from the primary flotation tailings.

Ore is ground at an alkaline pH around 8.5 so thiosalts are generated. The staff believes that thiosulfate levels are around 70-80 ppm in winter and higher in summer.

Too much collector added at the front end of the circuit ruins the selectivity of the first semi-bulk flotation. Consequently, the plant is run on "starvation" amounts of collector. This keeps Zn out of the Cu-Pb concentrate but results in a slightly reduced Cu-Pb recovery. Because recycle solutions are used in the primary flotation step, care must also be taken that collector does not recycle to the front end of the circuit.

Activated carbon is added to adsorb any extraneous collectors that may be present before the Pb-Cu separation step.

	ppm Zn	ppm Fe	ppm S_2O_3	ppm S/S	pH	ppm Cu
(AMD from Mine)	0.30	0.06	8.2	5.0	6.5	0.01-0.04 Max.
Reclaim Water	5.92	4.70	43.1	25.0	6.8	0.01-0.04
Tertiary Pond Effluent	0.24	0.08	-	8.0	10.3	0.01-0.04
Ret. Pond Effluent	0.80	0.10	-	7.0	10.0	0.01-0.04
Treated Tailings Effluent	0.76	0.48	-	Tr	10.2	0.01-0.04
Tailings Pond	0.36	0.32	-	7.0	9.4	0.01-0.04

During spring, the tailings pond water drops to pH 3.0.

- Composition of water streams in summer (July, 1984):

	pH	°C	ppm Cu	ppm Pb	Zn	Fe	S_2O_3	S/S
(Treated Effluent)	7.2	10°	0.01	0.01	0.1	0.06	Tr	1.0
Creek	6.4	10°	0.32	0.01	13.86	1.92	4.1	8.0

° Composition of water streams in summer (July, 1984), Continued:

	pH	°C	ppm Cu	ppm Pb	Zn	Fe	S_2O_3	S/S
Reclaim Water	7.1	16.5°	0.01	0.06	3.14	0.88	Tr	1.0
Tertiary Pond Effluent	10.8	15°	0.01	0.02	0.08	0.04	Tr	1.0
Ret. Pond Effluent	9.3	14°	0.01	0.02	1.32*	0.88	Tr	1.0
Treatment Plant Effluent	10.5	17°	0.01	0.02	0.20	0.04	4.1	Tr
Tailings Pond	3.5	14°	0.26	1.20	10.54	4.14	4.1	2.0
Open Pit Mine Discharge	11.1	-	0.04	0.02	0.80	0.06	Tr	15.0

* Atypical: Suspect Assay

° Lime is added to reclaim water and allowed to settle in a pond. pH must be increased, or it would corrode the steel line.

Cu-Mo Porphyry Operations in the Southwest U.S.A.

Somewhat sketchy information was gathered about water recycle at copper molybdenum flotation recovery operations from porphyry ore deposits in the desert southwest, U.S.A.

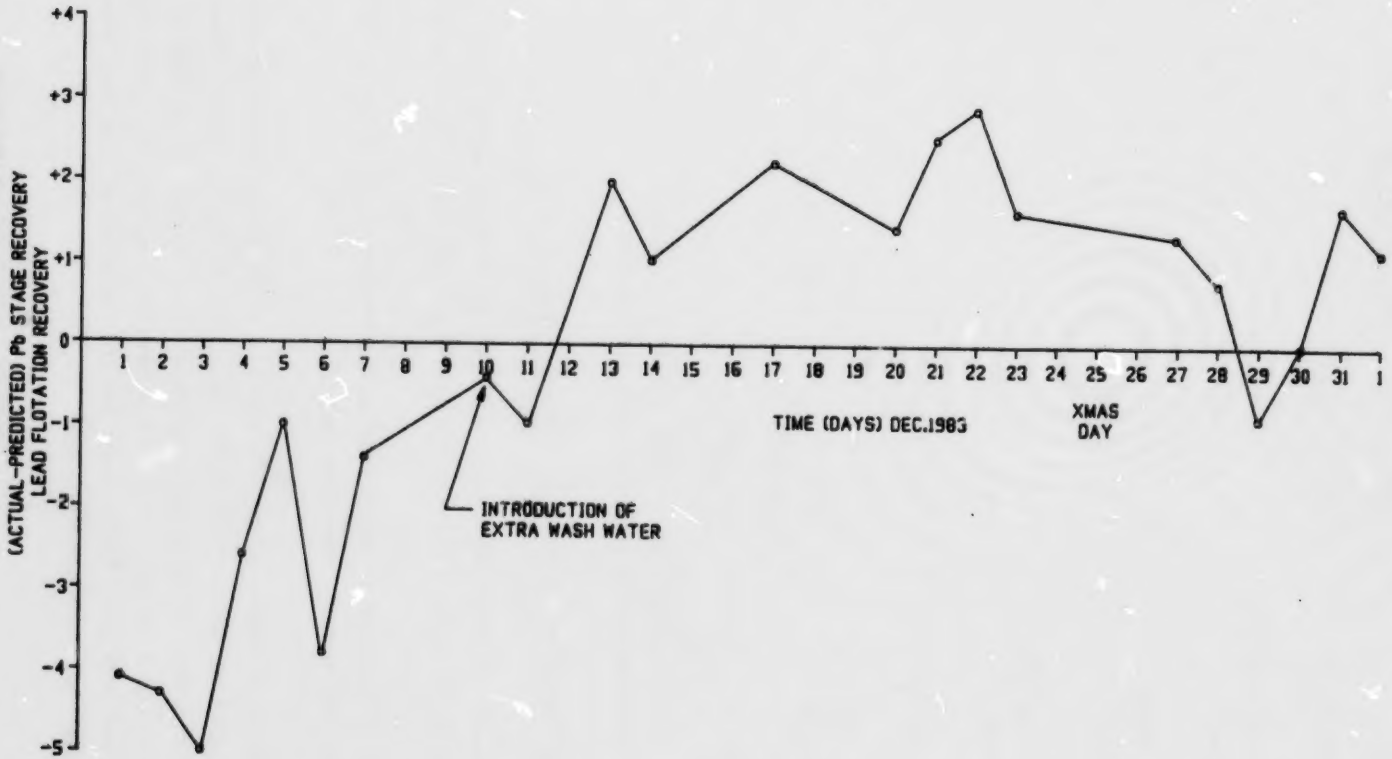
Water is recycled in the copper-moly flotation circuit in most instances, but almost never in the copper-moly separation step.

In almost al cases, no recycle water is used in the moly separation plant which is usually the point at which fresh water is added to the complex. However, at Phelps Dodge, Morenci plant, which uses ferrocyanide as a depressant instead of the conventional NaHS, recycle water is used. This is a new development, the plant having relatively recently changed over from fresh water for this application. So far, there has been no drop in recovery or grade according to:

PHELPS DODGE CORPORATION
Morenci Copper Operations
Morenci, AZ
(602) 865-4521

EFFECT OF FRESH WATER INCREASE AND IMPROVED WATER QUALITY

Black Mountain Mineral Development Company Limited



South American Copper-Molybdenum Producers

It is known that high TDS, poor quality water is used at some of the South American copper-moly producers. At the sulfide flotation operation at CODELCO's Chuquiquamata operations, it is believed that poor-quality recycle water is used, and that every possible source of secondary water and recycle water must be used. A reply to RANDOL's request for more information on this aspect is still awaited.

EXXON Crandon

The EXXON MINERALS CORP. planned operation at Crandon, Wisconsin, which will recover copper, lead, and zinc concentrations from a complex sulfide ore deposit, will be the first zero discharge operaton in a climatic region with net precipitation. It is too soon to tell what impact recycling of reclaimed tailings solution will have on the operation, although a general discussion on water recycling and treatment for new complex sulfide treatment plants was presented at the Randol Water Workshop at Beaver, Creek, Colorado, in October, 1984. Details on how water will be managed at Crandon have not yet been published.

Swedish Complex Sulfide Plants

Swedish companies, in particular BOLIDEN AB, have undertaken significant development research to define the effects of recycling water in complex sulfide flotation plants. Papers by FOSSBERG, et al. (1984) and BROMAN (?) are inserted in Chapter 54.

Black Mountain

BLACK MOUNTAIN MINERAL DEVELOPMENT (PTY) LTD. operates a Cu-Pb-Zn-Ag flotation plant near Aggeneys in Namaqualand, South Africa. This operation employs three main flotation circuits with nine different flotation reagents being added at up to 43 points. Lead and zinc flotation recoveries achieved their targets, but there were problems in achieving a satisfactory copper recovery.

Apart from initial problems of oil and grease getting in the ore, it has been found that disssolved oxygen levels are critical. Aeration of solutions was found to help considerably and also the use of dichromate to depress galena in the copper cleaner circuit. An excellent account of the complex tests and development work in the improvement of this complicated flotation plant has been given by TWIDLE and ENGLEBRECHT (1984). Additional information will be presented by TWIDLE, et al. (1985).

Data provided by the Black Mountain staff shows clearly that recovery of lead in their process is impaired by the use of more recycled water or, conversely, that it is improved by the use of more fresh water.

The Black Mountain flotation circuit arrangement and sequence is different to that used in massive sulfide treatment plants in Ontario and New Brunswick--probably because the Pb:Cu ratio is so much higher at Black Mountain which may require a different route and reagent selection. The Black Mountain flowsheet applies selective flotation of copper, then lead, and then zinc.

The backfill with cement, introducing calcium into the ore and water, seems to cause some detrimental effects on flotation as observed at INCO's Thompson plant and possibly at NORANDA's Geco operations. Data collected on Black Mountain is reviewed in a trip report in Appendix I.

Makeup water consumption at several copper and copper molybdenum operations is as follows:

Operation	Makeup Water at Full Capacity	Makeup Water at Partial Capacity	Gross Water Use per t Ore	% Recycle
Duval, Sierrita	217 U.S. gpt (0.82)	225 U.S. gpt (0.85 m^3/t) at 75% Capacity	-	-
Cypress Pima	245 U.S. gpt (0.92)	340 U.S. gpt (1.28 m^3/t) at 50% Capacity	-	-
ASARCO, Mission	205 U.S. gpt (0.77)	250 U.S. gpt (0.94 m^3/t) at 50% Capacity	-	-
ASARCO, Silver Bell	215 U.S. gpt (0.81)	275 U.S. gpt (1.04 m^3/t) at 50% Capacity	-	-
ANAMAX	215 U.S. gpt (0.81)	390 U.S. gpt (1.47 m^3/t) at 50% Capacity	-	-
MAGMA, San Miquel	234 U.S. gpt (0.9 m^3/t)		500 U.S. gpt (1.9 m^3/t)	52%
Phelps Dodge, Morenci	80-90 U.S. gpt (0.3-0.33 m^3/t)		600-700 U.S. gpt (2.3-2.7 m^3/t)	86%

Operation	Makeup Water at Full Capacity	Makeup Water at Partial Capacity	Gross Water Use per t Ore	% Recycle
Phelps Dodge, Metcalf	95-105 U.S. gpt (0.35-0.38 m3/t)		-	-

Foskor Ltd., Phalaborwa, South Africa

Foskor treats ore from two sources:

1) 25,000 TPD tailings from the PHALABORWA MINING CO. after PMC has removed the sulfide minerals by flotation. Foskor recovers apatite baddeleyite and magnetite. This "ore" is received at 50% solids, i.e., with 25,000 m^3/d water from PMC's circuit.

2) A further 25,000 TPD from a PMC ore stockpile which FOSKOR mills and floats to recover copper which is sent as a concentrate to the PHALABORWA MINING COMPANY. Then, phosphate minerals are recovered and, finally, baddeleyite is recovered by gravity.

Foskor discharges 20,000 m^3/d of water effluent to the Olifants River.

The 25,000 TPD flotation tailings transferred from PMC is accompanied by highly contaminated water containing F^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, $SO_3^=$, Cl^-, and Na. It has a TDS of around 5,000 ppm and 4 ppm F. Calcium and magnesium combined average 2,500 ppm.

The hardness of the water reacts with the fatty acids used in the flotation recovery of apatite and forms Ca and Mg oleates which are insoluble soaps and form a scum in the froth. As a result, excessive reagents are consumed.

In one circuit, poly glycol ether is used; in another circuit, poly glycol ether combined with a modified polysaccharide is used.

The chemically modified polysaccharide is made from quar beans in South Africa by TROCHEM (PTY) LTD. and is known by its trade name, ACROL LG21 and LG31.

The FOSKOR flowsheet and water balance is included in a trip report on the operation with a discussion of their water recycle and the effects thereof. The quality of the water in FOSKOR's circuits is a direct result of recycling of water at PMC which is then bled to FOSKOR with PMC tailings at 50% solids.

The cost of gangue depressants amounts to "millions of Rands" annually. A test using 50% fresh water with 50% recycled water failed to yield a big reduction in reagent needs.

In FOSKOR's case, the low price of water is not a deterent to using more water. Availability of water may be threatened by periodic droughts. A likely need for recycling is availability of supply.

FLUORSPAR FLOTATON

Martin Wilson of the U.S. BORAX AND CHEMICAL CORP. was awarded U.S. Patent 4248708 dated February 3, 1981, which provided an improved process for treating water obtained from a fluorspar flotation procedure which substantially reduces slimes and interferring soluble materials, allowing the water to be recycled in the process and also improving its quality to make it suitable for discharge to the environment.

The process refers to a specific combination of coagulants and flocculants to obtain a clear water for recycle without adverse affects on fluorspar recovery allowing recycle of in excess of 90% treated process water.

The reagents used are a combination of cationic polygalactomannan derivative as primary flocculant and a high molecular weight polyethylene oxide as a secondary flocculant. The polyglactomannans are polysaccharides composed of galacton and mannose units, usually found in the endosperm of leguminous seeds such as sugar, locust bean, honey locust, flametree, etc. The derivatives of use here are cationic. A copy of the patent is inserted into Chapter 54.

LEAD-COPPER SEPARATION USING HEXAVALENT CHROMIUM DEPRESSANT

Hexavalent chromium is a potent depressant of galena, even in very small quantities, and is commonly used for separation of galena from copper-lead bulk flotation concentrates.

Because of the toxicity of hexavalent chromium solutions, tailings containing this ion must be very carefully segregated and treated before discharge. If water used in the lead-copper separation step is not kept completely separate, there is the danger that it may get into the main recycle solution stream. Even traces of hexavalent chromium in the primary flotation circuit will cause a reduction in galena recovery.

Thiosulfate ions will reduce hexavalent chromium to trivalent chromium, but it would probably be dangerous to rely on this happening quantitatively in the tailings dam. This certainly did not happen at the NEWMONT MINING COMPANY's Idarado Mill near Telluride.

At the Missouri lead belt, dichromate is used for copper/lead separation. Water from this circuit is always kept separate except at the Magmont Mill where only 25 percent water is

recycled. In the early days of operations in the Missouri lead belt, deleterious results were experienced, possibly because of inadequate separation of dichromate-containing solutions.

It is concluded that if dichromate reagents are to be used in sulfide mineral flotation, then that part of the process and all water used should be kept completely separate from the rest of the plant.

Additional insight into this problem may possibly be available from:

NEWMONT MINING CORPORATION
200 Park Avenue
New York, NY 10166
(212) 953-6900
Leonard Harris, Vice President
Metallurgical Operations

AMERICAN CYANAMID COMPANY
859 Berdan Avenue
Wayne, NJ 07470
(201) 831-3900
Arnold Day

GOLD AND SILVER HEAP LEACHING

Heap leaching typically requires 0.004 gpm/ft^2-0.007 gpm/ft^2 (0.21 m^3/m^2/d-0.4 m^3/m^2/d) solution application. Efficient solution recovery and recycling is a funadmantal aspect of the process.

Solutions are usually spray irrigated onto the heaps which are often located in extremely arid climates with hot summers where evaporation rates are high. All solutions recovered from the lined heaps are recycled via a pregnant solution pond, metal recovery plant, and barren solutions pond.

Net water consumption in heap leaching can be as low as 0.2 m^3/t leached average for the year but will be higher than this average in summer. In winter, there can be a net gain in solution due to precipitation.

Some operations recover gold and silver by zinc precipitation; others use carbon adsorption. Zinc precipitation continuously adds zinc to the solutions. The addition of hydroxides, usually lime but in some cases NaOH or Na_2CO_3, adds to the TDS load of the recirculating solutions.

An interesting observation made at Tombstone Exploration, Inc., Tombstone, Arizona, is that despite the addition of 31 g Zn/m^3 solution on each pass, zinc levels build up to an equilibrium point and then stabilizes at a relatively low level in the "off" solution.

Recirculation of solutions, evaporation, and reagent addition does result in a TDS accumulation in heap leaching solutions. There is evidence that some dissolved salts drop out in the heaps, but the solutions can become scaling, and this could be expected to result in severe metallurgical problems due to fouling of carbon in columns or filters, pipelines, sprinklers, and the heaps themselves. Some plants have a much more serious scale problem than others due to water quality differences.

When fresh water is added to recycled solutions in metallurgical circuits, operators have noted that scale buildup seems to occur close to where the fresh water was added. An innovative way of reducing scale problems is implemented at one operation where the fresh water is mixed with recycle tailings solution in the "on" solution pond. Precipitate is allowed to form and to settle out before the solution reaches the heap or process.

Virtually all heap leaching operations for gold and silver use some form of scale inhibition. Examples are:

Operation	Reagent	Dose
Tombstone Exploration, AZ	NL Industries Barochem 535	--
Candalaria, NV	Drew Millsperse 802	50 cc/Min.
Cortez Gold Mine	Drew Millsperse 802	2-5 ppm

In Western Australia, available groundwater can contain 10,000 mg/l TDS and more, and yet is is used successfully in heap leaching projects.

Some operations experience more severe water problems than others. In the Mojave Desert, California, several small heap leaching operations were unsuccessful, reputedly due to the very poor water quality that interferred with the process. One company, AMERICAN MINE OPERATORS in Amboy, California, successfully heap leaches with a saturated calcium chloride solution which precipitates $CaCl_2$ crystals along the drainage ditches. More information about how success is achieved with such high TDS water may be available from their consultant:

EDMUND CAMPBELL
Consultant
Post Office Box 178
Harleybury, Ontario
(705) 672-3460

Scaling effect of carbon and heap leaching heaps have been carefully examined by water treatment chemical suppliers and heap leaching expert consultants, and these may well also provide a useful insight in how to deal with the problems that arise:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Frank Daniher
Bennet P. Boffardi
Russ Kirwin

NALCO CHEMICAL CORP.
2901 Butterfield Road
Oak Brook, IL 60521
(312) 887-7500
R. James Shield

DREW CHEMICALS CORP.
4625 South, 2300 East, #202B
Salt Lake City, UT 84107
(801) 278-2824
Charles Duke

NL BAROID
NL Industries, Inc.
Box 1675
Houston, TX 77251
(713) 527-1100

KAPPES-CASSIDY ASSOCIATES
Post Office Box 13687
Reno, NV 89507
(702) 356-7107
Daniel W. Kappes

COUNTER-CURRENT HEAP LEACHING

Research efforts are underway to develop a counter-current heap leaching process to generate pregnant solutions that have high enough gold and silver values for direct electrowinning. The stability of gold and silver in solution when in contact with ore on the heaps is an important aspect that has yet to be resolved, and it is likely to vary from case to case. This technology is the special study area of:

BUREAU OF MINES RESEARCH
LABORATORIES
U.S. Dept. of the Interior
1605 Evans Avenue
Reno, NV 89520
(702) 784-5391
Judy Eisele

Charles Escapule of the small state of Maine heap leaching operation in Tombstone, Arizona, observed that silver could be leached relatively easily from ore the first time around but that if it were allowed to precipitate back on the ore in the heap, dissolution was very much more difficult the second time around.

VAT LEACHING, AUSTRALIA

GRANTS PATCH PARTNERS in Australia uses whatever water is available for leaching gold from old tailings in vats followed by carbon adsorption. Their experience is that when copper and nickel concentrations get too high in the recycle solution, such a method loses its viability. They are, however, able to use water with up to 10,000 mg/l TDS which is often high in aluminum and requires large additions of lime to reach pH 9.5 used in cyanidation. Water quality has a significant impact on carbon recovery of gold from solution and on the cost of reagents used.

In this case, an added benefit of recycling solutions efficiently is that much smaller amounts of reagent are needed than if new high-TDS water were used each cycle.

CYANIDE SOLUBLE BASE METALS IN GOLD AND SILVER ORES

Water recycling is standard practice in gold and silver recovery using cyanidation. By recycling solutions, water is conserved and, particularly, lime and cyanide consumption reduced.

When gold and silver are cyanide leached from ores containing cyanide soluble base metals, these base metals also leach and accumulate in the recirculated barren solutions until they reach levels that interfere with both gold dissolution and zinc precipitation.

This is commonly experienced in gold operations treating ores with high base metal contents, e.g., Cu, Ni, Sb, As, etc., as occurs in western Australia, eastern Transvaal, and several operations on the Canadian Shield.

To overcome the problem, a barren bleed is necessary. The volume of barren bleed can exceed 50% of the fresh water intake. In order to leach gold and silver in the presence of high levels of copper and nickel, excessive amounts of cyanide must be added until this becomes a limiting factor in the profitability of the operation, especially if cyanides must be removed from the effluents. The degree to which solutions can be recycled is, of course, determined by the amount of base metals in solution.

If, however, a successful and economically attractive method of recovering base metals and regenerating cyanide from such solutions could be developed, the solutions would be recyclable indefinitely. Such a process seems now to be potentially available:

MNR REPROCESSING, INC.
Postfach 24
D-5940 Lennestadt 17
West Germany
(02721) 835-303
Dr. A. Bergmann

GEORGE M. POTTER
40 South Calcite
Tucson, AZ 85745
(602) 884-9609

Mahad Adh Dhahab Gold Mine

The Mahad Adh Dhahab Gold Mine and Mill that is being established in Saudi Arabia is an example of a mine that will be located in a desert a long way away from a water supply. Water will be pumped to the site by pipeline across the desert. In this case, even though CIP has been selected because of its improved metallurgical recovery, the tailings will be filtered before they reach the tailings pond as a way of recovering more water for reuse, thereby avoiding some of the evaporation losses that would occur if the normal system of decanting tailings were to be applied in the intense heat of the Arabian Desert. More information on this flow sheet and its estimated water needs can be requested from:

PETER J. LEWIS
Gold Fields Mahad Adh Dhahab
c/o Consolidated Gold Fields Ltd.
49 Moorgate
London EC2R 6BQ
(01) 606-1020

Western Mining Corp., Kambalda, WA

The Kambalda ore contains cyanide-soluble copper and nickel which would interfere with zinc precipitation but is at manageable levels for CIP. To reduce the interference of copper and nickel loadings on carbon at Kambalda, free cyanide levels are kept high in the pulp solution. Despite the very high cost of water used for this operation at A$1.00/m^3 or A$1 million per year, only 36% of the water can be reclaimed from the tailings pond for this reason.

CARBON ADSORPTION VS. MERRILL-CROWE AND WATER RECYCLING

The opportunity to recycle cyanide solution is very much different for CIP and zinc precipitation circuits. For one thing, to optimize gold adsorption on carbon from clean pulps, it is best to get free cyanide concentration as low as possible. This can be done by modifying the pH, air agitation and avoiding the use of excess cyanide in the first place. Also, there is no solid-liquid separation step ahead of the tailings pond, so the only opportunity to recycle solutions is by decanting the tailings in the pond. Residence in the tailings pond (especially in warm climates) will destroy much of the cyanide left in this solution.

On the other hand, when zinc precipitation is used, cyanide solution is separated from the ore solids and after gold recovery, can be recycled to the leach end of the process

without further cyanide losses. Of course, the zinc added builds up in solution as a zinc cyanide complex until a barren bleed is necessary.

In general, the conventional gold precipitation circuit arrangement offers the advantage of being able to use a little less water and of being able to reduce cyanide consumption compared with CIP.

Gold and Uranium Operations, Witwatersrand

In the current arrangement on the Witwatersrand, many of the mines and mills are zero discharge operations. Although no solutions are discharged as surface effluents, except surface runoff perhaps and sewage plant effluents, it is likely that solution is lost due to seepage from tailings and reclaim solution reservoirs in some cases. The chance of seepage losses from the older sand tailings is greater than from the more modern slimes dams, especially those using the "semi-dry" or "sub-aerial" disposal method and also depending on the permeability of the soil beneath the tailings impoundment.

If these seepages have to be prevented at some time in the future, then the water and salt balances will change accordingly.

Most gold mills on the Witwatersrand are associated with metallurgical plants which recover uranium by acid leaching. An interesting phenomenon is found in South Africa. When recycled water is used for washing the gold rotary filters, there is less blinding of the filter media than when Rand Water Board water is used.

Vaal Reefs Exploration and Mining Co. Ltd.

The Vaal Reefs mining and metallurgical complex treats nine million tons of ore annually in a series of gold and uranium recovery operations. Tailings are mined with uranium plant raffinate and 10 Kg lime/ton tailings and aerated prior to the tailings being pumped to the tailings dams. Water decanted from these dams is recycled to each of the metallurgical operations for reuse. This form of macro recycle is effective in that overall new water requirement for both gold and acid uranium leaching amounts to 0.9 m^3/ton ore, and the operation achieves zero discharge. Additional water, however, is added to the system in the form of treated sewage effluents from five sewage plants which represents a sizeable volume of water. The operations are located within a loop of the Vaal River, and monitored water analyses of the river water indicate that seepage and surface runoff from this mammoth operation is under control.

Rand Mines Milling and Mining Co. (Pty) Ltd. (RM3)

At RM3, secondary water sources are relied upon entirely in the recovery of gold and pyrite by flotation and CIP of the leached flotation tailings. Water is recycled to the

greatest possible extent as shown in a diagram in the trip report on RM3 in Appendix I. It is believed that gold recovery has not quite matched pilot test results due to water quality problems. First, one of the surface water sources upstream of the RM3 uptake is impacted by industrial effluents which seem to add organic constituents and oxygen consumers to the water. Second, the water in closed loop contact with the tailings undoubtably builds up levels of ferrous ions and partially oxidized sulfur and organic compounds which may impact both leaching and carbon adsorption of gold.

East Rand Gold and Uranium Company Ltd.

At ERGO, 1.6 million tons per month of tailings are reclaimed by repulping them using monitor hoses. Minewater from nearby deep underground mines is used together with tailings recycle water. After flotation of pyrite and gold at an acid pH, the tailings are neutralized and treated by CIP to recover gold. The last 7 stages of the 11-stage CIL train serve to remove cyanide from the pulp prior to tailings being pumped to a new tailings dam. Water from this dam is decanted and returned to the plant. The operation is described in Appendix I. Despite the degree of water recycling and high TDS, scale is not a serious problem in the tailings return solution lines, but it is in the monitor water lines, and special scale inhibiting measures are employed. Wherever cyanide is used to leach tailings or calcine for gold recovery, it is treated before being discarded to tailings to avoid cyanide returning to the flotation plant (where it would inhibit pyrite recovery) or becoming a pollutant.

GOLD AND SILVER RECOVERY, U.S.A.

Most gold and primary silver recovery operations are located in the drier western states of the U.S.A. where zero discharge is possible from a climatic point of view. At most of these oparations, water is recycled without serious effects. Two operations in the west where zero discharge is not achievable are the NORANDA Grey Eagle Mines in northern California and HECLA Mining's Knob Hill Mine at Republic, Washington, where precipitation exceeds evaporation. In the case of NORANDA Grey Eagle Mines, excess solution from the CIP tailings dam is treated by alkaline chlorination before it can be disposed of by spray irrigation to a field. At Knob Hill, the excess solutions are sprayed into the air to enhance evaporation. In both operations, tailings decant solution is also recovered for recycling to the mill.

At the Battle Mountain operation of DUVAL CORP. which uses CIP, recycling of solution is not possible as there are no topographic possibilities for a tailings pond at the same level as the mine and mill, both of which are located on top of a hill (mountain) while the tailings are disposed of in the valley floor below. Also, cyanide-soluble copper levels in the ore result in copper levels in solution close to the limit at which metallurgical problems would occur if the water was recycled without treatment. The Battle Mountain plant was converted to gold leach and recovery from a copper flotation operation. Had it

not been for the fact that abundant fresh water was available from a well near the minesite, their water management arrangements have had to make provision for water recycling as well.

Getty Mercur Mine, Tooele, Utah

The Getty Mercur Mine at Tooele, Utah, is interesting from a water recycling point of view. This is one of the few operations that recycles tailings decant solution back to the operation but where cyanide in the recycled solution is destroyed deliberately before reuse of the water.

The reason is that the Mercur ore is preg-robbing and, if cyanide were to get into the grinding circuit, gold would start leaching and would be adsorbed on the pregrobbing species in the ore. The aim at Mercur is for the ore to start leaching in cyanide only after it is brought in contact with activated carbon in a true carbon-in-leach arrangement.

Recycled solutions are treated with hypochlorite before being returned to the mill.

Rustenburg refiners, Rustenburg

Maximum use is made of recycled water at the Rustenburg Refinery which recovers a platinum group metal concentrate and copper, nickel, and cobalt salts from a roasted matte.

The water management program allowing the high degree of recycling is sophisticated and incorporates evaporation of the final metallurgical solutions to recover sodium sulfate crystals and water as well as reverse osmosis for the treatment of utility wastewater as a means of achieving zero discharge. The evaporators yield a salable sodium sulfate product. A lime-soda softening process is employed to treat reclaimed process water before it is returned to the process.

In this case, recycling of process water is so efficient that if chloride in incoming water is higher than usual, it builds up in the process solutions until eventually presenting a corrosion problem in the stainless steel autoclaves employed.

Efficient water recycling leads to efficient salt load accumulation which eventually must be bled in one or another way to maintain a balance.

Rustenburg Refiners' water management program is briefly discussed in Appendix I.

In the Rustenburg Platinum Complex, a tailings impoundment is used in which, because of efficient recycling, TDS levels are building up. The sulfate solutions have been

neutralized with lime and are close to saturation with $CaSO_4$. Underdrains for controlled release of water from tailings are an advanced design feature, but the metallurgical industry has not yet completely worked out how to avoid underdrain clogging due to scale formation, or under what conditions it will occur and what to do about it if it does.

ECONOMICS OF WATER RECYCLING

The economics of water recycling in mine-mill environments varies from site to site and cannot realistically be discussed here in quantitative terms. The extent of recycling should be increased in increments until the benefits no longer outweigh the costs. This is a tradeoff of the following factors.

Benefits of Recycling

1) Price of water saved.

2) Price of reagent savings, e.g., pH adjustment, cyanide, etc.

3) Cost of alternative water treatment or evaporation saved by recycling instead of discarding.

4) Value of incremental recoverable resource that would be lost were it not for recycling of solution after adjustment for the concentration enhancement due to recycling.

Cost of Recycling

1) Cost of reclaiming and pumping.

2) Extra cost of solution storage.

3) Incremental cost of scale or corrosion caused by recycling.

4) Cost of incremental impact on metallurgical efficiency recycling.

5) Cost of catering to problems such as the cementing up of multi-media polishing filters.

Of course, the economics of recycling are clearcut if an operating permit or water supply constraints are such that the operator has no option but to recycle as much water as possible in order to stay in business.

PROBLEMS ARISING FROM WATER RECYCLING

The problems that arise from water recycling were reasonable well documented in the above examples. These may be summarized as follows:

1) Buildup of TDS and contaminants.

2) Enhanced corrosiveness or scaling characteristics of recycled water.

3) Possible introduction to the front of the process of reagents that interfere with the front end processes, e.g., hexavalent chromium to Cu-Pb-Zn flotation or CN^- to mill treating a pregrobbing gold ore.

4) TDS increase in solutions as they are recycled, eventually resulting in problems such as in pregnant solution polishing ahead of metal recovery, e.g., SX for uranium or zinc precipitation for gold and silver. Fortunately, there are innovative new ways to polish solutions.

5) If metallurgical operations are operated for true zero discharge (in climates with a net evaporation), through efficient water recycling, then the salt load will also build up in tailings and process solutions. The concentrations of species such as $CaSO_4$ may exceed saturation, and there is a possibility of underdrains of tailings impoundments becoming scaled up. This is potential problem that is being studied by industry in the hope of finding answers before the problem occurs.

6) If water and salts contained in solutions are recycled, at some point there must be a salt bleed. Evaporation ponds are one way in areas where there is adequate space. In the future, increasing use will have to made of more sophisticated water recovery processes such as multi-effect evaporators, etc., as are used routinely in the chemical industry.

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CHAPTER 6

SUMMARY OF WATER QUALITY STANDARDS

The mining and mineral processing industry is impacted by several levels of water quality standards. These vary from country to country, state to state, county to county, and even site to site. In the U.S.A., the following seem to apply:

Federal Water Quality Standards
State Water Quality Standards
NPDES Permits for Effluent Discharges
Federal Drinking Water Standards
Federal Water Quality Objectives

A similar multi-level system of standards has also evolved in Canada where federal, provincial levels, and permit levels apply to a given project.

In South Africa, there are two and soon will be three National Standards relating to surface effluent discharge from industrial operations including mining. These are the so called general standard applicable everywhere, the special standard for the special protection of several disignated stretches of river which are said to be capable of supporting trout fisheries, and the new PWVS standard for operations in the Pretoria-Witwatersrand-Vereeniging-Sasolburg region where buildup of TDS in the Vaal Dam has necessitated more careful protection of surface water discharges.

In the United States, perhaps the most stifling of all is the pending regulation of solid waste disposal by mines and mills at the federal and state level since it is not yet established what these rules and criteria will be. Although the Beville Amendment rules that the federal RCRA laws governing hazardous waste do not apply, temporarily, to mining and mineral processing wastes, congress is busy working on a new set of rules designed to apply to the disposal of mining and mineral processing waste to prevent damage to surface and groundwater resources. Certain states, including the trend-setting state of California have established hazardous waste disposal laws that are even stricter than the RCRA rules, and in California the rules are applied to mining and mineral processing wastes. These rules are less of a water standard than a set of criteria by which to judge whether a particular waste is or is not to be classified as a "hazardous" waste. This is determined primarily by a short-term leach test using a weak acid (citric acid in California, acetic acid at pH 5 for the federal EP toxicity test). If judged to be hazardous by these criteria, then a special set of waste disposal regulations for "hazardous" waste disposal must be followed.

Apart from the questionable applicability of short-term acetic acid or citric acid leach tests as a realistic means of determining whether waste is hazardous or not, a major problem arises in that the list of elements and their criteria levels in the leachate has not been finally decided. The EPA reputedly is extending their list significantly. "hazardous waste" disposal rules are in varying stages of evolution state to state and for the next several years, these promise to continue to be a moving target. If one is contemplating a new mining and mineral processing operation in several parts of the U.S.A. at this time, it is not crisply defined what water quality standards will apply for effluents that have to be discharged nor what will be required in the way of groundwater protection for wasterock and tailings disposal.

Before discussing water quality standards themselves, it is important to recognize that in the U.S.A., the general rule is that there shall be no discharge of effluents at all from metallurgical and mineral processing operations except where precipitation exceeds evaporation in which case, effluents must be treated to meet the levels set out in the NPDES permit. In other words, all mineral processing and ore treatment operations must be zero discharge except where climatic constraints make this impossible. Minewater is subject to NPDES permitting and must be treated to meet permit requirements.

The way this works in practice is that water released from say a uranium mine in New Mexico may be released after treatment to meet NPDES permit requirements. Effluent from the mill or tailings pond decant may not be released because in New Mexico evaporation exceeds precipitation, and "zero discharge" can be achieved. In this case, mill process and tailings effluents must be impounded and evaporated.

At the Homestake Mining Company's McLaughlin project which is in a climate where, on average, evaporation exceeds precipitation, again no mill or tailings effluents may be discharged. A comprehensive NPDES effluent discharge permit is nonetheless required with extensive sampling and monitoring requirements for runoff that may occur from the affected area which covers several square miles. This NPDES permit is included in the McLaughlin trip report in Appendix I.

DISTINCTION BETWEEN EFFLUENT PERMITS AND OBJECTIVES

An important distinction neds to be made between the levels shown for contaminants in NPDES permits and various water quality objectives for environment protection. NPdES permit levels apply to concentrations of contaminants in the effluent itself. Water quality objectives and drinking water standards apply to the level of a contaminant in the receiving waters or drinking water itself. Another distinction between effluent limit permits and objectives is that the first describes a legal requirement while the second describes what the state would like to achieve if possible.

CERCLA - SUPERTHREAT

One aspect of the permitting and regulatory process in the U.S.A. should be of particular concern to mining companies operating in the U.S.A. CERCLA or Superfund rules are such that even if an operator fulfills all the requirements of their NPDES permits during the life of the operation, if years later after the operation has been shut down, the site is found to cause contamination of an aquifer or stream, lake, etc., then under CERCLA (Superfund) rules, the original owners of the operation can be persued by the state to pay for whatever measures are deemed necessary to stabilize the site and repair whatever damage has been done. Under CERCLA rules, the original operator may be sued for up to $50 million for "each occurrence" of contaminant release from the site. The meaning of "each occurrence" is believed about to be tested soon in court in Colorado.

What this seems to mean is that if an operation is successful at negotiating lenient permit requirements from regulators when he goes into production or if the measures required by the state at the time prove to be inadequate or inappropriate in the long run and damage results to the environment years later, then the state and private organizations representing "the people" may sue the owners of the operation for tens and even hundreds of millions of dollars in reparations.

One other point must be made before listing water quality standard and permit data. The data listed below refers to mining and mineral processing effluents. It does not apply to smelters, refineries, or metal finishing operations.

BASE METAL REFINERIES AND SMELTER EFFLUENT RULES - U.S.A.

For base metal refineries, the rules are now very much more complicated. The EPA has devised a series of technolog-based standards specifying not only the concentration of contaminants that can be released from smelters and refineries, but also the total amount of each contaminant that can be released daily in the total effluent from such plants including runoff. The regulations in the U.S.A. seem also to specify what type of treatment process shall be used. For a given type of works, the EPA has attempted to establish a "building block" framework for calculation of permissible amounts of contaminant release permitted daily. Each processing step in the plant is allowed to contribute a certain number of pounds per day of contaminant to the final effluent, and these allocations for the whole plant are then added to compute the maximum total amount of each contaminant in the final effluent. To bad if a new process step is used which is not included in the regulated list as for that part of the process, no contribution to the final effluent is allocated. Also, the allowable contaminant allocations for each step in the process are based on a production level at the plant. Presumably, if operations are suspended for a period of time, then the allowable effluent contamination drops to zero

for that period. The nature of the regulations governing discharges from smelters and refineries is so complicated that it is not practical to try to include them in the list of water quality standards tabulated below. Sponsors are referred to the Federal Register, Thursday, March 8, 1984, 40 CFR, Part 421, Part II, Environmental Protection Agency, titled "Nonferrous Metals Manufacturing Point Source Category; Effluent Limitation Guidelines, Pretreatment Statdards, and New Source Performance Standards; Final Rule," pp8741-8831. Although aspects of these effluent level determining procedures are subject to a suit filed by the American Mining Congress against the U.S. EPA, the final regulation document illustrates the complexity and unwieldiness of the present system for non-ferrous smelters and refineries in the U.S.A.

EFFLUENT LIMITS SPECIFIED IN PERMITS

	Homestake Mining Co. McLaughlin NPDES 1984 (Zero Discharge)		AMAX, Inc. Mount Emmons	Quivira Mining Mine/Mill	Homestake Lead, SD		St. Joe Minerals Monaca, PA 1984		Noranda Grey Eagle (Zero Disch.) California RWQCB	Cotter Corp. Schwarzwalder Palmer & Himsley
	30d Ave.	Daily Max.	Daily Max.		NPDES	Interim	Daily Max.	Daily Ave.	Order 84-108	(1984)
pH	6.5-9.0				6-9	6-9				
S/S	20	30	30	6-9	10					
Settlable Solids	1.0		5.0							
As_T	0.05		0.10	0.05	0.38		0.05		0.02	0.05
Cd_T	0.01	0.02	0.015		0.00025		14 lb/d	7.17 lb/d		0.0004
Cr_T	0.05	0.10			0.65					
Cu_T	0.15	0.30	0.04		0.009	0.009			0.20	0.005
Hg_T	0.001	0.002	0.0005		0.001		0.001	0.001		
Pb_T	0.05	0.10	0.15		0.28					0.032
Zn_T	0.75	1.5	0.06		0.02	0.02	187 lb/d	62.5 lb/d	0.01	0.05
NH_3 as N	N.S.	N.S.				2-8				
F										
Ni_T	0				1.25	1.25				
Residual Cl_2			0.002							
Total Fe			1.0						0.20	
Total Mn			1.0							
Total Mo			2.0							
Ra (PCI/l)				-3						5
U				-1						0.06
CN Available									0.02	
CNT					0.02	0.02				
Silver					0.001					
Se										
Barium										1.00
Boron										
Notes:	No incremental increase exceeding 10% of upstream levels of Hg, Cr, Cd, B, Cu, Ni.			Zero discharge mill; permit applies to minewater.	NH_3 limit depends on altitude and temperature.					

EFFLUENT LIMITS SPECIFIED IN PERMITS

	Climax Molybdenum Company 1981		Typical Arizona Copper Concentrations		New Mexico Water Quality Control Commission	Falconbridge Ltd. Onaping Ontario	Key Lake		Denison Mines Ltd. Elliott Lake AECB	Cominco Ltd. Con Mine Yellowknife, N.W.T.	
	24 Hr. Max.	30d Ave.	24 Hr. Max.	30d Ave.	August 27, 1971		Mo. Ave.	Max. Grab		Max. Ave.	Max. Grab
pH	6-9	6-9	6.5-8.6	6.5-8.6	*	6.5-8.5	6.0 Min.	5.0 Min.	6.5-9.5	6.0-9.5	
S/S	30.0	20.0	40	20			25.0	50.0	15 Grab 7 Mo. Ave.		
Settlable Solids			0.02	0.01							
As_T	1.0	0.5			0.05		0.5	1.0		0.5	1.00
Cd_T	0.1	0.05			0.01						
Cr_T					0.01						
Cu_T	0.1	0.05	1.0	0.5	0.05**	1.0	0.3	0.6	0.6*	0.30	0.60
Hg_T					0.001						
Pb_T					0.05	1.0	0.2	0.4	0.4*	0.20	0.40
Zn_T	0.2	0.1	2.0	1.0	0.10 mg/l**		0.5	1.0	1.0*	0.50	1.00
NH_3 as N						10.0	30				
F	3.0										
Ni_T					0.10	1.0	0.5	1.0	1.0	0.50	1.00
Residual Cl_2											
Total Fe	0.6		1.0	0.5							
Total Mn	1.0	1.0			0.1 mg/l						
Total Mo	2.0	1.0			0.1						
Ra (PCI/l)							10.0	30.0	5.0 Mo. Ave.		
U							0.50				
CN Available										0.40	0.80
CNT	0.04	0.02								1.50	3.00
Silver					0.05						
Se					0.01 mg/l						
Barium					1.0 mg/l						
Boron					0.75 mg/l						

Notes: COD = 50.0 24 Hr. Max.
25.0 30d Ave.

* Exception: Community Sewer Can Contain 0.1 mg/l Cu, 0.5 mg/l Zn.
** Cumulative Cu, Pb, Zn = 1.0 ppm Max.

* Exception: Community Sewer Can Contain 0.1 mg/l Cu, 0.5 mg/l Zn

EFFLUENT LIMITS SPECIFIED IN PERMITS

	Giant Yellowknife, N.W.T.		Wedge Mine, N.B. Guidelines 1977		Brunswick Mining N.B., 30d Ave. No. 6 Mine	Western Mines Myrah Falls, B.C. 1975	Effluents from Copper Mining 40 CFR 440, B USEPA		Anaconda Copper Butte, Mt. (1980) Copper
	Max. Ave.	Max. Grab	Mo. Ave.	Daily Max.			Max. Grab	30d Ave.	
pH	6.0	6.0 Min.	6.0 Min.	5.5 Min.	6.0 Min.	6.0-10.0	6-9	6-9	7-11
S/S	15.0	30.0					30	20	30
Settlable Solids									
As_T	0.80	1.60							0.05
Cd_T					0.05		0.01	0.05	
Cr_T									
Cu_T	0.8	1.6	0.3	0.45	0.30	0.3 (Soluble)	0.1	0.05	1.0
Hg_T							0.002	0.001	0.002
Pb_T	0.2	0.4	0.2	0.3	0.20	0.10 (Soluble)	0.2	0.1	0.1
Zn_T	0.20	0.40	0.5	0.75	0.50	5.0 (Soluble)	0.50	1.0	1.0
NH_3 as N	1.00	2.00							
F									
Ni_T	0.5	1.0							
Residual Cl_2	0.1	0.2							
Total Fe									
Total Mn									2.0
Total Mo									
Ra (PCi/l)									
U									
CN Available									
CNT									
Silver	1.50	3.00					0.02	0.01	
Se									
Barium						*$SO_4^{=}$ - 1,000 Max.			
Boron									

Notes:

SOUTH AFRICAN EFFLUENT STANDARDS

(mg/l Unless Otherwise Stated

	General Standard S.A. Water Act 54 Section 21, 1956 R553 Gov't Gazette 5 April, 1962	Special Standard S.A. Water Act 54 Section 21, 1956 R553 Gov't Gazette 5 April, 1962
pH	5.5-9.5	5.5-7.5
Dissolved O_2 (Min.)	75% Saturation	75% of Saturation
Faecal Coli	Nil	Nil
Total Organisms Colories/ml	-	-
Temperature	35°C'	25°C' Max.
COD	75 mg/l	30 mg/l
TDS	Intake + 500 mg/l and Other Limits	1.5% Increase Over Intake Water and Other Limits
Suspended Solids	25 mg/l	10 mg/l
Na	Intake + 90 mg/l and Other Limits	Intake + 50 mg/l and Other Limits
Soap, Oil, Grease	2.5 mg/l	Nil
Cl^- as Cl	-	-
Cl_2 Residual	0.1	Nil
Ammonia - N	10.0	1.0
Nitrates - N	-	1.0
Arsenic As	0.5	0.1
Boron as B	1.0	0.5
Hexavalent Cr	0.05	-
Cr_T	0.50	0.05
Cu	1.0	0.02
Phenolics as Phenol	0.1	0.01
Pb	1.0	0.10
Total Phosphates as P	-	2.0
Ortho Phosphate as P	-	-
Fe_T	-	0.30
Mn_T	-	0.10
CN_T as CN	0.50	0.50
Sulfides as S	1.0	0.05
Fluoride	1.0	1.0
Zn_T	5.0	0.30
Cd	-	-
Hg	-	-
Se	-	-
Mg	-	-
Sulfate	-	-
Total Hardness as $CaCO_2$		
Min.	-	-
Max.	-	-
Radioactivity	-	-

SOUTH AFRICAN EFFLUENT STANDARDS (Continued)

(mg/l Unless Otherwise Stated

	Proposed Standard PWVS-Witwatersrand Proposed Standard 1983 R553, Table 2	Drinking Water SABS 241-1971 Recommended	Max. Allowable
pH	5.5-9.5	6.0-9.0	5.5-9.0
Dissolved O_2 (Min.)	75% of Saturation	-	-
Faecal Coli	Nil	Nil	Nil
Total Organisms Colories/ml	-	-	-
Temperature	35°C' Max.	-	-
COD	75 mg/l	-	-
TDS	2,000 mg/l	500	2,000
Suspended Solids	25 mg/l	-	-
Na	Intake + 50 mg/l and Other Limits	-	-
Soap, Oil, Grease	2.5	-	-
Cl^- as Cl	-	250	600
Cl_2 Residual	0.1	-	-
Ammonia - N	10.0	-	-
Nitrates - N	-	10.0	-
Arsenic As	0.50	0.05	0.05
Boron as B	1.00	-	-
Hexavalent Cr	0.05	-	-
Cr_T	0.50	0.05	0.05
Cu	1.00	1.0	1.5
Phenolics as Phenol	0.10	0.001	0.002
Pb	0.10	0.05	0.10
Total Phosphates as P	3.00	-	-
Ortho Phosphate as P	1.00	-	-
Fe_T	-	0.3	0.7
Mn_T	0.40	0.1	0.4
CN_T as CN	0.50	0.01	0.2
Sulfides as S	1.0	-	-
Fluoride	1.0	1.0	1.5
Zn_T	5.0	5	15
Cd	0.05	0.05	0.05
Hg	0.02	-	-
Se	0.05	-	-
Mg	-	100	100
Sulfate	-	250	400
Total Hardness as $CaCO_2$			
Min.	-	20	-
Max.	-	200	1,000
Radioactivity	-	As laid down by International Commission for Radiological Protection	

BRAZIL

Effluent limits for industry, which include mine-mill operations in Brazil, are specified in site specific permits. The following general maximum guidelines are used in three industrialized provinces of Brazil:

Parameter	Unit	Rio	S. Paulo	Minas Gerais
pH	-	5-9	5-9	6-9
Sedim. Solids	ML/L	1.0	1.0	1.0
DB05	MG/L	(*)	60	60
Cyanide	MG/L	0.2	0.2	0.2
Arsenic	MG/L	0.1	0.2	0.2
Copper	MG/L	0.5	1.0	0.5
Lead	MG/L	0.5	0.5	0.1
Zinc	MG/L	1.0	5.0	1.0
Nickel	MG/L	1.0	2.0	1.0
Mercury	MG/L	0.01	0.01	0.01
Cadmium	MG/L	0.1	0.2	0.1
Chromium III	MG/L	1.0	5.0	1.0
Chromium VI	MG/L	1.5	0.1	ND
Fluorides	MG/L	10	10	10
Sulfides	MG/L	1.0	-	0.5
Oil and Grease	MG/L	20	100	20
Temperature Degc.		40	40	40

* Biological oxygen demand (5-day) depends on the receiving water quality (flowrate, flow pattern, and dissolved oxygen level).

Note: Priority pollutants such as carcinogens are submitted to specific legislation.

The above limits must not be exceeded for mine drainage, rain water runoff, and process effluents.

RANDOL is indebted to Natron, a leading firm of environmental engineers and consultants, for the above information.

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SWEDEN

No fixed limits of contaminants are specified in mine-mill discharges. These are set on a site specific basis through negotiation with licensing authorities. These are the Franchise Board in Stockholm and the Water Court of which there are several scattered across the country.

Examples of effluent limits which have been agreed upon include the following examples provided by BOLIDEN A/B:

pH	Case 1: pH 7 Case 2: pH 8
Suspended Solids	Max. 10 mg/l
Combined Cu, Pb, Zn, Cd, As, Hg	1 mg/l (Monthly Average)
Cr	0.1 mg/l
CN (Free)	0.5 mg/l (Monthly Average) 0.2 mg/l (From July, 1986)

INTRODUCTION

The U.S.A. initiated the wave of environmental awareness and the rapid growth of bureaucratic organizations to protect the environment. Mining and mineral processing is not the prime target of these bureaucracies who have had to deal with a wide range of industries, all at the same time, even though at times it feels to the industry as though they are. Regulation of mine and mill effluents as an environment protection measure has spread rapidly to other parts of the world, and there is virtually nowhere that a new mine could be started today without having to meet strict effluent discharge control regulations.

The huge Ok Tedi gold recovery operation in Papua New Guinea, had to meet effluent limits with respect to cyanide comparable with those in North America. U.S. environmental consultants were hired to advise both the Papua New Guinea, government and the owners of the project. When the Anglo American Corp. planned the recovery of gold from a new arsenopyrite gold deposit near Morro Velho, Brazil, the limits for arsenic that had to be met in their effluent (0.2 mg/l) were comparable with those in the U.S.A., although they were able to install a roaster which would be a questionable endeavor in North America at this time. This may have something to do with the shortage of sulfuric acid in Brazil.

South Africa is revising its regulations with respect to the protection of surface and groundwater quality, and the final ramifications of these regulations are not yet known. What is known is that they will be stricter than before, although the emphasis on the Witwatersrand will be more on preventing TDS buildup in the Vaal Dam which is the regional water supply to the industrial heartland of the country.

Most of Europe with its high population density has a well-developed environment protection regulatory system. Trout live successfully in a stream that receives effluents from the only gold cyanidation plant in France.

Australia is also very concerned with environmental aspects of mining and mineral processing. The Deep Leads, a gold resource in the state of Victoria which is suitable for in situ leaching, has not been exploited for lack of a permit to impact the aquifer in an agricultural region. In Kalgoorlie, Western Australia, there is some question as to whether another roasting plant would be permitted in the Golden Mile area. Regulatory requirements for environmental protection at uranium mines in the Alligator Ridge area of the Northern Territory have been as stiff or stiffer than those in the U.S.A.

In New Zealand, the public mostly appears to be against mining of any sort. Opponents to a mining operation which proposed to excavate only 50,000 tons used old photographs of Bingham Canyon to illustrate their cause. New Zealand is not a "mining country," and permits to open a metals mine there would be very difficult to obtain.

CHAPTER 7

SUMMARY OF CRITICAL RECULATIONS GOVERNING EFFLUENTS

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Some Considerations on Environmental Regulations Relevent to Hydrometallurgical Process Residue by SUN K. KIM and ROGER N. KUSH, AIME, Dallas, Texas, February 14-22, 1982 263

Canada is one of the major mining countries of the world along with South Africa and the U.S.A. Canada and South Africa are more alike in that both recognize the importance of the mining industry to their economies, while both also recognize the need for improved environmental protection. Environmental protection in both cases means protecting the quality of water. In fact, in Canada, the environment protection laws and effluent discharge permits are administered under the Fisheries Act.

Although alike in that both countries are concerned about the quality of mining and mill processing effluents, they are quite different in their motivation for water quality protection. Canada accommodates 37% of the world's fresh water resource while South Africa is a dry country with just a few oases. In Canada, rules are made primarily to protect valuable inland fisheries. In South Africa, the new modifications to effluent discharge regulations are aimed at protecting the quality of their limited water resources which have been recognized as a factor that will limit the future growth of their economy.

In the main mining countries of the world, motivation for environmental protection is reflected in the nature of the mine and mill effluent regulations, i.e., protection of fisheries in Canada, and protecting water quality in the Vaal Dam in South Africa. The U.S.A., however, although it is the leader in all aspects of understanding the environment, analyzing and monitoring techniques, and in the availability of equipment and technology to treat water and effluents, is possibly the furthest behind in developing a workable set of regulations for environmental control, i.e, preservation of surface and groundwater quality. Both Canada and South Africa recognize the need to keep their mining industries alive even if there is an environmental price to pay--within limits. The emphasis in these two countries is by and large placed on doing what can be done without destroying the industry or costing too many jobs.

U.S.A.

In the U.S.A., the two main areas of near term concern are the amended Resource Conservation and Recovery Act, RCRA, rules expected to govern "hazardous waste" disposal as applicable to solid waste from mines and mills, i.e., wasterock and mill tailings, and the CERCLA-Superfund Law implementation. RCRA rules may well also be applicable when metal precipitates or desalination concentrates are generated in effluent treatment processes, and it is conceivable that effluent treatment requirements may result in the generation of "hazardous" wastes requiring special disposal conditions. The EP toxicity test which is a criteria used to determine whether non-mining wastes are "hazardous" was described in EPA (1978). Toxicity is exhibited if any of the contaminants listed by the EPA exceed the limits established by the EPA (1980) and also listed by KIM and KUST (1982) at the end of this chapter which are 100 times the primary drinking water standards (PDWS). It is now rumored that the EPA is about to greatly expand the list of elements included in the EP toxicity test and to make the limits

Federal Register, Friday, December 3, 1982, Part II, Environmental Protection Agency Ore Mining and Dressing Point Source Category Effluent Limitations Guidelines and New Source Performance Standards 269

Clean Water Act - Regulatory Update, by JAMES R. WALPOLE, American Mining Congress, San Francisco, California, September 12-14, 1983 281

Review of Environmental Ligislation in the 98th Congress by DAVID C. RIDINGER, American Mining Congress, September 12-14, 1983, San Francisco 287

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Superfund/RCRA: An Environmental Jigsaw by LOUIS J. MARUCHEAU, American Mining Congress, September 12-14, 1983, San Francisco 299

EPA's Mine Waste Study by PENELOPE HANSEN, American Mining Congress, September 12-14, 1983, San Francisco 305

Superfund - Mining Sites on the National Priorities List by BRIAN L. MURPHY, WILLIAM W. BECK, and DENNIS F. UNITES, American Mining Congress, September 12-14, 1983, San Francisco 315

for the existing list of elements more stringent, but this has yet to be officially confirmed. There is such a potential "bite" to some of these regulations that they have already become a factor in scaring away potential foreign investment in U.S. minerals exploration and mining industry.

A major problem with BAT (Best Available Technology) regulations for metallurgical process effluents is that often as new treatment processes are demonstrated in laboratories by professors, the EPA latches onto them and sets a new limit--stricter than the last--based on the capabilities of the new technology demonstrated under ideal conditions rather than in real life mine environments. In effect, the regulations present a moving target.

One of the most difficult set of environmental protection regulations or pending rules for the U.S. mining industry to contend with is CERCLA--the Superfund regulations. The reason is that no matter whether or not an operation complied with all effluent and solid waste requirements at the time their tailings and wasterock were disposed of, if at some future point it is discovered that they are causing damage to the environment, the original owners of the operation can be sued years later for reparations to force them to pay for the repair of the damage and stabilization of the site. CERCLA suits run up to $50 million per occurrence and, with several possible contaminant release occurrences from the same property, Superfund suits run into hundreds of millions of dollars. The U.S. law also makes provision for citizen-suits against mining companies that cause environmental damage, or which fail to meet their permit requirements. Private groups in the U.S.A. also have the legal right to demand company files and reports lodged with regulators and, if they find incidences where permit requirements have not been met, they may force litigation against that company.

Most federal regulations are formulated in Washington where the mining industry is represented by lawyers working for the AMC (American Mining Congress). Regretably, there are indications that Washington is far removed from the practical problems and site-specific nature of the mining and mineral processing industry in the western states. The EPA headquarters in Washington seems bent on formulating a uniform set of regulations applicable to every mine in the country. Washington does not appear to want to listen even to their own people in the regional offices who have the field experience and know the site-specific nature of mining and mineral processing waste and of its impact on different types of environments in different topographies and climates. The industry awaits the pending new federal rules governing solid waste disposal by mines and mills with some apprehension.

Unlike any other country, in the U.S.A. new regulations are scrutinized also by publicly-funded organizations such as the Natural Resources Defense Council Inc., and others who take legal action which, in the recent past, has forced the issue successfuly, setting time limits for new regulations and contesting whether or not proposed regulations

are strict enough. Most of their actions are based on "eastern thinking" which seems to believe that all environmental impacts of mining can be solved overnight through technologies selected in Washington by lawyers. The result in the U.S.A. has been that regulators have tended to over regulate the mining industry while at least some of the mining industry has argued for no regulation with the result that a confrontational atmosphere has prevailed. This, in turn, has served neither the environment nor the mining industry constructively.

The public hearing process that goes into the granting of permits for mines and mills in the U.S.A. has also encouraged the evolution of vociferous anti-industry private groups that seem to oppose all industry on principle. These protestors pop up to oppose nuclear power, mining projects, automobile plants, and housing development. Very often, mining companies end up agreeing to do things to appease these anti-industry groups rather than because the agreed upon actions are reasonable or meaningful. These groups also influence public servants charged with regulating the mining industry.

Another significant trend in regulations that affects the U.S. mining industry is the shift in roles of Washington (i.e., the federal government) and state-level government. Although federal rulemakers continue to make new rules, the implementation of these rules is being shifted to the individual states. The way this is done is for jurisdiction to be transferred to state regulators once that state has enacted and can show it has the ability to enforce rules at least as stringent as the federal rules. This has two results. First, several states have enacted much stricter regulations than the federal rules; second, in those states that have limited experience with mining, it now takes "forever" to secure a permit while local regulators learn about the special needs and character of mining. A case in point is EXXON's Crandon project in Wisconsin which has been seeking a permit for a mine and mill for at least four years. In some counties of California, local ordinances have been passed recently which will make mining in those counties virtually impossible.

Fortunately for the industry, there are still states, such as Nevada, that welcome mining. However, for a mining company with nationwide interests, keeping up with and helping in the formulation of regulations concerning environmental protection (which means water) in all fifty states, has become a virtually impossible task. Much focus has been placed lately on the California Mining Association which strives to help mold some reason and perspective in regulations being formulated by that state, which is considered a trend-setting state. Although much progress has been made in tempering the California regulator's attitute toward mining, if California is trend-setting with respect to hazardous waste disposal by mines and mills, then the industry has much to be concerned about as other states model themselves on California. In the U.S.A., most states are electing to be "agreements states," that is, they agree to impose and regulate environmental (including water resources) rules at least as stringent as the federal regulations laid down by congress as proposed by the EPA.

The role of the U.S. EPA, it appears, is becoming more that of federal rule formulator to set the minimum standard and an advisor to the individual states when called upon. If a state fails to regulate the mining industry in accordance with its agreement, then the EPA, through its regional offices, will step in to do so.

In becoming an "agreement state," a state becomes eligible for federal funds for application in enforcing its regulations.

Another important trend in the U.S.A. is the new EPA focus on groundwater quality protection. This has a significant impact on solid waste disposal from all industries that could have an impact on groundwater through direct seepage or runoff followed by seepage from solid waste disposal sites. Consequently, it is clear that for the immediate future, significant attention will be focussed on mine waterock, mill tailings, evaporation ponds, and water/solution impoundments. This attention will be reflected in new regulations within the next one to two years. Some insight into this was obtained in a draft of EPA (1984) strategy.

In the U.S.A., generally, rainfall exceeds evaporation in the eastern half of the country and vice versa in the western states, except the very far northwest and Alaska.

A common denominator in U.S. regulations governing effluents is that there shall be no discharge of effluents from mineral processing where this is possible within climatic constraints. The impact of surface water related regulations was that much greater where effluent discharge could not be avoided, i.e., the east. The impact of anticipated groundwater-related regulations will be pretty much the same for all parts of the country.

The uranium mining and milling industry in the U.S.A. is regulated entirely by the Nuclear Regulatory Commission. Once again, however, individual state environment protection departments have the option to regulate this industry within their own states, provided their regulations and implementation thereof are at least as stringent as the NRC regulations. One of the most significant guidelines in uranium milling is a document known as the Generic Environment Impact Statement by uranium milling and waste disposal.

Uranium waste materials were specifically excluded from the RCRA rules governing hazardous waste disposal, but uranium mines and mills are not excluded from CERCLA (Superfund) regulations and, in fact, several uranium mill tailings and former mill sites have been listed as Superfund sites.

CRITICAL REGULATIONS - U.S.A.

KIM and KUST (1982) reviewed environmental regulations relevent to hydrometallurgical process residues.

At the American Mining Congress meeting in San Francisco, September, 1983, a session reviewed The Environment: Legislative and Regulatory Update, and Government Controls and the Environment: Superfund-Superproblem. This set of reports provides a good review of the critical regulations emerging in the U.S.A.

In addition, sponsors are referred to EPA (1982) on Ore Mining and Dressing, Point Source Category Effluent Limitations Guidelines, and New Source Performance Standards, and also a very confusing document, EPA (1984), on 40 CFR Part 421: Nonferrous Metals Manufacturing Point Source Category; Effluent Limitations, Guidelines, Pretreatment Standards, and New Source Performance Standards; Final Rule. The Preamble of this document is inserted below as it provides additional insight into the background of some of the important legislation that has recently been passed by congress.

PEDCo (1983) completed their report to the EPA on their analysis of solid waste (wasterock, mill tailings, precipitate sludges) and water that had been in contact with solid wastes. Based on the PEDCo (1983) report, congress will decide upon a new set of regulations designed to protect groundwater from solid waste generated by mining and mineral processing industries that EPA, Washington, is currently drafting, apparently with minimal help from EPA regional offices which are the ones that have direct field experience with industry.

As far as state regulations are concerned, California is leading the way with their set of regulations governing solid waste disposal.

A copy of a recent NPDES permit issued by the state of California to the Homestake Mining Company for their McLaughlin project is inserted below as an illustration of the types of requirements of such permits. It is to be borne in mind that this mine and metallurgical processing facility will be zero discharge, and the permit applies only to runoff surface runoff water not contained by the extensive collection system installed to prevent runoff from leaving the property.

The first Superfund lawsuits relating to mining and mineral processing suits are currently being served and in due curse, the outcome of these will determine to what extent CERCLA laws have a bite to them. Companies believed to be involved in Superfund sites are:

Anaconda Company	East Helena, Montana
ARGO Tunnel	Idaho Springs, Colorado
Asarco	Globe Smelter, Denver
Asarco	Leadville, Colorado
Cotter Corp.	Canon City, Colorado
Gulf & Western	Gilman Mine, Gilman, Colorado
Gulf & Western	Palmerton, Pennsylvania

Newmont Mining Co.	Idarado Mine and Mill, Telluride, Colorado
Union Carbide Corp./Umetco	Uranium Mill, Colorado
Vitro Uranium Tailings	Salt Lake City, Utah

There are many more Superfund sites, but the above sampling indicates the diversity of companies and industries involved.

Flotation mill tailings from selective flotation operations containing cyanide were originally listed in Appendix VII to Part 261 of IOCFR regulations as hazardous wastes from non-specific sources and given the "generic" waste number F013. During the commentary period, EPA agreed to delete this item from the regulation based on a comprehensive document prepared for AMAX Environment Services, Inc. by:

ENGINEERING SCIENCE, INC.
2785 North Speer Blvd.
Denver, CO 80211
(303) 455-4427
Allen L. Udin

"Pertinent Information Regarding Complexed Cyanides in Mineral Flotation Tailings," July 1980.

The hazardous waste regulations (RCRA) have been challenged in court by the mining companies, the American Mining Congress, and individually by companies such as AMAX, Inc., who object to the acetic acid EP leach criteria. This litigation was still in progress when RANDOL heard about it.

SOLID WASTE PROGRAM

For "non-hazadous" waste, congress encouraged the creation of effective solid waste management plans at the state level. The EPA was to promulgate guidelines for the development and implementation of state solid waste management plans. The controversial aspect of the program is included in Section 4005 of the Solid Waste Disposal Act, which provides that any solid waste management practice constituting "open dumping" is prohibited. To avoid constituting "open dumping," the disposal site would have to qualify as a "sanitary landfill" as defined by EPA promulgated criteria as found in 40CFR, Part 257. This subject is discussed in greater detail by MARUCHEAU (1983).

U.S. ACTS OF CONGRESS - FEDERAL LAW

CLEAN WATER ACT of 27 December, 1977) Sections 301, 304, 306, 307, 308, and 501 (The Federal Water Pollution Control Act, Amendments of 1972, 33, USC 1251, et sequ. as amended by the Clean Water Act of 1977, P.L. 95-217).

Sections 301(b)(2)A and 301(b)(2)C:

Require achievement by 1 July 1984 of the effluent limitations requiring application of BAT for toxic pollutants including the 65 priority pollutants declared toxic by Congress under Section 307(a) of the Federal Water Pollution Control Act of 1977.

Section 304(e):

Authorizes the Administrator of the EPA to prescribe "best management practices (BMP's) to control release of toxic and hazardous pollutants from plant site runoff; and spillages or leaks; sludge or waste disposal; and drainage from raw material storage associated with waste disposal; and drainage from raw material storage associated with or ancillary to the manufacturing or treatment process.

Section 301(b)(2)(E):

Establishes best conventional Pollutant Control Technology (BCT) for discharges of conventional pollutants from existing industrial point sources. Conventional pollutants are those defined in Section 304(a)(4) [biological oxygen demanding pollutants, total suspended solids, fecal coliform and pH as well as any other additional pollutants defined by the Administrator as conventional, e.g., oil and grease.].

Solid Waste Disposal Act, SWDA, of 1965, Section 4005:

"Open Dumping" of solid waste, i.e., other than in a sanitary landfill is prohibited.

The Clean Water Act of 27 December, 1977, Sections 301, 304, 306, 307, 308, and 501 (The Federal Water Pollution Control Act Amendments of 1972, 33, USC1251, et sequ. as amended by the Clean Water Act of 1977 P.L. 95-217).

Settlement Agreement in 'Natural Resources Defense Council, Inc. V. Train. 8ERC 2120 (DDC 1976) modified, 12ERC 1833 (DDC 1979). Requires EPA to promulgate BAT effluent limitation guidelines by a fixed date and NSPS covering 65 classes of toxic pollutants subsequently defined by EPA as 129 specific "priority pollutants."

Pollution Control Act Amendments of 1972, Section 301(b)(1)(A):

"By 1 July 1977 existing industrial dischargers were required to achieve "Effluent limitations requiring the application of the best practicable control technology currently available (BPT).

Federal Water Pollution Control Act Amendment of 1972, Section 301(b)(2)(A):

By 1 July, 1984, these dischargers were required to achieve "Effluent limitations requiring the application of best available technology economically achievable...which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants (BAT). These included 65 priority pollutants declared toxic by Congress under Section 307(a) of the Federal Water Pollution Control Act of 1977. Federal Water

Pollution Control Act Amendments of 1972, Section 306: New Source Performance Standards (NSPS) based on best available demonstrated technology (BADT).

RCRA:

Resource Conservation and Recovery Act of October 21, 1976, Section 8002(f) and Solid Waste Disposal Act Amendment of 1980, Section p: Mandate for the Study of the Impact of Solid Waste from the Mining Industry--Led to the PEDCo Study.

CERCLA:

Comprehensive Environment Response, Compensation, and Liability Act, 1980.

The Beville Amendment to RCRA:

Solid Waste Disposal Act of 1976 as amended 1980 under RCRA Deferred Regulation of Certain Wastes as "Hazardous" Wastes until at least 6 months after the submission to Congress by EPA of reports relating the results of studies on the exempted wastes. The exempted wastes include "solid wastes from the extraction, benefication, and processing ores and minerals, including phosphate rock and overburden from the mining of uranium ore." This refers to the PEDCo study mentioned above.

Federal Water Pollution Control Act Amendments of 1972, Section 402:

The requirements for direct dischargers of industrial effluents were to be incorporated into the National Pollution Discharge Elimination System (NPDES) permits issued under Section 402 of the Act.

Federal Water Pollution Control Act Amendments of 1972, Section 402(a)(1):

Authorizes the setting of requirements for direct dischargers on a case-by-case basis. Note: EPA claims that congress intended that control requirements would, for the most part, be based on regulations promulgated by the Administrator of the EPA.

Federal Water Pollution Control Act Amendment of 1972, Section 304(b):

Requires the Administrator of the EPA to promulgate regulations for effluent limitations setting forth the degree of effluent reduction attainable through the application of BPT and BAT.

Federal Water Pollution Control Act Amendment of 1972, Section 304(c) and 306:

Requires promulgation of regulations for NSPS (New Sources of Pollution).

Federal Water Pollution Control Act Amendment of 1972, Section 307(a):

Requires the EPA Administrator to promulgate effluent standards applicable to all dischargers of toxic pollutants.

Federal Water Pollution Control Act Amendment of 1972, Section 501(1):
Authorizes the EPA Administrator to prescribe any additional regulations "necessary to carry out his functions under the Act."

Clean Water Act of 1977, Section 304(b)(4)B:
Requires BCT limitations be assessed in light of a two-part "Cost Reasonableness Test." The first test compares the cost for private industry to reduce its conventional pollutants with the costs to publicly owned treatment works for similar reductions. Test 2 examines the cost effectiveness of additional industrial treatment beyond BPT. EPA must find that limitations are "reasonable" under both tests before establishing them as BCT. In no case may BCT be less stringent than BPT.

The complete Federal Water Pollution Control Act, including amendments under the Clean Water Act of 1977, is available in the form submitted to the Senate Committee on the Environment and Public Works:

FEDERAL WATER POLLUTION CONTROL ACT
Clean Water Act - Serial 95-12
Government Printing Office
Washington, DC

Attention is drawn to Section 101(f) of the Act:

"It is the National Policy that to the maximum extent possible, the procedures utilized for the implementing of this act shall encourage the drastic minimization of paperwork and inter-agency decision procedures and the best use of available manpower and funds, so as to prevent needless duplication and unnecessary delays at all levels of Government."

BILLS BEFORE CONGRESS

Clean Water Bill - James Howard (D-NJ), HR3282, 1983.
Clean Water Act, Amendment S-431 - Senator Chafee (R-RI), 1983.

U.S. FEDERAL REGULATIONS

Code of Federal Regulations = CFR, Title 40 - Environment

40 CFR, Part 257:
Under SWDA (1976) EPA Criteria for Sanitary Landfill. This regulation distinguishes legal disposal from "open dumping" which is prohibited by RCRA "non-hazardous waste" program.

40 CFR, Parts 260-271; May 19, 1980:
EPA Hazardous Waste Disposal Regulations, Implementing Section 3001 and Other Sections of RCRA, pp580-590.

40 CFR, Part 256:
EPA Guidelines for Solid Waste Management Plans.

40 CFR, Subchapter (N):
Effluent Guidelines and Standards - Part 415: Inorganic Chemical Manufacture; Part 421: Non-Ferrous Metals; Part 422: Phosphate; and Part 424: Ferro Alloys.

40 CFR, Subchapter (D):
Water Programs General - Pertinent to All Industries Listing Civil Penalties, Water Quality Regulations, NPDS System, State Program Requirements, Taxes on Effluent, Primary Drinking Water Standards, and Secondary Drinking Water Starndards.

40 CFR, Subchapter (J):
Solid Waste Disposal Act: RCRA.

40 CFR, Subchapter (I):
Hazardous Wastes, Parts 260-265; SWD Guidelines, Parts 240-257.

44 CFR, 44501, July 30, 1979:
Oil and Grease are defined by the EPA Administrator as "Conventional" and therefore subject to the Clean Water Act Section 304(a)4 and 301(b)(2)(E) subject to Best Conventional Pollution Control Technology (BCT).

44 CFR, 50732:
EPA published its methodology for carrying out BCT analysis.

40 CFR, 51722, 6 November, 1975:
EPA interim final regulations establishing BPT requirements for existing sources in the ore mining and dressing industry.

40 CFR, 51738; 6 November, 1975:
EPA proposed BAT, NSPS, and Pretreatment standards for ore mining and dressing.

41 CFR, 21191; 24 May, 1976:
EPA suspends parts of the interim final BPT regulations and solicits comments.

43 FR, 29711; 11 July, 1978:
EPA promulgates revised final BPT regulations for the Ore Mining and Dressing Industry.

44 FR, 7953; 8 February, 1979:
EPA published a clarification of the regulations as they apply to storm runoff.

44 FR, 11546; 1 March, 1979:
EPA amends final regulations by deleting the requirements for cyanide applicable to froth flotation mills in the base and precious metals subcategory.

U.S. Court of Appeals, 10th Cir., 10 December, 1979, Kennecott Copper Corp. vs. EPA, 612 F 2d 1232:
Upheld the BPT regulations rejecting challenges by five industrial petitioners.

Federal Register, 19 November, 1980, p76618:
Reports by EPA on various Mine and Metallurgical Wastes were due to be submitted by October, 1983. The Results of Assessment including Groundwater Monitoring of Waste Management at 8 Sites--"Study of Mineral Processing Waste," Section 8003(p) of the SWDA. "Mining and Milling Waste Study."

EPA (1982) Development Document for Effluent Limitations Guidelines and Standards for the Ore Mining and Dressing. Point Source Category, EPA 440/1-82/061, November 1982. "The BPT regulation provides for relief from effluent limitations including zero discharge during periods of precipitation. The basis of this upset or bypass (precipitation exemption) is that treatment facilities must be designed, constructed, and maintained to include the volume of water that would result from a 10-year, 24-hour precipitation event. The same provision is retained in BAT.

46 FR, 17567, 19 March, 1981:
EPA withdraws their proposed BAT, NSPS, and Pretreatment Standards.

14 June, 1982:
EPA proposed new BAT and NSPS standards and requested comments from the public.

47 FR, pp54598-54621, 3 December, 1982:
EPA promulgates final BAT and NSPS regulations for Ore Mining and Dressing, Point Source Category, Effluent Limitations. Guildelines and New Source Performance Standards.

NOTES ON REGULATION AND LICENSING OF MINING/MINERAL PROCESSING OPERATIONS IN CALIFORNIA

1. In California, mining and mineral processing waste has not been temporarily exempted from California laws regulating hazardous waste disposal.

2. Title 22 of the California Code of Regulations deals with hazardous waste management.

3. Matters relating to water quality fall under the jurisdiction of the California Water Board and the California State Government. The Porter-Cologne Act passed by the California state government defines the responsibilities of the California Water Board. There are overlapping responsibilities between California state and the California Water Board.

   The Hazardous Waste Management Branch of the California State Dept. of Health Services is responsible from the A1 soil zone up, and the Water Board is responsible for groundwater.

4. The California Occupational Safety and Health Administration regulates mine safety. The Hazardous Waste Management Branch becomes involved at the point of discharge of tailings at a mine-mill operation.

5. The Water Board is concerned with placer miners and any operation that could release silt or suspended solids to a stream.

6. The California Porter-Cologne Act has incorporated into it the federal National Pollutant Discharge Elimination System Act (NPDES).

7. In 1983, the California State Dept. of Health Services was trying to change the laws relating to mining and water to be similar to the federal laws but without the exemptions and using a modified EP toxicity test for determination of whether solid waste is hazardous or not. Within this structure, mine overburden would be exempted from jurisdiction by the State Dept. of Health Services but would be the responsibility of the Water Board.

8. Permits are required from the California State Regional Water Quality Control Board for all mine dumps. The California Regional Water Quality Control Boards examine all aspects of the operation that could have an impact on water quality.

9. Smaller placer mining operations employing up to 5-6 men are regulated by the California Fish and Game Dept.

10. Licensing fees are charged by the California State Dept. of Health Services. If over 500 acres are to be disturbed, the fee is $2,500. Between 50 and 500 acres, the fee is $5.00/acre. The minimum fee for less than five acres is $250.

11. The California Environmental Quality Act requires an Environmental Document. Effectively, this is an environmental impact statement on an operation which gets

circulated through a state clearing house to state authorities. All permit applications submitted at the county level are also sent via the clearing house to the state authorities.

It is the county's responsibility to inform the clearing house of all new operations. The county prepares the Environmental Document and issues one of three document types:

1) Exemption Certificate
2) A Negative Declaration - No Impact
3) An Environmental Impact Report

Items 2 and 3 are circulated through the state clearing house.

Although the county is responsible for the EIR, it usually hires consultants to carry them out. For example, the EIR on the Homestake Mining Company's McLaughlin Mine was prepared by:

ENGINEERING SCIENCE, INC.
Berkeley, CA

The consultants submit their fee to the mining company.

12. According to Dr. Takashi Asano:

OFFICE OF WATER RECYCLING
California State Water Research
Control Board
Post Office Box 2000
Sacramento, CA 95810

There are no guidelines for the recycling of water by the mining industry which in California is a minor user of water compared to other industries.

13. The Homestake Mining Company had to apply for over 281 permits for the McLaughlin operation, many of which directly or indirectly related to water management, e.g.:

- <u>Dam Approvals</u> — California Dept. of Water Resources, Divison of Dam Safety
- <u>Hazardous Waste Facility Permit</u> — California Dept. of Health Services
- <u>Solid Waste Disposal Facility Permit</u> — Lake County Solid Waste Board

° <u>Waste Discharge Requirement and NPDES Permit</u>	Central Valley Regional Water Quality Control Board (National Pollution Discharge Elimination System)
° <u>Water Appropriation</u>	State Water Resources Control Board
° <u>Stream Alteration Agreement</u>	California Dept. of Fish and Game

At the NORANDA Grey Eagle Mine at Happy Camp in northern California, the Regional Water Quality Control Board issued a cease and desist order when the company reported to them that a minor seepage of cyanide had been detected from the tailings dam. If the terms of the cease and desist order cannot be met, the case would be referred to the California Attorney General for prosecution. Fines up to $5,000/day can be imposed.

California Regional Water Quality Control Board
North Coast Region

ORDER NO. 84-108

WASTE DISCHARGE REQUIREMENTS

for

NORANDA, INC.
NORANDA GREY EAGLE MINES, INC.,
AND
SISKON CORPORATION

Siskiyou County

The California Regional Water Quality Control Board, North Coast Region, finds that:

1. On April 30, 1981, the Regional Board adopted Board Orders 81-51, 81-52, and 81-53, Waste Discharge Requirements for overall mine and mill activities, treated wastewater disposal activities, and tailings disposal activities, respectively. The adopted Orders reflect mining, milling, and waste disposal activities described in reports of waste discharge submitted by Mr. Steven A. Wulf, Vice President of Noranda Grey Eagle Mines, Inc., on January 19, 1981. On December 3, 1981, the Board adopted Order No. 81-222 amending Order No. 81-53 to provide financial assurances for closure and post closure activities regarding the tailings reservoir hazardous waste disposal facility. On May 31, 1984, the Board adopted Order No. 84-49, Waste Discharge Requirements, for tailings dam seepage control facilities.

2. Noranda Grey Eagle Mines, Inc., a Delaware Corporation, is a wholly owned subsidiary of Noranda, Inc., a Delaware Corporation. Noranda, Inc., is a wholly owned subsidiary of Noranda Manufacturing Inc., of Toronto, Ontario, Canada. Noranda Manufacturing Inc., is a wholly owned subsidiary of Noranda Inc., of Toronto, Ontario, Canada.

3. Siskon Corporation is the owner of patented and unpatented claims on which the Grey Eagle Mine is located. Noranda Grey Eagle Mines, Inc., is the sole owner of the lease to these claims. Noranda, Inc. (the owner of Noranda Grey Eagle Mines, Inc.), Noranda Grey Eagle Mines, Inc., and Siskon Corporation are hereinafter referred to as the discharger.

4. The Grey Eagle Mine is located within Section 14, T17N, R7E, HB&M in the watershed of Luther Gulch, tributary to Indian Creek thence the Klamath River in Siskiyou County. The mine is five miles north of Happy Camp. Facilities for treating wastewater and disposing of treated wastewater are located within Sections 14 and 11, T17N, R7E, HB&M in the watershed of Luther Gulch and Baker Gulch, both tributary to Indian Creek, thence Klamath River in Siskiyou County. The treatment and disposal sites are approximately five and six miles north of Happy Camp.

5. The Grey Eagle Mine, prior to the entry of NGEMI, was a continuous and chronic source of acid mine drainage which emanated from tunnels and waste

ore dumps remaining from its days of operation as a copper mine - concentrating mill during World War II. Acidic, dissolved metals-bearing drainage was toxic to all aquatic life in Luther Gulch Creek. The discharger has taken measures to reduce the effects of acid mine drainage. Measures include the sealing and flooding of tunnels and removal of waste rock from the stream system.

6. The Noranda Grey Eagle Mine is an open pit gold and silver mine. The overburden removed to expose the ore body was used to construct a tailings dam. The ore is processed at a carbon-in-pulp/cyanide leach mill and untreated tailings are discharged to the tailings dam reservoir for permanent disposal. Excess wastewater which accumulates in the tailings reservoir is treated and pumped to remote percolation basins for disposal. Pursuant to mining, milling, and waste disposal activities, the discharger has constructed:

   a. Mill and services buildings
   b. Open pit
   c. Tailings dam
   d. Diversion channel around tailings reservoir
   e. Tailings reservoir seepage control facilities
   f. Wastewater treatment facilities
   g. Export pipeline
   h. Land application site for treated wastewater
   i. Site roads
   j. On-site drainage facilities
   k. Topsoil storage site

7. Erosion control work to prevent discharge of earthen materials to surface drainages is performed by the discharger in accordance with reports submitted annually to the Regional Board.

8. The discharger receives, stockpiles, and uses in the mining-milling and waste treatment processes a number of hazardous or potentially hazardous raw materials and process chemicals including:

Material	On-Hand	Usage Rate (Resupply)
Chlorine	18 tons	5.5 tons/day
Lime	25 tons	150 tons/month
Lime Hydrate	10 tons	4 tons/month
Sodium Cyanide	20 tons	30 tons/month
Fuel Oil	5,000 gallons	6,000 gal/month
Acid (HCl)	2 drums	2 drums/year
Acid (Nitric)	5 drums	5 drums/year
Polyphosphate	5 drums	165 gal/month
Sodium Hydroxide	20,000 lb	10,000 lb/day
Polyacrilamide	5 tons	1.5 tons/month
Gasoline	2,000 gallons	3,000 gal/month

The discharger has submitted a contingency and spill prevention plan dated September, 1984, which describes spill prevention, containment, and cleanup measures.

9. The discharger has described sources of waste and wastewater from operations at the Noranda Grey Eagle Mine which include:

	Waste	Quantity	Disposal
a.	Process tailings slurry (solid and liquid phase)	650 ton/day (solid) 0.17 mgd (liquid)	tailings reservoir
b.	Treated wastewater effluent	0.35 mgd	land application site
c.	Wastewater treatment sludges	5 tons/month	tailings reservoir
d.	Tailings reservoir seepage	35 gpm	tailings reservoir
e.	Domestic waste (toilet)	1 gpm	leachfield
f.	Non-toilet domestic waste	5 gpm	tailings reservoir
g.	Mill site runoff	52 gpm (storm)	tailings reservoir
h.	Other site runoff	unknown	sedimentation ponds/ surface drainages

10. Facilities for treating excess wastewater in the tailings reservoir include the following unit processes:

a. chlorine oxidation
b. hydroxide precipitation
c. flocculant addition
d. sedimentation

The design capacity of the wastewater treatment plant was originally estimated at 159 gpm but improvements installed since the plant was constructed has enabled flow rates up to 400 gpm to be achieved.

Self-monitoring reports submitted by the discharger and verified by Regional Board staff indicated that water quality constituents which are present in the excess wastewater at levels of concern include:

a. cyanide
b. copper
c. iron
d. zinc

e. cadmium
f. lead
g. mercury
h. nickel

Performance records at the treatment plant indicate that treated effluent consistently attains State and/or EPA drinking water standards for all constituents with occasional exception of mercury. Process adjustments necessary to further reduce mercury levels have been shown to affect effluent levels for other constituents such that overall effluent quality is adversely affected.

The treated effluent typically exhibits high salt levels and alkaline pH.

The discharge of treated wastewater has been shown to increase salt levels in ground and surface waters of Baker Gulch, the affected drainage. This increase has not been shown to adversely impact beneficial uses of these waters.

11. The discharger has constructed the tailings dam and reservoir with the following dimensions:

a. height above cutoff trench — 240 feet
b. crest length — 950 feet
c. volume of fill — 2.5 million cubic yards
d. reservoir volume — 900 acre-feet
e. reservoir surface area (16 acres)
f. flood protection — 3 feet of freeboard above 2500 year recurrence rainfall event (190 acre-feet)

The dam has been built with special features, including:

a. Core — upstream face, compacted clays selected from suitable deposits on site. The core zone is anchored in a cutoff trench excavated to competent bedrock. Function is to control movement of water through dam.

b. A grout curtain was installed in bedrock underlying the core to impede migration of pollutants under the dam.

c. Chimney and blanket drain — behind core and above foundation area, imported drain rock. Function is to control movement of water through dam.

d. Random fill - structural embankment extending up to 1,300 feet downstream of chimney drain, overburden and waste rock from mining site.

e. Coarse rock armour — selected rock to protect fill from surface erosion, selected from random fill zone.

f. Clay plug - interior of dam, compacted clays selected to impound and divert tailings reservoir seepage from the chimney drain via discharge pipes which emerge at the toe of dam.

g. Diversion system - face of dam equipped with drainage control system to divert runoff and minimize infiltration.

h. Pumpback system — consists of a slurry wall, wet well, and pumping station at toe of dam to contain, collect, and return tailings reservoirs seepage to the reservoir.

12. The discharger has constructed an extensive diversion works which removes all runoff from the watershed above the reservoir and transports it to the North Fork Luther Gulch stream channel below the tailings dam. This diversion is covered by an appropriative water right filing, State Board Application No. 26450. The diversion and conveyance structures are sized to control a 2500-year storm runoff rate to assure that such flows will not enter the reservoir.

13. The design and construction of the tailings dam, reservoir, and diversion works described are subject to regulatory jurisdiction of the California Department of Water Resources, Division of Dam Safety (DDS). A certificate to impound water was awarded by DDS on November 14, 1983.

14. Wastes discharged to the tailings reservoir include water and soluable (dissolved) residues from various waste streams and solids which consist largely of gangue (unreacted minerals from mining/mill processes) and sludges from water and wastewater treatment facilities.

The discharger has reported that, on a daily average basis, 650 tons per day of solid phase and 0.17 mgd of water phase is discharged to the tailings reservoir. At the end of mining and ore processing activities, the discharger estimates that 560 acre-feet of tailings will be accumulated. The discharger has submitted reports which confirm the presence of the following constituents in the water phase:

Heavy metals (as cations or components of complexes) - Cu, Fe, Zn, Pb, Na, Hg, Ni, Al and traces of As and Cd

Cations - Na, Ca, Mg, K

Non-metals (as anions or components of complexes) - $SO_4^{=}$, Cl^-, HCO_3^-, $CO_3^{=}$ cyanide (free and complexed) thiocyanate

15. The discharger has reported the quantities and qualities of solid and liquid wastes which have been continuing to be discharged to, recycled from, removed for treatment and disposal off-site, and retained as solid waste in the tailings reservoir. These wastes contain dissolved and/or soluble components such as heavy metals and free and complexed cyanides which, if discharged to surface waters or usable groundwaters, would adversely affect the quality of those waters. The waste is a Group 1 waste as classified in Section 2520 of the California Administrative Code, Title 23 - Waters.

16. The tailings dam and reservoir is a hazardous waste disposal facility as defined by California Administrative Code, Title 22, and permitted by California Department of Health Services (DOHS). A Hazardous Waste Facility Permit was issued by DOHS on April 20, 1982.

17. The discharger has constructed control facilities at the toe of the tailings dam to impound and return tailings reservoir seepage back to the reservoir. The seepage contains pollutants which originate in the tailings reservoir. Control facilities consist of an impermeable slurry trench excavated to bedrock to impound underground flows, a wet well with french drains to collect the seepage, three pumps (lead, backup, and standby), auxiliary power source, and export pipeline to the tailings reservoir/wastewater treatment plant.

18. The discharger has partially constructed seepage treatment and disposal facilities for long term control of tailings reservoir seepage. The facility employs the alkaline-chlorine process and when completed will consist of chemical storage, reactor vessels, clarification, sand filtration, and pH adjustment with discharge by gravity to percolation beds adjacent to Indian Creek. The discharger has demonstrated that the existing wastewater treatment facility in conjunction with the seepage control facilities is capable of processing all anticipated flows until termination of ore-processing activities when the tailings reservoir will be reclaimed. Therefore, long term seepage treatment and control facilities will not be activated until mining and milling activities are terminated.

19. The discharger's description of natural and man-made features which prevent lateral and vertical continuity between liquids in the waste and surface waters meets the criteria for classification as a Class II-1 disposal site as established in Section 2511 of the California Administrative Code, Title 23 - Waters. Section 2532 of said Code provides that the disposal of certain Group 1 wastes may be allowed in a Class II-1 site by a regional board, when in the judgment of the board, such disposal will not unreasonably affect water quality. Such restricted disposal of specific Group 1 wastes shall be subjected to terms and conditions considered appropriate by the Regional Board.

20. The discharger submitted an operations plan with the original reports of waste discharge on January 19, 1981. These documents contain analyses of alternative methods of site closure.

    The report of waste discharge and operations plans describe the activities which will occur after the mining operations terminate. Excess stored water will be treated and discharged to the off-site percolation beds and the solid phase wastes will be allowed to consolidate. A gravel layer will be placed over the tailings to bar upward capillary movement of water. A compacted clay cap will be placed over the gravel and tailings to bar downward movement of rainfall. A layer of topsoil (stockpiled during the

initial mine-mill development) will be placed over the clay cap and revegetated with native plants to prevent erosion of the clay cap and top soil material. Monitoring and periodic maintenance/repair will be provided.

In September and October, 1981, the discharger submitted estimates of costs for site closure and post-closure monitoring and maintenance assurances of financial responsibility for closure and post-closure activities.

On January 15, 1984, the discharger submitted a report of waste discharge and revised Operation Plan to reflect the necessity of constructing long term seepage treatment and disposal facilities. Detailed cost estimates for operation and maintenance of these facilities were submitted on May 8, 1984.

Final cost estimates for all closure and post closure activities were submitted on _____, 1984, in the amount of $_____.

Exhibit A, appended and hereby made a part of this Order is a summary of the estimated costs of closure and post-closure activities.

Exhibit B, appended and hereby made a part of this Order is a copy of a statement which describes the financial condition of Noranda Inc., of Toronto, Canada.

Exhibit C, appended and hereby made a part of this Order is Guarantee by Noranda, Inc., in favor of the State of California, Regional Water Quality Control Board, North Coast Region, on behalf of Noranda Grey Eagle Mines, Inc., whereby Noranda Inc., guarantees that it will assume the financial responsibility for closure, reclamation and monitoring of the Grey Eagle Mine tailings disposal site in the event that Noranda Grey Eagle Mines, Inc., fails to comply with Regional Board Orders.

21. The Regional Board adopted the Water Quality Control Plan for the Klamath River Basin (1A) on March 20, 1975, and last amended in September 1983.

22. Beneficial uses of waters of the Klamath River Basin include:

    a. municipal and agricultural water supply
    b. industrial water supply
    c. groundwater recharge
    d. freshwater replenishment of lakes and streams
    e. hydropower generation
    f. water contact and non-water contact recreation
    g. warm freshwater habitat
    h. cold freshwater habitat
    i. wildlife habitat
    j. migration route for anadromous fish
    k. fish spawning area.

23. In order to protect the beneficial uses of the Klamath River Basin, the Basin Plan prohibits the discharge of waste to all surface, freshwater

impoundments, and their tributaries, with the exception of the Lower Lost River system.

24. On October 28, 1968, the State Water Resources Control Board adopted Resolution No. 68-16, the Non-Degradation Policy. The Policy provides that:

    a. Whenever the existing quality of water is better than the quality established in policies as of the date on which such policies become effective, such existing high quality will be maintained until it has been demonstrated to the State that any change will be consistent with maximum benefit to the people of the State, will not unreasonably affect present and anticipated beneficial use of such water and will not result in water quality less than that prescribed in the policies; and

    b. Any activity which produces or may produce a waste or increased volume or concentration of waste and which discharges or proposes to discharge to existing high quality waters will be required to meet waste discharge requirements which will result in the best practicable treatment or control of the discharge necessary to assure that (a) a pollution or nuisance will not occur and (b) the highest water quality consistent with maximum benefit to the people of the State will be maintained.

25. The Board has notified the discharger and interested agencies and persons of its intent to prescribe waste discharge requirements for this discharge.

26. The discharger has stated and the Board finds that all local agencies with jurisdiction has approved use of the site for the intended purposes.

27. The County of Siskiyou, in accordance with the California Environmental Quality Act, has prepared and circulated the following:

    •Notice of Preparation; May 15, 1980
    •Draft Environmental Impact Report; August, 1980
    •Supplement to Draft EIR — Comments and Responses; October 1, 1980

    The County Use Permit, issued October 27, 1980, requires conformance with state/local/federal regulations.

    The United States Klamath National Forest has prepared Environmental Assessments related to various project elements as follows:

    • Road Improvements, Environmental Assessment dated September 9, 1980. Operations Plan for Noranda Mining Operations on Public Lands, Environmental Assessment dated February 9, 1981.

    • Seepage treatment and disposal facilities, Finding of No Significant Impact dated April 24, 1984.

28. The Regional Board has determined that compliance with the provisions contained in these requirements will mitigate the potential adverse water quality impacts identified in the Environmental Impact Report.

29. The Board in a public hearing on October 25, 1984, in Rohnert Park, California, heard and considered all comments pertaining to the discharge.

THEREFORE, IT IS HEREBY ORDERED THAT Board Orders 81-51, 81-52, 81-53, 81-222, and 84-49 are hereby rescinded and that Noranda, Inc., and Noranda Grey Eagle Mines, Inc., shall comply with the following:

A. DISCHARGE PROHIBITIONS

1. There shall be no discharge of treated or untreated domestic sewage, industrial waste; runoff from ore stockpiles, or process chemical storage/receiving areas; or other solid waste or any deleterious material to the surface waters of the Klamath River Basin.

2. There shall be no discharge of any waste except domestic (toilet and urinal) to septic tank/leachfield treatment/disposal facilities.

3. The creation of a nuisance or a pollution, as defined in Section 13050 of the California Water Code, as a result of any waste collection, treatment, and disposal is prohibited.

4. There shall be no discharge of soil, silt, bark, slash, sawdust, or other organic and earthen material from any logging, construction, or associated activity of whatever nature into any stream or watercourse in the basin in quantities deleterious to fish, wildlife, or other beneficial uses.

5. There shall be no placing or disposal of soil, silt, bark, slash, sawdust, or other organic and earthen material from any logging, construction, or associated activity of whatever nature at locations where such material could pass into any stream or water course in the basin in quantities which would be deleterious to fish, wildlife, or other beneficial uses.

B. EFFLUENT LIMITATIONS

1. Treated industrial process wastewaters discharged to the land disposal site shall meet the following limits:

Constituent	Units	Maximum Concentration
Arsenic	mg/l	0.002
Copper	mg/l	0.20
Iron	mg/l	0.20
Cyanide (free)	mg/l	0.02
Zinc	mg/l	0.01

Constituent	Units	Maximum Concentration
Lead	mg/l	0.05
Nickel	mg/l	0.40
Cadmium	mg/l	0.01
Mercury	mg/l	0.002
Aluminum	mg/l	0.5
pH	pH units	6.5 - 7.5

C. PROVISIONS

1. The discharger shall comply with the Contingency Planning and Notification Requirements, Order No. 74-151 and the Monitoring and Reporting Program No. 84-108 and the General Provisions for Monitoring and Reporting, and any modifications to these documents as specified by the Executive Officer. Such documents are attached to this Order and incorporated herein.

2. The discharger shall submit a report of waste discharge to the Regional Board at least 120 days before initiating any new discharge or making any material change in the character, location, or volume of any waste discharge.

3. The discharger shall protect from erosion all disturbed soil areas, protective dikes, diversion facilities, stream crossings, and other water quality control facilities.

4. The discharger shall provide proper sanitary facilities at appropriate locations in project construction areas. The design, installation, and use of any domestic waste disposal system shall be in compliance with any and all more restrictive Siskiyou County health ordinances and regulations.

5. Collected screenings, sludges, and other solids removed from liquid wastes shall be disposed of at a legal point of disposal, and in accordance with the provisions of Division 7.5 of the California Water Code. For the purpose of this requirement, a legal point of disposal is defined as one for which waste discharge requirements have been prescribed by a regional water quality control board and which is in full compliance therewith.

6. The discharger shall maintain in good working order and operate as efficiently as possible any facility or control system installed by the discharger to achieve compliance with the waste discharge requirements.

7. In the event the discharger is unable to comply with any of the conditions of this Order due to:

   a. breakdown of waste treatment equipment;
   b. accidents caused by human error or negligence; or
   c. other causes such as acts of nature;

   the discharger shall notify the Executive Officer by telephone as soon as he or his agents have knowledge of the incident and confirm this notification in writing within two weeks of the telephone notification. The written

notification shall include pertinent information explaining reasons for the noncompliance and shall indicate what steps are taken to correct the problem and the dates thereof, and what steps are being taken to prevent the problem from recurring.

8. The requirements prescribed herein do not authorize the commission of any act causing injury to the property of another, nor protect the discharger from his liabilities under federal, state, or local laws.

9. The discharger shall permit the Regional Board:

   a. Entry to the project area and upon premises in which a waste source or waste discharge is located or in which any required records are kept;

   b. Access to copy any records required to be kept under terms and conditions of this Order;

   c. Inspection of monitoring equipment or records; and

   d. Sampling of any discharge.

10. The discharge of any pollutant not identified and authorized by the waste discharge requirements or the discharge of any pollutant in a manner or quantity which differs from that stated in the report of waste discharge is prohibited.

11. The discharger shall implement the contingency and spill prevention, containment, and planning measures as described in the report entitled "Hazardous Material Spill Prevention and Preparedness Plan" dated September 1982, updated November 1983. This report shall be updated annually and submitted to the Executive Officer. Failure to comply with these measures is a violation of this Order.

12. In the event of any change in control or ownership of land or waste discharge facilities presently owned or controlled by the discharger, the discharger shall notify the succeeding owner or operator of the existence of this Order by letter, a copy of which shall be forwarded to this Board.

13. Group 1 waste materials shall not be disposed of outside of the tailings reservoir.

14. The Group 1 waste disposal area shall be protected from any washout or erosion of wastes or covering material, and from inundation, which could occur as a result of floods having a predicted frequency of once in 2500 years.

15. The discharge of Group 1 wastes to the tailings reservoir shall be limited to the materials produced by the discharger in the cyanide processing of gold and silver ores from the Grey Eagle Mine.

16. Group 1 waste materials and any water that has contacted the waste shall be contained in the area designed for Group 1 wastes including seepage control facilities.

17. A minimum freeboard of three feet shall be maintained in the tailings reservoir at all times.

18. Waste confinement barriers shall be protected and maintained to ensure their effectiveness.

19. All site facilities used to contain Group 1 waste shall be designed and constructed to minimize damage to the graded foundation or the structures which control leachate, surface drainage, erosion and gas due to the maximum credible earthquake.

20. There shall be no overflow from the waste holding facilities used for Group 1 waste.

21. A leachate collection and disposal system shall be constructed and maintained downgradient from the disposal area to prevent any leachate or other liquid waste from entering ground or surface water. Leachate volumes contained by liquid control barriers shall be maintained below a volume equal to 75 percent (or a lesser amount if necessary because of specific site conditions) of the total liquid storage capacity of the barrier.

22. The leachate control facility shall consist of at least two feet of compacted clay, soil cement (having a permeability of 1×10^{-6} cm/sec or less), or other equivalent material approved by the Executive Officer. The thickness of the barrier must be based on the anticipated life of the site and the threat of the specific waste to the beneficial use of the waters of the basin.

23. Long term tailings reservoir seepage treatment and disposal facilities shall be completed and operable within three months of terminating ore processing activities.

24. The discharger shall maintain a copy of this Order at the site so as to be available at all times to site operating personnel.

25. The discharger shall file with this Board an updated operation plan when substantial changes in operations are made. A letter indicating conformance with existing plans shall be submitted annually. For the purpose of these requirements, this includes any proposed change in the boundaries, contours, or ownership of the disposal area.

26. The owner or operator of the disposal site shall provide assurances that monies are available in an amount estimated by the Board to be sufficient to ensure the closure and subsequent post closure maintenance of the disposal site in a manner that will not pose an adverse threat to the environment. The cost estimate and, if necessary, the financial assurances shall be updated on an annual basis. Post closure maintenance costs shall be estimated for a period of thirty years following site closure.

27. The dischargers shall comply with provisions of the water right permit issued by the State Water Resources Control Board pursuant to Application No. 26450. Failure to comply is a threatened violation of this Order.

28. The dischargers shall comply with requirements of the California Department of Water Resources, Division of Dam Safety. Failure to comply is a threatened violation of this Order.

29. The dischargers shall comply with all permits issued by the Department of Health Services. Failure to comply is a threatened violation of this Order.

30. The discharger shall implement the Reclamation Plan as approved and as may be revised by County of Siskiyou. Failure to implement the Reclamation Plan is a threatened violation of this Order.

Certification

I, David C. Joseph, Executive Officer, do hereby certify that the foregoing is a full, true, and correct copy of an Order adopted by the California Regional Water Quality Control Board, North Coast Region, on October 25, 1984.

_____

David C. Joseph
Executive Officer

California Regional Water Quality Control Board
North Coast Region

MONITORING AND REPORTING PROGRAM NO. 84-108

FOR

NORANDA GREY EAGLE MINES, INC.

Siskiyou County

MONITORING - WATER QUALITY

Grab samples shall be collected at monitoring stations listed below and described on Attachment "A" and analyzed as follows:

STATION	LOCATION	ANALYSES*	FREQUENCY
1.	South Fork Luther Gulch Above Tailings Reservoir	—	Discontinue Sampling
2.	North Fork Luther Gulch above South Fork Confluence	—	Discontinue Sampling
3.	Luther Gulch Below Toe of Tailings Dam	A B	Monthly Quarterly
4.	Luther Gulch at Green Gate	—	Discontinue Sampling
5.	Luther Gulch Above County Road Crossing	—	Discontinue Sampling
6.	Indian Creek 100 feet above Luther Gulch Confluence	—	Discontinue Sampling
7.	Indian Creek 100 feet below Luther Gulch Confluence	—	Discontinue Sampling
8.	Indian Creek 1.3 miles below Luther Gulch	—	Discontinue Sampling
9.	Tailings Reservoir (Return Line)	A, B,	Monthly
10.	Monitoring Well South Abutment of Dam	A	Quarterly

STATION	LOCATION	ANALYSES*	FREQUENCY
11.	Monitoring Well North Abutment of Dam	A	Quarterly
12.	Chimney Drain North Discharge Pipe (D2)	A B	Monthly Quarterly
13.	Chimney Drain South Discharge Pipe (D2)	A B	Monthly Quarterly
14.	Blanket Drain Discharge at Toe of Dam (D4)	A B	Monthly Quarterly
15.	Monitoring Well at Toe of Dam	A B	Monthly Quarterly
16.	Spring Below Land Application Site	A, B	Monthly
17.	Water Treatment Plant Effluent	A, B	Monthly
18.	East Monitoring Well at Land Application Site	A, B	Quarterly
19.	Southwest Monitoring Well at Land Application Site	A, B	Quarterly
20.	North Monitoring Well at Land Application Site	A, B	Quarterly
21.	West Well at Proposed Indian Creek Perc Field	EC, TDS, TCN	Quarterly
22.	South Well at Proposed Indian Creek Perc Field	EC, TDS, TCN	Quarterly
23.	East Well at Proposed Indian Creek Perc Field	EC, TDS, TCN	Quarterly

* Group A analyses = Total cyanide, free cyanide, copper, iron, zinc, sulfate, chloride, sodium, pH, EC, and TDS
Group B analyses = arsenic, cadmium, lead, mercury, nickel, aluminum

FLOW/LEVEL MONITORING

Static levels in groundwater monitoring wells shall be recorded at the time of sample collection. Flow rate shall be measured at Stations 12, 13, 14, and the road crossing (water hole) on Luther Gulch Creek at the approximate time of sample collection.

Flow rate for the pumpback system shall be recorded daily.

Reservoir volume, remaining capacity, and static elevation of surface shall be recorded weekly.

MONITORING - EROSION CONTROL

The discharger shall observe and record erosion/slope stability problems and sediment control basin performance. Monitoring records shall be related to storm events.

REPORTING

Monitoring reports shall be submitted to the Regional Board for each month by the 15th day of the following month. Reports shall include results from all water quality analyses performed and shall be signed by a responsible official of Noranda Grey Eagle Mines, Inc. The report shall include a detailed narrative summary of erosion control monitoring during the month and a description of proposed corrective measures implemented or proposed. The erosion control monitoring summary shall be supplemented with photographs as necessary to accurately describe both problems and corrective measures.

Ordered by _____
David C. Joseph
Executive Officer

October 25, 1984

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

ORDER NO. _____

NPDES NO. CA0081477

WASTE DISCHARGE REQUIREMENTS
FOR
McLAUGHLIN MINE
HOMESTAKE MINING COMPANY
AND
US BUREAU OF LAND MANAGEMENT
YOLO, LAKE AND NAPA COUNTIES

The California Regional Water Quality Control Board, Central Valley Region (hereafter Board), finds that:

1. Homestake Mining Company (hereafter Discharger) submitted a report of waste discharge, dated 15 April 1983, to discharge waste under the National Pollutant Discharge Elimination System.

2. The proposed mining operation will operate in part on public lands administered by the US Bureau of Land Management (hereafter Discharger).

3. The Discharger proposed to discharge water in contact with mine activities from five sedimentation ponds into Hunting Creek and Knoxville Creek, both tributary to Lake Berryessa, a water of the United States.

4. Homestake Mining Company proposes to develop a gold mine and mineral extraction facility (mill) to process about 4000 tons of ore per day. Units of the mine include: mine pit, waste rock site, grinding and crushing area, mill, low grade ore storage, slurry line, tailings disposal facility, water supply reservoir, interconnecting roadways and electrical transmission corridor.

5. The mining process will begin at an open pit mine which will ultimately be one mile long, one-half mile wide and 400 feet deep. Higher grade ore bearing rock will be crushed, ground and piped through a 4-1/2 mile slurry pipeline to the mill site. Waste rock from the mine pit will be disposed of on 342 acres some of which are public lands administered by the US Bureau of Land Management. The pipeline slurry will undergo a cyanide leach process to extract gold at the 35 acre mill site. Processed slurry will be discharged to the 546 acre tailings disposal facility.

6. The discharge to land of all mining activities, including the tailing disposal reservoir, is regulated through separate waste discharge requirements.

7. The report of waste discharge describes the water discharge as follows:

Pond	Discharge Point Serial Number	Description
T_1	001	Sediment trap for topsoil stockpile taken from the tailings reservoir. T_1 will function primarily during the first three years before the topsoil is revegetated and again towards the end of project during the reclamation phase. During most of the operating life of the project, the sediment yield to the pond is expected to be minimal. The pond will be maintained for the entire project and reclamation period.
T_2	002	Same as pond T_1.
W_1	003	Sediment trap for the waste rock disposal facility from stormwater runoff and waste rock subdrainage. This pond will be required for the life of the project.
W_2	- -	Sediment trap within the waste rock disposal facility. This pond may or may not be required. If constructed, it would flow only into pond W_1, and therefore would not be an NPDES discharge point.
M_1	004	Sediment trap for the grinding facility area during the mine construction period only (i.e., the first 1 to 2 years). Thereafter, the pond will be used as a water-recycling pond and will not be an NPDES discharge point.
M_2	005	Sediment trap for the early years of development at the south pit. This pond will be required for approximately the first 7 years of mining. Thereafter, all runoff from pit disturbance will be contained within the pit and the pond decommissioned.

8. The Board, on 25 July 1975, adopted a Water Quality Control Plan for the Sacramento River Basin (5A). These requirements are consistent with the Plan.

9. The beneficial uses of Lake Berryessa are municipal, industrial, and agricultural supply; recreation; esthetic enjoyment; navigation; ground water recharge; fresh water replenishment; hydroelectric power generation; and preservation and enhancement of fish, wildlife and other aquatic resources.

10. The beneficial uses of the ground water downstream of the project are municipal and agricultural supply.

11. The chemical quality of the ground and surface waters in the immediate vicinity of the tailings disposal facility and the waste rock disposal facility is generally poor, when compared to EPA Primary and Secondary Drinking Water Standards. Boron levels frequently exceed the recommended levels for continuous irrigation use.

12. Effluent limitation standards established pursuant to Sections 301, 302, and 304 of the Federal Water Pollution Contol Act and amendments thereto are applicable to the discharge.

13. On 6 July 1983, the Napa County Planning Commission certified the final Environmental Impact Report/Environmental Impact Statement (EIR/EIS) for the Homestake Mining Company McLaughlin Gold Project in accordance with the California Environmental Quality Act (CEQA) Public Resources Code Sections 21000, et seq. The EIR/EIS discloses that the project may have the following significant impacts on water quality:

    a. Increased erosion during construction.

    b. Landslides along the perimeter of the water reservoirs.

    c. Increased sedimentation to streams during construction.

    d. Increased TDS and heavy metals concentration to Hunting Creek downstream of the waste rock dump.

    e. Contamination of Hunting Creek from accidental spills of mill reagents or tailings disposal facility rupture.

14. The Board has reviewed the EIR/EIS. These waste discharge requirements provide protection to water quality equal to or more effective than the mitigation measures in the EIR/EIS relating to water quality. Compliance with these waste discharge requirements will mitigate or avoid the following significant impacts on water quality listed in Finding 13:

    a. Landslides along the perimeter of the water reservoir. Mitigation of this potential impact is required by turbidity, sedimentation and erosion controls contained in these requirements.

    b. Increased TDS and heavy metals concentration to Hunting Creek downstream of the waste rock dump. Mitigation of this potential impact is accomplished by receiving water limitations on heavy metals and the requirement to implement best available technology (BAT) to limit mineralization.

15. The following impacts will be mitigated to some extent by these requirements, but the EIR/EIS identifies these as unavoidable potentially significant environmental impacts:

    a. Increased erosion during construction.

b. Increased sedimentation to streams during construction.

c. Contamination of Hunting Creek from accidental spills of mill reagents or tailings disposal facility rupture.

While these significant detrimental impacts may occur, the Board finds these impacts are outweighed by the potential benefits of the project. This decision is based on the two potential benefits to water quality listed in the EIR/EIS:

a. Long-term improvement to Knoxville Creek water quality downstream of mine pit due to the ultimate elimination of poor quality runoff from the mine pit area.

b. Long-term reduction in sedimentation to Davis Creek downstream of the reservoir through dam releases of better-quality water than that presently existing.

16. Subsequent to the preparation of the final EIR/EIS, Discharger and the Solano Irrigation District (SID) entered into an Agreement (the SID Agreement) which provides for a comprehensive monitoring program and a series of response mechanisms designed to preclude any potential adverse environmental impacts on water quality which might otherwise occur in connection with the project. Pursuant to the SID Agreement, Discharger has agreed to comply with specified requirements in order to assure nondegradation of the water quality of any surface or subsurface waters flowing or draining into or through Hunting, Soda, Knoxville, Putah or Eticuera Creeks into Lake Berryessa.

17. The Board has notified the Discharger and interested agencies and persons of its intent to prescribe waste discharge requirements for this discharge and has provided them with an opportunity for a public hearing and an opportunity to submit their written views and recommendations.

18. The Board, in a public meeting, heard and considered all comments pertaining to the discharge.

19. This Order shall serve as a National Pollutant Discharge Elimination System permit pursuant to Section 402 of the Federal Water Pollution Control Act, or amendments thereto, and shall take effect ten days from the date of hearing, provided EPA has no objections.

IT IS HEREBY ORDERED, Homestake Mining Company and the property owner, in order to meet the provisions contained in Division 7 of the California Water Code and regulations adopted thereunder and the provisions of the Federal Water Pollution Control Act and regulations and guidelines adopted thereunder, shall comply with the following:

A. Prohibitions:

1. The discharge of domestic sewage, industrial wastes and runoff from ore stockpiles and process chemical storage/receiving areas, which is deleterious to fish, wildlife or other beneficial uses, is prohibited.

B. Effluent Limitations:

1. The discharge of an effluent in excess of the following limits is prohibited:

Constituents	Units	30-Day Average	Daily Maximum
Suspended Solids	mg/l	20	30
Settleable Solids	ml/l	1.0	5.0
Arsenic	mg/l	0.05	0.10
Cadmium	mg/l	0.01	0.02
Chromium	mg/l	0.05	0.10
Copper	mg/l	0.15	0.30
Mercury	mg/l	0.001	0.002
Lead	mg/l	0.05	0.10
Zinc	mg/l	0.75	1.5

Metals shall be analyzed and reported as totals.

2. The discharge shall not have a pH less than 6.5 nor greater than 9.0.

3. The Discharger shall use the best available technology to limit mineralization to no more than a reasonable increment.

4. Discharge to surface waters shall be limited to discharge from the sediment control ponds.

C. Receiving Water Limitations:

1. The Discharger shall not cause the dissolved oxygen concentration in Hunting or Knoxville Creek to fall below 5.0 mg/l.

2. The discharge shall not cause visible oil, grease, scum, foam, floating or suspended material in the receiving waters or watercourses.

3. The discharge shall not cause a measurable increase, over upstream levels of the receiving waters, of the following constituents: Arsenic, Lead.

4. The discharge shall not cause a statiscally significant, incremental increase of more than 10% (or, if greater than 10%, the minimum percentage increase that may be accurately measured) over upstream levels of the receiving waters, of the following constituents: Mercury, Chromium, Cadmium, Boron, Copper, Nickel.

5. The discharge shall not cause sedimentation or concentrations of any materials in the receiving waters which are deleterious to human, animal, aquatic, or plant life.

6. The discharge shall not cause esthetically undesirable discoloration of the receiving waters.

7. The discharge shall not cause fungus, slimes, or other objectionable growths in the receiving waters.

8. The discharge shall not cause bottom deposits in the receiving waters.

9. The discharge shall not increase the turbidity of the receiving waters by more than 10% over immediately upstream levels.

10. The discharge shall not alter the pH of the receiving water more than 0.5 units from immediately upstream levels.

11. The discharge shall not increase the temperature of the receiving water more than 5°F (3°C) from immediately upstream levels.

12. The discharge shall not cause a violation of any applicable water quality standard for receiving waters adopted by the Board or the State Water Resources Control Board as required by the Federal Water Pollution Control Act and regulations adopted thereunder. If more stringent applicable water quality standards are approved pursuant to Section 303 of the Federal Water Pollution Control Act, or amendments thereto, the Board will revise and modify this Order in accordance with such more stringent standards.

13 This permit shall be modified, or alternatively, revoked and reissued, to comply with any applicable effluent standard or limitation issued or approved under Sections 301(b)(2)(C), and (D), 304(b)(2), and 307(a)(2) of the Clean Water Act, if the effluent standard or limitation so issued or approved:

(a) Contains different conditions or is otherwise more stringent than any effluent limitation in the permit; or

(b) Controls any pollutant not limited in the permit.

The permit as modified or reissued under this paragraph shall also contain any other requirements of the Act then applicable.

D. Provisions:

1. Neither the discharge nor its treatment shall create a nuisance or pollution as defined in Section 13050 of the California Water Code.

2. The settling ponds shall be designed to contain the flow from the 10 year frequency storms in a 24 hour period.

   Annually, prior to the rainy season, the settling ponds shall be inspected and maintained to ensure the design capacity is provided.

3. The Discharger shall comply with all the items of the "Standard Provisions and Reporting Requirements (NPDES)", dated 1 January 1982, which are part of this Order.

4. The Discharger shall comply with the attached Monitoring and Reporting Program No. _____ as ordered by the Executive Officer.

5. This Order expires on 1 August 1988 and the Discharger must file a Report of Waste Discharge in accordance with Title 23, California Administrative Code, not later than 180 days in advance of such date as application for issuance of new waste discharge requirements.

6. In the event of any change in control or ownership of land or waste discharge facilities presently owned or controlled by the Discharger, the Discharger shall notify the succeeding owner or operator of the existence of this Order by letter, a copy of which shall be forwarded to this office.

7. The provisions of this Order are not intended to, and shall not limit or reduce any obligations or requirements which are additional to, or more stringent than, those created pursuant to this Order and which are imposed on the Discharger pursuant to (a) the terms of any agreement to which the Discharger is a party, including but not limited to, that certain agreement dated as of 30 June 1983, by and between the Discharger and the Solano Irrigation District, or (b) the requirements and controls imposed by any governmental agency or other authority having jurisdiction with respect to the Project. Nothing in this paragraph shall be construed to release or excuse the Discharger from full and timely compliance with the requirements of this Order or amendments or supplements hereto.

I, WILLIAM H. CROOKS, Executive Officer, do hereby certify the foregoing is a full, true, and correct copy of an Order adopted by the California Regional Water Quality Control Board, Central Valley Region, on _____.

_____
WILLIAM H. CROOKS, Executive Officer

CKV:dg
Revised 9/02/83

Attachments

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

MONITORING AND REPORTING PROGRAM NO. _____

NPDES NO. CA0081477

FOR
McLAUGHLIN MINE
HOMESTAKE MINING COMPANY
AND
US BUREAU OF LAND MANAGEMENT
YOLO, LAKE AND NAPA COUNTIES

Sample stations shall be established such that the samples are representative of the volume and nature of the discharge.

EFFLUENT MONITORING

During each discharge period, the discharge from each settling pond (discharges 001, 002, 003, 004, 005) shall be sampled and analyzed according to the following schedule:

Constituent	Units	Type of Sample	Frequency
Flow	Gallons per day	Estimate	Daily
Temperature	°C	Grab	Daily
TDS	mg/l	Grab	Daily
EC	umhos/cm	Grab	Daily
pH (field)	pH units	Grab	Daily
pH	pH units	Grab	Daily
Suspended Solids	mg/l	Grab	Daily
Settleable Solids	ml/l	Grab	Daily
Total Alkalinity	mg/l	Grab	Daily
Calcium	mg/l	Grab	Daily
Chloride	mg/l	Grab	Daily
Nitrate	mg/l	Grab	Daily
Sulfate	mg/l	Grab	Daily
Ammonia	mg/l	Grab	Daily
Boron	mg/l	Grab	Daily
Arsenic	mg/l	Grab	Daily
Barium	mg/l	Grab	Daily
Beryllium	mg/l	Grab	Daily
Cadmium	mg/l	Grab	Daily
Chromium	mg/l	Grab	Daily
Copper	mg/l	Grab	Daily

Constituent	Units	Type of Sample	Frequency
Iron	mg/l	Grab	Daily
Lead	mg/l	Grab	Daily
Magnesium	mg/l	Grab	Daily
Manganese	mg/l	Grab	Daily
Mercury	mg/l	Grab	Daily
Nickel	mg/l	Grab	Daily
Sodium	mg/l	Grab	Daily
Selenium	mg/l	Grab	Daily
Vanadium	mg/l	Grab	Daily
Zinc	mg/l	Grab	Daily

Metals shall be analyzed and reported as totals.

RECEIVING WATER MONITORING

Receiving water samples shall be collected daily during periods when discharge is occurring. All samples shall be grab samples taken near mid-stream, where safety permits. Samples shall be taken from each sampling station and analyzed for the following constituents:

Station	Description
R-1	Hunting Creek, upstream of tailings disposal pond or at the northern end of the tailings stormwater diversion ditch
R-2 (HC-9)	Hunting Creek, 1/2 mile downstream of tailings dam
R-3 (HC-5)	Hunting Creek, 1/2 mile upstream of Waste Rock Disposal area
R-4 (HC-10)	Hunting Creek, 1/2 mile downstream of Waste Rock Disposal area
R-5 (KC-3)	Knoxville Creek, 1/4 mile west of Knoxville

Constituent	Units
Flow	Gallons per day
Temperature	°C
TDS	mg/l
EC	umhos/cm
pH (field)	pH units
pH	pH units
Suspended Solids	mg/l
Settleable Solids	ml/l

Constituent	Units
Total Alkalinity	mg/l
Calcium	mg/l
Chloride	mg/l
Nitrate	mg/l
Sulfate	mg/l
Ammonia	mg/l
Boron	mg/l
Arsenic	mg/l
Barium	mg/l
Beryllium	mg/l
Cadmium	mg/l
Chromium	mg/l
Copper	mg/l
Iron	mg/l
Lead	mg/l
Magnesium	mg/l
Manganese	mg/l
Mercury	mg/l
Nickel	mg/l
Sodium	mg/l
Selenium	mg/l
Vanadium	mg/l
Zinc	mg/l
Turbidity	NTU

Metals shall be analyzed and reported as totals.

REPORTING

In reporting the monitoring data, the Discharger shall arrange the data in tabular form so that the date, the constituents, and the concentrations are readily discernible. The data shall be summarized in such a manner to illustrate clearly the compliance with waste discharge requirements.

Monthly monitoring reports shall be submitted to the Regional Board by the 15th day of the following month.

If the Discharger monitors any pollutant at the locations designated herein more frequently than is required by this Order, he shall include the results of such monitoring in the calculation and reporting of the values required in the Discharge Monitoring Reporting Form. Such increased frequency shall be indicated on the Discharge Monitoring Reporting Form.

The Discharger shall submit a report to the Board by 30 January of each year containing both tabular and graphical summaries of the monitoring data obtained during the previous year. In addition, the Discharger shall discuss the compliance record and the corrective actions taken or planned which may be needed to bring the discharges into full compliance with the waste discharge requirements.

The Discharger shall implement the above monitoring program on the effective date of this Order.

Ordered by _____
WILLIAM H. CROOKS, Executive Officer

_____
(Date)

GKV:dg
7/12/83

ASARCO INCORPORATED-
WATERLOO PROJECT
San Bernardino County

EXAMPLE OF 1982 CALIFORNIA DISCHARGE SPECIFICATIONS

Board Order No. 6-82-35

I. DISCHARGE SPECIFICATIONS

1. The discharge of wastewater or tailings except to the designated disposal sites is prohibited.

2. The wastewater evaporation pond shall be effectively sealed[a/] to prevent the exfiltration of any liquids from the pond.

3. The disposal of tailings and wastewater shall be in accordance with the plan described in the D'Appolonia report referenced in footnote "a".

4. The use of a flocculant with similar characterisitcs to the type used in the tailings test and reported on in the D'Appolonia report is required to increase the specific retention of the tailings.

5. The "emergency" tailings disposal site shall effectively be sealed[b/] to prevent the exfiltration of any liquids from the site.

6. The discharge of liquids of any type to the tailings disposal site is prohibited except for limited quantities of freshwater for dust control.

7. At no time shall tailings having a moisture content in excess of 32 percent be disposed of at the tailings disposal site.

8. The average[c/] water content of tailings disposed of at the tailings disposal site shall not exceed 30 percent.

9. The disposal of tailings is limited to only those areas of previous tailings disposal where the measured moisture content of the previous lift falls below the "moisture control curve" as shown on Figure 18j in the July 1981 D'Appolonia report.

10. In the event that wastewater is detected in the evaporation pond underdrain system, the February 24, 1982 "System Failure Contingency Plan" shall be implemented.

11. In the event that (1) the measured moisture content within the placed tailings in any moisture detection well exceeds the specifications as defined in Figure 18j (Moisture Control Curve) of the July 1981 D'Appolonia report, or (2) the measured moisture content in the foundation soils increases by more than 4 percent above the background at a depth of five (5) feet (as measured prior to tailings disposal), then the "System Failure Contingency Plan" dated February 24, 1982, shall be implemented and a report as specified in the "Plan" be provided to the Regional Board within four weeks.

a/ As an acceptable minimum, construction of the pond liner shall consist of a 30-mil thick hypalon membrane covered with one foot (0.3 m) of soil as specified in "Tailings Disposal Plan" dated July 1981 and prepared by D'Appolonia Consulting Engineers, Inc.

b/ The emergency tailings disposal site shall be sealed with a 30-mil hypalon liner as specified in the January 26, 1982 "Lined Emergency Disposal Facility Design and Tailings Compaction Specifications", prepared by D'Appolonia Consulting Engineers.

c/ The arithmetic mean of daily water content averages measured during any 30 consecutive-day period.

12. The tailings disposal area shall at all times be sloped to a minimum grade of 0.5 percent to provide adequate drainage and prevent ponding of precipitation.

13. Diversion ditches shall be constructed upgradient of the tailings disposal area and shall be maintained by ASARCO, Inc. both during the project and following its completion as specified in the D'Appolonia report.

14. Collection ditches to collect surface runoff from the tailings disposal area shall be constructed and shall be maintained by ASARCO, Inc. both during the project and continuously following its completion as specified in the D'Appolonia report.

15. There shall be no discharge, bypass or diversion of tailings or wastewater from the collection, transport, or disposal facilities to adjacent land areas.

16. There shall be no surface flow or visible discharge of wastewater or tailings from the designated disposal sites to adjacent land areas.

17. All facilities used for collection, transport, or disposal of waste shall be adequately protected against damage resulting from overflow, washout or inundation from a storm or flood having a recurrence interval of once in 100 years.

18. The vertical distance between the water surface elevation and the lowest point of a pond dike or the invert of an overflow structure shall not be less than 1.5 feet (0.46 m).

19. The discharge shall not cause a pollution or a nuisance.

II. PROVISIONS

1. Site closure and maintenance shall be implemented in accordance with the discussion of "Abandonment/Reclamation" in the D'Appolonia report and as described further in a December 1, 1981 letter from ASARCO, Inc. to the Regional Board.

2. The discharge shall comply with Monitoring and Reporting Program No. 82-35 as specified by the Executive Officer.

3. The discharger shall immediately notify the Regional Board by telephone whenever there are any accidental spills of wastes containing cyanide or any other toxic materials on the subject property, or when any other adverse condition occurs as a result of this discharge; written confirmation shall follow.

4. Any proposed material change in the character of the waste, manner or method of treatment or disposal, increase of discharge, or location of discharge shall be reported to this Regional Board at least ninety (90) days in advance of implementation of any such proposal.

CANADA

In Canada, generally, precipitation exceeds evaporation and, ultimately, the discharge of an effluent from a tailings impoundment cannot be avoided using conventional tailings disposal techniques.

Canada's water quality protection laws fall under their Fisheries Act because effluents find their way into the huge lake and river system of Canada which supports major fishing and recreaton industries related to fishing.

As in the U.S.A., Canadian regulations are established on a federal level based on recommendations by Environment Canada, Environment Protection Service. Each province has its own Ministry of the Environment. In the case of some of these, e.g., British Columbia, environment protection, including mine-mill effluents, are regulated by the province. In the case of others, e.g., Ontario, the province maintains a strong advisory service and, although it is empowered to issue directives which can shut an operation down or force it to rectify a problem, the regulation and permitting of mines and mills is left to Environment Canada.

Although in Canada the regulators have and do exert their powers to close down operations if regulations are not adhered to, the impression gained is that regulators are much more conscious of the role of mining in their national and local economies. There appears to be a greater awareness amongst regulators of the need to preserve employment. Also, Environment Canada studies numerous site-specific cases to determine their needs and, working with industry, will test and promote the development of improved technologies to solve environmental problems in real life situations.

Environment Canada first goes out to define a problem, in several cases representing the range of industry-wide conditions. It then finds out, based on real field tests, what can be done to solve the problem and what it will cost. Then finally, it proposes regulations which oblige industry to solve the problem using the practical solutions it has demonstrated.

This contrasts with the EPA and states in the U.S.A. which have been known to regulate a problem by dictating what results must be achieved before a practical solution is available or known.

RANDOL INTERNATIONAL LTD., in the course of this investigation, found the Canadian federal and provincial authorities much more accessible, more helpful, and generally better informed about the environment protection problems and the nature and needs of the mining industry. They were also more problem solving-oriented than in the U.S.A. where the regulators seem to concentrate on the problems and regulations rather than

finding and suggesting practical answers. In short, the Canadian system appears to be more service oriented as reflected in the name, Environment Protection Service.

In Canada, regulation of uranium mines and mills falls under the Atomic Energy Control Board although provincial ministries of the environment have the right to issue control orders if they find the AECB measures inadequate in specific instances.

In Canada, details of regulations governing effluents would be available on request from the Federal Environment Protection Services, Environment Canada, and from each province as to their provincial regulations:

ENVIRONMENT PROTECTION SERVICE
Environment Canada
Water Pollution Control Directorate
Place Vincent Massey
351 St. Joseph Blvd.
Hull, Quebec K1A 1C8
(819) 997-2270
Jim Scott

MINISTRY OF THE ENVIRONMENT (ONTARIO)
35 St. Clair Street West, #100
Toronto, Ontario M4V 1P5
(416) 965-6954
John Hawley

SOUTH AFRICA

The South African government in a rare and commendable example of resisting an opportunity to create yet another bureaucracy; intelligently combined environment protection into the Dept. of Water Affairs and changed its name to the Dept. of the Environment. Environment protection and water resource management and protection are, after all, synonymous. The change in name, however, reflects the emphasis that the South African government has decided to place on water resource protection.

Apart from a change in the environment protection regulations affecting water quality, there has been a recent beefing up in enforcement of the existing regulations and a general tightening in these interpretation. For example, in February, 1984, the Dept. of the Environment was advertising for 15 new water inspection professionals with experience in the mining industry.

The Water Research Commission, a state funded organization, has sponsored several major studies on the future needs of water for growth projected in the South African economy. It also surveyed the impact of point source mine effluents on the quality of water in the Vaal Dam which serves as the main regional water supply to the industrial heart of the country, and further research into the impact of diffuse source effluents, e.g., runoff

and seepage from slimes and sand dumps created by gold and uranium mining and milling operations.

The National Institute for Water Research of the CSIR is yet another state funded research organization whose mandate is to develop improved technology for water treatment.

The Dept. of the Environment is the permitting and policing agency for all major water users and dischargers of effluents.

Most of the South African metal mining areas experience net evaporation climates, and metallurgical operations and tailings can be designed for zero discharge if necessary. Minewater is pumped to the surface in very large quantities--far too large to be wasted in a water deficient country.

One of the main indicated new directions of the Dept. of the Environment's proposed changes to regulations is clearly the prevention of TDS buildup in Vaal Dam water and in promotion of water conservation measures within industry. Since mining and metallurgical operations are major users and dischargers of water containing high TDS, the implementation of the new regulations can be expected to be focused on this industry.

In South Africa, uranium is recovered from the same ore as gold; therefore due to practical considerations, the environmental aspects of both are regulated by the Dept. of the Environment. The Atomic Energy Board does not get involved in mine/mill tailings management or effluent treatment and discharge.

The South African government will never let the Dept. of the Environment stifle the mining industry on which the whole country's economy relies, but there will be much tougher and more expensive rules to live within.

SOUTH AFRICAN REGULATIONS

Regulations concerning water discharge by mines are contained in "Effluent Standards promulgated in terms of Section 21 of the Water Act, Act 54, 1956, as amended. Various additional amendments include those published in the Government Gazette:

R1029, 18 June, 1976:
On sewage effluent measurement and reporting of water analyses from mines.

R287, 20 February, 1976:
Control measures for control of surface water showing existing and planned minerals, tailings, wasterock dumps, and slimes dams for the following five years.

Para 6.1: The manager of a mine or works shall, unless otherwise authorized in writing by the Secretary, prevent the pollution of any water, cause effective measures to be taken to prevent effluent, including water pumped from underground or which flows naturally from a mine or works, to flow or seep beyond the boundaries of the property on which the mine or works is situated.

Para 7: The manager of a mine or works shall make adequate provision to the satisfaction of the Secretary to prevent as far as reasonably practicable runoff from eroding slimes dams and mineral tailings and wasterock dumps due to rain.

Para 8: All runoff due to rainfall on a property on which a mine or works is situated must be controlled in such a manner by a system of storm water dams that it flows clear of slimes dams, mineral tailings, or wasterock dumps and other sources of pollution. Provision shall be made for the maximum precipitation expected over 24 hours on a 100-year frequency. A freeboard of at least 0.5 m shall be provided throughout the system above the expected maximum water levels.

Para 9: All waterways on a property on which a mine or works is situated shall be fenced in and protected to prevent pollution of any water.

Para 10: Prevention of any extraneous liquid or other material from entering any evaporation dam, storm water drain, or other entering the evaporation dam, storm water drain, etc.

Para 11.1: All slimesdams, mineral, tailings, and wasterock dumps to be so designed and constructed or modified that all rainwater precipitated thereon is retained thereon. Barrier dams and evaporation dams shall be provided to collect any runoff. Storage capacities shall provide at least 0.5 m freeboard above water level based on average monthly figures over 24 hours (100-year flood).

Para 11.2: Rainwater from tailings dumps and the appurtenat barrier dams and water used in any process at a mine or works shall be recycled wherever possible.

Para 11.3: Trench drains and ditches to catch seepage water and carry it to evaporation dams or sumps for recycling shall be constructed at all tailings dumps whenever possible.

Para 11.4: All pumps and pumping installations, including catchment dams for the recycling of water shall be of a design and of adequate capacity to prevent the uncontrolled release of water at any time.

Para 12: Mining, tailings, wasterock dumps and any slimes barriers or evaporations dams, waterways, etc. shall be designed to minimize the possibility of damage thereto due to past, present, or future operations at the mine works.

Para 13: Maintenance by the mine manager of the dam wall of storm-water drains and other waterways.

Para 14: "Best practicable means" as determined by the Secretary shall be implemented to prevent erosion of material from the sides of tailings dumps and slimes dams.

Para 15: Collection and evaporation of seepage from outcrops or sub-outcrops occurring on a property on which a mine or works is situated and which does not conform to the standard prescribed in terms of Section 21(1)(a) of the Act.

Para 16.1: Siting of mineral, tailings, or wasterock dump, slimes dam, evaoration dam, or any other dam or furrow containing polluted water shall not be near any spring or with 45 meters from 50-year flood waterline of any river or watercourse.

Para 16.2: No mineral, tailings, or wasterock dump or slimes dams or evaporation dams to be sited on waterlogged ground or ground likely to become waterlogged.

Comprehensive regulations regarding most aspects of water in and around mines and mills.

Regulations are in place. Change in the degree of strictness with which they are enforced makes a big difference.

R553, 5 April, 1962, Regional Standards for Industrial Effluents which include Mines: Regulatory standards for any waste water or effluent produced by or resulting from the use of water for industrial purposes in catchment areas draining to the rivers or portions of rivers. Summary:

Special Standard: Stricter than the General Standard and Special Standards apply to only certain specific rivers or sections of rivers where trout exist. These are listed in the previous chapter in addition to the proposed new standard applicable to the PWVS Region (Vaal Dam Drainage).

New Regulations and Changes Pending

The Water Act itself is under a broad review in Parliament. There are several changes under consideration as well as some new regulations.

1. New regulation proposed to set new standards for heavy metals, lead, chromium, mercury, and cadmium. The standard proposed has not yet been finalized to a degree that is firm enough to be reported on.

2. Proposed new regulation which would limit TDS of effluent streams to 250

milliSiemens/m. This is the equivalent to around 2,000 ppm TDS and would mean that the mining industry would have to evaporate more effluents or install desalination plants. Government Notice R1567, 1 August, 1980.

3. Standard limiting $PO_4^{=}$ as soluble orthophosphates to 1 ppm max. in certain catchments from 1 August, 1985, i.e., Vaal River upstream and including Bloemhof Dam, Pienaars River and Crocodile River upstream of their confluence, Great Olifants River upstream and including the Loskop Dam, The Umgeni River, Umlaas River, Buffalo River to Bridle Rift Dam, and the Berg River.

4. Regulations R287 of 20 February, 1976, pertaining to the Water Act are currently under review. This review is in its initial stages.

5. New mine plans must now be submitted to the Government Mining Engineer who consults the Dept. of the Environment. The plan must include restoration on completion of operations. Restoration factors are critical with respect to water aspects.

Conclusions - South Africa

1. Water use by the mining and metallurgical industry and discharge of effluents by mines and mills will come under increasing scrutiny in South Africa. This is quite evident in the statements of Mr. Hendrik J. Best, Director of Water Pollution Control of the Dept. of the Environment in the SA Mining & Engineering Journal 1984 inserted below.

2. The mining industry contributes 12% of the volume of water draining into the Vaal River but contributes 30% of the TDS. Mine effluents are point sources which are easy to identify.

3. Water cost to the mining/metallurgical industry will go up. Costs include purchase, pumping, and disposal.

4. New regulations will be much sricter toward the mining industry, and existing regulations will be more strictly enforced. Before a new mine can start up, its plans will be scrutinized. New methods of analysis and new water treatment technology is becoming available which the enforcement officials should be implemented.

5. Needed: Guideline document on how a closing down mine should be restored for abandonment.

6. When a mine has been passed for abandonment, it becomes the responsibility of the SA Dept. of the Environment.

7. Dept. of Environment and Water Research Commission seem to be heading toward encouraging the use of desalination for mine/mill effluent treatment. A SRK study showed that evaporation is probably cheaper. Conclusion: More evaporation dams will be needed.

8. Apparently so far, the South African regulators have focused minimal attention on groundwater quality and monitoring.

Implications of amendments to the Water Act

No pool or stream is sacrosanct when people seek to dump unwanted junk or even poisonous chemicals. The amendments to the Water Act, however seek to remedy this.

The far-reaching implications of the amendments to the Water Act (Act 54 of 1965) — regarding the use of water and measures imposed to prevent pollution — have been detailed for SA Mining and Engineering Journal by Mr H I Best, Director of Water Pollution Control of the Department of Environment Affairs.

Mr Best outlined the consequences of the amended legislation particularly in so far as the use of water by industry and mining is concerned and the steps laid down for the disposal of effluent.

He outlined the following sections of the Act, with the reasons for their amendment.

Section 12:

Before amendment the Act required any person intending the use of water for industrial purposes, or to expand such use, to inform the Department of Water Affairs beforehand of his proposed method of purification of effluent and, if the quantity of public water to be used exceeded 300 m³ on any one day, or an average of 250 m³ per day during any month, to obtain from the Minister a permit authorising such use.

In terms of the amended Act no person may use more than 150 m³ of any water on any day for industrial purposes (as defined in Section 1), whether private or public water, or underground water, or sea water brought ashore, without a permit, irrespective or whether or not any waste water is returned to any public stream. However, any person who at the date of the amending legislation lawfully used more than 150 m³ of water a day is entitled to a permit, subject to such conditions as the Minister may deem fit to impose.

Appliction forms for permits are obtainable from the head office and all regional offices of the Department.

Section 12A:

This section is an addition to the Act and places a prohibition on the construction or enlargement of any water work used for the purification, treatment or disposal of effluent, including sewage.

Regulations are to be promulgated shortly describing the minimum number of personnel with their minimum qualifications, to be employed for the operation of the various classes of water care works. Before promulgation the draft regulations will be published in the Government Gazette to give the public an opportunity of commenting on them.

Section 20:

In this section the alteration to the course of a public stream is prohibited, unless authorised by permit, mainly to regularise river deviations for the purposes of open-cast coal mining. These provisions do not affect the activities of a local authority within its area of jurisdiction or the construction of a soil conservation work in terms of the Conservation of Agricultural Resources Act, 1983.

This picture tells its own story.

Section 21:

This section deals with the purification, treatment and disposal of effluent occasioned by the use of water for industrial purposes. The amendments do not deviate materially from original objectives, except that —

- previously any industry discharging its effluent into the sewer of a local authority concerned was responsible for such compliance. Now, however, the Minister may direct that any particular industry shall not be so exempted, and each case will be treated on its own merits and
- any effluent discharged into a canal, sewer or other conduit controlled by a local authority, body or person having authority to undertake the purification, treatment or disposal of effluent, is deemed to be effluent produced by or resulting from the use of water by that local authority, body or person for industrial purposes. This means that a local authority will henceforth be responsible for the purification, treatment and disposal in accordance with the provisions of Section 21 of the Act, of any effluent released with or without its consent or knowledge into a stormwater drainage system under its control.

Section 22:

This is a new provision. Subsection (1) states:

"Any person who has control over land on which anything was or is done which involves a substance capable of causing water pollution, whether such substance is a solid, liquid, vapour or gas or a combination thereof, shall take such steps as may be prescribed by regulation under Section 26 in order to prevent:

- any public or private water on or under that land, including rainwater which falls on or flows over or penetrates such land, from being polluted by that substance, or if that water has already been polluted, from being further polluted by that substance; and
- any public or private water on or under any other land, or sea, from being polluted, or if that water has already been polluted, from being further polluted, by water referred to in the previous paragraph, which became polluted in the circumstances described."

Regulations will be framed shortly to compel industrialists to take the precaustions outlined above.

Section 24:

This is also a new section, which vests in the Minister and the Director-General certain powers to prevent water pollution before it can take place.

The Director-General may authorise any person to enter upon any land referred to in Section 22 (1) or on which water is used for industrial purposes or on which effluent is disposed of and to conduct on such land such investigation as the Director-General may determine (It should be mentioned that such authority is subject to a prohibition, in terms of Section 166A of the Act, on the disclosure of information gained during the investigation).

If the Director-General, as a result of such investigation, is of the opinion that any steps carried out on such land to prevent water pollution are in the particular circumstances inadequate or ineffective, he may direct the person responsible for carrying out those steps to take such additional or other steps as are deemed necessary for the prevention of water pollution. Any person aggrieved by such direction may appeal to the Minister.

If a person fails to comply with such direction within a period specified, the Minister may isntruct the steps to be carried out and recover the cost incurred from the person to whom the direction was issued.

In terms of this Section the Mininster may by notice in the Government Gazette direct that the manufacture, marketing or use of any substance which, in his opinion could cause water pollution, be terminated or restricted, or he may subject the manufacture, marketing or use thereof to the conditions specified in such notice.

If a person:

- uses water for industrial purposes contary to the provisions of Section 12;
- fails to comply with any provision of 21 (1) or 22 (1); or
- fails to comply with an direction issued to him under Section 24; the Minister may direct that the supply of water to such person for industrial purposes, whether from a Government water works or any other water works, be suspended or reduced. In such event the State, the Minister or any person carrying out such direction is not responsible for any loss or damage caused thereby.

Section 30:

Before the amendment to the Act the owner of a mine was entitled to remove from the mining area any water found underground if such removal was necessary for mining operations or the safety of his employees and, unless the Minister otherwise directs, to use such water for mining operations. In terms of the amending legislation such use is subject to the provisions of Sections 12 and 21. Therefore the mine owner may not use such water unless he is authorised to do so under permit (if the quantity exceeds 150 m^3 on any day) and he is obliged to treat any effluent resulting from such use in accordance with the provisions of Section 21.

Section 41:

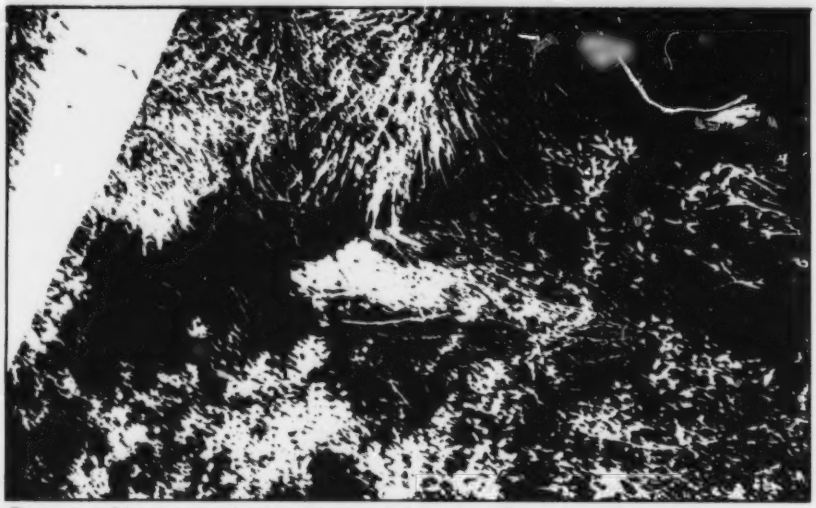
In terms of the amendment a mine owne: will henceforth be entitled to claim a servitude under the Water Act for the purposes of disposing of water found underground and removed from the mining area.

Section 170:

The penalties prescribed for offences under the Water Act have been enhanced considerably in the amending legislation. As far as water pollution is concerned the maximum penalty for a first offence is increased from R2 000 to R10 000 and for a subsequent offence from a minimum of R1 000 to a maximum of R20 000. Alternative imprisonment is increased from six to 12 months. In the case of a continuing offence the penalty is increased from R100 to R200 in respect of every day the offence continues.

An addition to the Act reads as follows:

"Whenever any person is convicted of an offence under this Act, the court convicting him may summarily enquire into and assess the monetary



Severe penalties are contained in the amended Act for offences regarding use of water and pollution.

value of any advantage gained by such person in consequence of that offence and, in addition to any punishment imposed in respect of that offence, impose on that person a fine equal to the amount so assessed or, in default of payment, imprisonment for a period not exceeding one year."

Section 171:

Although there are only slight amendments to this section, mention is made thereof in view of its implications. Whenever any person is convicted of an offence under the Water Act and it appears that such person has thereby caused a loss or damage to any other person, the court may, at the request of the said other person determine the amount of the loss or damage and order the conviced person to compensate the person who has suffered loss or damage, in addition to any punishment imposed in respect of the offence.

BRAZIL

Brazil has a Federal Environmental Protection Agency. Each state has its own environmental agency with specific legislation on effluent discharge limits.

The permitting process in Brazil includes three main steps requiring licensing authority approval for all of them.

1. Preliminary license based on general aspects about process units and proposed environmental control measures. An environmental impact assessment may be required, depending on the plant location, capacity, raw materials to be processed, products, and by-products, etc.

2. Installation license based on environmental control systems and basic design of effluent treatment equipment.

3. Operating license based on plant inspection and effluent monitoring.

The licensing agency addresses for three main mining states, and the federal agency are shown below. The federal agency can provide complete detailed information.

1. Federal Agency:

SECRETARIA ESPECIAL DO MEIA AMBIENTE
Av. W-3 Norte-Quadra 510
70.570 Brasilia-DF
Telex: (061) 1429

2. Rio de Janeiro:

FUNDACAO ESTADUAL DE ENGENHARIA
DO MEIO AMBIENTE
Rua Fonseca Teles, 121-15 Andar
20940 Rio de Janeiro RJ

3. Sao Paulo:

COMPANHIA DE TECHNOLOGIA DE
SANEAMENTO AMBIENTAL
Av. Prof. Frederico Hermann, Jr., 345
05459 Sao Paulo SP
Telephone: (011) 22246

4. Minas Gerais:

COMISSAO DE POLITICA AMBIENTAL
Rua da Bahia, 916 - and Andar
30.000 Belo Horizonte MG
Telephone: (031) 1775

There is no specific legislation on environmental control for mines and mills. U.S. EPA criteria are often used as guidelines or for contaminant levels in permits. State liquid effluent discharge limits must be met for mine drainage, rainwater runoff, and process effluents. A guiding rule is that ground water must be protected against infiltration by contaminated wastes.

Mine area reclamation is required as well as "proper" transportation and disposal of solid wastes.

Effluent discharge limits for some contaminants as laid down by three Brazilian states are as follows:

Parameter	Unit	Rio	S. Paulo	Minas Gerais
pH	-	5-9	5-9	6-9
Sedim. Solids	ML/L	1.0	1.0	1.0
DB05	MG/L	(*)	60	60
Cyanide	MG/L	0.2	0.2	0.2
Arsenic	MG/L	0.1	0.2	0.2
Copper	MG/L	0.5	1.0	0.5
Lead	MG/L	0.5	0.5	0.1
Zinc	MG/L	1.0	5.0	1.0
Nickel	MG/L	1.0	2.0	1.0
Mercury	MG/L	0.01	0.01	0.01
Cadmium	MG/L	0.1	0.2	0.1
Chromium III	MG/L	1.0	5.0	1.0
Chromium VI	MG/L	1.5	0.1	ND
Fluorides	MG/L	10	10	10
Sulfides	MG/L	1.0	-	0.5
Oil and Grease	MG/L	20	100	20
Temperature Degc.		40	40	40

* Depending on receiving water quality in terms of flowrate, flowpattern, and dissolved oxygen.

Note: Priority pollutants such as carcinogens are submitted to specific legislation.

The above information was provided by a leading form of environmental and engineering consultants in Brazil, namely:

NATRON CONSULTORIA E. PROJETOS SA
Environmental Control Dept.
Rua Teofilo Otoni, 63 - 11 Andar
20090 Rio de Janeiro RJ
Brazil
Telex: 2123510 NATR BR
Paulo Campos Gimenez

CHILE

In Chile, the Ministry of Mines approval must be granted for all mine-mill projects.

The National Health Service approval is needed for tailings disposal plans as they affect water quality protection.

The Ministry of Mines approval is required of tailings disposal plans with respect to their safety.

Effluent limitations are not prescribed in Chile.

RANDOL is indebted to Utah International, Inc. for providing the following copy of relevant Chilean regulations governing mine-mill wastes.

(106) DECREE NUMBER 86 of JULY 31, 1970

APPROVES THE REGULATIONS FOR THE CONSTRUCTION AND OPERATION OF TAILING PONDS

(Published in the Official Record Num. 27,722 of Aug. 13, 1970)

(Considering the need to specify more exactly the concepts and technological demands for the construction of tailing ponds the following decree is issued.)

(107) TITLE I

BASIC DEFINITIONS

Article 1 (Director = Director of Service of Mines

Relave = Suspension of solids in liquids which are thrown out in plants of humid concentration of pure and waste minerals which have gone through one or several stages in fine milling. The word will also be applied to the solid fraction of the pulp which has been described in the suspension mentioned above.

Article 2 Tranque de relave (tailing pond) means the layout for the storage of the tailings which fills the function of locating the solid fraction in a stable structure, and arranging, at the same time, for the partial suspension of solids in liquids and for a liquid fraction, capable of being maintained in safe conditions in respect to possible overflows and other disturbances.

Article 3 The area of the tailing pond in which the finest solid grains will accumulate -by the process of sedimentation- shall be called the muddy (slimy) accumulation.

Article 4 The area of the tailing pond in which the larger solid grains shall accumulate will receive the name sandy accumulation.

Article 5 The area of the tailing pond where muddy accumulation takes place and where the gradual process of sedimentation allows the accumulation of clear water on the surface shall be called the sedimentation pool.

Article 6 The peripheral area of the tailing pond constructed artificially, which complements the natural perimeter to shape inside it the tailing pond and, at the same time, part or all of the sandy area of the pond will be called the resistent prism (Spanish=prisma resistente).

Article 7 The device set up for the collection of clear water from the tailing pond, which is obtained from the sedimentation pool and/or for the collection of water which extrudes from the tailing pond as it solidifies as the water which fills the inergranule spaces is eliminated, will be called the drainage system.

Article 8 The elements set up for the purpose of placing the complete tailings and/or its muddy and sandy components, under conditions of executing an hydraulic fill, will be called the distribution system.

TECHNICAL DEFINITIONS PARAGRAPH II

Article 9 The condition of moisture content in which the granules are resting upon one another, the spaces are completely filled with liquid will be defined as a state of total saturation.

Article 10 Ground water level is the height above sea level at which poihts the molecule water has a pressure equal to zero.

Article 11 The device which measures the ground water level shall be called a piezometer.

Article 12 The constant which determines the permeability of a soil or of any area of the tailing pond, by the expression : $k = v/i$, in which v is the velocity of discharge of water through the soil, and i is the hydraulic gradient is called the "coefficient of permeability".

Article 13 The quantitative description of the distribution of the
(108) sizes of the solid components of the tailings, in reference either to the complete tailings or to a prior separation into a sandy fraction and a muddy fraction, will be called the granulometry of the tailings.

Article 14 (Defines density of tailings)

Article 15 (Defines compaction of the tailings)

Article 16 (Defines density <u>in situ</u>)

Article 17 (Formulae for degree of compaction.)

Article 18 (Formula for resistance capacity to fatigue.)

Article 19 (Measurement of resistance to penetration.) Resistance is expressed as the number of blows of a 65 kilo hammer falling freely from a height of .75 meters required to sink the tube 0.30 meters deep, the indicated sampler having an external diameter of 0.05 meters and its cutting points 60°.

Article 20 (Defines slope angle of supporting prism.)

(109) Article 21 and 22 (Define certain reference lines.)

TITLE II

GENERAL PROVISIONS

Article 23 (State Mining Service has overseeing responsibilities for all projected and operating tailing ponds.)

Article 24 (State Mining Service also has responsibility for assuring that users follow all rules for Industrial Safety.)

Article 25 (User of tailing pond responsibility for all consequences resulting from bad use of tailing ponds.)

Article 26 (The user of the tailing pond shall have preferential treatment vis a vis a third party who later want to build structures at the foot of the tailing pond.)

TITLE III

MAINTENANCE AND OPERATION

Article 27 (Information which the user must report periodically to the Service;

a) Details of monthly maintenance work

b) Details of monthly operation

c) Relative density at 1/3 and 2/3 depth at the extreme slope of the resistent prism, with no less than one determination for each 100 meters of length of the prism.

d) Granulometry over 48, 60, 100 and 150 Tyler mesh and under 150 Tyler mesh in percentage, once per month.

e) Subtotals of sands and muds in aggregate tons for the month, for the year and the total since the beginning of the work.

Article 28 (In certain cases specified by the Director user may operate under one of the following: out water system
(110) or mixed system)

Article 29 The sands will be emptied towards the exterior of the pond and above the level of the outside slope, spreading them in such a way that they are spread uniformly, and, in certain cases, compacting in layers no thicker than 30 cm., under moist conditions when possible, to obtain a Proctor percentage equal to or above the limit set by the Director.

Article 30 (The mud will be emptied toward the surface of the mud zone. Other requirements that no water may run into pond. And special cases where the tailings may completely be spread on the sandy and muddy areas.)

Article 31 (Sedimentation pool to be kept clear.)

Article 32 (Measures may be taken by director to maintain freatic level within limits set.)

TITLE IV

EMERGENCY TASKS

Article 33 (User must pay for emergency measures required by Service.)

Article 34 (Service may adopt following means:

a. Rupture of lower drainage system, resulting in mixture of mud with clear water, loose or sacked stone will be dropped at the outlet until problem is corrected;

(111) b. Rupture of distribution system, plant shut down until fixed.

c. Heavy snow causing ice on slopes may necessitate stoppage of sand spreading or temporary work stoppage.

d. Earthquakes causing structural damage will cause suspension of use.

TITLE V

DESIGN AND OPERATION STANDARDS

Article 35 (Tailing ponds to be designed in accordance with the principles of Soil Mechanics and Foundation Engineering.)

Article 36 Waters which run permanently, temporarily or accidentally will be deflected to assure fulfilment of Article 30. Therefore the design will include necessary civil works and the justification for their dimensions.

Article 37 (Requirement to achieve an increase in the permeability of the soil to meet Article 32.)

(112) Article 38 (Definition and formula for a safety factor.)

Article 39 (Drainage of resistent mass)

Article 40 (What information must appear in the request to construct a tailing pond.)

(113) Article 41 (Director will set periodic information.)

Article 42 (Director will set relative density factor.)

Article 43 (User will furnish information on all auxiliary works.)

TITLE VI
SCOPE OF APPLICATION

Article 44 (Present regulation applicable to tailing ponds under construction and those already operating which have populated areas below them.)

Article 45 (Formula for determining danger distance.)

Article 46 (The Director may reduce the requirements or establish exceptions under the following conditions.

a) Length of supporting prism is less or a most equal to 0.2 of the perimeter of the pond;

b) (Sandy fraction and/or constituents of the frontal prism represent together 150% of the muddy fraction.)

c) (Sedimentation to be developed in rotational manner thus limiting tonnage in face of possible liquification.)

d) (a) or b) above require achieving revetment of 6 meters and or berm above or equal to 15 meters.)

e) (In areas with less than 500 mm of annual precipitation and with a maximum of no more than 50mm. of rain in 24 hours, the vertical development of the pond will be less then or at the most equal to 1/2 cm. per day.)

Article 47 (Users who will undertake to construct tailing ponds under articles 44 to 47 must have preliminary, provisional approval of plans by the Director, and later meet requirements of Article 40.)

Article 48 (Users have 6 months to conform.)

Article 49 (Director has the authority to change procedures herein as the science of soil mechanics developes.)

TITLE VII

SANCTIONS

Article 50 (Reference to Decree 32, Article 316 for sanctions)

(023) Article 30. In no case can industrial or mine tailings, or water contaminated with toxic products, be put into the ground water system, irrigation canals, aquaducts, rivers, swamps, streams, lakes, lagoons, reservoirs, general water flows or masses, unless they have first been purified or neutralized by treatment prescribed, in each case, by the National Health Service.

Article 31. In no case can solid materials, which may come from industrial establishments or general work areas, or seeds harmful to agriculture, be discharged into general water courses or masses.

Article 32. The final elimination and disposition of waste and resulting residual products, be they organic or inorganic, solid or liquid, putrescible or not, from diverse industrial processes, that are not eliminated through the culvert system, must be carried out in the form and under the conditions determined by existing Regulations or, in special cases assessed by the National Health Service, in a way determined by that same agency.

Dust, garbage, trimmings, and waste in general, will be regularly removed in such a way as to avoid any bother or inconvenience to the industry personnel and the neighborhood. Where harmful or toxic solid products are handled, sweeping should be done outside of working hours by personnel with adequate protection.

SWEDEN

All mines and mills in Sweden require a permit. The licensing authority is the Water Court and/or the Franchise Board.

The permit regulates, for example, the maximum annual ore production rate and, in some cases, the maximum amount of discharge permitted under special conditions.

No fixed limits on contaminants are set but are decided upon cases by case, based on site specific aspects.

BOLIDEN MINERAL A/B operations are still in an investigation stage to determine what effluent limits will be set. To date, very few limits have been set.

pH at two of BOLIDEN's dailings dam effluents has been set at 7.0 and 8.0 respectively. There are guidelines for maximum allowable concentrations of Cu, Pb, Zn, Cd, As, Hg, Cr, and CN. Regulated maximum contaminant levels have been laid down only in exceptional cases.

The limit for suspended solids is 10 mg/l in the one case where it is regulated. In one regulated case, the combined Cu, Pb, Zn, Cd, As, and Hg monthly average is maximum 1 mg/l.

In one case, a limit guideline for chromium has been set at 0.1 mg/l (monthly average). A free cyanide level of max. 0.5 mg/l has been set from July, 1986, and the target level is 0.2 mg/l for one of BOLIDEN's operations.

The address of the Franchise Board is:

KONCESSIONSNAMNDEN FOR MILJOSKYDD
Box 34067
S-100 26 Stockholm
Sweden

There are several Water Courts. One of them in the county of Stockholm has the following address:

STOCKHOMS TINGSRATT
Vattendomstolen
Box 510
S-10126 Stockholm
Sweden

RANDOL INTERNATIONAL is indebted to Torbjorn G. Ransson of BOLIDEN for the above summary.

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SOME CONSIDERATIONS ON ENVIRONMENTAL REGULATIONS RELEVENT TO HYDRO-METALLURGICAL PROCESS RESIDUE

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Abstract. Hydrometallurgical processes are not free of environmental regulations. A clear understanding of the regulations under which the minerals industry operates delineates processing requirements at early stages. This paper deals with federal environmental regulations with emphasis on the hazardous waste regulations promulgated in May, 1980. The procedure of EP toxicity test and an example of the test are described. Brief account is given of the current trend and future outlook of regulations.

Introduction

Profound changes have taken place and more are expected in the minerals industry due to the emergence of environmental awareness both in the general population and elected representatives. Ambient air regulations on sulfur dioxide have been major contributors to the trend away from the traditional pyrometallurgical processes which is evident now. Additional motivation has been furnished by the Occupational Safety and Health Administration (OSHA) in the case of some metals, like lead and zinc. Hydrometallurgical processes have been regarded as the means of circumventing these environmental problems. However, hydrometallurgical processes themselves are not free of regulation which is the subject of this paper.

The technical feasibility by which existing and emerging processes are measured includes their environmental acceptability as a large component. Such concerns have major effects on process economics and viability. A clear understanding of the regulations under which the minerals industry operates would facilitate the technical tasks by delineating processing requirements at early stages.

This paper is designed to present a brief overview of the Federal environmental regulations relevant to hydrometallurgical process residues as promulgated by EPA. It does not include local or State requirements or others that could by derived, for example, from OSHA regulations. Brief descriptions are included of those approaches the EPA is following in applying the existing regulations to the mineral industries and in promulgating new ones in the future. At the present time, the subject is complex and in a state of flux with major uncertainties derived from the newly promulgated hazardous waste regulations.

General Description of the Regulations

Regulations concerning the protection of the environment are codified under the Title 40 of the Code of Federal Regulations (CFR)(1). Title 40 consists of seven volumes covering regulations on air pollution to procedures for certification of low-emission vehicles. Only those regulations which apply to the mineral industries are included as follows.

Solid Wastes

Parts 240 to 243 of title 40 give guidelines for the thermal processing, the storage and collection of solid wastes. These regulations do not apply to hazardous and mining wastes.

Hazardous Wastes

Parts 260 to 265, which were published recently in the Federal Register(2), are the new hazardous waste regulations. The new Federal "cradle-to-grave" waste monitoring system was effective beginning November, 1980. Since these regulations are of interest to the minerals industries, they will be reviewed in more detail.

The definition of solid waste is given in Section 261.2. A solid waste is any garbage, refuse, sludge, or other waste material, which is not excluded under Section 261.4(a).

Section 261.4 lists special cases which are excluded from the regulations (e.g., mining overburden returned to the mine site). Wastes from processing of ores are not included in these special cases.

Section 261.3 defines what a hazardous waste is. A solid waste is a hazardous waste if:

1) It is not excluded from the regulation as a hazardous waste under Section 261.4(b).
2) It is listed as a hazardous waste in Subpart D of Part 261 and has not been excluded from the lists under Sections 260.20 and 260.22.
3) It is a mixture of solid waste and one or more hazardous wastes listed in Subpart D of Part 261.
4) It exhibits any of the characteristics of hazardous waste identified in Subpart C of Part 261.

Sections 260.20 and 260.22 describe general requirements regarding petitions to modify or revoke any provisions in Part 260 through Part 265 or to amend Part 261 to exclude a waste produced at a particular facility.

Section 261.5 states special requirements for hazardous wastes generated by small quantity generators. If a person generates in a calendar month a total of less than 1000 kg of hazardous wastes, those wastes are not subject to the regulation. Later, EPA revised this paragraph replacing "person" with "generator" (3).

Section 261.6 describes special requirements for hazardous wastes which are recycled. If a hazardous waste is recycled or reclaimed, it is not subject to these regulations.

Subpart C of Part 261 states four characteristics of hazardous waste: ignitability, corrosivity, reactivity, and toxicity.

Section 261.24 describes the characteristics of "Extraction Procedure (EP) toxicity". A solid waste exhibits characteristics of EP toxicity if, using the test method described in the Appendix II of Part 261, the extract from a representative sample of the waste contains any of the contaminants listed in Table 1 at a concentration equal to or greater than the respective value given in that table.

Hazardous wastes from nonspecific sources are listed in Section 261.31 (e.g., spent cyanide bath solutions from metals recovery operations).

Section 261.32 lists hazardous wastes from specific sources (e.g., electrolytic anode slimes/sludges from primary zinc production).

Listed in Section 261.33 are the generic names of commercial chemical product which are hazardous if discarded (e.g., arsenic trioxide).

Appendix II of Part 261 describes the EP toxicity test which can be briefly summarized as follows:

A representative sample is first obtained using the methods specified in Appendix I of Part 261. The sample is separated into its liquid and solid phases. After preparing the solid material for extraction, it is placed in an extractor with 16 times its weight of deionized water. The pH of the solution is continuously adjusted to 5.0 during the 24 hour extraction period. After extraction, deionized water is added, and the material is separated into liquid and solid phases. The liquid is combined with the liquid obtained previously and is analyzed for the presence of any contaminants specified in Table 1 using the analytical procedures designated in Appendix III of Part 261. The separation procedures are described in Appendix II.

Parts 264 and 265 describe standards applicable to owners and operators of hazardous waste treatment, storage, and disposal facilities.

The regulations under Part 265 establish requirements applicable during the interim status period (the period after an owner or operator has applied for a permit, but prior to final disposition of the application) for existing facilities.

These interim regulations require a ground water monitoring system for any surface impoundment, landfill, or land treatment facility which is used to manage hazardous wastes. The owner or operator of a facility has to establish the background ground-water quality of the underlying aquifer. The owner or operator has to determine the concentration or value of the parameters characterizing the suitability of the ground-water as a drinking water supply. Also, the owner or operator has to determine the parameters establishing the ground water quality such as chloride, iron, etc. and the parameters used as indicators of ground-water contamination such as pH, the amount of total organic carbon, etc. Table 2 shows the EPA drinking water standards to be adhered to during the interim status period. Sections 265.90-265.94 describe how to install a ground-water monitoring system and do the sampling and analysis, recordkeeping, and reporting.

The Part 264 regulations include the first phase of the standards to be used to issue permits for hazardous waste treatment, storage, and disposal facilities. Included are requirements relating to preparedness for and prevention of hazards, contingency planning, and emergency procedures, the manifest system, and recordkeeping and reporting. Also included are general requirements relative to identification numbers, required notices, waste analysis, security at facilities, inspection of facilities, and personnel training.

In conformance with the recently enacted Solid Waste Disposal Act Amendments of 1980, EPA amended the regulations to exclude solid waste from the extraction, beneficiation, and processing of ores and minerals (including coal), including phosphate rock and overburden from the mining of uranium ore (3).

Effluent Guidelines

Parts 400 to 460 of Title 40 describe effluent guidelines and standards. These parts of the regulations were proposed pursuant to the Federal Water Pollution Control Act whereas the previous parts regarding hazardous wastes were promulgated based on the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act (RCRA) of 1976. These effluent guidelines give "effluent limitations" which means any restrictions established by EPA on quantities, rates, and concentrations of chemical, physical, biological, and other constituents which are discharged from point sources into navigable waters, contiguous zone of water or the ocean. The term "point source" means any discernible, confined and discrete conveyance from which pollutants are discharged. Here "pollutant" means solid waste and other industrial, municipal, and agricultural wastes discharged into water.

Section 401.15 lists toxic pollutants. In the list are base metals and compounds of arsenic, cadmium, copper, lead, mercury, selenium, silver, and zinc. Section 401.15 lists conventional pollutants such as grease and oil. Part 136 describes test procedures for pollutants.

EPA listed 21 industrial categories which were believed to discharge the pollutants of greatest environmental concern. Hydrometallurgical processes fall within two categories, ore mining and nonferrous metal manufacturing.

Subparts D, E, and F of Part 421 (nonferrous metals manufacturing category) deal with the categories of primary copper smelting, primary copper refining, and secondary copper refining, respectively. They do not apply to facilities recovering copper from the ore by hydrometallurgical methods.

Subparts G and H treat the categories of primary lead and primary zinc, respectively.

Subpart H is applicable to discharge resulting from the production of primary zinc by either electrolytic or "pyrolytic" means. Table 3, taken from Subpart H, shows effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable for the zinc industry according to EPA.

Section 440.22 (ore mining categories) gives effluent limitations guidelines for base and precious metals. It says for instance that there shall be no discharge of process water from vat leach processes for the extraction of copper from ores.

Application of the Regulations and EPA's Future Approach

Application

Residue toxicity varies widely with the materials processed and the process used. As an example of the hydrometallurgical process, the jarosite process was considered to treat a bulk concentrate of zinc, copper and lead. Jarosite was produced in the laboratory and subjected to the EP toxicity test. Table 4

shows the result of the test. As can be seen in the table, the jarosite in this case must be considered to be a toxic waste due to high concentration of lead.

From the processing point of view, it may be advantageous to dischard this residue outright. Contained metal values are comparatively minor, and furthermore the addition of water (as would be required for washings to recover values in the entrained liquid) could create extensive water balance problems. By definition the residues are hazardous unless the concentrations in the EP toxicity test are below those in Table 1. Of immediate concern in this respect is the residual liquid, which is considered part of the solid waste (section 261.2, "Other waste material is any solid, liquid, semi-solid or contained gaseous material....") and would be covered by the hazardous waste regualtions because of its metal content, in particular lead. Flexibility in the process design would be lost if recovery or removal of these metals were attempted and other options would need to be considered.

When the new hazardous regulations were promulgated on May 19, 1980, they did not exclude wastes from the processing of ores. In conformance with the recently enacted Solid Waste Disposal Act Amendments, EPA amended the hazardous regulations to exclude from the regulation solid wastes from the extraction, beneficiation and processing of ores(3). EPA, for the time being, is interpreting the scope of these exclusions broadly but is unsure that this interpretation is consistent with the intent of the Congress. EPA may further narrow the exclusion in subsequent rulemaking.

Even before the Congressional Amendment, EPA was aware that application of the full set of proposed waste management standards would not be appropriate for such wastes as beneficiation wastes, uranium and other mining wastes because (p. 33173 of Ref. 2):

1) The total annual quantity of each of these wastes is very large and individual disposal facilities tends to involve large piles or ponds. Should large volumes of the wastes be hazardous, the size of the facilities could make the application of some of the regulations technically infeasible or impracticable.
2) Any portion of the wastes which fail the proposed hazardous waste characteristics are thought to be on the margin of failure. Thus the hazardous portions of the wastes appear to have relatively low intrinsic hazard relative to other wastes.
3) EPA does not have sufficient information to propose specific alternate waste management requirements without additional studies.

Approach Taken by Environmental Protection Agency

The following comments on EPA's outlook are based on the Federal Register(4).

EPA is particularly concenred with the standards for land disposal facilities because of the effects of wastes on groundwater. EPA has begun to develop a comprehensive groundwater protection strategy that will guide many of its programs. In developing such a strategy, EPA examined four principal alternatives: facility design requirements, containment strategies, specific ambient health and environmental performance standards, and non-numerical health and environmental standards. Of these approaches, currently EPA intends to pursue the possibility of using specific design requirements in future regulations.

EPA could establish specific design requirements applicable to all land disposal facilities. For example, the regulations could require all landfills to install liners meeting minimum specification (e.g. the equivalent of 20 ft (6.1 m) of clay having a permeability of 10^{-7} cm/sec.), leachate collection systems capable of removing 98% of the leachate generated in the facilities, and highly impermeable covers. Also, EPA currently intends to use the approach of nonnumerical health and enfironmental standards that lay out broad objectives which permittees must seek to meet.

In the future, EPA will establish technical design requirements that reduce the risk of groundwater and surface water contamination. EPA will also require that disposal facilities do not degrade surface waters and groundwaters below certain established ambient health and environmental performance standards (e.g. water quality standards). EPA will use non-numerical health and environmental standards to protect against any potential adverse effects not addressed by the other types of standards.

EPA has developed a specific outline for protecting groundwater from the adverse effects of land disposal facilities(4). The key elements of the approach include:

1) It is unacceptable to allow a facility to cause any contamination of a down gradient water supply used for any purpose (drinking water, agricultural, industrial,etc.)
2) The regulations would require that the facility owner or operator employs certain management practices and design features that would control adverse effects on groundwater and surface water, as well as prevent or minimize other surface environmental effects.
3) While EPA believes that the non-degradation goal must be the starting point in the regulations, it recognizes that in some circumstances it may be possible to show that limited degradation will not adversely affect the public health or the environment.

EPA is considering applying this scheme to all new facilities.

Current Trend

The EPA is in the process of passing on to state environmental bodies the authority for enforcing hazardous waste handling regulations. EPA authorities estimate that

many States are ready to take up Resource Conservation and Recovery Act (RCRA) enforcement(5). However, some States may choose not to, in which case the federal agency will remain the enforcing body.

Each state is free to make its standards which should be at least equivalent to Federal standards. Some states set their standards even stricter than the Federal standards. For example, South Carolina has a toxicity standard of only ten times the Safe Drinking Water Act guidelines (Toxicity standard of Federal regulations is 100 times the Safe Drinking Water Act guidelines). Federal regulation defines a waste generator as any generator which produces more than 1000 kg/month of waste, New York's proposed definition of a waste generator is much stricter than EPA's, 100 kg/month. California applies a guideline based on chemical content. They have identified close to 900 hazardous substances, and something that contains one of these substances would be considered a hazardous waste. Therefore, we should look closely at this RCRA decentralization in the future.

Conclusion

Residues from hydrometallurgical processes are excluded temporarily from the new hazardous waste regulations. However, we have to follow the effluent limitations guidelines and also state and local environmental regulations.

It is not known yet whether EPA will resume implementation of the new hazardous regulations to the minerals industry or will make the current exemption permanent. EPA may propose modified regulations in the future. EPA lacks long-term experience with advanced waste management technologies. Therefore, it may take several years to adequately develop nationally applicable detailed technical standards on certain specific issues. EPA has begun to develop a comprehensive ground-water protection strategy and intends to pursue the possibility of using specific design requirements and several other strategies in promulgating new regulations. State authorities rather than federal are likely to play an important role in implementing hazardous waste handling regulations in the future.

References

1. U.S. Environmental Protection Agency, 1981, Code of Federal Regulations, Title 40, U.S. Government Printing Office, Washington, D.C.

2. U.S. Environmental Protection Agency, May 19, 1980, "Federal Register," Vol. 45, No. 98, U.S. Government Printing Office, Washington, D.C.

3. U.S. Environmental Protection Agency, November 19, 1980, "Federal Register," Vol. 45, No. 225, U.S. Government Printing Office, Washington, D.C.

4. U.S. Environmental Protection Agency, October 8, 1980, "Federal Register," Vol. 45, No. 197, U.S. Government Printing Office.

5. N. Basta, June, 1981 "The RCRA Law-When the States Take Over," Chemical Engineering, pp. 24-27.

Table 1. Maximum Concentration of Selected Contaminants for EP Toxicity(2)

Contaminant	Maximum Concentration (mg/L)
As	5.0
Ba	100.0
Cd	1.0
Cr	5.0
Pb	5.0
Hg	0.2
Se	1.0
Ag	5.0

Table 2. EPA Interim Primary Drinking Water Standards for Selected Contaminants(2)

Parameter	Maximum Level (mg/L)
As	0.05
Ba	1.0
Cd	0.01
Cr	0.05
Fluoride	1.4-2.4
Pb	0.05
Hg	0.002
Nitrate (as N)	10.0
Se	0.1
Ag	0.05

Table 3. Effluent Limitations Guidelines Representing the Degree of Effluent Reduction Attainable by the Application of the Best Available Technology Economically Achievable (Electrolytic or "Pyrolytic" Production of Zn According to EPA) (1).

Effluent Characteristic	Effluent Limitations	
	Maximum of any one day	Average of daily values for 30 consecutive days shall not exceed -
	Metric Units (kg/kkg of product)	
Total Suspended Solids	0.28	0.14
As	1.1×10^{-3}	5.4×10^{-4}
Cd	5.4×10^{-3}	2.7×10^{-3}
Se	0.054	0.027
Zn	0.054	0.027
pH	Within the range of 6.0 to 9.0	

Table 4. Results of EP Toxicity Test of Jarosite Produced from Zinc Bulk Concentrate

Contaminant	Concentration (mg/L)
As	<1.0
Cd	0.24
Cr	<1.0
Pb	5.0
Se	<1.0
Ag	<1.0

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Part II

Environmental Protection Agency

Ore Mining and Dressing Point Source Category Effluent Limitations Guidelines and New Source Performance Standards

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 440

[WH-FRL 2232-1]

Ore Mining and Dressing Point Source Category Effluent Limitations Guidelines and New Source Performance Standards

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This regulation limits the discharge of pollutants into navigable waters of the United States from exisitng and new sources in the ore mining and dressing industry. The Clean Water Act and a Consent Decree require EPA to issue this regulation.

The purpose of this regulation is to establish "best available technology" limitations (BAT) and "new source performance standards" (NSPS) for direct dischargers. Pretreatment standards for both existing and new sources are not being issued since no known indirect dischargers exist nor are any known to be planned. Effluent limitations for "best conventional technology" (BCT) are reserved pending application of the new BCT cost methodology.

DATES: In accordance with 40 CFR 100.01 (45 FR 26048), this regulation will be considered issued for purposes of judicial review at 1:00 P.M. Eastern time on December 17, 1982. It will become effective January 17, 1983 publication date, except § 440.104(b)(2)(ii) which contains information collection requirements which are under review at OMB.

Under Section 509(b)(1) of the Clean Water Act, any petition for judicial review of this regulation must be filed in the United States Court of Appeals within 90 days after the regulation is considered issued for purposes of judicial review. Under Section 509(b)(2) of the Clean Water Act, the regulation may not be challenged later in civil or criminal proceedings brought by EPA to enforce its requirements.

ADDRESS. Technical information may be obtained from Mr. B. Matthew Jarrett, at the address listed below, or by calling (202) 382-7164. The economic information may be obtained from Mr. John Kukulka, Office of Analysis and Evaluation (WH-586), Environmental Protection Agency, 401 M Street SW., Washington, D.C. 20460, or by calling (202) 382-5388.

On December 24, 1982, copies of the development document and the NSPS economic analysis will be available for public review in EPA's Public Information Reference Unit, Room 2404 (Rear) (EPA Library), 401 M Street SW., Washington, D.C. On February 7, 1983, the complete Record, including the Agency's responses to comments on the proposed regulation will be available for review at the Public Information Reference Unit. The EPA information regulation (40 CFR Part 2) allows the Agency to charge a reasonable fee for copying. Copies of the development document and the economic analysis may also be obtained from the National Technical Information Service, Springfield, Virginia 22161 (703) 487-6000. A notice will be published in the **Federal Register** announcing the availability of these documents from NTIS. (This should occur within 60 days of today's date.)

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I. Legal Authority

The regulations described in this notice are promulgated under authority of Sections 301, 304, 306, 307, 308, and 501 of the Clean Water Act (the Federal Water Pollution Control Act Amendments of 1972, 33 USC 1251 et seq., as amended by the Clean Water Act of 1977, P.L. 95-217) (the "Act"). These regulations are also promulgated in response to the Settlement Agreement in *Natural Resources Defense Council, Inc.*, v. *Train*, 8 ERC 2120 (D.D.C. 1976), *modified*, 12 ERC 1833 (D.D.C. 1979).

II. Scope of This Rulemaking

A. *Overview.* This regulation applies to facilities engaged in mining and processing of metal ores. The industry includes facilities which mine or process the ores of 23 separate metals and is segregated by the U.S. Bureau of the Census Standard Industrial Classification (SIC) into nine major codes: SIC 1011, Iron Ore; SIC 1021, Copper Ores; SIC 1031, Lead and Zinc Ores; SIC 1041, Gold Ores; SIC 1044, Silver Ores; SIC 1051, Aluminum Ore; SIC 1061, Ferroalloy Ores including Tungsten, Nickle, and Molybdenum; SIC 1092 Mercury Ores; SIC 1094 Uranium, Radium, and Vanadium Ores; and SIC 1099 Metal Ores, Not Elsewhere Classified including Titanium and Antimony.

Over 500 active mining and over 150 milling operations are located in the United States and most are in remote areas.

The industry includes facilities that mine ores to produce metallic products and all ore dressing and beneficiating operations at mills operated either in conjunction with a mine operation or at a separate location. A detailed overview of the ore mining industry can be found in the proposed regulation (47 FR 25682).

B. *Prior EPA Regulations.* On November 6, 1975, EPA published interim final regulations establishing BPT requirements for existing sources in the ore mining and dressing industry (see 40 FR 51722). These regulations became effective upon publication. However, concurrent with their publication, EPA solicited public comments with a view to possible revisions. On the same date, EPA published proposed BAT, NSPS, and pretreatment standards for this industry (see 40 FR 51738). Comments were also solicited on these proposals.

On May 24, 1976, as a result of the public comments received, EPA suspended certain portions of the interim final BPT regulations and solicited additional comments (see 41 FR 21191). EPA promulgated revised, final BPT regulations for the ore mining and dressing industry on July 11, 1978, (see 43 FR 29711, 40 CFR Part 440). On February 6, 1979, EPA published a clarification of the BPT regulations as they apply to storm runoff (see 44 FR 7953). On March 1, 1979, the Agency amended the final BPT regulations by deleting the requirements for cyanide applicable to froth flotation mills in the base and precious metals subcategory (see 44 FR 11546).

On December 10, 1979, the United States Court of Appeals for the Tenth Circuit upheld the BPT regulations, rejecting challenges brought by five industrial petitioners. *Kennecott Copper Corp.* v. *EPA*, 612 F. 2d 1232 (10th Cir. 1979).

The Agency withdrew the proposed BAT, NSPS, and pretreatment standards on March 19, 1981 (see 46 FR 17567). On June 14, 1982 the Agency proposed the BAT, BCT, and NSPS limitations and standards which are the subject of this rulemaking.

C. *Description of This Regulation.* As a result of the Clean Water Act of 1977, the emphasis of EPA's program has shifted from "classical" pollutants to the control of a list of toxic substances. Therefore, in this rulemaking, EPA efforts are primarily directed toward ensuring the achievement of limitations based upon the best available technology economically achievable (BAT) by July 1, 1984.

The BPT effluent limitations are included as part of this regulation for the convenience of the reader. Since there are no substantive changes in the BPT effluent limitations as sustained by the 10th Circuit, the BPT effluent limitations are not subject to further judicial review.

BAT limitations are established for seven subcategories in the ore mining and dressing point source category. The BAT effluent limitations are being promulgated as they were proposed on June 14, 1982 (47 FR 25682). The technology basis for BAT is discussed in the proposed regulation and is discussed in greater detail in the development document supporting the proposed regulation and in the development document supporting this final regulation.

BCT effluent limitations are not being promulgated in this rulemaking. As discussed further in Section V, Changes from Proposal, BCT for this point source category is instead being included as part of the proposed regulation on the new BCT cost methodology. (47 FR 49176, October 29, 1982).

NSPS are established for seven subcategories. A NSPS for froth flotation mills extracting copper, lead, zinc, gold, silver, or molybdenum was proposed as zero discharge, but the standard is being amended to allow for a bleed in the mill circuit. Also, the upset and bypass storm provision for new sources requiring zero discharge is being changed and made identical to the provision for existing sources. All other standards of performance and general provisions are established essentially as proposed. This is discussed further in Section V, Changes from Proposal.

Finally, this regulation does not establish pretreatment standards because, as discussed in the proposed regulation, the Agency knows of no existing facilities which discharge to publicly owned treatment works and does not expect that any new sources will do so.

III. Summary of Legal Background

A. *The Clean Water Act.* The Federal Water Pollution Control Act Amendments of 1972 established a comprehensive program to "restore and maintain the chemical, physical and biological integrity of the Nation's waters" (Section 101(a)). To implement the Act, EPA was required to issue effluent limitations guidelines, pretreatment standards and new source performance standards for industrial dischargers.

The Act included a timeable for issuing these standards. However, EPA was unable to meet many of the deadlines and, as a result, in 1976, it was sued by several environmental groups. In settling this lawsuit, EPA and the plaintiffs executed a court-approved "Settlement Agreement." This Agreement required EPA to develop a program and adhere to a schedule in promulgating effluent limitations guidelines and pretreatment standards for 65 "priority" pollutants and classes of pollutants, for 21 major industries. [*See Natural Resources Defense Council, Inc.* v. *Train*, 8 ERC 2120 (D.D.C. 1976), *modified*, 12 ERC 1833 (D.D.C. 1979)].

Many of the basic elements of this Settlement Agreement were incorporated into the Clean Air Water Act of 1977 ("the Act"). Like the Settlement Agreement, the Act stressed control of the 65 classes of toxic pollutants. In addition, to strengthen the toxic control program, Section 304(e) of the Act authorizes the Administrator to prescribe "best management practices" (BMP) to prevent the release of toxic and hazardous pollutants from plant site runoff, spillage or leaks, sludge or waste disposal and drainage from raw material storage associated with, or ancillary to, the manufacturing of treatment process.

Under the Act, the EPA program is to set a number of different kinds of effluent limitations. These are discussed in detail in the proposed regulation and development document. The following is a brief summary:

1. Best Practicable Control Technology Currently Available (BPT). BPT limitations generally are based on the average of the best existing performance at plants of various sizes, ages and unit processes within the industry or subcategory. In establishing BPT limitations, we consider the total control of applying the technology in relation to the effluent reduction derived, the age of equipment and facilities involved, the process employed, the engineering aspects of the control technologies, process changes and the nonwater-quality environmental impacts (including energy requirements). We balance the total cost of applying the technology against the effluent reduction.

2. Best Available Technology Economically Achievable (BAT). BAT limitations, in general, represent the best existing performance in the industrial subcategory or category. The Act establishes BAT as the principal national means of controlling the direct discharge of toxic and nonconventional pollutants to navigable waters. In arriving at BAT, the Agency considers the age of the equipment and facilities involved, the process employed, the engineering aspects of the control technologies, process changes, the cost of achieving such effluent reduction and nonwater-quality environmental impacts. The Administrator retains considerable discretion in assigning the weight to be accorded these factors.

3. Best Conventional Pollutant Control Technology (BCT). The 1977 Amendments added Section 301(b)(2)(E) to the Act establishing "best

conventional pollutant control technology" (BCT) for discharges of conventional pollutants from existing industrial point sources. Conventional pollutants are those defined in Section 304(a)(4) [biological oxygen demanding pollutants (e.g., BOD5) total suspended solids (TSS), fecal coliform and pH] and any additional pollutants defined by the Administrator as "conventional," i.e., oil and grease. (See 44 FR 44551: July 30, 1979.)

BCT is not an additional limitation but replaces BAT for the control of conventional pollutants. In addition to other factors specified in section 304(b)(4)(B), the Act requires that BCT limitations be assessed in light of a two part "cost-reasonableness" test. *American Paper Institute* v. *EPA*, 660 F. 2d 954 (4th Cir. 1981). The first test compares the cost for private industry to reduce its conventional pollutants with the cost of publicly owned treatment works (POTWs) for similar levels of reduction in their discharge of these pollutants. The second test examines the cost-effectiveness of additional industrial treatment beyond BPT. EPA must find that limitations are "reasonable" under both tests before establishing them as BCT. In no case may BCT be less stringent than BPT.

EPA published its methodology for carrying out the BCT analysis on August 29, 1979 (44 FR 50732). In the case mentioned above, the Court of Appeals ordered EPA to correct data errors underlying EPA's calculation of the first test, and to apply the second cost test. (EPA had argued that a second cost test was not required.)

EPA recently proposed a new methodology on October 29, 1982 and simultaneously proposed BCT limitations for ore mining and dressing. (47 FR 49176).

4. *New Source Performance Standards (NSPS).* NSPS are based on the best available demonstrated technology. New plants have the opportunity to install the best and most efficient production processess and wastewater treatment technologies.

5. *Pretreatment Standards for Existing Sources (PSES), and Pretreatment Standards for New Sources (PSNS).* Pretreatment standards (PSES and PSNS) are designed to control the discharge of pollutants into publicly owned treatment works. Pretreatment standards were not proposed for the ore mining and dressing category since no known indirect dischargers exist nor are any known to be planned. Ore mines are located in rural areas, generally far from a POTW. EPA expects that the cost of pumping mine and mill wastewater to a POTW would be prohibitive in most cases, and on-site treatment is more cost effective in virtually every instance.

IV. Methodology and Data Gathering Efforts.

The methodology and data gathering efforts used in developing the proposed regulation were discussed in the preamble to the proposal, 47 FR 25682 (June 14, 1982). In summary, before publishing the proposed regulation the Agency conducted a data collection, analytical screening, and analytical verification program for the ore mining and dressing industry. This program stressed the acquisition of data on the presence and treatability of the 65 toxic pollutants and classes of toxic pollutants discussed previously. The 65 toxic pollutants and classes of pollutants potentially include thousands of specific pollutants. EPA selected 129 specific toxic pollutants for study in this rulemaking and other industry rulemakings. (Analytical methods are discussed in *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants* (U.S. E.P.A., April 1977)). Based on the results of that program, EPA identified several distinct treatment technologies, including both end-of-pipe and in-plant technologies, that are or can be used to treat ore mining and dressing industry wastewaters.

For each of these technologies, the Agency (i) compiled and analyzed historical and newly-generated data on effluent quality, (ii) identified its reliabilities and constraints, (iii) considered the nonwater quality impacts (including impacts on air quality, solid waste generation and energy requirements), and (iv) estimated the costs and economic impacts of applying it as a treatment and control system. Costs and economic impacts of the technology options considered are discussed in detail in two separate documents. *The Economic Impact Analysis of Promulgated New Source Performance Standards for the Ore Mining and Dressing Industry* and *The Economic Impact Analysis of Promulgated BAT Effluent Limitations and Standards for the Ore Mining and Dressing Industry.* A more complete description of the Agency's study methodology, data gathering efforts and analytical procedures supporting the regulation can be found in the *Final Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Point Source Category* (U.S. EPA, November 1982).

V. Summary of Promulgated Regulation and Changes From Proposal

The final regulation does not change the proposed BAT regulations but does change the standards for new sources. The changes are the result of the Agency's consideration of public comments provided in response to the proposal and further evaluation of the information upon which the proposal was based.

A. *Subcategorization.* The proposed subcategorization scheme was similar to the subcategorization scheme found in the 1978 BPT regulations. That scheme subcategorizes the industry primarily on the basis of ore type. Each subcategory is further subdivided on the basis of whether the discharge is from a mine or a mill and, in some cases, according to the type of beneficiation process employed. In these final regulations the Agency is retaining the proposed subcategorization scheme with a few modifications resulting from comments received on the proposed regulation.

The 1978 BPT regulations contained a Ferroalloy Ores subcategory that addressed discharges from facilities mining or milling chromium, cobalt, columbium, tantalum, manganese, molybdenum, nickel, tungsten, and vanadium (recovered alone, rather than as a by-product of uranium mining or milling). The BPT regulations also contained a Base and Precious Metal Ores subcategory that addressed the discharges from facilities mining or milling copper, lead, zinc, gold, or silver. Prior to proposing the BAT and NSPS regulations, EPA found that the wastewater discharges from molybdenum mines and mills were more like the discharges from facilities in the Base and Precious Metals Ores subcategory than the discharges from the Ferroalloy subcategory. Consequently the proposed BAT and NSPS regulations placed molybdenum mines and mills into the Base and Precious metals subcategory, which was renamed the Copper, Lead, Zinc, Gold, Silver, Platinum and Molybdenum Ores subcategory. The proposal also eliminated the Ferroalloy subcategory and replaced it with the Nickle Ores subcategory, the Tungsten Ores subcategory, and the Vanadium Ores subcategory (recovered alone, not as a by-product of uranium mining and milling). For clarification, however, the proposal retained the old subcategorization scheme for the BPT limitations.

From the comments received, it is apparent that retention of the old BPT subcategorization scheme for the BPT

limitations has only confused, rather than clarified matters. The commenters suggested that, to eliminate this confusion, the Agency should use an identical subcategorization scheme for all the limitations and standards. Accordingly, in this final regulation, the Agency is eliminating a separate subcategorization scheme for the BPT limitations, and is, instead, using the same scheme for all the BPT, BAT, and NSPS limitations. This change is solely for the purpose of clarification and will not alter in any way the actual numerical limitations which apply to facilities covered by the BPT regulations.

One additional modification to the subcategorization scheme is being made. The Agency is taking platinum ore out of the new Copper, Lead, Zinc, Gold, Silver, and Molybdenum Ores subcategory and establishing a new subcategory for these mines and mills. The Agency received comments that a new platinum mine and mill is being considered that will be substantially different than the existing mines and mills upon which the Agency based best demonstrated technology. The Agency is, therefore, establishing a new subcategory addressing platinum ore mines and mills and is reserving the new source performance standard.

B. Applicability. As discussed in the proposal, the Ore Mining and Dressing effluent guidelines limitations and standards are applicable to facilities discharging wastewater from ore mining and milling operations. They do not, however, provide a complete basis for calculating the limitations of operations known as "complex facilities," which combine wastestreams from processes such as refining and smelting with ore mining and milling wastestreams and then treat this combined stream before discharge. Each facility will be given effluent limitations that are derived from the BAT mine and mill guidelines and the smelter and refining guidelines and other applicable guidelines.

The Agency received voluminous comments from developers of a molybdenum mine and mill in southeastern Alaska. The developers argued that the mill differs substantially from the existing molybdenum mills upon which the Agency based the proposed NSPS. Specifically, they argue that precipitation is greater than at other facilities and that the terrain is unusually steep, necessitating the construction of a dam much larger than tailings impoundments at existing facilities. They further argue that since the mine and mill are located in the environmentally sensitive Misty Fjords National Monument, construction of a massive tailings impoundment may result in greater long term environmental degradation than at existing facilities. In a related vein, they point out that the mine and mill are being developed in accordance with the dictates of the Alaska National Interest Lands Conservation Act (ANILC), which requires an intensive study of the overall environmental impact of the mine and mill before construction begins. Finally, they note that the mine and mill are in an earthquake area, and that construction of a large tailings dam raises concerns for safety of the population below the dam.

The Agency disagrees with the commenter's assertions that the proposed molybdenum mine and mill differ significantly in topography and climate from existing mines and mills. Nevertheless, given the possibility that compliance with the zero discharge NSPS would result in substantial non-water quality environmental impacts, and given the fact these impacts are being subjected to an intense environmental scrutiny, the Agency believes it would be premature to subject the mine and mill to regulation at this time, before the environmental review process is fully completed.

Also, as the Agency stated in the preamble to the BPT regulations and in the proposed regulation for BAT and NSPS, under no circumstances will an owner or operator be required to violate applicable safety standards to meet the requirements of BPT, BAT, or NSPS. As discussed in these regulations, the Agency is confident that the national applicable effluent limitations guidelines and standards of performance do not pose a concern for the overall safety related to the water impoundments that may be required by the regulations. However, it would be premature to regulate this mine and mill before the potential for earthquake and avalanches in a deep mountain terrain has been completely evaluated by Federal and State agencies and others responsible for conducting a thorough study of the impacts of this proposed new mine and mill. Accordingly, the Agency is excluding this mine and mill from the regulations applicable to molybdenum mines and mills, thereby postponing consideration of the appropriate limitations for this facility until the permit proceedings.

The BPT limitations established a subpart for gold placer mines, but reserved effluent limitations because the Agency did not have sufficient technical or economic data. The proposal similarly reserved effluent limitations and standards for the gold placer mine subpart because the data generated prior to proposal were not sufficiently comprehensive.

EPA still has no data upon which to base an economic assessment of gold placer mines and does not have sufficient technical data to promulgate or propose limitations for gold placer mines. The Agency is, therefore, continuing to reserve the subpart for gold placer mines in the promulgated regulation.

C. Best Practicable Technology Limitations. The BPT limitations for the ore mining industry were promulgated in 1978, were completely upheld in the Courts, and are repeated in this regulation solely for clarity. EPA received a few comments which recommended that the Agency relax the current BPT regulations. These comments are discussed in the response to public comments document.

D. Best Available Technology Limitations. EPA proposed BAT limitations equal to the BPT regulations currently applicable to this industry.

The rationale for setting BAT effluent limitations equivalent to BPT effluent limitations is discussed in the proposal (47 FR 25682), the development document supporting the proposed rule, and the development document supporting this final rule. In summary, the Agency established BAT equal to BPT either because BPT already specified zero discharge of process wastewater, or because application of candidate BAT did not reduce the level of the toxic or nonconventional pollutants, or because BPT removed a very high percentage of the relevant pollutants. Almost all the commenters agreed with EPA's decision to propose BAT equal to BPT. Accordingly, the Agency is finalizing the BAT limitations as proposed. The comments addressing the BAT limitation are discussed in the response to public comments document.

E. Best Conventional Technology Limitations. The Agency proposed BCT limitations equal to the BPT limitations for conventional pollutants. This was done even though the Agency had not established a new cost effectiveness test for conventional pollutant removal as directed by the Fourth Circuit Court of Appeals decision in *American Paper Institute* v. *EPA*, F. 2d (4th Cir. 1981). In the proposal the Agency reasoned that since BPT is the minimum level of control required by law, no possible reassessment of BCT pursuant to the Court's remand could result in BCT limitations for conventional pollutants less stringent than the BPT limitations.

A number of commenters took issue with the Agency's decision to propose BCT limitations in the absence of a new BCT methodology. The Agency agrees with these criticisms and has accordingly decided to withdraw the BCT limitations proposed on June 14, 1982. Instead, BCT Limitations for the ore mining and dressing point source category are being included as part of the proposed regulation on the new BCT methodology. This proposed regulation was published in the **Federal Register** on October 29, 1982. (47 FR 49176). Comments on the proposed BCT limitations must be submitted during the comment period for the BCT rulemaking.

F. New Source Performance Standards. EPA proposed new source performance standards (NSPS) equal to the BAT limitations for all elements of the ore mining and dressing industry with the exception of froth flotation mills in the copper, lead, zinc, gold, silver, platinum and molybdenum subcategory and the uranium mill subcategory. The Agency proposed NSPS requiring zero discharge for these latter two segments as discussed below.

1. Froth Flotation Mills. The proposed zero discharge requirement for new froth flotation mills was based on the fact that 46 out of 90 existing facilities for which we have data achieve zero discharge through total recycle and evaporation of process wastewater.

Industry commenters raised a number of objections to this proposal. First, they argued that most of the mills achieving zero discharge are in net evaporation areas with flat topography and that it was inappropriate to extrapolate from the treatment performance of mills in these areas to mills located in rainy or mountainous areas. They contended that in rainy or mountainous areas, the costs of constructing the tailings impoundment necessary to achieve zero discharge and the costs of transporting recycle water back to the mill could be prohibitive. They implied that this problem was greatly exacerbated by the proposed storm exemption for new sources, which granted relief to a facility only upon the occurrence of a ten year, twenty-four hour storm.

Second, they argued that EPA improperly assumed that new sources, unlike existing sources, would not experience extensive retrofit costs. They pointed out that the Agency's proposed definition of new source embraces both virgin or "greenfield" facilities and facilities constructed in conjunction with existing sources. These latter facilities, they stated, will incur substantial retrofit costs to achieve zero discharge.

Finally, they asserted that the Agency neglected to take into account the buildup of reagents and other contaminants in the recycle water of a total recycle system. They claimed that these contaminants would interfere with the froth flotation process and cause severe loss of product, necessitating either the addition of fresh make up water or the treatment of the recycle water. They added that treating the recycle water may not always prove to be an effective solution because of the buildup of contaminants from the treatment of the recycle water. They pointed out the Agency had not calculated the costs of treating the recycle water or building the bigger impoundment to hold and recycle the wastewater.

The Agency disagrees with the commenters' first criticism that EPA failed to adequately take into account topographical and climatic constraints in proposing a zero discharge requirement for new sources. Mills currently achieving zero discharge are located in areas ranging from flat to extremely steep and mountainous. Zero discharge is thus demonstrated for a wide spectrum of topographical constraints. Similarly, although the majority of mills achieving zero discharge are located in dry areas, 15 are located in relatively wet areas. Zero discharge is thus demonstrated for wet areas as well as dry areas. Moreover, the standards promulgated for new source froth flotation mills allow a discharge of wastewater equivalent to the net precipitation (precipitation less evaporation) subject to the discharge limitations for mine drainage, e.g. 440.104(2)(i). By permitting the discharge of excess rainwater and runoff, this provision substantially minimizes the effect of climate on a facility's ability to meet zero discharge.

An assumption of the commenters' arguments is that the zero discharge requirement imposes significantly greater costs than the BPT requirement under the same set of topographical, climatic and land availability constraints. Many commenters implied that constructing a tailings pond necessary to achieve zero discharge in mountainous or rainy areas would be much more expensive than constructing a similarly situated pond to meet BPT requirements. Although there might have been some merit to this argument under the Agency's proposed storm exemption for new sources, this is no longer the case. Now that the Agency has amended the proposed storm provision to make it identical to the provision for existing sources, the pond required to meet BPT requirements will be approximately the same size as the pond required to meet zero discharge. (See Development Document for further discussion).

One commenter, whose existing tailings pond is located several miles from the mill and several thousand feet below it, argued that, if this mill were a new source, the costs of recycling water to the mill to achieve zero discharge would prove much more expensive than meeting the BPT requirements. The Agency, however, considers such situations to be extremely rare. If a new source had to operate under similar constraints, the Agency would entertain a petition to modify the new source standard or create a new subcategory for this type of facility.

With respect to industry commenters' second criticism, EPA agrees with their claim that there would be retrofit costs associated with meeting zero discharge where a new source is constructed at the site of an existing source. It is not clear, however, whether this problem is anything but theoretical. EPA specifically asked industry to provide it with examples of construction at the site of an existing source which might constitute a new source under EPA's proposed criteria for "new source" (45 FR 59343, September 9, 1980). After evaluating these examples, EPA has concluded that only one of the examples provided by industry would constitute a "new source" under the proposed criteria—and this example involved construction at a "green field" site. (These examples are specifically discussed in the Response to Comments document). Nevertheless, EPA has redone its economic analysis to embrace situations where construction at the site of an existing source would clearly create a new source (i.e. total replacement of a mill). EPA has concluded that in such situations, the costs of achieving zero discharge will not cause an adverse economic impact.

EPA agrees with the commenters' third contention that we did not adequately consider the buildup of contaminants in the recycle water. Commenters have come forward with data demonstrating that the buildup of reagents and other contaminants can in fact interfere with the extractive process, causing severe loss of product. They have also demonstrated that treatment of the recycle water may not always be an economically viable option for dealing with this interference problem. Unfortunately, this interference is a complex phenomenon, which appears to be related to the characteristics of the ore at particular sites, making it impossible to carve out a subcategory of facilities afflicted with this problem. Accordingly, to

accommodate the problem, the final NSPS contains a special "bleed" provision which will allow facilities to discharge wastewater (subject to the NSPS mine drainage standards) if they can demonstrate to the permitting authority that total recycle would cause a major interference in the extractive metallurgical process and that appropriate treatment of recycle water is not adequate to remedy this interference. This provision will allow such facilities to substitute some fresh water for recycle water as industry stated and their data indicated was necessary, thereby avoiding the losses associated with buildup of contaminants in the recycle water. Specification of the exact amounts of water discharged and the appropriate treatment of recycle water will, of course, be left to the permitting authority. The Agency has, however, evaluated the costs and economic impact of at least two forms of treatment of recycle water. The first is pH adjustment (lime addition) and settling. Assuming a 24-hour retention time and a 10 percent safety factor, the Agency has concluded that the costs of such treatment of recycle water would not be significant enough to deter investment for a new mill with a tailings pond used for primary settling. The Agency has further determined that additional treatment consisting of a mixed media filter would not constitute a barrier to entry for such mills. The development document and economic document supporting this regulation discuss in more detail the Agency's considerations in creating the bleed provision and what treatment was considered as appropriate treatment of recyle water.

2. Uranium Mills. The Agency proposed zero discharge for new uranium mills based on data demonstrating that 18 of 19 existing mills do not discharge wastewater. The single existing mill which discharges, recycles over 80 percent of the requirement for its intake water. Zero discharge for new uranium mills is based on recycle, evaporation, and a combination of recycle and evaporation.

Industry commented that our data represented mills in arid areas and that we did not consider new mills that may locate in areas of high rainfall. They also requested that flexibility should be allowed to accommodate changes in the extractive processes currently used to recover uranium. Finally they commented that we should allow an effluent discharge because such a discharge is considered a valuable commodity in water short areas.

The ability of uranium mills to achieve zero discharge is well demonstrated and is recognized by Federal and State regulating authorities dealing with the uranium industry. It is true that existing uranium mills are located in arid areas. However, we know of no plans for construction of new mills in non-arid areas, although some firms have conducted exploration in such areas. Should any new mills locate in areas of high net precipitation, they can take advantage of the net precipitation provision and the storm exemption. If, despite these provisions, a uranium mill locates in an area where it is impossible to achieve zero discharge the facility can petition the Agency to change NSPS or create a separate subcategory for that type of facility.

The Agency does not believe that it needs to provide any additional flexibility to accommodate changes in the extractive processes used to recover uranium. Industry commenters failed to provide EPA with any information concerning new or different extractive processes. Furthermore, the current regulations only apply to certain identified extractive processes and thus would not apply to processes unrelated to processes used today.

Nor does the Agency believe that the zero discharge requirement will adversely affect water conservation. Even if there were a slight increase in water consumption attributable to compliance with zero discharge, that increase would not be significant when compared to the benefits derived from the use of recycle and evaporation systems. Accordingly, the zero discharge requirement for new uranium mills is promulgated as proposed.

3. *Storm Exemption.* The Agency proposed a storm exemption for new sources subject to zero discharge which would allow a discharge of excess wastewater upon the occurrence of a 10-year 24-hour precipitation event. Industry stated that the provision of the exemption imposed an impossible design requirement on them and should be changed to the requirement for existing sources.

After reviewing the industry comments, and data developed by the Agency, EPA has concluded that the industry comments are valid. Conditioning the storm exemption on the actual occurrence of a 10-year, 24-hour storm is inappropriate because overflows can occur from facilities designed, maintained, and operated to handle a 10-year, 24-hour precipitation event as a result of recurring storms or excessive snowmelt even though no individual event were equivalent to a 10-year, 24-hour precipitation event. The proposal would have required facilities to engage in the extremely difficult task of anticipating all such combinations of precipitation events. Accordingly, we have modified the storm exemption for new sources subject to zero discharge so that it is identical to the exemption for existing sources.

The Agency received requests for further explanation of the considerations to be taken into account in the design and construction of a facility which may be granted relief under the storm exemption. As a result of these requests we have made some clarifying changes in the language of the exemption. The first change is designed to clarify the nature of the operator's responsibilities during an upset or bypass overflow event. The storm exemption is designed to provide a limited exception to the requirements applicable to mines and mills under normal operating conditions. It grants relief from excess discharges which occur during and immediately after any precipitation or snowmelt—the intensity of the event is not specified. The storm exemption was not intended to grant the operator the option of ceasing or reducing efforts to contain or treat the runoff resulting from a rainfall or snowmelt, i.e., the operator does not have the option of turning off the lime feed to a facility at the start of or during a precipitation event, regardless of the design and construction of the facility. The operator must, instead, take all reasonable steps during and after the precipitation event to treat or contain the wastewater discharge and to limit the amount of overflow or excess discharge.

The second change is intended to clarify the nature of the design requirement for sources subject to a zero discharge limitation and to emphasize the fundamental differences between that requirement and the requirement for sources not subject to zero discharge. The storm exemption applicable to sources which are allowed to discharge requires the facility to be able to contain the maximum volume of wastewater which would be generated by the facility during a 24-hour period plus the volume of water which would result from a 10-year, 24-hour rainfall or treat the flows associated with these volumes. The rationale behind the containment requirement is that a facility with such capacity, even if full at the beginning of the storm, would be able to treat the storm runoff and normal plant discharge by providing at least a 24-hour retention time for settling

of the wastewaters before the water is discharged.

The design concept for the storm exemption applicable to sources subject to zero discharge requirements must, however, be different, because such sources are not permitted to discharge. Such sources must, therefore, be able to contain the amount of water equal to the volume of water in the pond under normal operating conditions (which includes water which is recycled or will be evaporated) plus the volume generated from a 10-year, 24-hour rainfall. In other words, the source must provide a freeboard over and above normal pond levels which can accommodate the water generated by a 10-year, 24-hour rainfall. Simply being able to hold the normal volume of wastewater from the mill process without discharge plus the 10-year, 24-hour rainfall will not suffice, unless the normal process wastewater is a fair measure of the volume of water in the pond under normal operating conditions.

The third change is designed to clarify the relationship between the storm exemption and the general upset and bypass provisions set in the consolidated permit regulations [See, 40 CFR 122.60]. The relationship between them should be set out more clearly. In the preamble to the proposal, we said that the storm exemption supersedes the general upset and bypass provisions with respect to precipitation events; that is, an operator wishing to obtain an excursion from the BAT or NSPS requirements during precipitation events must comply with the the prerequisites of the storm exemption. We did not, however, state whether an operator also had to comply with any of the upset and bypass provisions contained in the consolidated permit regulations as well. To clarify this, the storm exemption is being changed to specifically require compliance with the notice provisions of the general upset and bypass provisions, in accordance with the Agency's original intent. In addition, we have added a sentence to clarify that the storm exemption, like the general upset and bypass provision, simply provides an affirmative defense to an enforcement action. Consequently, the burden of proving compliance with the conditions of the storm provision rests with the operator, just as in the case of the general upset and bypass exemptions.

Additional explanation of the storm exemption is offered in the development document supporting this rulemaking.

G. *General Provisions and Definitions.* As the result of the comments received on the proposed BAT and NSPS, the Agency is adding a definition for "in situ leach methods" applicable to the Uranium, Radium and Vanadium Ores subcategory. This definition makes it clear that the no discharge standard of performance for in situ leach methods is applicable to the process wastewater used in and resulting from the actual in situ operation itself. In situ mine and mill process wastewater does not include discharges from wells from within or surrounding in situ mines used to restore aquifers after all actual mining activity (extraction of the ore, or pregnant liquor from the in situ process) has been completed. Such discharge would be from an inactive mine area and effluent limitations guidelines and standards of performance would not be directly applicable. Effluent limitations and standards are directly applicable to "active mining areas." During the actual working of the mine, if the discharge originates from an area outside of the in situ process area but directly associated with the "active mine area" such discharges are considered "mine drainage" and are subject to the effluent limitations or standards of performance for mine drainage from uranium mines. Mine drainage from areas outside of the areas used for the in situ process area include: drainage from development areas of a deep mines, and surface mine and runoff from mine and mill areas that are not directly involved in in situ leaching. Additional explanation is offered in the development document supporting this rulemaking.

The Agency received comments requesting that the Agency further explain the general provision having to do with waste streams which are combined for treatment from various subparts and segments of Part 440. We stated in the original provision that the quantity and quality of each pollutant or pollutant property in the combined discharge shall not exceed the quality and quantity of each pollutant or pollutant property that would have been discharged had each waste stream been treated separately. Further, the flow from the combined discharge shall not exceed the volume that would have been discharged had each wastestream been treated separately. An example that industry wished clarified is whether mine drainage commingled with the discharge from a new froth flotation mill is subject to the zero discharge requirements for new froth flotation mills. Such combined waste streams may be discharged subject to the limitations on mine drainage but the volume of the discharge cannot exceed the volume of mine drainage that would have been discharged had the mine drainage and the mill discharge been treated separately. It is immaterial whether the mine drainage is introduced to the treatment system simultaneously with the discharge from the mill, e.g. two separate pipes leading to the tailings pond, or whether the mine drainage is introduced as part of the feed water and intake to the mill itself. Further explanation and guidance is provided in the development document supporting this final regulation.

One commenter suggested that EPA provide a special allowance, similar to the net precipitation provision, for underground water which seeps into the tailings impoundment, this commenter asserted that such seepage constituted a large portion of the water collecting in its impoundment. The Agency knows of only this one example of underground seepage at existing facilities subject to zero discharge and believes that the fundamentally different factors variance provision provides an avenue of relief for existing sources. To accommodate new sources, however, the Agency is adding a provision which will allow the permit writer to grant an additional discharge allowance in the case of significant groundwater infiltration, subject to the limitations on mine drainage.

There were requests from industry that a separate definition for "new source" applicable to ore mines and mills be included in the final regulation. The Agency feels that there is no reason to do so. As part of the consolidated permit regulations, Paragraph 122.66(b), the Agency promulgated criteria for determining what is a new source. On September 9, 1980, these criteria were withdrawn and new criteria were proposed. When finalized, these criteria will apply to the mining industry.

VI. Costs and Economic Impact

Executive Order 12291 requires EPA and other agencies to provide regulatory impact analyses for rules that result in an annual cost to the economy of $100 million dollars or more, cause major price increases to the consumer and cause significant adverse effects on competition, employment, investment, productivity and the balance of trade. In addition, the Clean Water Act specifies that best available technology limitations must be economically achievable. The Regulatory Flexibility Act requires EPA to consider the effects of this rule on small entities, and if they are significant and affect a substantial number of small entities, to prepare a Regulatory Flexibility Analysis. The Agency has concluded that this is not a major rule and will not have a significant impact on a substantial number of small entities and, therefore,

a Regulatory Impact Analyses and a Regulatory Flexibility Analysis are not required.

The BAT limitations promulgated today do not reflect any treatment requirements beyond the treatment required for existing direct dischargers under the BPT rule promulgated July 11, 1978 (43 FR 29711). Additionally, EPA is not establishing pretreatment standards because no known indirect dischargers exist nor are any known to be in the planning stage. Accordingly, EPA expects no incremental costs or impacts for existing plants from this rulemaking. The costs for New Source standards are not expected to be a deterrent to investment and are not expected to change the rate of entry into the industry or slow the industry growth rate.

In developing this rule, the Agency considered various technology options and analyzed their economic impacts. This economic analysis is presented in two documents. One is the *Economic Impact Analysis of Promulgated New Source Performance Standards for the Ore Mining and Dressing Industry* which addresses new sources. The second document is *The Economic Impact Analysis of Promulgated BAT Effluent Limitations Guidelines for the Ore Mining and Dressing Industry* which addresses existing sources and is presently subject to a confidentiality requirement discussed previously. For each of the options considered during rulemaking, these analyses detail the investment and annual costs for the industry as a whole and for typical plants; assesses the impact of effluent control in terms of price and production changes, plant closures and employment effects; and assesses the potential impacts on the small plants in this industry.

VII. Nonwater Quality Environmental Impacts

The elimination or reduction of one form of pollution may aggravate other environmental problems. Therefore, sections 304(b) and 306 of the Act require EPA to consider the nonwater quality environmental impacts (including energy requirements) of certain regulations.

In compliance with these provisions, EPA has considered the effect of these regulations on air pollution, solid waste generation, land requirements, water consumption and energy requirements.

Because this regulation does not impose any additional pollution control requirements on existing sources, implementation will not result in any substantial increase in air pollution, energy use, solid waste generation, land requirements or water consumption.

The Agency similarly, determined that the pollution control requirements for new sources, where they differ from existing sources requirements, will not result in adverse non-water quality impacts which would require alteration of the requirements.

In those subparts for which NSPS is more stringent than BAT, the increase in solid waste generated should not be greater than one percent.

In addition, section 7 of the Solid Waste Disposal Act Amendments of 1980 has exempted under Subtitle C of RCRA solid waste from the extraction, beneficiation, and processing of ores and minerals. This exemption will remain in effect until at least six months after the Administrator submits a study on the adverse environmental effects of solid waste from mining. The study is required to be submitted by October 21, 1983 (see 42 U.S.C. 6982).

Imposition of NSPS is not expected to create any significant adverse impacts on land requirements beyond those associated with BAT effluent limitations.

Achievement of NSPS will not result in a significant net increase in energy requirements. The main use of energy is for pumping, mixing, and control instrumentation. Wherever feasible, gravity flow is used in treatment facilities for mine drainage and mill process wastewater. Recycle at new froth flotation mills and new uranium mills will require electric power for pumps, but the Agency concludes that the impact of the energy consumed from compliance with the standards is justified by the benefits derived from the standards.

There should be no net water loss attributable to compliance with zero discharge of process wastewater from froth flotation mills and uranium mills. Moreover, even if there were a slight loss, it would not be significant when compared to the benefits derived from the use of recycle and evaporation systems.

VIII. Pollutants and Subcategories Not Regulated

Paragraph 8 of the modified Settlement Agreement, approved by the District Court for the District of Columbia on March 9, 1979 (12 ERC 1833), contains provisions authorizing the exclusion from regulation, in certain circumstances, of toxic pollutants and industry categories and subcategories.

A. Exclusion of Pollutants. As discussed in greater detail in the proposal June 14, 1982 and in the development document supporting the rule, paragraph 8[a][iii] of the Revised Settlement agreement allows the Administrator to exclude from regulation toxic pollutants not detectable by Section 304(h) analytical methods or other state-of-the-art methods. This provision includes pollutants below EPA's nominal detection limit. In addition, Paragraph 8[a][iii] allows the exclusion of pollutants that were detected in amounts too small to be effectively reduced by technologies known to the Administrator. Pollutants excluded under these provisions are listed in Appendices B, C and D. One hundred and thirteen toxic organics, cyanide and six toxic metals are excluded from regulation under these provisions.

Paragraph 8[a][iii] also allows the Administrator to exclude from regulation pollutants detected in the effluent of only a small number of sources within the category and uniquely related to those sources. The toxic organic pollutant, 2,4-dimethylphenol, was detected in the effluent at only one facility and 2,4-dimethylphenol is excluded under this provision.

Paragraph 8[a][iii] also allows the Administrator to exclude from regulation pollutants that are effectively controlled by the technology upon which other effluent limitations and guidelines are based. Effluent limitations for TSS will effectively control the toxic pollutant asbestos (chrysotile). Arsenic and nickel found in discharges from ore mining and dressing are adequately controlled by the incidental removal associated with the control and removal of other metals found in the discharges from this industry, e.g., copper, lead, mercury, and zinc.

In addition to the toxic pollutants excluded for all subcategories, EPA is excluding certain toxic pollutants from particular subcategories and subparts because they were either not detected or detected in amounts too small to be effectively reduced by technologies known to the Administrator. See Appendix G for pollutants excluded by subcategory and subpart.

B. Exclusion of Subcategories. Paragraph 8(a)(iv) of the revised settlement Agreement allows the Administrator to exclude a category or subcategory from regulation if the amount and toxicity of each pollutant in the discharge does not justify developing national requirements in accordance with the schedule contained in the agreement. EPA is excluding the mill subpart in the Uranium, Radium and Vanadium subcategory from development of BAT regulations

ecause there is only one existing ischarger and development of national egulations are not warranted for this ngle plant. EPA is excluding the Nickel ubcategory, the Vanadium subcategory nined alone and not as a byproduct) nd, the Antimony subcategory from evelopment of BAT and NSPS because here is only one known discharger in ach of these subcategories and no new ources are expected. EPA is excluding he Platinum subcategory from evelopment of NSPS because the one lentified new source must use an ntirely different treatment system than hat was identified as best emonstrated technology and EPA lacks ata on the system. EPA is differing egulations of the gold placer mine ubpart of the Copper, Lead, Zinc, Gold, ilver, and Molybdenum subcategory ntil it completes data gathering efforts or this subpart.

Paragraph 8(b) of the Settlement greement allows the Administrator to xclude from regulation pretreatment tandards for all point sources within a oint source category. Pretreatment tandards for both existing and new ources in this point source category are ot justified because no indirect ischargers exist nor are any known to e planned.

X. Best Management Practices

Section 304(e) of the Clean Water Act ives the Administrator authority to rescribe "best management practices" BMPs). BMPs are not addressed in this egulation.

X. Upset and Bypass Provisions

A recurring issue is whether industry uidelines should include provisions uthorizing noncompliance with effluent imitations during periods of "upset" or "bypass." An upset, sometimes called an "excursion," is an unintentional oncompliance occurring for reasons beyond the reasonable control of the permittee. It has been argued that an upset provision in EPA's effluent imitations is necessary because such upsets will inevitably occur even in properly operated control equipment. Because technology-based limitations require only what technology can achieve, it is claimed that liability for such situations is improper. When confronted with this issue, courts have disagreed on whether an explicit upset or excursion exemption is necessary, or whether upset or excursion incidents may be handled through EPA's exercise of enforcement discretion. Compare *Marathon Oil Co.* v. *EPA*, 564 F. 2d 1253 (9th Cir. 1977) with *Weyerhaeuser* v. *Costle*, 590 F. 2d 1011 (D.C. Cir. 1978) and *Corn Refiners Assn., et al.* v. *Costle*, 594 F. 2d 1223 (8th Cir. 1979). [See also *American Petroleum Institute* v. *EPA*, 540 F. 2d 1023 (10th Cir. 1976); *CPC International, Inc.* v. *Train*, 540 F. 2d 1320 (8th Cir. 1976); *FMC Corp.* v. *Train*, 539 F. 2d 973 (4th Cir. 1976).]

An upset is an unintentional episode during which effluent limits are exceeded; a bypass, however, is an act of intentional noncompliance during which waste treatment facilities are circumvented in emergency situations. We have, in the past, included bypass provisions in NPDES permits.

We determined that both upset and bypass provisions should be included in NPDES permits and have promulgated Consolidated Permit Regulations that include upset and bypass provisions. [See 40 CFR 122.60, 45 FR 33290 (May 19, 1980).] The upset provision establishes an upset as an affirmative defense to prosecution for violation of technology-based effluent limitations. The bypass provision authorizes bypassing to prevent loss of life, personal injury, or severe property damage.

The Agency has received several inquiries on the relationship between the general upset and bypass provisions set forth in the consolidated permit regulations and the storm exemption contained in the regulations for ore mining and dressing. This relationship is discussed in Section V of this preamble.

XI. Variances and Modifications

Upon the issuance of this regulation, the effluent limitations for the appropriate subcategory must be applied in all Federal and State NPDES permits thereafter issued to direct dischargers in the ore mining and dressing industry. For the BPT effluent limitations promulgated on July 11, 1978, the only exception to the binding limitations is EPA's "fundamentally different factors" variance. [See *E.I. du Pont de Nemours & Co.* v. *Train*, 430 U.S. 112 (1977); *Weyerhaeuser Co.* v. *Costle*, *supra*.] This variance recognizes factors concerning a particular discharger that are fundamentally different from the factors considered in this rulemaking. Although this variance clause was set forth in EPA's 1973–1976 industry regulations, it is now included in the NPDES regulations and will not be included in the ore mining and dressing industry BAT regulation. (See the NPDES regulations at 40 CFR Part 125, Subpart D.)

The BAT limitations in this regulation are also subject to EPA's "fundamentally different factors" variance. BAT limitations for nonconventional pollutants are subject to modifications under Sections 301(c) and 301(g) of the Act. These statutory modifications do not apply to toxic or conventional pollutants. To apply for these modifications a discharger must be in compliance with BPT. Because this rule will make BAT equal to BPT, EPA does not expect any applications for Section 301(c) or 301(g) modifications. [See 43 FR 40895 (September 13, 1978).] NSPS are not subject to EPA's "fundamentally different factors" variance or any statutory or regulatory modifications. [See *E. I. du Pont de Nemours and Co* v. *Train*, supra.)

XII. Relationship to NPDES Permits

The BAT limitations and NSPS in this regulation will be applied to individual ore mines and mills through NPDES permits issued by EPA or approved state agencies, under Section 402 of the Act. As discussed in the preceding section of this preamble, these limitations must be applied in all Federal and State NPDES permits except to the extent that variances and modifications are expressly authorized. Other aspects of the interaction between these limitations and NPDES permits are discussed below.

One issue that warrants consideration is the effect of this regulation on the powers of NPDES permit-issuing authorities. The promulgation of this regulation does not restrict the power of any permitting authority to act in any manner consistent with law or these or any other EPA regulations, guidelines or policy. For example, even if this regulation does not control a particular pollutant, the permit-issuer may still limit such pollutant on a case-by-case basis when limitations are necessary to carry out the purposes of the Act. Where manufacturing practices or treatment circumstances warrant additional controls, such limitations may be technology-based in conformance with the legislative history of the Act. However, such limitations are subject to administrative and judicial review as part of the permit issuance process. In addition, to the extent that State water quality standards or other provisions of State or Federal law require limitation of pollutants not covered by this regulation (or require more stringent limitations on covered pollutants), such limitations must be applied by the permit-issuing authority.

A second topic that warrants discussion is the operation of EPA's NPDES enforcement program, many aspects of which were considered in developing this regulation. We emphasize that although the Clean Water Act is a strict liability statute, the initiation of enforcement proceedings by EPA is discretionary. We have exercised

and intend to exercise that discretion in a manner that recognizes and promotes good-faith compliance efforts.

XIII. Public Participation

The Agency solicited public comment on the proposed rules published in the Federal Register on June 14, 1982, (47 FR 25682). In addition, the Agency accepted public comment on the development document and economic analysis supporting the proposed rules. The Agency received over fifty comment submittals.

Individual public comments received on the proposed regulation, and our responses, are presented in a report, "Responses to Public Comments, Proposed Ore Mining and Dressing Industry Effluent Guidelines and Standards," November 1982, which is part of the public record for this regulation.

Most of the major comments and the Agency's response are discussed in Section V of this preamble, Summary of Promulgated Regulation and Changes from Proposal.

XIV. Small Business Administration (SBA) Financial Assistance

The Agency is continuing to encourage small manufacturers to use Small Business Administration (SBA) financing as needed for pollution control equipment. Three basic programs are in effect: the Guaranteed Pollution Control Program, the Section 503 Program, and the Regular Guarantee Program. All the SBA loan programs are only open to businesses with net assets less than $6 million, with an average annual after-tax income of less than $2 million and with fewer than 250 employees.

The guaranteed pollution control program authorizes the SBA to guarantee the payments on qualified contracts entered into by eligible small businesses to acquire needed pollution control facilities when the financing is provided through pollution control bonds, bank loans and debentures. Financing with SBA's guarantee of payment makes available long-term financing comparable with market rates. The program applies to projects that cost from $150,000 to $200,000.

The Section 503 Program, as amended in July 1980, allows for long-term loans to small and medium-sized businesses. These loans are made by SBA-approved local development companies, which for the first time are authorized to issue Government-backed debentures that are bought by the Federal Financing Bank, an arm of the U.S. Treasury.

Through SBA's Regular Guarantee Program, loans are made available by commercial banks and are guaranteed by the SBA. This program has interest rates equivalent to market rates.

For additional information on the Regular Guarantee and Section 503 Programs contract your district or local SBA Office. The SBA coordinator at EPA headquarters is Ms. Frances Desselle who may be reached at (202) 382-5373.

For further information and specifics on the Guaranteed Pollution Control Program contact: U.S. Small Business Administration, Office of Pollution Control Financing, 4040 North Fairfax Drive, Rosslyn, Virginia 22203, (703) 235-2902.

XV. List of Subjects in 40 CFR Part 440

Metals, Mines, Water pollution control, Waste treatment and disposal.

XVI. Availability of Technical Assistance

The justification for the proposed regulation is detailed in four major documents available from EPA. Analytical methods are discussed in (1) *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants.* EPA's technical conclusions are detailed in the (2) *Development Document for Final Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Point Source Category.* The economic analysis for new sources is detailed in *Economic* (3) *Analysis of New Source Performance Standards for the Ore Mining and Dressing Industry.* The economic analysis for existing sources is detailed in the *Economic Impact Analysis of* (4) *Promulgated BAT Effluent Limitations Guidelines for the Ore Mining and Dressing Point Source Category.* The data contained in the analysis is covered by a third party agreement between the Agency and industry members who supplied the data. These data are confidential and can not be released until cleared by a confidentiality review panel. The Agency anticipates the BAT economic analysis will be made available to the general public shortly after this rule is promulgated.

A summary of the public comments received on the proposal and EPA's responses is presented in "Summary of (5) Comments and Responses on the June 1982 Proposed Regulations for the Ore Mining and Dressing Industry," which is part of the public record for this regulation.

XVII. OMB Review

The regulation was submitted to the Office of Management and Budget for review as required by Executive Order 12291.

In accordance with the Paperwork Reduction Act of 1980 (P.L. 96-511), the reporting or recordkeeping provisions that are included in this regulation will be submitted for approval to the Office of Management and Budget (OMB). They are not effective until OMB approval has been obtained and the public notified to that effect through a technical amendment to this regulation.

Dated: November 5, 1982.

Anne M. Gorsuch,
Administrator.

APPENDIX A

Abbreviations, Acronyms and Units Used in This Notice

Act—The Clean Water Act.

Agency—The U.S. Environmental Protection Agency.

BADT—Best available demonstrated technology under sections 304(c) and 306.

BAT—The best available technology economically achievable, under section 304(b)(2)(B) of the Act.

BCT—The best conventional pollutant control technology, under section 304(b)(4) of the Act.

BMP's—Best management practices under section 304(e) of the act.

BPT—The best practicable control technology currently available, under section 304(b)(1) of the Act.

CWA—The Federal Water Pollution Control Act Amendments of 1972 (33 U.S.C. 1251 et seq.) as amended by the Clean Water Act of 1977 (P.L. 95-217).

FWPCA—Federal Water Pollution Control Act.

MSHA—The Department of Labor, Mine Safety and Health Administration.

NPDES Permit—A National Pollutant Discharge Elimination System permit issued under section 402 of the Act.

NSPS—New source performance standards under section 306 of the Act.

POTW—Publicly owned treatment works.

RCRA— Resource Conservation and Recovery Act (PL 94-580) of 1976, Amendments to Solid Waste Disposal Act.

UNITS

gpd—gallons per day.
mgd—million gallons per day.
mg/l—milligram(s) per liter.
µg/l—microgram(s) per liter.

APPENDIX B

Toxic Organic Compounds Not Detected During Sampling

1. Acenaphthene.

2. Acrolein.
3. Acrylonitrite.
4. Benzidene.
5. Carbon Tetrachloride.
6. 1,2,4-Trichlorobenzene.
7. Hexachlorobenzene.
8. 1,2-Dichloroethane.
9. Hexachloroethane.
10. 1,1-Dichloroethane.
11. 1,1,2-Trichloroethane.
12. 1,1,2,2-Tetrachloroethane.
13. Chloroethane.
14. Bis(Chloromethyl) Ether.
15. Bis(2-Chloroethyl) Ether.
16. 2-Chloroethyl Vinyl Ether.
17. 2-Chloronaphthalene.
18. 2,4,6-Trichlorophenol.
19. Parachlorometa Cresol.
20. 2-Chlorophenol.
21. 1,2-Dichlorobenzene.
22. 1,3-Dichlorobenzene.
23. 1,4-Dichlorobenzene.
24. 3,3-Dichlorobenzidene.
25. 1,1-Dichloroethylene.
26. 2,4-Dichloro-phenol.
27. 1,2-Dichloropropane.
28. 1,3-Dichloropropylene.
29. 2,4-Dinitrotoluene.
30. 2,6-Dinitrotoluene.
31. 1,2-Diphenylhydrazine.
32. Fluoranthene.
33. 4-Chlorophenyl Phenyl Ether.
34. 4-Bromophenyl Phenyl Ether.
35. Bis(2-Chloroisopropyl) Ether.
36. Bis(2-Chloroethoxy) Methane.
37. Methyl Chloride.
38. Methyl Bromide.
39. Bromoform.
40. Dichlorodifluoromethane.
41. Chlorodibromomethane.
42. Hexachlorobutadiene.
43. Hexachlorocyclopentadien.
44. Isophorone.
45. Naphthalene.
46. Nitrobenzene.
47. 2-Nitrophenol.
48. 4-Nitrophenol.
49. 2,4-Dinitrophenol.
50. 4,6-Dinitro-O-Cresol.
51. N-Nitrosodimethylamine.
52. N-Nitrosodiphenylamine.
53. N-Nitrosodi-N-Propylamine.
54. Benzo(A)Anthracene.
55. Benzo(A)Pyrene.
56. 3,4-Benzofluoranthene.
57. Benzo(K)Fluoranthene.
58. Chrysene.
59. Acenaphthylene.
60. Anthracene.
61. Benzo(G,H,I)Perylene.
62. Phenathrene.
63. Dibenzo(A,H)Anthracene.
64. Indeno(1,2,3-C,D)Pyrene.
65. Pyrene.
66. Trichloroethylene.
67. Vinyl chloride.
68. Chlordane.
69. 4,4-DDT.
70. 4,4-DDE.
71. 4,4-DDD.
72. Endosulfan-Alpha.
73. Endosulfan-Beta.
74. Endosulfan Sulfate.
75. Endrin Aldehyde.
76. Heptachlor Epoxide.
77. γBHC(Lindane)-Gamma.
78. PCB-1242 (AROCHLOR 1242).
79. PCB-1254 (AROCHLOR 1254).
80. PCB-1221 (AROCHLOR 1221).
81. PCB-1232 (AROCHLOR 1232).
82. PCB-1248 (AROCHLOR 1248).
83. PCB-1260 (AROCHLOR 1260).
84. PCB-1016 (AROCHLOR 1016).
85. Toxaphene.
86. 2,3,7,8-Tetrachlorodibenzo-p-Dioxin.

APPENDIX C

Toxic Organic Compounds Detected at Least One Facility but Always 10 μg/l or Less

1. Chlorobenzene.
2. Dichlorobromoethane.
3. Fluorene.
4. Aldrin.
5. Dieldrin.
6. Endrin.
7. Heptachlor.
8. 1,1,1-Trichloroethane.
9. Chloroform.
10. Ethylbenzene.
11. Trichlorofluoromethane.
12. Diethyl Phthalate.
13. Tetrachloroethylene.
14. Toluene.
15. αBHC-Alpha.
16. βBHC-Beta.
17. ΔBHC-Delta.

APPENDIX D

Toxics Detected at Levels Too Small To Be Effectively Reduced by Technologies Known to the Administrator

1. Antimony.
2. Beryllium.
3. Silver.
4. Thallium.
5. Selenium.
6. Chromium.
7. Cyanide.
8. Benzene.
9. 1,2-Trans-Dichloroethylene.
10. Phenol.
11. Bis(2-Ethylhexyl) Phthalate.
12. Butyl Benzyl Phthalate.
13. Di-N-Butyl Phthalate.
14. Di-n-Octyl Phthalate.
15. Dimethyl Phthalate.
16. Methylene Chloride.
17. Pentachlorophenol.

APPENDIX E

Toxic Organic Compounds Detected From a Small Number of Sources and Uniquely Related to These Sources

2,4-dimentylphenol.

APPENDIX F

Pollutants Effectively Controlled by the Technology Upon Which Other Effluent Limitations and Guidelines Are Based

1. Asbestos.
2. Arsenic.
3. Nickel.

APPENDIX G

Pollutants Excluded by Subcategory and Subpart

Uranium Ore Subcategory—Mine Drainage

Cadmium (not detected).
Copper (present in amounts too small to treat).
Lead (present in amounts too small to treat).
Mercury (present in amounts too small to treat).

Tungsten Ore Subcategory—Mine Drainage

Lead (not detected).
Mercury (present in amounts too small to treat).

Tungsten Ore Subcategory—Mill Process Water

Mercury (not detected).

Mercury Ore Subcategory)—Mine Drainage.

Cadmium (not detected).
Copper (not detected).
Lead (not detected).
Zinc (not detected).

Titanium Ore Subcategory—Mine Drainage

Cadmium (not detected).
Copper (present in amounts too small to treat).
Lead (present in amounts too small to treat).
Mercury (not detected).
Zinc (present in amounts too small to treat).

Titanium Ore Subcategory—Mine Drainage

Cadmium (not detected).
Copper (present in amounts too small to treat).
Lead (present in amounts too small to treat).
Mercury (not detected).

Titanium Ore Subcategory—Mill with Dredges

Cadmium (present in amounts too small to treat).
Copper (present in amounts too small to treat).
Lead (present in amounts too small to treat).
Zinc (present in amounts too small to treat).

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CLEAN WATER ACT—REGULATORY UPDATE

by

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INTRODUCTION

Several years ago I presented a paper to this group describing the Clean Water Act requirements on mining operations, and we all know these requirements continue to increase. This year I have been asked to mention some of the notable regulatory developments under the act that have occurred during the past year. In the time available, it is not possible to discuss these matters in any detail so I will outline the developments and try to answer any question during the question and answer period.

By way of background, the Clean Water Act was originally passed in 1948 and has been amended numerous times since then. The most important amendments occurred in 1972, 1977 and 1978. The law as it is now written is designed to improve and maintain the quality of the nation's waters by eliminating the discharge of pollutants, by providing for the protection and propagation of fish, shellfish and wildlife and providing for recreation, and by prohibiting the discharge of toxic pollutants in toxic amounts. It directs the Environmental Protection Agency (EPA) to issue a wide range of standards and regulations for the control of discharges into U.S. waters from point sources (e.g., pipes, ditches, discrete conveyances) and non-point sources (e.g., runoff). An individual state may assume some of EPA's permitting authority if it submits an acceptable plan to the agency. The act also directs the Corps of Engineers to control the program that regulates the dredge and fill material in so-called "wetland" areas.

EFFLUENT GUIDELINES

The law prohibits the discharge of pollutants into waters of the U.S. without a permit. To obtain a permit, a person must agree to comply with effluent guidelines which are, generally speaking, EPA regulations that define the level of wastewater treatment a facility must provide before a discharge is allowed. These guidelines limit the amount of pollutants that can be discharged from a point source. These standards apply nationally and can be revised at any time.

National effluent guidelines have been set for more than 40 industrial categories, including ore mining and dressing, coal mining, smelting and refining, iron and steel, cement manufacturing, explosives manufacturing, and oil and gas extraction. They contain limitations for such things as total suspended solids, oil and grease, manganese, iron, copper, zinc, pH, COD and cadmium. I would now like to focus my remarks on the recently published proposed or final effluent guidelines for ore mining and dressing, smelting and refining, and coal mining. The regulations contain several levels of treatment that are specifically defined in the act: best practicable control (BPT),[1] best available control (BAT),[2] best control of certain conventional pollutants (BCT),[3] standards of performance for new sources (NSPS).[4] Those of you familiar with Clean Water Act permits no doubt are familiar with these.

Ore mining and dressing

Between 1975 and 1979 EPA issued effluent guidelines for ore mining and dressing facilities that required the application of the best practicable control technology currently available (BPT). They contained requirements for facilities processing: iron ore, base and precious metals (such as copper, lead, zinc, gold

and silver), aluminum, ferroalloy ores, uranium, radium, vanadium, mercury and titanium. These regulations were modified July 11, 1978 and Mar. 1, 1979.[5] Last year, on June 14, EPA proposed three sets of regulations for the ore mining and dressing industry: BAT standards, BCT standards and standards for new sources (NSPS).

There were several items of concern to the industry in the proposed regulations which were reviewed carefully by the American Mining Congress staff and members of its Water Quality Control Subcommittee. Probably the major concern was in regard to the new source performance standards for copper, lead, zinc, gold, silver, platinum and molybdenum processing. The proposed standards required zero discharge for the facilities.

The AMC comments pointed out that wastewater management technologies in the mining industry have a number of constraints, including climate, topography, geology, hydrology, land availability, waste management requirements. They went on to describe technical reasons why zero discharge was not an appropriate standard, and requested a variance provision be included in the regulations.

The final regulations were issued Dec. 3, 1982 and contained requirements for processing iron ore, aluminum ore, tungsten ore, nickel ore, vanadium ore mined alone, antimony ore, copper, lead, zinc, gold, silver and molybdenum ores, and platinum ore. The preamble to the regulations specifically recognized that a build-up of contaminants in the recycle water can significantly interfere with ore recovery and cannot be eliminated through appropriate treatment of the recycle water. The regulations now provide that the permitting authorities may allow a discharge of the process wastewater in the amount necessary to correct the interference problem after installation of appropriate treatment facilities.[6]

Smelting and refining

Another important set of effluent guidelines are those for smelting and refining. Between 1975 and 1980, EPA issued a series of BCT and BAT guidelines for the nonferrous metals manufacturing point source category, which is generally referred to as the "smelting and refining" category.[7] This category includes bauxite refining, primary aluminum smelting, secondary aluminum smelting, primary copper smelting, primary copper refining, secondary copper processing, primary lead smelting and refining, primary zinc processing, and metallurgical acid plants associated with certain processing operations.

On Feb. 17, 1983 EPA published proposed effluent guidelines as well as proposed new source performance standards, pretreatment standards for existing sources, pretreatment standards for new sources, and BCT effluent guidelines.[8] In addition to the subcategories listed above, the proposal adds the following subcategories: primary tungsten processing, primary columbium-tantalum processing, secondary silver processing, and secondary lead processing.

The February 1983 proposal addresses the 12 subcategories listed above and is the "Phase I" portion of the smelting and refining guidelines. Later this year, EPA intends to publish Phase II proposed regulations containing an additional 21 primary metals, 15 secondary metals and bauxite refining.

The proposal contains provisions of significant concern to smelting and refining facilities, especially primary copper, lead and zinc facilities. One major concern is that the data base used by EPA in developing the proposed regulations ignores wastewater chemistry and effluent reduction achievements occurring at existing facilities. Also, EPA reviewed and relied to some extent on data from other industries in developing the smelting and refining guidelines. AMC objected to this data in comments submitted to EPA and in fact provided the agency with further, extensive wastewater data developed by the Water Quality Subcommittee.

The proposed regulations require, among other things, reductions in concentration of pollutants and flow rate of effluent streams. However, many existing facilities simply cannot be operated in such a way as to reduce the concentration and flow to the limits proposed. Further, the EPA proposal would require lime and settle treatment as well as the additional requirement of filtering. This ignores the fact that several facilities have implemented tertiary treatment (such as filtering or polishing) without being able to meet the proposed limits. Another matter of concern is that the proposal would require segregation of stormwater to prevent it from flowing into treatment facilities. However, any existing plants treat combined process water and stormwater, and the operators question the effectiveness, as well as the cost, of installing separate stormwater systems.

AMC staff and members of the Water Quality Control Subcommittee have met with EPA to discuss these and other concerns, although there is no indication at this time whether the proposal will be modified. It is expected that final regulations will be issued sometime in early 1984.

Coal mining

On Apr. 26, 1977, EPA issued BPT effluent guidelines for the coal mining category[9] and published new source performance standards for this category July 12, 1979.[10] Revisions of the BPT and standards for new sources were proposed Jan. 13, 1981 along with BCT effluent guidelines.[11] On Oct. 13, 1982 EPA issued revised BPT effluent guidelines and new source performance standards for the coal mining point source category along with BCT effluent guidelines.

These regulations were challenged by several parties in the U.S. Court of Appeals for the Fourth Circuit. Briefing was stayed in the case so that negotiations could take place. After months of negotiations, the parties reached agreement and filed a settlement agreement with the court Aug. 1, 1983. It requires EPA to propose and issue amendments to the regulations and also publish specified preamble language. Time does not permit me to provide details of this agreement although I will mention that some of the matters dealt with include the definitions of new source coal mines, coal refuse disposal piles, controlled surface mine discharge, and abandoned mines. The proposed regulations are expected soon. If the final regulation and accompanying preamble are consistent with the agreement, the challenges will be dismissed.

DREDGE AND FILL REGULATIONS

The Clean Water Act provides for the issuance of permits for the discharge of dredge and fill material into navigable waters at specified disposal sites. These permits are issued by the U.S. Army Corps of Engineers. EPA, however, is authorized to issue guidelines for the designation of disposal sites.

The act authorizes the corps to issue permits "for the discharge of dredged or fill material into the navigable waters," and the corps has defined the terms "dredge material," "discharge of dredge material," "fill material" and "navigable waters" quite broadly.[12] Depending on the location, various activities undertaken in connection with a mining operation may require a corps permit, including constructing a road or bridge to move equipment, constructing an office, mill or mining site, constructing a tailings pond or water storage area, diverting streams, or construction of tunnels or pipelines.

On Sept. 19, 1980, the corps proposed dredge and fill regulations[13] and on July 22, 1982 it issued regulations for its dredge and fill program.[14] The new regulations establish 25 types of general or "nationwide" permits for which no permit application is required for a qualifying operation. Nationwide permits are available for a number of activities related to mining, including certain work associated with surface coal mining, surveying activities (e.g., core sampling, seismic exploratory operations, plugging seismic shot and other exploratory-type bore holes), minor road crossing fills, certain structures associated with discharges permitted under the Clean Water Act, certain utility line construction, and structures on work associated with surface coal mining activities authorized under the Surface Mining Control and Reclamation Act.[15]

While the industry expressed some concern over individual provisions, the overall approach taken in the new regulations was strongly supported by the mining industry.

On December 22, 1982, sixteen environmental and conservation groups challenged the Corps of Engineers regulations and requested the court to declare a number of provisions invalid and to enjoin the corps from implementing or enforcing certain of the provisions.[16] Three of the nationwide permit regulations challenged are of interest to the mining industry: i.e., 1) for activities conducted above headwaters of streams and rivers, 2) for activities near isolated waters (not part of a surface tributary system) and 3) for surface coal mine activities authorized by the federal Office or Surface Mining.[17] AMC and several other industry groups petitioned to intervene in the case, and the plaintiffs have opposed intervention of some industry groups, including AMC. The court has scheduled a status conference for Sept. 16, 1983 to decide on a briefing schedule, consider motions for intervention and other matters. Preliminary settlement discussions have taken place among the parties but, as yet, no issues have been resolved.

Also, on May 12, 1983, the corps proposed another series of regulations regarding dredge and fill activities. The proposal deals with many aspects of the regulations including the reimposition of the 10-acre lake limitation for headwaters and isolated water permits, and the addition of two new categories of nationwide permits.[18] The public comment period closed Aug. 31, 1983, and it is not certain when the final regulations will be issued.[19]

NPDES DISCHARGE PERMIT REGULATIONS

In 1980 EPA issued a comprehensive set of regulations setting forth the administrative procedures and requirements for obtaining a discharge permit.[20] These regulations were very controversial and the subject of protracted litigation by many companies and trade associations. In June 1982, a settlement agreement was reached whereby EPA agreed to propose and then issue a number of modifications to the regulations. On Nov. 18, 1982 EPA proposed extensive changes to the permit regulations.[21] The proposal includes many significant matters including stormwater runoff, net vs. gross limitations, pre-permit construction, and evidentiary hearing procedures. Final agency action on the regulations is expected soon.

PROPOSED REVISIONS TO WATER QUALITY STANDARDS

The Clean Water Act provides for the establishment of water quality standards.[22] These standards define the water quality goals of a water body (or portion) by designating the use or uses to be made of the water, and by setting the criteria necessary to protect the uses. The standards are adopted by the states to fit individual bodies of water and are the foundation of a state's water quality management process. These EPA standards are important because state standards are based on them.

On Oct. 29, 1982, EPA proposed revisions to its water quality standard regulations. The proposal allowed consideration of site-specific factors affecting a water body and it allowed consideration of seasonal uses of a stream. While there were some problems with the proposal, AMC submitted comments that were generally favorable.

Since the proposal, however, legislation was introduced in the Senate and House designed to preempt any significant change by EPA of the existing water quality standard regulations. The legislation in the Senate would codify the "antidegradation" provision in the existing regulations limiting how a water body may be classified. It would also eliminate certain discretionary authority now residing with EPA. Consequently, there have been discussions between EPA and congressional staff on the matter to see if a compromise can be worked out. It appears if EPA will modify its proposed regulations, the Senate committee may be willing to withdraw its legislative proposals. Many people feel EPA will modify its regulations to avoid legislation on this matter. If the regulations are so changed, the agency may find it necessary to repropose the regulations rather than simply issuing final regulations. A Senate markup on the Clean Water Act legislation is scheduled for Sept. 15 when this item may be discussed.

EPA GROUNDWATER POLICY

Several federal laws contain provisions designed to reduce contamination of groundwater, e.g., Resource Conservation and Recovery Act, Safe Drinking Water Act, Superfund, Uranium Mill Tailings Radiation Control Act. During the last three or four years, EPA has attempted to develop an overall groundwater policy to coordinate and set priorities for groundwater protection efforts. For a variety of reasons, this policy has never been finalized.

Recently EPA administrator Ruchelshaus announced the establishment of a task force to look into the matter. It will have three responsibilities: 1) to assess the differences in major policies, regulations and operational practices of groundwater programs such as RCRA, UIC and Superfund; 2) to study how the agency should coordinate groundwater policy development and program implementation throughout the country and 3) to review EPA policies and actions in light of their effect on state programs to protect groundwater. A report is to be submitted this fall and the administrator will then select an appropriate operational plan for the agency.

Protection of groundwater is a matter of extremely high priority at EPA, so

the report of the task force will be an important indication how the agency staff views the problems and solution. Once the report is submitted, the admininstrator will decide on further action to be taken in the development of an overall agency policy. It will be important for members of the mining industry to follow closely the report of the task force and any subsequent action taken by the agency.

References

[1]CWA §304(b)(1), 33 U.S.C. 1314(b)(1).

[2]CWA §304(b)(2), 33 U.S.C. 1314(b)(2).

[3]CWA §304(b)(4), 33 U.S.C. 1314(b)(4).

[4]CWA §306(a)(1), 33 U.S.C. 1316(a)(1).

[5]See 40 Fed. Reg. 51722, 43 Fed. Reg. 29711, and 44 Fed. Reg. 11546, respectively. These regulations appear in 40 C.F.R. Part 440. See also the withdrawal of proposed BAT and NSPS regulations. 46 Fed. Reg. 17567 (Mar. 19, 1981).

[6]40 C.F.R. 440.104(b)(2).

[7]See 40 C.F.R. Part 421.

[8]48 Fed. Reg. 7032-7126.

[9]42 Fed. Reg. 21380.

[10]44 Fed. Reg. 2586. Revisions were made Dec. 28, 1979 (44 Fed. Reg. 76788) and June 29, 1980 (45 Fed. Reg. 43413).

[11]46 Fed. Reg. 3136. On May 29, 1981 the proposal was amended. 46 Fed. Reg. 28873.

[12]33 C.F.R. 323.2(b), (i), (j), (k).

[13]45 Fed. Reg. 62732-62777.

[14]47 Fed. Reg. 31794-31834. These regulations were issued in "interim final" form. The modify regulations in 33 C.F.R. Parts 220-230.

[15]33 C.F.R. 330.5.

[16]National Wildlife Federation, et al. v. Marsh, No. 82-3632, D.D.C., 1982.

[17]33 C.F.R. 330.4(a)(1), (a)(2) and (a)(21).

[18]48 Fed. Reg. 21466.

[19]AMC filed comments supportive of the proposed changes and particularly of the nationwide permit regulations that are the subject of the litigation mentioned above.

[20]40 C.F.R. Parts 122-125.

[21]47 Fed. Reg. 52072.

[22]Clean Water Act, §303, 33 U.S.C. 1313.

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REVIEW OF ENVIRONMENTAL LEGISLATION IN THE 98TH CONGRESS

by

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The advent of the Reagan administration and the confirmation of Anne Gorsuch (now Burford) as EPA administrator in 1981 gave the industrial community great hope for sweeping rewrites of the environmental laws due for reauthorization. After nearly two years of lengthy hearings and emotional debate, the 97th Congress adjourned at the end of 1982 without having passed any comprehensive environmental amendments into law. Widespread publicity surrounding allegations of mismanagement at the Environmental Protection Agency in the beginning of 1983 led to a reorganization of key EPA personnel and increased public fears of pollutants in the environment. Now the 98th Congress is reluctant to pass any amendments that could be perceived as being "pro-industry" and appears to be heading toward passage of further restrictive and complicated controls.

Following is a review of five of the major areas of environmental legislation -- Clean Air, Clean Water, Safe Drinking Water, RCRA and CERCLA (Superfund) -- and their status in the 98th Congress.

CLEAN AIR

To properly review the current status of Clean Air Act amendments, it may be helpful to briefly highlight some of the activities of the 97th Congress in 1981 and 1982.

The Clean Air Act, along with the Clean Water Act and RCRA, was due for reauthorization in 1981, and both the Senate and House seemed eager to, and did, schedule hearings early in the session in an attempt to get the legislative process in motion. Following confirmation of the Reagan administration's EPA appointments, industry representatives approached Congress armed with lists of Clean Air Act amendments. Little did we realize that the reauthorization of the nation's major air pollution control law would turn into a bitter confrontation, with business and industry groups in constant conflict with environmental and public health groups.

The Senate Environment and Public Works Committee approved a bill in August 1982 that made modest changes in the existing Clean Air Act and added new provisions aimed at controlling acid rain and hazardous air pollutants. The Senate bill was met with mixed emotions by both the environmentalists and industry. Sections of the bill pertaining to acid rain, prevention of significant deterioration (PSD), hazardous air pollutants, visibility, etc. were unacceptable to industry. The environmentalists felt that the bill did not go far enough and were particularly opposed to an amendment in the Senate bill giving nonferrous smelters relief under Sec. 119. Although the Senate committee was able to report its bill to the Senate floor, very little time remained for the full Senate to consider the measure, and it died a natural death at the end of the 97th Congress.

On the House side, Henry Waxman's (D-CA) Subcommittee on Health and Environment kept a bill stalled for over 15 months before reporting its version to the full Energy and Commerce Committee. At the committee level, chairman John Dingell (D-MI) was expected to shepherd Waxman's version through a series of corrective amendments supported by industry, most of which were contained in a bill authored by Tom Luken, Democrat from Ohio. To chairman Dingell's surprise -- in fact, to the surprise of many of the environmentalists as well -- he was defeated on several key amendments, often by a mere one or two vote margin. The committee did manage to pass a nonferrous smelter amendment similar to the one contained in the Senate bill. However, on the very day the Senate committee ordered its bill reported, the Energy and Commerce Committee deadlocked on a hazardous air pollutants amendment. The House committee never resumed mark-up after that day and never reported a Clean Air bill during the 97th Congress.

This brings us to 1983 and a new Congress, the 98th, and some new committee members to deal with. In the 1982 election, liberal Democrats picked up a number of seats on the Energy and Commerce Committee, and the mining industry lost a valued supporter with the defeat of Jim Santini in his race for the Senate.

Although the 1982 election left the Republican numerical majority in the Senate intact, the Senate Environment and Public Works Committee picked up two more pro-environmentalist members. Since key votes on air act amendments were won or lost by only a one or two vote margin last year, even a slight shift or increase in the "swing" voters on either committee is significant. The Reagan administration, which disappointed industry during the last Congress by failing to come forth with a legislative package, is treading cautiously again this year, and it has given no clear signal that it will present specific legislative recommendations to Congress this time around, with the possible exception of acid rain.

Only one comprehensive Clean Air Act amendment bill has been introduced in Congress this year -- S. 768 -- introduced by Sen. Robert Stafford (R-VT), chairman of the Environment and Public Works Committee. S. 768 is essentially the same as the bill that the committee reported in 1982 and contains the same provisions for controlling acid rain, hazardous air pollutants, PSD and visibility. No hearings have been held on this year's bill. It appears that the Senate committee is waiting for some sign of activity from the House before embarking on the lengthy hearing and mark-up process. There have been reports that Congressmen Dingell and Waxman are collaborating on drafting Clean Air Act amendments for unveiling later this month. It is speculated that Dingell and Waxman intend to negotiate out of the spotlight of public hearings and mark-ups this year. A Dingell-Waxman compromise bill is probably the only vehicle that would stand a chance of moving through the factioned Energy and Commerce Committee.

Although there has been only one comprehensive Clean Air bill introduced this year, there have been numerous legislative initiatives specifically aimed at controlling acid rain. Following is a summary of proposed acid rain control strategies pending in Congress:

S. 768 and S. 769 by Stafford (R-VT)

S. 768 is the Environment and Public Works Committee bill mentioned above. One of its worst features is an acid rain provision that would require a reduction of eight million tons per year of sulfur dioxide emissions to be achieved over a 12-year period.

The purpose of S. 769, also by Sen. Stafford, is to raise the ante to 12 million tons per year over 15 years and to place caps on SO_2 and NO_x emissions by the year 2000. Both bills apply to a 31-state region east of the Mississippi.

S. 766 by Randolph (D-WV)

This bill calls for the submission of a report to Congress by August 1987, with recommendations on how to deal with acid rain. During the reporting period, the bill would place a cap on SO_2 emissions from all stationary sources at actual 1982 levels, assuming the bill passes in 1983. The Randolph bill applies to a 48-state region.

S. 145 by Mitchell (D-ME), H.E. 132 by Gregg (R-NH) and H.R. 2794 by St. Germain (D-RI)

These are identical bills, requiring a 10 million ton reduction in annual SO_2 emissions within 10 years of enactment. All three bills apply to a 31-state region.

S. 454 by Byrd (D-WV) and H.R. 1405 by Rahall (D-WV)

These identical bills require submission of a report to Congress by 1987, similar to the Randolph bill. Unlike the Randolph bill, however, the Byrd and Rahall bills do not place caps on SO_2 emissions. These bills also provide for mitigating grants to states or interstate agencies for neutralizing lakes, streams, etc.

H.R. 3251 by D'Amours (D-NH)

This bill calls for an 85 percent reduction in SO_2 emissions from the 50 largest power plants in the United States.

H.R. 3400 by Waxman (D-CA), Sikorski (D-MN) and Gregg (R-NH)

H.R. 3400 requires 48 states to collectively reduce SO_2 emissions by 10 million tons below 1980 levels by the year 1995. In addition, H.R. 3400 requires

the installation of scrubbers by the year 1990 on the 50 largest SO_2 emitting power plants in the U.S. that burn medium or high sulfur coal. The sponsors of the bill believe that the scrubber requirement would reduce SO_2 emissions by an additional seven million tons. Scrubbers are now only required on new plants. A scrubber requirement for existing plants would mean that utilities would have no incentive to switch to low-sulfur coal, according to the sponsors.

H.R. 3400 would establish a user fee on electricity generated from power plants in 48 states. The money would be channeled into a trust fund to reimburse utilities for 90 percent of the cost of installing scrubbers.

There have been reports that Sen. Durenberger (R-MN), a member of the Environment and Public Works Committee, is ready to introduce acid rain legislation calling for a 10 million ton SO_2 emissions reduction over 48 states. The costs of reduction would be funding by an emissions tax on SO_2 and NO_x nationwide.

There seems to be general agreement over only one aspect of the Clean Air debate: that there will be some kind of acid rain legislation passed by the 98th Congress before the Presidential elections, and quite possibly, before the end of 1983. The acid rain issue has become highly visible and political, and most legislators would rather have it out of the way before the campaigns heat up. Both House subcommittee chairman Waxman and Senate committee chairman Stafford are committed to passing an acid rain control program and will focus their attention on this issue as a prelude to a comprehensive look at Clean Air Act amendments. If acceptable compromises can be found for the controversial, and often uncertain, areas of the acid rain issue, the two committees may then consider the other Clean Air Act issues that divide their members in the 97th Congress, issues such as PSD, hazardous air pollutants, visibility and auto emissions.

CLEAN WATER

Prior to recessing in August, the Senate Committee on Environment and Public Works reported a bill to amend the Clean Water Act, the nation's principal law for controlling water pollution.

The bill, S. 431, was introduced by Sen. Chafee (R-RI) and is expected to be considered on the floor of the Senate this fall. As approved by the committee, S. 431 forces greater clean-up of water pollutants and rejects most of the Reagan administration's proposal to ease requirements on industrial and municipal dischargers.

On the House side, a Clean Water bill sponsored by James Howard (D-NJ), H.R. 3282, has been introduced but has not yet been considered by the Public Works Committee. However, the Public Works Committee chairman, Robert Roe (D-NJ), did not sign on as a co-sponsor to the Howard bill and is expected to hold hearings and mark-ups on his own set of Clean Water Act amendments this fall.

There are five major areas of the Clean Water debate:

BAT (best available technology)

A great deal of the Clean Water debate in 1982 centered around proposals to allow chemical and other industries to bypass tough technology requirements if they could demonstrate that less costly treatment (best practical technology) would not harm water quality. This year, the waiver of BAT requirements has been soundly rejected in both House and Senate bills. The environmental groups would like to require industrial dischargers to go even beyond BAT if the best technology fails to clean up polluted waters.

Pretreatment

In 1982, both municipal sewage treatment authorities and industries were on their way toward getting amendments passed that would allow the substitution of local pollution control programs for national pretreatment requirements governing industries pumping wastes into public disposal systems. Proponents of this measure advocated placing more authority at the local level, so that publicly-owned treatment works could tailor their programs to their particular problems and avoid unnecessary or duplicate treatment of wastes first by industry, then by municipality. This year, Sen. Chafee's bill (S. 431) does not allow for any waivers for publicly-owned treatment works (POTWs), and Congressman Howard's bill (H.R. 3282) allows waivers only in very limited situations and only after strict tests are passed.

Some industries are still pushing for a pretreatment provision in the Senate bill, and the issue may come up as a floor amendment.

Non-point pollution

Control of non-point pollution -- that which runs off farm lands or city streets, for example -- was not much of an issue last year. This year, however, the Senate committee bill contains a comprehensive, $150 million annual program to control agricultural and urban water pollution. The House bill does not contain a provision for non-point controls, but the sponsor of that bill, Congressman Howard (D-NJ), has stated that he is working on a proposal that will reduce non-point pollution "as effectively as the Clean Water Act has dealt with point sources."

Sec. 404 dredge and fill permit program

The Sec. 404 dredge and fill permit program of the Clean Water Act is one of the few existing laws that provides for the protection of wetlands. Environmental groups have been trying hard to have this section of the law strengthened. Certain industry groups have been trying to have the definition of "wetlands" narrowed to apply to only truly navigable waters. Under the present law, anyone wanting to fill in a swamp for development, drill an oil well, expand a port or dump any material in a waterway must go through a lengthy and complicated process of obtaining a permit from the Army Corps of Engineers.

Senators Chafee (R-RI) and Bentsen (D-TX) have drafted amendments to the Senate Clean Water bill which they are expected to offer on the floor. These amendments would make it possible for the states to administer part of the dredge and fill permit program, strengthen the involvement of the Fish and Wildlife Service and the Commerce Department in permit issuing decisions, and bring Sec. 404 within the scope of the "citizens suits" provision of the Clean Water Act.

Water quality standards

There is a continuing dispute between the Senate Environment and Public Works Committee and the EPA over water quality standards. In October 1982, the EPA issued proposed regulations to revise the current water quality standards. These proposed new standards were greeted favorably by industry, but they were not acceptable to several members of Congress and the environmental community who viewed the regulations as "weakening" the Clean Water Act. The EPA is currently working on a revised set of standards, but it has not issued another notice of proposed rulemaking to date. As a result, both S. 431 and H.R. 3282 contain provisions to codify the existing stringent water quality standards. This amendment could be deleted from both bills if the EPA proposes new water regulations that are acceptable to both the Senate and House committees.

The Senate bill, S. 431, contains an additional provision that would allow for stormwater run -off at mining operations to be considered as "non-point source" and therefore not subject to point-source regulations, if such stormwater run-off does not contain mining contaminants. Efforts are being made to have this provision introduced as an amendment to the House Clean Water bill.

SAFE DRINKING WATER

A bill to amend the Safe Drinking Water Act was introduced by Dennis Eckart, Democrat from Ohio, and co-sponsored by Congressman Waxman (D-CA). This bill, H.R. 3200, would force the EPA to regulate more drinking water contaminants, accelerate enforcement efforts and take initial action to protect groundwater supplies.

Specifically, H.R. 3200 would:

- Require EPA to set standards within 18 months for 14 organic chemicals found in drinking water but currently unregulated;
- Require establishment of a monitoring program for up to 129 additional water pollutants which EPA is required to regulate under the Clean Water Act;
- Require lining and groundwater monitoring of surface impoundments and landfills;
- Severely restrict, and may totally prohibit, deep-well injection of hazardous wastes beneath formations containing drinking water aquifers;
- Expand the definition of "drinking water source" to include water which may be anticipated to be capable of supplying any public water system, if such system were to use advanced technology treatment that may become available;

- Provide money for technical assistance programs to help public water system operators to attain standards. Under the present regulations, systems which cannot afford to comply now are allowed variances from the standards and told to comply as soon as possible. This bill would set strict requirements for compliance.

- Provide grants to states to identify groundwater sources and begin planning for their protection and use.

H.R. 3200 is heavily supported by environmental and conservation groups, but most major industries are concerned that, among other restrictions, this bill could ban all underground injection of wastes -- now an important alternative to landfilling. Public water suppliers disagree with the bill's presumption that all organic chemicals found in drinking water are hazardous and must be regulated. No doubt there will be considerable debate on this issue before a final bill can be passed.

The Health and Environment Subcommittee held hearings on H.R. 3200 this past summer and is expected to begin mark-up later this month. The bill should reach the full Energy and Commerce Committee before the session ends. As yet, corresponding legislation has not been introduced in the Senate.

RCRA

RCRA is the principal law governing the management and disposal of hazardous waste. Like the Clean Air and Water Acts, RCRA was due for reauthorization in 1981. And, like the air and water issues, RCRA amendments became entangled in debate in the 97th Congress and had to be carried over into the 98th.

In 1982, the House passed a comprehensive RCRA reauthorization bill sponsored by Congressman Jim Florio (D-NJ) and intended, in his own words, to "close the loopholes" in the hazardous waste management system. However, a companion measure in the Senate died when the Environment and Public Works Committe could not reach a consensus on tightening regulations for generators of small quantities of hazardous waste.

This year, debate over RCRA amendments seems to be focusing not on whether requirements in existing hazardous waste management law should be narrowed but on how quickly that should be done. Both the Senate Committee on Environment and Public Works and the House Energy and Commerce Committee have already reported RCRA bills this year.

On May 12, Energy and Commerce unanimously approved Congressman Florio's (D-NJ) H.R. 2867, a bill to reauthorize RCRA and give the EPA control over an additional 40 million metric tons of hazardous waste per year. The bill was debated on the floor of the House for one day before the August recess and has not yet passed.

On July 28, the Senate Environment and Public Works Committee, by a vote of 14-1, approved S. 757, a RCRA reauthorization bill introduced by Sen. Chafee (R-RI), who was also the author of last year's RCRA effort.

This year the Senate bill is closer in content to the House version. Both bills contain provisions which would:

- Require EPA to issue regulations for small quantity generators of 100 kg of hazardous waste or more per month;

- Prohibit the disposal of liquid hazardous waste;

- Prohibit the land disposal of certain hazardous waste;

- Prohibit the underground injection of hazardous waste close to drinking water sources;

- Regulate the burning and blending of hazardous waste as fuel;

- Require land disposal operators to install double liners, leakage capture systems and underground monitoring systems as a condition to obtaining a permit or renewal of a permit.

The double liner requirement is a major concern for the mining industry. When the House continues its floor debate on RCRA, Congressman Billy Tauzin (D-LA) is expected to introduce an amendment which will remove mining wastes from the application of the double liner requirement by referring to the Bevill amendment. The Bevill amendment was added to RCRA in 1980 and defers regulation of mining and smelting wastes pending completion of a study by EPA. The Tauzin amendment will also

direct EPA to develop appropriate standards for each facility, together with groundwater monitoring. The sponsor fo the House RCRA bill, Congressman Florio, has indicated that he will support the Tauzin amendment on the floor. The Senate bill contains a committee-approved amendment by Sen. Simpson (R-WY) that retains the double liner requirement but allows EPA to exempt landfill operators, on a case-by-case basis, from installing double liners if it can be proven that an alternate method offers equal protection for ground and surface water. Another provision in the Senate bill instructs EPA to determine if double liners are appropriate for mine wastes and, if not, to develop alternative methods that are adequate to protect human health and the environment.

The small generator exemption is another major concern in both the Senate and House bills. Under current law, businesses which produce less than 1000 kg per month of hazardous waste are considered "small generators" and are not subject to RCRA regulations. The House bill, as reported out of committee, calls for regulating sources that produce as little as 100 kg of hazardous waste per month. It further requries that generators of 25 kg of hazardous waste or more must notify their transporters that the waste is hazardous.

When H.R. 2867 was debated on the floor of the House, several amendments were adopted in deference to requests by EPA to ease the enormous regulatory burden the bill would place upon that agency; however, the 100-kg regulation and the 25-kg notification requirements were kept in the House bill.

The Senate bill, S. 757, as reported by the committee, also requires the regulation of generators which produce 100 kg or more per month, but contains a 100-kg threshold (instead of the 25 in the House bill) for notification of hazardous waste shipments.

Another RCRA bill has been introduced, S. 1363, by Sen. Gary Hart (D-CO). In many areas, this bill is even more stringent than either S. 757 or H.R. 2867; it requires the use of best available technology for hazardous waste management and a waste-end tax on disposers of hazardous waste. Sen. Hart has offered some sections of his bill as amendments to S. 757 in committee, and some of them were adopted. He is expected to continue to offer amendments when the bill is debated on the Senate floor.

COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY ACT (CERCLA)

Congressman Florio has been quoted as saying that, without a tough RCRA, the way would be cleared for the creation of more abandoned hazardous waste sites. This, in turn, would mean a greater need for the Comprehensive Environmental Response, Compensation and Liability Act of 1980, better known as Superfund. Superfund is now a five-year, $1.6 billion program set to expire in 1985. It would appear that it is too soon for legislators to consider extending Superfund when other environmental laws are overdue for reauthorization, but recent public fears and prolific reports about toxic wastes in the environment have precipitated a major congressional review of EPA's Superfund program. Allegations that EPA officials mishandled the toxic waste clean-up program led to a major housecleaning at EPA this year and could lead to further tightening of federal laws governing hazardous and toxic materials.

Proposals have already been introduced to extend funding of Superfund and to expand the law to provide compensation to persons injured or diseased by exposure to toxic substances in the workplace. Among the bills under consideration is H.R. 3129, introduced by Claudine Schneider (R-RI) and Ron Wyden (D-OR), which would replace the existing Superfund fee on petrochemical feedstocks with a fee on land disposal of hazardous wastes. Similar bills have been introduced in the Senate by William Proxmire (D-WI) - S. 1779, and by Gary Hart (D-CO) - S. 860. Sen. Hart's RCRA bill, S. 1363, also contains a provision to levy a waste-end tax on the disposer, the proceeds of which would be used for Superfund clean-up. Environmental groups are strongly in favor of this approach, since it would place the costs of clean-up upon those disposing of the waste.

Other CERCLA bills, S. 816 by Senator Bradley (D-NJ) and H.R. 1615 by Representative LaFalce (D-NY) would extend Superfund to 1990 and greatly increase the present funding level of $1.6 billion.

Victim's compensation is another area of the Superfund debate. When the Superfund law was originally proposed in 1980, it contained a provision to allow those persons injured or diseased because of hazardous or toxic waste to be compensated from Superfund for their medical costs. This provision was dropped from the final law. At that time, legislators were fearful that countless claims would be lodged against the fund, at a considerable cost to the petrochemical industry, which

now contributes some 85 percent of the Superfund. Other industries and the federal government contribute the remaining 15 percent.

The original Superfund act set up a panel composed of legal experts to study victim's compensation and make a report to Congress. The panel's report, which was released in September 1982, found that there are not enough effective legal remedies in our judicial system to compensate victims for injuries which may not become manifest until years after the victim was exposed to a toxic substance. The report recommended the establishment of a federally-managed, industry-financed fund to provide no-fault compensation for medical expenses and death benefits. Using the panel's findings, several members of Congress have now re-opened the victim's compensation issue.

Legislation to establish a federal victim's compensation trust fund has been introduced by Sen. Mitchell (D-ME), S. 945 and S. 946; Congressman LaFalce (F-NY), H.R. 2330 and H.R. 2482; and Sen. Stafford (R-VT), S. 917. The bills have many similar provisions, with the Mitchell and LaFalce bills setting three-year statutes of limitations on claims, and the Stafford bill setting a six-year statute of limitations. In addition, the Stafford bill, S. 917, deletes the Bevill amendment mining waste exclusions from Superfund.

Another bill, H.R. 2582, has been introduced by Congressmen Florio (D-NJ) and Markey (D-MA). While this proposal drops the establishment of a federal no-fault compensation trust fund, it contains provisions to make it easier for victims to win damages from the companies they sue in federal court. Congressman Markey may offer this bill as an amendment to the RCRA bill currently under consideration on the floor of the House.

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SUPERFUND: PRESENT AND FUTURE FOR THE MINING INDUSTRY

by

Donald L. Ritter
U.S. Representative from Pennsylvania

Being a technical professional surrounded by attorneys in Washington, D.C. is sometimes a lonely vigil. There are three technical professionals and about 250 attorneys out of 435 congressmen in the system. Each has a different way of going about dealing with problems.

An engineer, a technical person, really looks to solve problems. An attorney looks to advocate one side or another of those problems, not necessarily solving it. An engineer tries to get all the information he can and takes a look at it to see if there is a possibility of getting the right answer or something that approaches the right answer. A good attorney gets all of the information that he can and then throws out that which doesn't agree with his position of advocacy.

It's a very different skill, and frankly, the U.S. Congress is woefully short of people who have technical backgrounds and it shows.

Many of you at this session are probably aware of how, on occasion, or perhaps frequently, badly it shows.

I think, by the way, having this convention here in San Francisco is symbolic. I mean, right in this area is the center of high tech; Silicon Valley is a stone's throw. And yet basic American heavy industry has got its convention here.

I am one of those people who firmly believes that in spite of the clamor and all the noise about high tech being the saviour of this country in terms of our economics, our basic industries had better well be part of the future of this country. Otherwise, we are going to be dealing with the impoverishment of America.

I serve as vice chairman of an 80-member Republican task force on high tech and high tech initiatives. It is interesting that my counterpart, the chairman, is a very bright young man out of Silicon Valley named Edwin Zschau, a freshman. He comes from Computerland, and I come from basic manufacturing America-land. I have a deeply labor dominated industrial district--first Republican in 50 years, and probably the only Republican in the House from such a district who thinks, talks and acts and votes the way I do.

Our view of high tech--and I have tried to bring this idea into the task force--is that our basic industries will use high tech, that a fantastic market for the high tech products are our basic industries, and that there are just so many home computers that are going to be out there.

The big systems and the high productivity systems--the sensors, the communications systems, the robots--all will be applied in the realm of basic manufacturing America and that will be the high tech revolution.

Obviously, these basic industries cannot be ignored as some of the philosophers from the social sciences, who never spent a day in their lives working in a basic industry, are pointing out. Neither can they be regulated out of existence. It would be a great tragedy if, through ignorance and fear and the lack of proper communication of difficult subject matter to the American people, we lost a goodly chunk of basic manufacturing America. It's not impossible.

The Superfund legislation is going to be reauthorized by 1985. How that reauthorization comes about will depend, to a great extent, on a far higher level of knowledge on the part of the American public on this subject of hazardous waste. It will depend to a great extent on a far greater effort on the part of people like yourselves to promote understanding and communication in this difficult field.

One great message that came out of the luncheon speech was if things are not going right according to what you think and you believe, your first amendment rights are there and you've got to speak up. If you don't speak up, the doomsayers and those who prosper on fear and ignorance will be victorious.

In the present situation, there is a good deal of confusion over just what constitutes a hazardous substance. There are a couple of conflicting definitions. One is a broad definition that says, for example, that a mining waste could be classified as a hazardous substance. That same definition says it is possible that a mining waste, even though it may contain elements or compounds that are classified hazardous, may not be finally adjudged to be a hazardous substance. Bill Hedeman from this panel has been personally active in opting for the broad decision.

It is, I think, positive for this industry and people who work for it that the EPA has taken a selective approach. A more restrictive view would be that, after all, these mining wastes do contain hazardous substances and therefore they should be classified as hazardous. Therefore, the accompanying rules and regulations of the law should be imposed.

Obviously you are familiar with some of the great differences between mining wastes and wastes generated, say, from the chemical industry. But the writers and the generators of the original law were not necessarily taking mining wastes into account, and that is why some of the confusion has resulted.

For instance, the volumes are quite different. An EPA generated Mitre study ranks potential hazard and talks about 10,000 drums as being an upper limit. As you know, 10,000 drums of waste material could be generated in an hour at some mining operations.

The study talks about 0.1 percent of heavy metal being the upper limit for heavy metal concentration, yet 0.1 percent is commonly included as a threshold limit and 0.1 percent is commonly available in mining wastes.

The question is, What does it mean? Is it, in that particular situation, dangerous? Is it really hazardous or is it to some extent insoluble? Is it stable? Does it work its way into the soil without getting into groundwaters?

These kinds of questions will be asked of you. If they are not asked, you should be presenting them and the answers to your representatives. Now is the time for people in this industry to take an active role with subcommittee members, committee members, and members of Congress in general so that there is no rush to judgment, so that there is no finale of crescendo one month final law writing, and all of a sudden everybody's trying to get their ideas across.

There is some time out there, and that time gives you an opportunity.

The question of certain new bills which impose a waste end tax is going to come up, and I am certain that there is going to be a good deal of congressional support for taxing the wastes generated as opposed to a particular feed stock.

Well, the kinds of wastes and the character of the wastes that are involved in mining have to be explained to the people involved in the legislative process. The impact on imports and the import sensitivity of the mining industry have to be explained to my colleagues.

I think that will give you opportunity to have some input.

There is good reason to believe that in and around the time of reauthorization of Superfund, the horror stories will start coming out and that the media will tend to look at the question from one side, which has happened not infrequently on this question of hazardous waste.

Again, you are going to find yourselves in a position of, in a sense, attack. I think the best defense is going to be a good offense. If you've got a case to make, you are going to have to make it. You are going to have to make it with the media, with the local politicians, with the state people, and with the federal people, because although Superfund is a federal issue, there will be great local pressure to tie up the various members of Congress and there will be much activism in the media.

I believe that it is possible to gain a better handle on this question of what is hazardous and what is not hazardous. It involves the assessment of risk and it involves putting that risk, once assessed, into some perspective for the public to understand in terms of what it does on an everyday basis, and I think we are going to come out ahead.

I know there is a lot of fear of laying this stuff on the line but, in my mind, after five years of being involved with these questions, the worst possible situation is rising out of ignorance.

I have had many experiences back in my own congressional district where the person on the street believes that we are drowning in a sea of chemical carcinogens and corporate America is getting away Scot free somehow, and if we don't do something about it real fast, you know, our kids, ourselves, our grandchildren, our heritage are in trouble.

That is more or less the present situation combined with the media looking for disaster and fear. Fear and disaster sells, along with white knight politicians in shining armor on grand steeds coming to save the people from the impending danger. These are the pitfalls out there, and I think much of what Superfund is going to turn into is going to depend on whether people like yourselves are out there in the trenches working, educating, communicating.

As I understand it, the question of hazardous and the definition of hazardous as defined by EPA relevant to the mining industry is not going to be settled as of October 1983, but there will be some delay, which means more and more that the next sets of changes will come with reauthorization of Superfund.

I would also like to point out there is a controversy, and many of you are aware of it, between the chemical industry and the mining industry over the potential of waste and legislation. I think the chemical industry doesn't want to see funds it contributed into Superfund go into massive projects to clean up certain mines.

I think people in the mining industry would be willing to fairly appropriate those funds once the hazard is judged to be significant and not unwilling to make their fair share of contribution.

By the way, on the significance of hazard, my bill H.R. 3840 has recently been reintroduced. This is on risk assessment research, demonstration and development projects, and it has the full support of the administration. It has six cosponsors including three leading Democrats on the Science and Technology Committee and three Republicans who are on both that committee and leaders in the technology field. I urge your support of that legislation as the alternative for intelligently assessing risk and involving the public in understanding the extent of the risk.

We are already spending hundreds of millions of dollars out of fear and ignorance and political realities that go with fear and ignorance. I am not blaming anybody, but we have got too much fear and ignorance right now.

You know, it is the ultimate dream of the Club of Rome promoters and the no-growth people--to cut off growth and cut off production and cut off economic activity that they view as the evil of modern technological society.

Think of it. It is one thing to tell the people we shouldn't produce, but it is another thing to tell people that this waste is bad, that anything we can do with it is insufficient, that its location near you is going to cause you serious and irreparable harm. At that point, things stop happening. There are certain spheres of this economy today which have already stopped producing because at some point, at some threshhold cost, production is not profitable. That is, at some threshhold cost of dealing with a waste problem, production is not possible.

You know, today people get away from the idea that production of wealth had something to do with natural resources. Somehow production of wealth is simply ethereal. Garbage. Absolute garbage.

Production of wealth is the use of all and each and every resource that a country has, and if we eliminate the basic natural resource production of this country, the prosperity will disappear. We are not Japanese. Nor are we about to be Japanese.

It is going to be a long time between simply importing feedstock and creating out of our wonderous brain power final products that will support the kind of lifestyle this country has. That Japan is going very well, thank you. But if you look at the way the average Japanese engineer and worker and middle management person lives, it is nowhere near the way we in this country live.

Think about it. Mining is one industry whereby with the vast millions, literally billions of tons of waste generated, if wrong moves are made in Washington, we could regulate you out of existence. We have already regulated several other

basic industries out of existence, or virtually so, such as the foundry industry. It could happen to mining.

As Reed Irvine says, there is nothing wrong with people like yourself exercising your first amendment rights and, as Superfund comes down the line, education of community people, politicians, media people, friends, neighbors, demonstrators, and the like, is going to be an essential ingredient to a--from your perspective--successful outcome.

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SUPERFUND/RCRA: AN ENVIRONMENTAL JIGSAW

by

Louis J. Marucheau
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INTRODUCTION

Until not very long ago, solid waste management in the mining industry only concerned a few regulatory programs, such as applicable state mined land reclamation requirements and various types of land use controls. Although the federal government had established comprehensive programs regulating air and water discharges, it had no comparable program for solid waste.

This situation changed dramatically in 1976 when Congress passed the Resource Conservation and Recovery Act (RCRA) and the Surface Mining Reclamation and Control Act (SMCRA). While SMCRA was to have a profound impact on coal mining, it was the passage of RCRA that marked the beginning of full federal involvement in the regulation of solid waste.

Congressional concern with solid waste and its effect on the environment has increased over the years and led to enactment of additional laws, most notably the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (known as Superfund). Superfund established federal authority over any release of hazardous substances to the environment and imposed liability on persons associated with such releases.

The result is that federal laws such as RCRA and Superfund have tremendous legal and financial ramifications for the mining industry. To assess present impacts on the industry and to be able to anticipate and help frame future changes to these programs, it is necessary to understand the history of these programs, their general scope and content, and the way in which they deal with mining waste.

FEDERAL SOLID WASTE DISPOSAL ACT

Development of federal law regulating solid waste

In the United States, solid waste disposal, as typified by the city or county "dump," was long considered a matter of local concern. Consequently, early federal solid waste legislation (such as the Solid Waste Disposal Act of 1965) merely encouraged proper management of solid waste by the state. However, after continuing instances of environmental damage caused by improper solid waste handling and disposal, Congress concluded that more forceful legislation was required.

Passage of RCRA. By the fall of 1976, both the House and Senate had developed legislative proposals to completely rewrite the existing Solid Waste Disposal Act (SWDA) to create comprehensive solid waste management requirements (H.R. 14496 and S. 3622). However, the House bill was reported out of committee so late in the session that it was scheduled to be debated and voted on only four days before Congress was to adjourn for the November national elections.

Since there was no time to resolve differences between the two bills, staff members of the House Commerce Committee and the Senate Public Works Committee held meetings over the weekend (it is said in a Capitol Hill bar) and drafted a compromise bill. The following Monday a substitute bill (a 1-in. thick typed manuscript with handwritten notations) was introduced in the House, which quickly passed it without even having enough time to read the bill. The day before Congress adjourned, the Senate adopted the compromise bill, which was entitled the "Resource

Conservation and Recovery Act of 1976." RCRA became law when it was signed on Oct. 21, 1976.[1]

Post-RCRA amendments to the SWDA. As one might expect of a law hastily written over a weekend, a number of amendments have been made since 1976,[2] of which the most significant are the Solid Waste Disposal Act Amendments of 1980. The 1980 amendments expanded EPA's enforcement authority over hazardous waste but, at the same time, exempted from regulation certain categories of waste.

Congress, due to the requirement that the Solid Waste Disposal Act be reauthorized from time to time, is currently conducting a thorough review of the law. While legislation has yet to be finalized, it is clear from H.R. 2867 (which was reported to the floor of the House) and the latest Senate version that substantial amendments will be made by this Congress to the Solid Waste Disposal Act. These amendments will address, among other items of congressional concern, certain perceived "gaps" in the hazardous waste regulatory program, such as the small quantity generator exemption, exemption of burning of hazardous waste as fuel, and the lack of limitations on landfilling of hazardous waste.

Description of RCRA programs

RCRA completely rewrote the Solid Waste Disposal Act and established two separate programs for solid waste management--one for federally-designated "hazardous" waste; another for "non-hazardous" solid waste.

Hazardous waste program. For management of "hazardous" waste, Congress mandated a comprehensive "cradle-to-grave" regulatory program. The law requires federal standards for those who generate, transport, treat, store, or dispose of hazardous waste. In addition, permits are required for any owner or operator of a facility that treats, stores, or disposes of hazardous waste (known as TSD facilities). While individual states may administer this program, the state program must be "equivalent" to the federal program established by the U.S. Environmental Protection Agency (EPA).

The hazardous waste regulations promulgated by EPA may be found at the Code of Federal Regulations, Title 40, Parts 260-271. The regulations deal with general matters (Part 260), the identification of hazardous waste (Part 261), generator requirements (Part 262), transporter requirements (Part 263), requirements for permitted TSD facilities (Part 264), requirements for unpermitted TSD facilities which qualify for interim status (Part 265), temporary standards for permitted land disposal facilities (Part 267), permitting procedures (Part 270), and procedures for state assumption of the program (Part 271). Although these regulations are much too complex to be discussed in any detail here, several aspects of the program should be noted.

When assessing the impact of this program, one must look at each residual produced and how it is managed. EPA asserts authority over many industrial residuals not usually considered waste (e.g., "by products" which are sold). On the other hand, specific wastes (e.g., oil and gas wastes) and specific waste management practices (e.g., wastewater treatment units) may be exempt from regulation or subject to less onerous requirements. Only a thorough knowledge of these complicated regulations will enable one to properly determine the extent of their applicability.

Generators have limited requirements, such as reports and record keeping, but must ensure that all hazardous waste is sent with the proper manifest to facilities allowed to receive the residuals (authorized TSD or recycling facilities). Generators should, however, be careful not to accumulate hazardous wastes longer than authorized, lest they become a storage facility and thereby require a permit to legally operate. Since hazardous waste is considered a "hazardous material," transporters need do little more than follow the applicable Department of Transportation regulations.

In contrast to generators and transporters, the owners and operators of TSD facilities are subject to strict requirements. Besides a host of procedural requirements, including providing assurances of financial responsibility, these facilities must meet specified design and operating standards which are particularly stringent for surface impoundments, waste piles, land treatment facilities and landfills. For these types of facilities, there is a regulatory policy of total containment of the waste, which (subject to limited exceptions) results in requiring a liner, groundwater monitoring at the boundary of the waste management area, and corrective action if leachate exceeds specified concentration limits.

The hazardous waste regulations have been challenged by a large number of companies and trade associations, including the American Mining Congress, but the

issues have yet to be briefed and argued in court. Due in large part to the extensive settlement negotiations in this litigation that have been conducted since 1980, EPA has made numerous changes to the regulations. Further changes will undoubtedly be made, not only because of the litigation, but also due to adjustments by EPA after it has more experience with the program, due to future congressional directives, and due to possible expansion of the program to include currently exempt wastes.

Solid waste program. For "non-hazardous" solid waste, Congress used a more traditional incentive program to encourage the creation of effective state solid waste management plans. EPA was to promulgate guidelines for the development and implementation of state solid waste management plans. States were required to identify planning regions and agencies responsible for developing and implementing such plans, but they did not have to actually develop plans. Should a plan comply with the guidelines and be approved by EPA, the state would then be eligible for federal financial and technical assistance. EPA's guidelines are found at the Code of Federal Regulations, Title 40, Part 256.

The most controversial aspect of this program involves Sec. 4005 of the SWDA, which provides that any solid waste management practice constituting "open dumping" is "prohibited." Disposal practices constitute "open dumping" if the disposal site would not qualify as a "sanitary landfill" as defined by EPA-promulgated criteria. EPA's criteria for "sanitary landfills" (found at 40 CFR Part 257) may be difficult to meet because they require, in part, that leachate from the waste cannot cause drinking water standards to be exceeded in any groundwater beyond the solid waste boundary. The important legal issue concerning this provision is whether the prohibition can be directly enforced against the responsibile facility.

Because EPA's guidelines require the closure of "open dumps," it is clear that in states with EPA-approved solid waste management plans, citizens can require state agencies to enforce the prohibition. As for EPA enforcement, EPA contends that it has no authority to directly enforce the prohibition of "open dumping," but has stated that the prohibition is separate from the state planning process and can be directly enforced by citizen suit. Although there has been one federal court agreeing with this proposition,[3] a recent decision by another federal district court held, after a thorough review of the legislative history of RCRA, that the prohibition of "open dumping" has no effect apart from an EPA-approved state solid waste management plan. The court said that, even where such plan is approved, no citizen can directly enforce the prohibition against the facility.[4] While this 1983 decision is well reasoned, this issue will be open to litigation in other districts.

Application of RCRA programs to mining waste

Mining waste and the hazardous waste program. The Solid Waste Disposal Act Amendments of 1980 deferred regulation of certain wastes as "hazardous" wastes until at least six months after the submission to Congress by EPA of reports relating the results of studies of the exempted wastes. Among the wastes exempted are "solid waste from the extraction, beneficiation and processing of ores and minerals, including phosphate rock and overburden from the mining of uranium ore." This exemption, known as the "Bevill Amendment" after the representative who introduced it during floor debate on H.R. 3994, currently governs the applicability of the federal hazardous waste program to the mining industry.

In November 1980, EPA published an explanation of this exemption and so amended the hazardous waste regulations.[5] EPA stated that it would broadly interpret the amendments to exempt waste from the exploration, mining, milling, smelting and refining of ores and minerals (including coal). While EPA indicated that this exemption would include wastewater treatment sludges and air emission control dusts, it qualified the exemption by stating that it would not apply to wastes "not uniquely associated with these mining and allied processes," such as spent solvents and discarded commercial chemical products, and by further indicating that it fully intended to reconsider the scope of the exclusion.

The reports, which must be completed before EPA can regulate mining waste, are due to be submitted in October 1983. The EPA study of mining and milling waste (under Sec. 8003(f) of the SWDA) involved the assessment, including groundwater monitoring, of waste management practices at eight mining sites. This assessment, which was monitored by the American Mining Congress, has been submitted in draft form to EPA by its contractor, but it does not appear that the required report will be submitted on time. The study of mineral processing waste (under Sec. 8003(p) of the SWDA) has just been contracted by EPA and will be delayed even further than the mining and milling waste study.

There are some signs that the extent of the mining and mineral processing waste exemption is being called into question. EPA has given some recent indications that in the future it might determine that certain smelting and refining wastes may not be covered by the exemption. Also, although the legislative history of the "Bevill Amendment" appears quite clear that it was intended to cover smelting and refining wastes, there is a reference in the recently published House Report No. 98-198, Part 1, that indicates that current congressional staffers may not believe that all types of smelting waste are exempt. Only time will tell if the exemption will be modified.

Mining waste and the solid waste program. Presently, mining waste is subject to the "sanitary landfill" criteria, and certain mining disposal practices could be prohibited as "open dumping." When EPA promulgated its criteria for "sanitary landfills," the American Mining Congress sued EPA for improperly applying the criteria to mining waste. Although it appeared from the legislative history that Congress intended that the "sanitary landfill" criteria, as its name implies, was only intended to apply to municipal and industrial landfills, the United States Court of Appeals for the D.C. Circuit held that the "sanitary landfill" criteria applied to mining waste.[6]

Even though mining and milling waste disposal sites have not yet appeared on the inventory of "open dumps" published periodically by EPA, the possibility exists that they may be included and could be subject to closure, either under state laws passed to comply with EPA solid waste management plan guidelines or by citizen suit. Although EPA has yet to classify different wastes and develop specific criteria for each class, such separate criteria would be appropriate for mining waste and such classification is encouraged by the SWDA.

FEDERAL SUPERFUND

Development of the federal Superfund legislation

Although Congress believed that the passage of RCRA would result in proper management of hazardous waste in the future, there were growing concerns that past disposal practices had already caused severe adverse environmental effects. Cleanup of these sites was slow in coming because responsible parties could either not be found (so-called "orphaned or abandoned" sites) or were financially insolvent. Even if a solvent responsible party could be found, it was believed that cleanup could only be achieved through protracted and difficult litigation.

Consequently, in 1980 various bills were developed in both the House and Senate to create a fund to clean up hazardous waste sites and to impose liability for releases of hazardous substances into the environment. In September 1980, the House had passed two bills--H.R. 85, which established a fund and imposed liability for discharges of oil and hazardous substances to navigable waters, and H.R. 7020, which established a fund and imposed liability concerning inactive hazardous waste sites. By the time Congress recessed for the November national elections, a more stringent Senate bill (S. 1480), which had been reported out of the Senate Committee on Environment and Public Works in July 1980, had not yet reached the floor of the Senate.

When the 96th Congress reconvened after the elections to conduct the 1980 "lame duck" session, the Senate sponsors of S. 1480 encountered strong opposition to their bill and were forced to introduce a less stringent version on Nov. 18, 1980. However, due to continued opposition, the senators and their staffs quickly drafted a new compromise which was introduced on Nov. 24, 1980 and, after agreeing to limit amendments to a single amendment by Sen. Helms to stop collection of the fees for the fund after a certain date, was passed with virtually no debate.

In sending the bill to the House, the Senate leaders notified the House that any amendment, no matter how minor, would kill the bill if it was returned to the Senate. The House then considered the bill under a suspension of the rules and approved it on Dec. 3, 1980. On Dec. 11, 1980, outgoing President Jimmy Carter signed into law the Comprehensive Environmental Response, Compensation, and Liability Act of 1980. Thus, many provisions of Superfund are not addressed by either a committee report, a conference report, or floor debate.

There are currently several efforts to further amend Superfund. The compromise that removed those provisions imposing liability for injury to persons (Superfund only covers cleanup costs and damages to natural resources) also required a study to assess whether the present legal system adequately provided compensation to victims of exposure to toxic substances (the Sec. 301(3) study). In completing this study, a panel of 12 attorneys indicated that some compensation system was needed and recommended a two-tiered approach whereby victims could

receive administrative compensation (similar to workmen's compensation) and seek damages in the judicial system, modified somewhat to make recovery easier to achieve. This report may encourage a legislative response from congressmen, such as Sen. Mitchell who stated during the brief Superfund debate that "at least as to the Superfund, it's all right to kill people, but not trees."[7] In addition, there is an increasing belief in Congress that the present fund may not be adequate to clean up all the hazardous sites presently identified.

Description of Superfund program

Although Superfund is best known for its creation of a large fund to finance cleanup of hazardous substances from disposal sites (hence the name "Superfund"), the greatest impact of Superfund on industry is from its provisions dealing with actual and potential releases of hazardous substances into the environment. In order to encourage quick response to releases of hazardous substances into the environment and to inventory sites where such releases may have occurred, Superfund established certain notification requirements. First, any person in charge of a facility must report immediately to the National Response Center any release into the environment of a hazardous substance in excess of a designated reportable quantity, unless the release is federally permitted. Second, the owner or operator of any facility where hazardous waste was ever managed must have notified EPA by June 1981 of the existence of the site.

Having established procedures whereby government agencies are made aware of situations where hazardous substances may have been released into the environment, Superfund then provides authority for the government to respond to such releases. Whenever there is a release or threat of release of either a designated hazardous substance or, in the case of an imminent and substantial danger, a "pollutant or contaminant," the government has broad authority to take actions to clean up or otherwise mitigate the harm from such release, unless it is determined that a responsible party will properly carry out such action. Superfund provides for payment of government response costs, subject to certain limitations. One of the major limitations is that, for permanent cleanup actions, the site must be on the National Priorities List and the state must provide 10 percent of the cleanup costs and all future maintenance of the site.

In addition to authorizing government cleanup actions, the Superfund contains provisions facilitating government legal actions against parties responsible for the release. Where there is an imminent and substantial danger, the government can issue abatement orders to a responsible party, requiring him to take cleanup actions. Failure to comply with an abatement order can subject a party to treble damages in addition to the cleanup costs. Subject to a few limitations, Superfund also imposes, regardless of fault, liability for cleanup costs and damages to natural resources on (1) past and present owners or operators of sites where a release occurs, (2) generators who arranged for disposal of hazardous substances at the release site, and (3) transporters who selected the release site for disposal.

A major legal issue yet to be resolved is whether the liability imposed by Superfund is joint and several, i.e., whether each responsible party, regardless of the extent of his involvement with the site, is fully liable for all cleanup costs and damages to natural resources. Although one federal district court has held that non-negligent past generators are not subject to abatement orders,[8] the court indicated that the generators still would be liable for cleanup costs.

The heart of Superfund and the origin of its nickname is the provisions which established two massive funds. First, Superfund created a Hazardous Waste Response Trust Fund to provide a source of revenue to conduct cleanup activities where responsible parties were unknown or were unable or unwilling to conduct immediate cleanup. Claims against this fund may be made by any party carrying out cleanup actions in accordance with the National Contingency Plan and by state or federal governments for damages to natural resources. This fund is to be financed by federal appropriations (up to $220 million), by an environmental excise tax on certain chemicals, metals and oil (up to $1.38 billion), and by penalties collected from responsible parties.

Second, Superfund created a Post-Closure Liability Trust Fund to be financed from a tax on certain hazardous waste received at disposal sites after Sept. 30, 1983. All liability, whether under Superfund or "other law," arising from properly closed permitted hazardous waste disposal facilities is transferred to this fund. Congress believed that this would encourage siting of new hazardous waste disposal sites by providing a dedicated fund to take care of any problems which might develop after a site was closed.

Mining waste and the Superfund

When defining "hazardous substance" Congress referred to lists of substances identified under various federal laws and included hazardous waste, "but not including any waste the regulation of which under the Solid Waste Disposal Act has been suspended by Act of Congress." As described above, the Solid Waste Disposal Act Amendments of 1980 (passed less than two months before Superfund) exempted from regulation as hazardous waste, "solid waste from the extraction, beneficiation, and processing of ores and minerals." The legislative history makes it clear that exempted wastes are not considered "hazardous substances" even though they may contain substances designated elsewhere as hazardous.[9] To interpret the law otherwise would make all dirt and animal and vegetable matter "hazardous" because they contain small amounts of metals listed under the Clean Water Act because they are toxic in high concentrations. This issue is currently before the courts in litigation filed recently.[10]

Thus it would appear that mining and mineral processing wastes would not have much to do with Superfund. Such is not the case. While the government may only issue abatement orders for releases of hazardous substances, the government may take response actions for sites releasing "pollutants or contaminants," provided there is an imminent and substantial danger, and may, therefore, include them on the National Priorities List. When EPA formally proposed the National Priorities List, 17 of 418 sites were mining or mineral processing waste sites.[11] EPA has recently announced the addition of 133 sites to the list that, after other deletions and additions, result in a proposal for 539 sites, of which 22 are mining or mineral processing sites. Although sites may be listed, liability of responsible parties under Superfund only attaches to releases of "hazardous substances." Thus, while EPA may engage in response actions at such sites, the use of Superfund's special liability to recover cleanup costs may be restricted and the government may have to resort to other statutes or common law to recover.

In addition to being subject to Superfund response actions, mining industry facilities may also be subject to release notification requirements. Assuming EPA's current interpretation of the exemption for mining and mineral processing wastes is correct, releases such as spills of process chemicals or products such as sulfuric acid must be reported. Failure to report may result in criminal action against the person in charge of the facility.

CONCLUSION

To respond to perceived serious public health problems, Congress hastily enacted the two major laws affecting waste disposal--RCRA (which rewrote the federal Solid Waste Disposal Act) and Superfund. Mindful that the laws were intended to respond primarily to problems from past chemical waste disposal sites, Congress made some accommodation to certain types of low hazard, large volume waste such as that found in the mining industry. However, ambiguities in the program caused by the hasty enactment of the governing statutes and the desires of state agencies and EPA to address unresolved pollution problems, such as mine drainage, clearly indicate that the mining industry will, to some extent, be affected by these laws. Currently, the effect is limited primarily to (1) hazardous waste regulation of so-called non-indigenous waste, (2) potential future application of the "sanitary landfill" criteria, and (3) response actions under Superfund. However, litigation, further administrative action, or future amendments to the laws themselves may dramatically alter the current status.

References

[1]For a discussion of the legislative history of RCRA, see Kovacs & Klucsik, "The New Federal Role in Solid Waste Management: The Resource Conservation and Recovery Act of 1976," 3 Columbia Law Journal 205 (1977).

[2]PL 95-609, Nov. 8, 1978; PL 96-463, Oct. 15, 1980; PL 96-482, Oct. 21, 1980; PL 96-510, Dec. 11, 1980; and PL 97-272, Sept. 30, 1982.

[3]O'Leary v. Moyer's Landfill, 523 F. Supp. 642 (E.D. Pa. 1981).

[4]City of Gallatin v. Cherokee County, 13 ELR 20395 (E.D. Tex. 1983).

[5]45 Federal Register 76618, Nov. 19, 1980.

[6]Chemical Manufacturers Ass'n v. EPA, 673 F.2d 507 (D.C. Cir. 1982).

[7]126 Congressional Record S. 14973, daily ed. Nov. 24, 1980.

[8]U.S. v. Wade, 546 F. Supp. 785 (E.D. Pa. 1982).

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EPA's MINE WASTE STUDY

by

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Mining wastes are one of the largest national waste streams. There is a lot of argument as to whether mining wastes or agricultural wastes are the nation's largest waste stream. It doesn't really matter which is because both are significantly large.

We think there are approximately 30 billion tons that are accumulated and also that about 2.3 billion tons additional are accumulated each year.

The Congress has had a great deal of interest in this subject in the last five years or so. The first two laws, SMCRA and UMTRCA as we call them, are aimed specifically at coal waste and uranium mill tailings waste, respectively.

The last two laws are the ones that have been under discussion so far this afternoon. The Resource Conservation and Recovery Act of 1976 mandated that the agency study mining waste. Basically it was large, its constituents were not well known, and the Congress said, "We want the agency to take a look at what's going on here."

That provision was in Sec. 8002(f) of RCRA. The Solid Waste Disposal Act amendments of 1980 added a new provision and that was Sec. 8002(p). This was basically another mining waste study. It is very similar to 8002(f).

The major difference is that 8002(p) has tied to it the exclusion from the hazardous waste regulations. The agency is precluded from regulating mining industry waste until six months after we complete our studies and submit a report to the Congress.

Clearly, 8002(p), then, focused very heavily on potentially hazardous wastes.

The congressional study calls for eight major points, which we have condensed into five here. We are to look at the source and volume of the wastes associated with the mining industry, we are to look at the current disposal practices and the alternatives to those disposal practices, and the costs for both present and perhaps alternative practices.

We are to look at the potential danger of both disposal and reuse of mining wastes, and to determine if any damages have taken place in the past.

The impact of the various disposal alternatives on the use of natural resources is one of the items that we have not looked at and that we will not be looking at until we determine whether the need for hazardous waste regulation is existent.

And finally, the current and potential uses of the waste--we have already completed that study, and we submitted it to the American Mining Congress and to the industry for review, I believe, about a year ago.

There are some segments of the mining industry that are not being addressed in this program. The first is the coal mining industry. The second is the uranium industry, because of the previously listed laws, which address those industries specifically.

We are not looking at oil shale because our study has been focused on active industries, and the oil shale industry is not what one would call active.

In situ mining we are also not looking at because that is covered by the Underground Injection Congrol Program at EPA.

Now, our study had basically three phases. The first thing we did was to characterize the waste streams from 600 sites. This resulted in the taking of approximately 400 waste samples and full-scale analysis of those samples.

Then, we selected sites for a year of monitoring and we selected eight sites. That was probably one of the most difficult things that we have had to do in this project.

Last but not least is Phase III, which is beginning now. We will do additional waste characterization sampling and analysis at 25 new sites, and we are also taking a look at contamination instances of the past which, as I had mentioned previously, is one of the line items that Congress required.

I would like to go through some of the data on our presurvey results, because clearly what's in a waste is very important to its definition as to whether it is defined in the legal sense as being a hazardous waste, or not being a hazardous waste.

Gold and silver. We took 14 tailings samples, which is by far the largest number of samples that we took for this particular industry. Gold was of particular concern because of cyanide and the cyanidization process. There is no primary drinking water standard for cyanide so we have expressed that in terms of a range, 0.6 to 41 ug/g (see fig. 1).

For the tailings pond liquid, of which we took six samples, we had cyanide that ranged from 12 to 76 mg/l.

There were a few samples also which exceeded for other things. There were three samples that were in the elevated range, which we define as being 20 to 99 times the primary drinking water standard, given the EP toxicity test.

For each of these parameters, there was one each, with the exception of the cadmium where there were two, that exceeded the 100 times drinking water standard.

Now, let me be very clear about this standard. EPA set up self-testing procedures for waste streams so that the regulated community could determine for themselves whether they had, by these test procedures, a hazardous waste. One hundred times the drinking water standard is that self-diagnostic, if you will, criteria. Between 20 and 100 is what we generally worry about as being an elevated range. This is considered to be a high range, and normally a clearly hazardous waste.

Now, mining wastes are, of course, excluded, so these are not hazardous wastes in the legal sense of the term now.

For the copper industry, probably the most interesting numbers are the ones for arsenic and lead from the leach liquors (see fig. 2). These numbers were a factor in deciding to evaluate this particular management practice for the copper industry.

There were two samples that exceeded 100 times drinking water standards. One exceeded 100 times drinking water standards for cadmium. Four of six samples exceeded the 100 times the drinking water standard for selenium.

In the lead-zinc industry, as one might expect, the parameters of concern were lead (see fig. 3). For the tailings of the 25 samples which we took, seven exceeded 20 times the drinking water standards, or were within that elevated range, and 5 exceeded 100 times the drinking water standard.

For moly, we had a couple of samples that were in the elevated range (fig. 4). None were in the high range, and we did show some cyanide ranges, but again, not very high for this industry. Obviously, much higher for the gold-silver industry.

In phosphate, there were a few elevated parameters, but we took many samples (fig. 5) and there were none that were in the high range.

For uranium, again, a large number of samples was taken--30 mine waste rock low grade ore (fig. 6). Again, tailings were considered here because (AMTRCA) handles that problem and we address only the non-tailings waste associated with the uranium industry.

We looked at iron and tungsten, taking 44 samples for those two industry segments, and basically found none that were either elevated or high for any RCRA parameter (fig. 7).

Fig. 8 shows the results from a study done by the Effluent Guidelines Division in which they took samples at mining sites for several industry segments and applied the RCRA testing procedure. Not quite as many samples were taken as we had for the other areas, but still a goodly number associated with these smaller industries in general. The only number that sort of jumps out at you is the 3 exceeding the 100 times drinking water standard of the eight associated with the antimony industry.

Another "contaminant of concern" that is associated with phosphate and uranium is radium 226 (see fig. 9 and 10). There is no RCRA standard for this, but clearly it is something that, at least in the literature, was an environmental concern when we began doing this study.

We have simply defined, to put it in a common context, elevated as being from 10 to 49 pico curies per gram and high as being over 50 pico curies per gram. There were none for phosphate. In general, I would say that the phosphate results turned out to be significantly lower in radium 226 than the literature at that time present would have led you to believe.

We have defined elevated in terms of a liquid sample as being between 100 pico curies per liter and roughly 500, and over 500 as being high; there was nothing in that range at all associated with phosphate. Even the number you might define as being elevated is comparatively small compared to the large number of samples that were taken.

Now, for uranium, there was a significantly larger number, as you might expect (fig. 10). Of the mine water samples, five of the eight exceeded, as far as pico curies per liter are concerned, the elevated definition. In solid uranium mine waste samples, 16 of the 30 samples were elevated. For the low grade ore, we have 11 of 13 in the high category and 6 of 12, roughly half for the mine water pond settled solids.

The next item that we come to, and this is a very brief summation, is how we selected sites for monitoring. To give you some idea of the magnitude of the difficulty here, it is generally conceded that there are somewhere between 12,000 and 20,000 mining disposal sites in the United States, active. Associated with the metal mining industry, there are somewhere between 5,000 and 6,000 sites.

Deciding which industry to focus on, and then getting down to the point of which sites to go to was clearly an intellecutal job of enormous proportion. I think to defend it, that we did it the only way we could. I will briefly run through the methodology that we used to select these sites. There is a much fuller explanation and a nice thick document that gives much more detail on how they were chosen. If you would like a copy of that, we can get it for you.

The first step was to determine which of the approximately 56 industry segments that are out there, which of those 56 we should focus on.

We took this first step prior to doing the pre-survey, before having the benefit of the data contained in fig. 1 to 10. This was based on literature, and we used two basic criteria. The first was size. Clearly Congress had set this industry aside primarily because of its gigantic size. The second one was waste characteristics, primarily toxicity, corrosivity and radioactivity.

The result of that step was to choose the copper, uranium, phosphate, lead, zinc, gold, silver, molybdenum, and iron industries to focus on as the major industries of our concern.

I think the justification is obvious there. For most of them it was size; for some it was toxicity and corrosivity; for two phosphate and uranium, radioactivity was also taken into consideration.

The second step was to determine which waste management practices and which wastes within those industries to monitor. Again, we chose size as our first major characteristic. Waste characteristics were the second. And the potential for transport, the particle size, and particularly the presence of water as a sort of a self-conducting medium was used in this step to determine which management practice to focus on.

After we decided which management practice to focus on, we then went to a substep, which was picking the major producing districts in which to pick our sites.

Of the various management practices that are present within the industries, there are two that are universal. Everyone has mine waste rock, overburden, etc. And everyone uses tailings ponds. Again, uranium was not considered applicable here but, of course, they have tailings ponds.

For other industries and other wastes, there were different kinds of management practices; for example, low grade ore dumps in copper and uranium. Almost unique to the phospahte industry are sand tailings piles.

So looking at the management practices and going through the criteria just mentioned, we basically chose these management practices to focus on and waste streams.

Of course, there are a lot of tailings ponds; we chose copper tailings ponds, phosphate, gold, silver and lead/zinc (fig. 11). We chose phosphate mine waste dumps primarily because of the radioactivity. And we chose leach dumps associated with the copper industry primarily because of toxicity. Mine water ponds for uranium, again, radioactivity.

This makes it sound like it was a very simple process. This was probably the most difficult step; that is, to make this cut and choose these wastes and practices to focus our research on.

We then did a series of maps, laying out where in the United States these industries were located, and what percentage of present production they represented. Fig. 12, for gold and silver, suggests that, if you were going to pick two states for study, you would probably pick South Dakota and Nevada, and that's what we picked. Some of them were not quite that clear.

Nonetheless, by laying all this out we came to our choices for tailings ponds with the copper industry as being Arizona and New Mexico and Utah (fig. 13). We were going to choose at least one site in those states. Same for the leach dumps.

For uranium, we had New Mexico and Wyoming for mine water ponds. For phosphate mine waste dumps, Idaho and Florida, and for phosphate tailings ponds, clearly Florida. That's where 90 some odd percent of the industry is located.

Having made those choices, we then went to Site Selection Step III (fig. 14).

Step III was fundamentally different from Step I and II. In Step I, we were trying to determine which part of the mining industry would be the most likely to have wastes that could impact the environment. Step II is to determine which waste management practices and specific wastes associated with those industries were the most likely to affect the environment. In Step III we specifically backed away from looking for the worst case actors, and we tried to find waste management practices that, based on our pre-survey data, were in the mid-range of toxicity or radioactivity or whatever the contaminant of concern was. Also, to find settings that were typical of the industry that we were trying to evaluate.

Last but not least were monitoring considerations; all sites associated with the mining industry are difficult in terms of interpreting the data simply because of their mammoth size. For some sites, it is probably impossible. And when sites came up in our typicality range that had particularly difficult topographies in terms of evaluating the data, those were rejected.

So we look for sites that were typical of the industries and practices we were trying to evaluate, and we did take into consideration the monitoring considerations and the monitoring complexities that we might see.

The sites selected, as given in fig. 15, are the botton line. I would like to take this opportunity to thank these companies who were very generous in their time and allowed us to put in monitoring wells and monitoring stations for both ground water and surface water.

Fig. 16, a schematic of the Fort Green site in Florida, gives an idea of the kind of monitoring done.

Shown are the disposal facilities, which are enormous impoundments, surface water monitoring stations (triangles on fig. 16), and each of the black dots represents a groundwater monitoring well. These kinds of schematics were done for all of the eight sites.

Our contractor, Pedco, has created reports on each one of these eight sites. Those reports have gone back to the industry, to the owners of these facilities for their comments, and we have received comments from three of the eight. We are waiting for the other five. We will modify our conclusions etc. based on those comments--those that we take to be valid, clearly. We will then distribute for peer review a three-volume report on this $2.8 million study. We have asked the American Mining Congress to be one of those peer reviewers, and they have accepted. Those reports should be out next month.

But let me give you a few sort of bottom line preliminary findings if you can have such a thing. These are preliminary in that, as I said, we have not received the comments back from most of the facilities, and we intend to take those comments very seriously. But in general, this is what I think we can say are legitimate preliminary findings.

First, surface water was not apparently impacted at any of the sites that we monitored. That is a rather significant finding.

Radioactivity is apparently not impacting ground to surface water at either the uranium mine water ponds or at the phosphate site. The most pressing concern for both those industry segments is radioactivity, and it does not appear to be reaching groundwater--at least, not at the present time.

There was evidence of seepage at all of the impoundments that we monitored. I think that is more or less to be expected. Clearly, impoundments carry their own mode of transportation in that they do have a constant head. They are covered with water, and as a consequence, I don't think that is a surprising conclusion.

The next one is not a surprising conclusion either; hydrologists and geologists know it to be true, and this study which we have conducted is one of many that confirms that the local hydrology controls the rate of seepage, and the local geochemistry controls the extent of the contaminants, how far they move into the environment and at what concentration.

We evaluated seepage collection systems--two or three varieties. We found that if they are properly installed and operated, they can be a very effective mitigative control for keeping pollutants from ground water.

Last but not least is another fact that was confirmed: acidic wastes and/or environments significantly increase the probability of groundwater contamination.

As I said before, we are going into another phase of this study. We are going to be reviewing state files as the Congress directs us in the study to determine instances of contamination and instances of releases of pollutants to the environment from mining waste.

We are going to be reviewing the Superfund data, and this is supposed to take place over the next six months. We had the kick-off meeting last week. It is conceivable that we should get that work done by March 1984.

In addition, we have done a statistical analysis of the waste characterization data that we have on the various segments of the mining industry. We have determined that we are deficient in having enough samples for some of the industry segments, which we intend to address in our report to Congress.

Our report to Congress, which I expect to be there this time next year, will not address the entire mining industry. We hope to address all of the metal mining segments and phosphate and asbestos.

We then hope to begin a new study, although probably not as exhaustive as this study has been, of the nonmetal mining industry other than phosphate and asbestos.

The 25 sites as selected in phase III of our study and 125 samples will be taken over the next six months. You may be contacted by our contractors. We have two working with us on this particular phase--a contractor from Cambridge, and Pedco again will be participating in this part of the study. With these additional

25 sites, we hope we will have a statistical representation of all of the wastes associated with the metal mining industry, phosphate and asbestos.

Now I would like to clarify, particularly in the context of the previous speakers, the options for mining waste regulation under the present law.

First, if any of the mining wastes are determined to be hazardous, any of them, we have two choices. We can either apply the full range of the Subtitle C standards as they exist today, the hazardous waste regulations as they exist today, or we can propose in the Federal Register and hopefully promulgate at some point waste specific, but still mandatory, standards under Part 266.

Part 266 is a piece of the regulation that has been saved for special kinds of problem wastes that don't fit into the normal structure of hazardous wastes. Just to give you an example of that, waste oil will have its own 266 regulations because that is a waste stream that just doesn't fit into the normal ebb and flow of hazardous waste as we commonly think of it.

I have always felt that if we determined that any of the wastes that we have studied are hazardous wastes and need not the full, but Subtitle C control, national hazardous waste control, that in all probability Part 266 regulations would be the route that we would take.

If and I shouldn't say if, because right now all mining wastes are in this category, and once we send our report to Congress, if we determine that only a few of the mining wastes need to be controlled as hazardous wastes--a few or none, I should certainly add the caveat "or none"--then all mining wastes would be in the second column of fig. 18. They would be nonhazardous wastes by the meaning of the law.

I would like to stress as a personal observation that the terms hazardous and nonhazardous have been one of the greatest problems with RCRA and probably with Superfund as well. If you open a pop-top can, drop it on a beach and I step on it, that to me is a hazardous waste. What we are talking about is the continuum of risk, starting with probably the first one that comes to mind--say dioxin--and moving all the way through to that innocuous little pop-top. But it depends on where it is and what is done with it as to how "hazardous" it is.

Nonetheless, this is the legal framework that we must deal with and, therefore, according to RCRA, it has to go into one category or the other.

So getting back to the nonhazardous category, if we took no action, then the wastes would stay as they are today in the nonhazardous category controlled by the Subtitle D land disposal criteria, subject to the open dump inventory, with the states bearing fully implementation and responsibility.

Or, and again there is a high probability that this will happen, we can write waste specific advisory guidelines to the states based on this research, telling them what we found and what we think are the best management practices for mining wastes.

It is conceivable that we could end up in a situation where we have some mining wastes in all four of these, because clearly mining wastes are not monolithic. They differ widely in their chemical and physical characteristics and they certainly differ enormously in their size, which I believe is really what got them the special distinction to begin with.

Nonetheless, these are the four options--legally, I think there are no others. Mining wastes, all mining wastes, will end up in one of these four categories.

It is important for the agency to determine which category they want them in, but it is also very important to get input from the industry as to which category you think they belong in.

Fig. 1

- GOLD/SILVER INDUSTRY -

Waste Type (No. Sampled)	Parameter	No. Elevated (20 to 99 x PDWS)	No. High (>100 x PDWS)
Mine Waste (3)	Lead	1	1
Low-Grade Ore (5)	Lead	-	1
Tailings (4)	Lead	3	1
	Mercury	-	1
	Selenium	-	1
	Cadmium	-	2
	Cyanide	From 0.6 to >1.0 mg/l	
Tailings Pond-Liquid (6)	Arsenic	-	1
	Chromium	-	1
	Mercury	2	1
	Selenium	1	-
	Cyanide	From 12.0 to 76.0 mg/l	

Fig. 2

- COPPER INDUSTRY -

Waste Type (No. Sampled)	Parameter	No. Elevated (20 to 99 x PDWS)	No. High (>100 x PDWS)
Mine Waste (21)	Cadmium	1	-
Tailings (11)	Selenium	2	-
	Cadmium	-	1
	Cyanide	From 0.12 to 1.7 mg/l	
Leach Liquors (6)	Arsenic	4	-
	Cadmium	2	2
	Chromium	2	-
	Lead	4	-
	Selenium	1	4
Mine Water (6)	Cadmium	1	-
Mill Waste Water (1)	Selenium	1	-

Fig. 3

- LEAD/ZINC INDUSTRY -

Waste Type (No. Sampled)	Parameter	No. Elevated (20 to 99 x PDWS)	No. High (>100 x PDWS)
Underground Mine Waste (4)	Cadmium	1	1
	Lead	1	-
Tailings (25)	Mercury	1	-
	Lead	7	5
Mine Water (5)	Lead	-	1
Mine Water Pond Solids (2)	Lead		1

Fig. 4

- MOLYBDENUM INDUSTRY -

Waste Type (No. Sampled)	Parameter	No. Elevated (20 to 99 x PDWS)	No. High (>100 x PDWS)
Tailings (2)	Cyanide	From 0.14 to 1.92 mg/l	
Tailings Pond Liquid (1)	Cyanide	From <0.02 to 0.16 mg/l	
Untreated Mine Water (5)	Cadmium	1	-
	Selenium	1	-

Fig. 5

- PHOSPHATE MINING INDUSTRY -

Waste Type (No. Sampled)	Parameter	No. Elevated (20 to 99 x PDWS)	No. High (>100 x PDWS)
Surface Mine Waste (26)	Mercury	1	-
Tailings (25)	Selenium	1	-
	Cadmium	1	-
	Mercury	1	-
Tailings Pond Liquid (1)	Cadmium	1	-
	Selenium	1	-

Fig. 6

- URANIUM MINING INDUSTRY -

Waste Type (No. Sampled)	Parameter	No. Elevated (20 to 99 x PDWS)	No. High (>100 x PDWS)
Mine Waste Rock (3*)	Mercury	2	
Low Grade Ore (13)	Selenium	1	
Mine Water Pond Settled Solids (12)	Barium	2	-

Fig. 7

IRON INDUSTRIES
AND
TUNGSTEN INDUSTRY

* None of the no samples exhibited elevated or high levels of toxicity

Fig. 8

- OTHER INDUSTRY SEGMENTS -

Industry Segment	No. Samples	No. Elevated (20 to 99 PDWS)	No. High (>100 x PDWS)
Tungsten	7	1	-
Platinum	8	1	5
Aluminum	10	-	-
Nickel	10	-	-
Chromium	13	2	-
Tungsten	4	-	-
Titanium	12	-	-

Fig. 9

- PHOSPHATE MINING INDUSTRY -
(RADIUM 226)

WASTE TYPE (NO. SAMPLES)	NO. ELEVATED (5 TO 49 PCI/G)	NO. HIGH (>50 x PCI/G)
SOLIDS		
TAILINGS POND SETTLED SOLIDS (18)	-	-
SURFACE MINE WASTE (25)	[illegible]	-
LOW-GRADE ORE [illegible]	-	
WASTE LAND [illegible]		
	NO. ELEVATED (50 TO 499 PCI/G)	NO. HIGH (>500 x PCI/G)
LIQUIDS		
TAILINGS WATER (10)	1	-

Fig. 10

- URANIUM MINING INDUSTRY -
(RADIUM 226)

WASTE TYPE (NO. SAMPLES)	NO. ELEVATED (5 TO 49 PCI/G)	NO. HIGH (>50 x PCI/G)
SOLIDS		
MINE WATER POND SETTLED SOLIDS (12)	2	6
MINE WASTE ROCK (30)	26	-
LOW-GRADE ORE (27)	2	11
	NO. ELEVATED (50 TO 499 PCI/G)	NO. HIGH (>500 x PCI/G)
LIQUIDS		
MINE WATER (8)	5	-

Fig. 11

WASTE MANAGEMENT PRACTICES CHOSEN

	Copper	Uranium	Phosphate	Gold/Silver	Lead/Zinc	Molybdenum	Iron
Mine waste dumps	X	X	●	X	X	X	X
Low grade ore dumps	X	X		X			X
Mine water ponds		●			X	X	
Tailings ponds	●	N/A	●	●	●	X	X
Leach dumps	●						
Sand tailings piles			●				

● CHOSEN

Fig. 12

EXAMPLE PRODUCTION MAP FOR MINING DISTRICT SELECTION--
GEOGRAPHIC DISTRIBUTION AND GOLD/SILVER ORE PRODUCTION
CONTRIBUTIONS OF MAJOR PRODUCING STATES

Fig. 13

WASTE MANAGEMENT PRACTICES CHOSEN

	Copper	Uranium	Phosphate	Gold/Silver	Lead/Zinc	Molybdenum	Iron
Mine waste dumps	X	X	NV,FL	X	X	X	X
Low grade ore dumps	X	X		X			X
Mine water ponds		NM,WY			X	X	
Tailings ponds	AZ,NM, UT	N/A	FL	NM,NV	NM,NV	X	X
Leach dumps	AZ,NM, UT						
Sand tailings piles			X				

Fig. 14

SITE SELECTION METHOD

STEP I - Determine mining industry segments to study

STEP II - Determine waste management practices and location within each segment for monitoring

STEP III - Select sites typical of management practices within each segment for monitoring

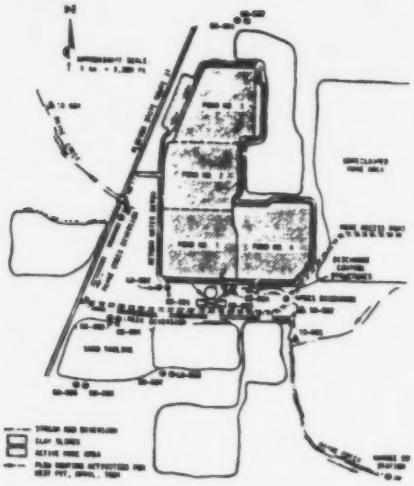
- Toxicity (waste, ooziing, etc.)
- Monitoring considerations

Fig. 15

SITES SELECTED FOR MONITORING STUDIES

Industry Segment	Management Practice	Site	Ground Water	Surface Water
Copper	Tailings Pond	Cyprus Pima, AZ	X	
Copper	Dump Leaching	Kennecott Chino, NM	X	
Lead/Zinc	Tailings Pond	St. Joe Viburnum, MO	X	X
Gold/Silver	Tailings Pond	Newmont Carlin, NV	X	X
Gold/Silver	Tailings Pond	Homestake Lead, SD	X	X
Uranium	Mine Water Pond	Kerr-McGee Churchrock, NM	X	
Phosphate	Mine Waste Pile	Stauffer Wooley Valley, ID		X
Phosphate	Mine Waste, Clay and Sand Tailings	Agrico Fort Green, FL	X	X

Fig. 16



EXAMPLE MONITORING SITE CONFIGURATION--
LOCATION OF MONITORING STATIONS
AT AGRICO'S FORT GREEN SITE

Fig. 17

FUTURE RESEARCH
ACTIVITIES

- Survey of contamination instances
  - Review state files
  - Review Superfund data
  - September 83-March 84
- Additional industry and waste characterization
  - 25 sites
  - 125 samples
  - October 83-April 84

Fig. 18

FUTURE ALTERNATIVES
FOR MINING WASTE MANAGEMENT
UNDER RCRA

HAZARDOUS	NONHAZARDOUS
APPLY FULL RANGE OF SUBTITLE C STANDARDS	NO ACTION-SUBTITLE D CRITERIA APPLY. STATES IMPLEMENT
OR	OR
WASTE SPECIFIC, MANDATORY STANDARDS UNDER PART 266	WASTE SPECIFIC, ADVISORY GUIDELINES TO STATES UNDER SECTIONS 1008/4004

WASTE CHARACTERIZATION SUMMARY

Mining Segment	Total No. Sites	No. Sites Sampled (%)	No. New Sites To Be Sampled
Bauxite	7	1 (14)	0
Copper	91	11 (12)	4
Gold/Silver	150	13 (9)	6
Iron/Taconite	28	5 (18)	0
Lead/Zinc	37	10 (27)	4
Titanium/Ilmenite	5	1 (20)	1
Tungsten	5	2 (40)	0
Uranium	200	16 (8)	4
Antimony	1	1 (100)	0
Beryllium	1	0 (0)	1
Mercury	2	1 (50)	0
Molybdenum	3	3 (100)	0
Nickel	1	1 (100)	0
Rare Earths	1	0 (0)	1
Vanadium	1	1 (100)	0
Asbestos	3	0 (0)	2
Phosphate	33	11 (33)	2

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SUPERFUND—MINING SITES ON THE NATIONAL PRIORITIES LIST

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On December 20, 1982, 418 sites were placed on the National Priorities List (NPL). (Times Beach, Mo. has since become the 419th site and further additions to the list are expected on about Aug. 1, 1983.) This was the culmination of an effort by the Environmental Protection Agency and numerous state agencies to identify the hazardous waste disposal sites in the United States which present the greatest risk to human health and/or the environment.

Sites believed to present a hazardous waste problem are designated for the NPL by a two-step procedure:

1) The states nominate sites for the NPL. Under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), which established this procedure, each state must have at least one site on the NPL.

2) An intendedly objective scoring system developed by the Mitre Corp. for EPA (the "Mitre model") is then used to select sites. Mitre model scores are furnished by the states with their nomination. In reality, EPA or EPA contractors did the scoring for the states in many cases.

EPA has estimated that there may be 10,000 to 20,000 hazardous waste sites potentially covered by CERCLA. Of these, 690, or about 5 percent, were nominated for the NPL. Thus, the winnowing process in Step 1 is much greater than in Step 2 (418/690 = 61 percent). For mining sites, 31 locations were nominated, of which 17 sites were selected. Presumably, like the other sites, the mining sites nominated represent only a small fraction of the total population.

The second step of the listing process is the comparison of Mitre model scores to compose the NPL. The model calculates scores for five "pathways" of potential human exposure: ground water, surface water, air, direct contact, and fire and explosion. The first three pathways are combined (by taking the square root of the sum of the squares) into an overall "migration" score. The migration score is essentially the determinant for listing on the NPL. According to the National Contingency Plan (47 FR, 137, 31180, July 16, 1982), placement of sites on the NPL is based primarily on the migration score. The fire and explosion and direct contact score may be used to determine if emergency attention is needed.

The score for each of the three migration pathways is the product of scores for three "factors":

1) The existence or likelihood of a release. An "observed release" which is basically a measurement of concentration above background at any location automatically produces the maximum score.

2) A "characteristics" score, which is the sum of scores for quantity and toxicity/persistence for water pathways and quantity, toxicity and reactivity, and incompatibility for the air pathway. The score for "quantity" is determined by the total volume of waste while the score for parameters like "toxicity/persistence" is determined by the most toxic and persistent component.

3) Characteristics of the population or sensitive environment at risk such as distance to point of exposure and number of people involved. Potential scores for population factors are much larger than for purely environmental factors.

In this paper, mining sites are defined by whether the practices at the site would qualify an operator for membership in the American Mining Congress. These practices include extraction, smelting, and refining but not fabrication into a final product. Only sites where mining practices are responsible for most of the Mitre model score are analyzed. Under these criteria, the 31 mining sites analyzed, including 17 NPL sites, are shown in table 1.

This paper is concerned solely with the technical validity of the listing process. Legal issues, such as the propriety of including mining sites in Superfund, are not considered. Nor are site-by-site characterizations a primary concern; this is done only to the extent necessary to provide perspective on the validity of the Mitre model results.

NOMINATION OF SITES BASED ON EXTENT OF EXISTING INFORMATION

In generating Mitre model scores to be submitted for a site's nomination, a general result is: the more information available, the higher the score. This result is as true for sites not causing any signficant harm to the environment as it is for genuine problem sites.

The Mitre model score rises with the available information for the following reasons. The instructions for using the model specify that where there is no data for a factor, it is assigned a value of zero. Further, where data is lacking for two or more factors, the entire pathway score (air, ground water, or surface water) is set to zero. Finally, the maximum score for any pathway can only occur for a measurement, or other conclusive evidence, of a concentration above background (irrespective of whether the concentration is significant in terms of health standards and criteria).

Most of the 31 mining sites nominated for NPL have prior studies; some have a history of EPA and/or state negotiations and in a few cases consent decrees. Further evidence that these sites are well known is the fact that all of the 17 NPL sites and 10 of the 14 additional sites have "observed" (that is, measured) releases in some route category. Although a site may be well known for some environmental impact, it may not be in an area scored by the Mitre model. For mining sites, for example, acid mine drainage and its effect on aquatic life are often of concern; this is the case at 8 of the 17 NPL sites. No score is given for acidity in the Mitre model.

The following table shows which routes contributed to scoring at the 31 sites.

Mitre Model Scoring

	Air (%)	Ground Water (%)	Surface Water (%)
NPL Sites (17)			
Considered	41	94	88
Highest Score	18	65	18
Non-NPL Sites (14)			
Considered	0	100	100
Highest Score	0	71	29

Unlike ground water and surface water, the air route only contributes when there is a measured release (rather than a likely release). The reason the air pathway does not occur for the non-NPL sites is that they generally do not have as extensive measurements as the NPL sites. Almost all mining sites consider both ground water and surface water pathways in the scoring with the highest scores generally being obtained for the ground water.

Overall structure of the model in combining source, release and population information is shown in fig. 1. Note that,as illustrated, the information required is designed to be readily available rather than self consistent.

To gain some insight into what distinguishes the NPL from the non-NPL sites, a sensitivity analysis was performed for each parameter occurring in each pathway score. This was done by decreasing each parameter score by 50 percent and calculating the overall change in the total score. An example will make this procedure clearer. At the first entry in table 1, the Anaconda smelter site in Anaconda, Mont. the total migration score is 58.7. In obtaining this result, "quantity of waste" in the ground water pathway was scored as 8 points. Had quantity of waste

been scored as 4 points the migration score would drop by 6.0 points to 52.7. For the parameter "toxicity/persistence" in the surface water pathway, a score of 18 was recorded. Had this score recorded as 9 points, the migration score would drop by 2.7 points to 56.0. Hence the overall score is more sensitive to the value of the first parameter. Table 2 shows the results when all pathways are combined so that "observed release" represents any of the three pathways, etc. The different pathways were combined because they basically all behave the same way. Numbers in table 2 may add to more than 17 horizontally, because more than one pathway is considered.

The fact that the maximum number of sites occurs along the diagonal in table 2 indicates a consistent pattern of parameter importance. Whether or not there is an observed release is almost always (16 times out of 17) the most important factor; population factors and distance to well or intake are usually the second most important factor and so on.

This picture of how the Mitre model works can be simplified even further by just considering the top four parameters in table 2 and recognizing that for parameters such as distance to well/population served or distance to stream/population, the population portion of the parameter is a good indicator of this whole factor (of course, it is the whole factor for the air pathway) since people require wells or surface water. The population figure used is the figure mentioned in scoring that pathway at that site.

Results are shown in the following table for the rule: "Observed release, population greater than 100 and (near) maximum toxicity, persistence, and quantity in any one pathway produces an NPL site--failure to satisfy these conditions does not":

Percentage of sites satisfying the selection rule

NPL site*	94%	(One site not an observed release, 16 satisfy the rule)
Non-NPL sites	6%	(13 sites satisfy the rule, one does not)

* One NPL site has next to maximum score in the dominant pathway for the toxicity/persistence parameter. Score in this pathway is based on copper rather than cadmium, which was used in the other pathway and which would have produced a maximum score. All the others score the maximum in these categories.

The two sites not satisfying this rule are of particular interest. Alden mill has the highest score of any non-NPL site, higher in fact than several of the NPL sites, but it is based on "unproven" arsenic content of the waste. This may be why it is an exception to the selection rule and was not listed. The NPL site not satisfying the rule is Celtor Chemical. It scores maximum on toxicity, persistence, quantity and has a population nearby of more than 100, but it is an inferred rather than an observed release. It has the second lowest score (the lowest scoring NPL site is the Mountain View Mobile Homes asbestos site) of the NPL sites and in fact is lower than the score for Alden mill. The Celtor Chemical site scores fairly high on direct contact, however, and is said to be a children's play area on the Hoopa Indian Reservation. Although the direct contact hazard to children does not enter into the migration score calculation, it may be the reason why this site is an exception to the selection rule.

MINING SITE CHARACTERISTICS LEADING TO LISTING

In summary, the way the Mitre model treats mining sites can be represented by the equation:

Mitre Model Score	=	Observed Release Score	x	Quantity Toxicity, Persistence Score	x	Population Score

As illustrated in fig. 2:

- Mining sites almost automatically receive the maximum quantity, toxicity, persistence score based on total amount of tailings, spoils, slag or discharge and on the presence of small amounts (relative to bulk waste) of metals, etc. Of the 31 sites, 26 had maximum or next-to-maximum scores in some pathway for this factor.

- A mining site which is nominated for the NPL will tend to have maximum score for an "observed release" in at least one pathway (27 of the 31 did) because only sites that have been previously studied tend to be nominated and any concentration measurement above background (no matter how small) constitutes an observed release.

- With maximum scores in these two areas, the total score will be high enough for listing on the NPL unless there are virtually no people in the area. Twenty-five out of 31 sites had more than 100 people within three or four miles.

WHY 14 SITES WERE NOT LISTED

Table 3 presents the specific reasons, in terms of the three factors comprising the rule, why the 14 non-NPL sites failed to score high enough for listing. Results are given only for the highest scoring pathway.

Lack of an observed release and little or no population nearby are the most common reasons for low scores. Of the five cases where quantity and toxicity/persistence scores were not (near) maximum, two of the sites were tram sites and the quantity of waste is actually relatively small. At another two of the five sites, the toxicity and persistence scores were based on sulfuric acid and cyanide rather than trace metals in the waste. Had the scorer selected metals, maximum toxicity/persistence scores would have been achieved.

VALIDITY OF MODEL APPLICATION TO MINING

After reviewing the 31 sites nominated for the National Priorities List, the authors of this paper are convinced that what distinguishes NPL sites from non-NPL sites is not primarily degree of hazard. Rather, the distinction is based mainly on how much prior study has been done at a site and how rural the surroundings are. It could be argued that both of these factors correlate to some extent with degree of hazard. This is true, but the model then must be viewed as assessing risk in an extremely indirect way.

As has been noted, special characteristics of mining sites that contribute to high Mitre model scores are the large amounts of waste involved and the presence of trace metals in the waste. These characteristics tend to produce maximum scores in one of the three scoring areas--ground water, surface water or air. Thus, scores in the other two areas that are too small to produce listing at a chemical dump may be sufficient to list a mining site.

It is concluded that the Mitre model is not a useful tool for assessing or ranking hazards at mining sites because the score is produced by factors which have little to do with the actual hazards at the site. The Mitre model seems to have been developed with chemical dumps in mind. In that context, its scoring system may be more useful. For example, maximum quantity of waste may indicate more than 10,000 drums of chemical present rather than, as for mining, more than 2500 tons of spoils, slag or tailings. Maximum toxicity at a chemical dump may indicate presence in concentrated form of very toxic or carcinogenic compounds rather than, as at many mining sites, the normal or unconcentrated elements in the earth at the site.

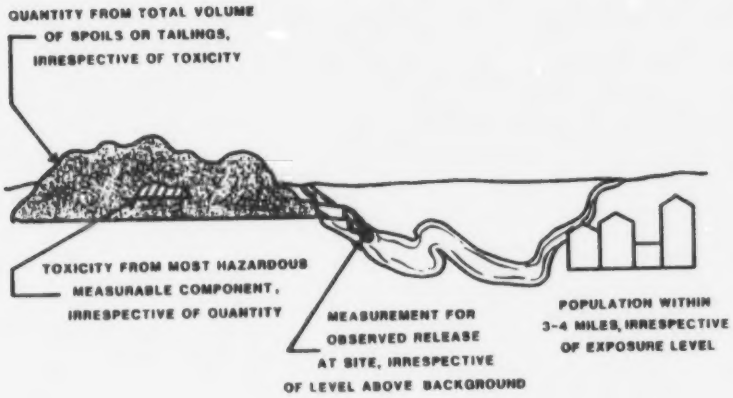

Figure 1. Overview: Mitre Model Methodology

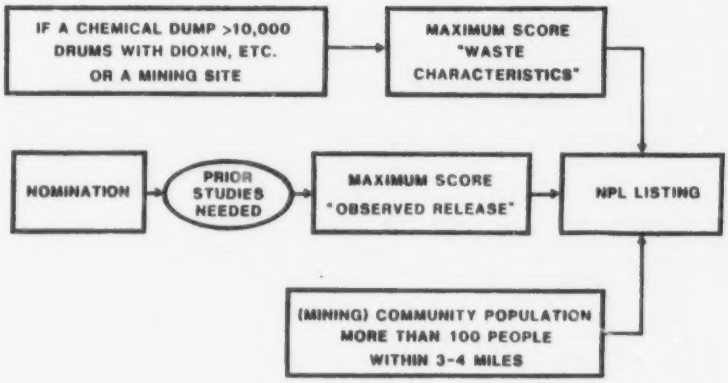

Figure 2. National Priorities List (NPL) Overview: Mitre Model Logic

TABLE 1

SITES ANALYZED

NPL Sites	Mining Activity[2]
1. Anaconda Smelter Anaconda, MT	Copper smelter
2. Bunker Hill Smelter Smelterville, ID	Lead and zinc smelter
3. California Gulch Leadville, CO	Metal mines
4. Celtor Chemical Humboldt County, CA	Metals reclamation mill
5. Central City - Idaho Springs Clear Creek and Gilpin Countries, CO	Gold mines
6. Commencement Bay Tacoma, WA	Metal smelting
7. Homestake Mining Milan, NM	Uranium mill
8. Iron Mountain Mine Shasta County, CA	Copper mines
9. Millitown Reservoir Millitown, MO	Copper mines and smelter
10. Mountain View Mobile Homes Globe, AZ	Asbestos mills
11. Palmerton Zinc Palmerton, PA	Zinc refinery and smelter
12. Silver Bow Creek Silver Bow and Deerlodge Counties, MT	Metal mines and mill
13. Tar Creek - Kansas Cherokee County, OK	Lead and zinc mines
14. Tar Creek - Oklahoma Ottawa County, OK	Iron and zinc mines
15. United Nuclear Churchrock, NM	Uranium mill
16. U.S. Titanium Nelson County, VA	Mine and refinery
17. Whitewood Creek Black Hills, SD	Gold mines and mill
Recommended by States but Not NPL Sites	
18. Alder Mill Twisp, WA	Metals mill
19. Anaconda Copper Weed Hts, NV	Copper mine
20. Anaconda Refinery Great Falls, MT	Copper and zinc refinery
21. ASARCO Globe Facility Commerce City, CO	Metal recovery (smelting)
22. Blackbird Mine Cobalt, ID	Mine
23. Gateway Mill site Gateway, CO	Vanadium mill
24. Hendricks Mine Boulder, CO	Radium and fluorspar mill
25. Golden Mine Golden Village, WA	Metals mine
26. Loma Mill Loma, CO	Vanadium mill
27. Placerville Tram Placerville, CO	Vanadium tram/ore bin
28. Rio Tinto Mountain City, NV	Copper mine
29. Sawpit Tram Sawpit, CO	Vanadium tram/ore bin
30. Silver Mountain Mine Loman, WA	Gold and silver mine
31. Vanadium Mill Site Vanadium, CO	Vanadium mill

2 This is the mining activity mainly responsible for the Matrix Model score. At some sites, non-mining uses also contribute to the score. At other sites, the use has now changed from that listed.

TABLE 2

SENSITIVITY ANALYSIS FOR 17 NPL SITES

	Parameter Importance				
	1st	2nd	3rd	4th	5th
"Observed release"	16	1	-	2	4
Distance to well or intake/population	-	12	5	1	3
Toxicity, persistence	-	4	11	2	-
Quantity	-	-	1	8	4
Water/land use	-	-	-	3	4
Containment	1	-	-	1	1

TABLE 3

REASONS WHY 14 MINING SITES ESTIMATED HERE NOT SELECTED FOR THE NATIONAL PRIORITIES LIST -- PROPERTIES OF HIGHEST SCORING PATHWAY

Site Number	No Observed Release	Less Than (Near) Max. Quantity and Toxicity	Population Within 100	Less Than 3-9 Miles	Other
18			X		X[7]
19			X		
20			X		
21	X				
22			X		
23	X				
24	X				
25		X	X		
26	X				
27	X	X[8]			
28	X	X[9]			
29	X	X[9]			
30		X[10]			
31	X		X		
TOTAL	8	5	6		1

[7] "Unproven Arsenic Content of Waste," see text.
[8] Tram site
[9] Based on sulfuric acid not metals.
[10] Based on cyanide solution not metals.

CHAPTER 8

DEVELOPING A COOPERATIVE APPROACH TO ENVIRONMENTAL REGULATION

In the past in the U.S.A., when a representative of the environment protection agency introduced the purpose of his visit as, "I am here to help you," this invariably led to a series of problems and new cost items for the operator of a mine or mill. This happened so often that the EPA man's, "I am here to help you," has become ingrained in the joke about the three most commonly used lies.

When a mining company opens its doors to the EPA, the information gained by the regulator may result in more expense and problems for that company. The older generation of senior mining company management has pretended for so long that if one ignores the problems presented by regulators, they will go away.

Consequently, since the mining industry was not exactly forthcoming in helping regulators develop the means to cause them grief, the regulatory movement had to develop its own information and effluent treatment technology. When regulations based on this technology were imposed on industry, industry lawyers emphatically claimed that the rules and technology for treatment requirements imposed were out of context.

Mining companies and the American mining industry through the American Mining Congress has sued the EPA many times over proposed or promulgated regulations. The EPA and state governments have and are suing numerous mining companies over environmental damage at their operations. Throughout all this, private environmental organizations have become intertwined in the action suing both the EPA and the mining companies who have involved themselves by voicing objections at virtually every public hearing held to discuss a mining company permit application or proposed new regulation.

The result, in the U.S.A. at least, is a degree of bitterness and a general spirit of mistrust and confrontation between mining companies, regulators, and environmental groups. Even within the mammoth regulatory bureaucracies, there is a well-ingrained hierarchy in each division and group and some degree of mistrust between one bureaucratic group and another, or between the regional offices and Washington, or one branch of government and another, as each possessively guards its area of jurisdiction or invades for that of another. The result is not constructive and does not serve the environment, the people, or the mining industry's best interests.

It is high time to spend whats left of shrinking resources available on the environment itself rather than on supporting huge hierarchial bureaucracies with overlapping responsibilities, especially rather than on litigation and lawyers.

All groups need to find some common ground and work together toward the common goal of minimizing, as far as cost effective, the impact of mining and mineral processing on the environment.

In this context, the following paper by EDELMAN and WALLINE (1982) is refreshing and deserves a chapter on its own in this report.

LAURENCE H. EDELMAN*
ROBERT E. WALLINE†

Developing a Cooperative Approach to Environmental Regulation[1]

Amidst charges and counter-charges concerning the efficacy of the United States Environmental Protection Agency's (EPA's) enforcement efforts, it is all too easy to lose sight of the real issue, environmental results. While the rhetoric often centers on numbers of enforcement cases filed and amounts of fines collected, from a technical viewpoint, a better measure of effectiveness is the number of environmental problems solved and the degree of positive environmental benefits achieved.

The case of *U.S. v. Homestake Mining Company*[2] is illustrative of the potential benefits to be derived from developing a cooperative approach to solving an environmental problem. This article traces the history of the Homestake case from its genesis as an EPA enforcement action, through a confrontational litigative phase involving eight separate civil proceedings, to its resolution in an innovative Consent Decree that holds the promise for development by Homestake of a state-of-the-art water pollution treatment system.

I. HISTORICAL BACKGROUND

The Black Hills of South Dakota is an area rich in mining history. Though overshadowed by tales of the California Gold Rush, the 1874–79 rush in the Black Hills was proportionately of equal magnitude.[3] Spurred by reports of the Custer expedition's gold discoveries in 1874, miners flocked to the Central and Northern Black Hills locating placer claims on the streams, and later, staking out lode claims seeking the gold ore from which the placer deposits had originated.

In 1876 an outcrop of gold ore, Homestake Lead, was discovered in an

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The views expressed herein are those of the authors and do not necessarily represent those of EPA.

[2]Civ. No. 78-5094 (D.S.D. 1978).

[3]The colorful history of South Dakota's gold rush and the Homestake mine is portrayed in PARKER, GOLD IN THE BLACK HILLS, University of Oklahoma Press (1966), and DEADWOOD: THE GOLDEN YEARS, University of Nebraska Press (1981).

area now encompassed by the town of Lead, South Dakota. By 1877 the Homestake Mining Company had been incorporated by California investors led by George Hearst, and the Homestake was to become the financial foundation of the Hearst publishing empire.

Early mining at Homestake was done on the surface in open cuts, but underground mining followed closely. On-site milling began in 1878 with the use of stamp mills. Gradually, the Homestake mine and mill complex expanded and modernized, becoming what is today the largest gold-producing facility in the Western Hemisphere.

Mineral development in the Black Hills was not without significant environmental impacts. The smaller mining operations resulted in erosion and leaching of metals into the streams and rivers. Homestake, following the traditional mining practice, discharged its untreated mining and milling wastes directly into Gold Run Creek, a tributary of Whitewood Creek and the Cheyenne River drainage. In 1881 the Territory of Dakota recognized by law the local customs providing for use of streams for mining and milling purposes, including waste disposal. Later, Whitewood Creek was classified for industrial waste disposal pursuant to South Dakota state law.[4] One historical account of the environmental impact created by the Black Hills mining rush contains this vivid description:

> The pollution produced by the Homestake—and indeed by all of the mines—first stained the creek waters red from the cement ores and placers, then grey with the slimes of the mills, and the reek of cyanide hung over the valleys of Deadwood and the Whitewood like a curse.[5]

Not only did Whitewood Creek bear the impact of Homestake's effluent, but the towns of Lead and Deadwood also discharged their raw sewage to the creek. By 1976 the use of Whitewood Creek as an open sewer for mill tailings, toxic chemicals, and municipal waste had become a one hundred year tradition.[6] Even the oldest citizens of the area could not recall a time when the stream had supported aquatic life.

II. BREAKING WITH MINING TRADITION—IMPACT OF THE FEDERAL WATER POLLUTION CONTROL ACT

During the 1960s general public awareness of environmental issues heightened. This new environmental consciousness and desire for environmental quality spread west to confront the time-honored traditions of the

[4]South Dakota 1935 Session Laws, chapter 174 § 4; SDCL 46-25-5 (1967).

[5]PARKER, DEADWOOD: THE GOLDEN YEARS, *supra* note 3 at 112.

[6]In November, 1981 South Dakota nominated a portion of Whitewood Creek as its number one priority for investigation under the Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S.C. 9601 (Superfund). In August, 1982 EPA, Homestake and South Dakota entered into a voluntary agreement to study the potential hazardous environmental effects of the tailings historically deposited in and along the stream.

miners. By the mid-1950s there appeared to be a general consensus among the Lead-Deadwood locals that the discharge of Homestake's untreated mining wastes and the raw municipal sewage to Whitewood Creek was unacceptable. Discussions among local, state, federal, and company officials concerning the Whitewood Creek water pollution problem, took place throughout this period but no remedial actions resulted.

Not until passage of the 1972 Federal Water Pollution Control Act Amendments (FWPCA) was a regulatory process established that would change past practices.[7]

The National Pollutant Discharge Elimination System (NPDES) permit program created in section 402 of the FWPCA[8] required Homestake, for the first time, to obtain a federally enforceable permit for the discharge from its operations. Moreover, by the July 1, 1977, statutory deadline, Homestake's discharge was to meet effluent limitations derived from the technology-based guidelines set by EPA, as well as potentially more stringent water quality standards based on classification of Whitewood Creek as a fishery by South Dakota in accordance with section 303 of the FWPCA.[9]

Homestake's NPDES permit was issued by EPA on September 3, 1976. The permit established effluent limitations for total suspended solids, cyanide (which is present in the discharge because of the use of a cyanidation milling process), and heavy metals and incorporated the July 1, 1977, compliance date of the FWPCA.

For Homestake attaining compliance with the requirements of the FWPCA would prove no small task. Elimination of the mill tailings discharge necessitated construction of a major $25 million tailings impoundment in Grizzly Gulch. In addition to eliminating the tailings discharge, a final treatment system for suspended solids, cyanide, and heavy metals was necessary to treat the remaining wastewater discharge. Given the magnitude of such an undertaking, Homestake, like many major industrial dischargers, did not meet the July 1, 1977, FWPCA deadlines.

In late 1977, EPA and Homestake entered into a Consent Decree and Stipulation, *U.S. v. Homestake Mining Company*,[10] that allowed Homestake a time extension to complete its tailings impoundment by December 1977 and the necessary treatment system by April, 1978. Homestake completed the multimillion dollar tailings pond on schedule and began diverting the tailings discharge to Grizzly Gulch.

[7] 33 U.S.C. 1251 *et seq.* (1976) The FWPCA was significantly amended in 1977 by Pub. L. No. 95-217, 91 Stat. 1566 (1977) and is now commonly referred to as the Clean Water Act.

[8] *Id.* at § 1342.

[9] The FWPCA also forced construction of a municipal wastewater treatment system for Lead-Deadwood.

For detailed judicial summary of the FWPCA's regulatory provisions and the interrelationship between technology-based limitations and state water quality standards, *see* EPA v. California *ex rel.* State Water Resources Control Board, 426 U.S. 200 (1976); United States Steel Corp. v. Train, 556 F.2d 822 (1977).

[10] Civ. No. 78-5002 (D.S.D. 1977).

The treatment system, however, was another story. Homestake's traditional mode of operation with its emphasis on production provided a minimum of staff for pollution control. The design of the original treatment system was attempted by Homestake production staff who drastically underestimated the complexity of the wastewater treatment problem. Reality became painfully clear when the ozonation unit, which Homestake initially installed for cyanide destruction, actually resulted in more cyanide in the effluent than was going into it in the untreated wastewater.

With the dismal failure of its treatment system Homestake was in violation of the Consent Decree and faced not only stipulated penalties, but also fines for violations of permit limits on expiration of the Decree. Homestake, therefore, requested that EPA modify its permit to relax critical limitations and subsequently also moved the district court for relief from the Decree, touching off what was to become a Donnybrook of litigation involving EPA, Homestake, and South Dakota.

III. FROM LEGAL CONFRONTATION TO TECHNICAL COOPERATION.

EPA denied Homestake's NPDES permit-modification request on the basis that Homestake had not shown any new evidence supporting a modification. Homestake petitioned the court of appeals for review of EPA's decision, but that petition was subsequently dismissed as time-barred.[11]

Meanwhile, the federal district court had granted Homestake's motion for relief from the Consent Decree under Rule 60(b) of the Federal Rules of Civil Procedure. EPA responded by appealing the court's ruling, and later filing a separate civil enforcement action in the district court, for penalties and injunctive relief based on Homestake's continuing NPDES permit violations after the Consent Decree had expired on July 1, 1978.[12] South Dakota intervened as plaintiff. Homestake countered by challenging EPA's approval of South Dakota's water quality standards and by directly challenging the South Dakota standards in state court.[13]

[11] Homestake Mining Company v. EPA, 584 F.2d 862 (8th Cir. 1978). The court refused to address either the merits of Homestake's petition or EPA's position that its denial of the permit modification request was unreviewable. The court found that Homestake's petition was four days late, even when calculated from the date of EPA's denial, and, hence, dismissed the petition.

[12] In U.S. v. Homestake Mining Company, 595 F.2d 421 (8th Cir. 1979), the court vacated the district court's order granting Homestake relief from the Consent Decree. The court ruled that Homestake was not entitled to a compliance extension under section 309(a)(5)(B) of the Clean Water Act, because its permit limitations were governed by state water quality standards rather than technology-based guidelines. The court, however, did not rule out a future good faith equitable defense by Homestake under Rule 60(b).

[13] In Homestake Mining Company v. EPA, 477 F. Supp. 1279 (D. S.D. 1979), the district court upheld EPA's approval of South Dakota's water quality standards under 33 U.S.C.

During the course of all this legal maneuvering, it became clear to EPA, Homestake, and South Dakota officials involved that little was being gained by any party or the public. From Homestake's perspective, the litigation was not successfully providing any basis for long-term corporate planning, and it certainly was not aiding its corporate image. Moreover, Homestake's potential liability in civil penalties was growing by the day. From EPA's and South Dakota's perspectives, the litigation was not producing any tangible environmental results, and it was merely delaying constructive efforts to address the technical problems in engineering a wastewater treatment system that would treat effectively the cyanide and heavy metals in Homestake's effluent.

Several meetings were held among EPA, Homestake, and South Dakota during which a clear change in attitudes became apparent on both sides of the negotiating table. The discussions began to center, not on the legal positions, but on the technical issues. The lawyers holstered their six-shooters as the engineering staffs explained that the chemistry of Homestake's effluent was posing unique treatment problems.

As an outgrowth of this new attitude, the respective technical staffs arranged to meet for candid technical discussions without the lawyers present. They agreed that a solution to the treatment problem would require a major research and development program by Homestake, and further recognized that the treatment process development would be most productive with the close involvement of EPA and South Dakota. All parties agreed that pending litigation should be settled, and the lawyers were charged with drafting what was to be characterized as an "engineer's" Consent Decree that would maximize engineering flexibility within the confines of an enforceable document. As part of the settlement Homestake would also pay a stipulated fine of three hundred and ninety thousand dollars, of which three hundred and fifty thousand dollars would go to South Dakota for a Whitewood Creek rehabilitation project.

IV. THE TECHNICAL PROBLEM

Because the Homestake facility at Lead is a combined mine/mill complex, Homestake uses the excess mine water (which must be pumped from the mine) and recycled process water from the tailings pond[10] in its milling process. The net volume of mine water, however, exceeds the mill's requirement for process water, thereby preventing total recycle and necessitating a

§ 1313(c)(2), finding that, under the FWPCA, states could adopt stringent technology-forcing standards without necessarily considering economic and social factors. In Homestake Mining Company v. Board of Environmental Protection, S.D., 289 N.W. 2d 561 (1980), the South Dakota Supreme Court reversed and remanded on procedural grounds a circuit court decision that had generally upheld South Dakota's standards. The circuit court action was later settled.

[10]The mill tailings consist of the ground ore remaining after the gold has been removed. The tailings are transported in slurry form and the water in the slurry contains heavy metals and process reagents, principally cyanide.

discharge. Homestake's discharge consists of a mixture of mine water and tailings pond decant water. While the mine water is of comparatively better quality than the decant water, it also contains heavy metals and cyanide. The mine water picks up cyanide from the sand fraction of the mill tailings that are used in the mine to backfill open areas. As cyanide drains from the filled areas, it mixes with other mine water.

When Homestake's NPDES permit was developed, the flow limit and effluent limitations were based on the more stringent of either the existing Best Practicable Technology (BPT) guidelines or the numeric limits calculated to comply with the State Water Quality Standards for a fishery. For the most part, the water quality standards were controlling. Table I shows a comparison of these values.

TABLE I

Parameter	BPT Limit (40 CFR 440.22)* mg/l	WQS Limit mg/l	Permit
Total Suspended Solids	30	10	10
Arsenic	N/A	0.38	0.38
Cadmium	0.1	0.00025	0.00025
Chromium	N/A	0.85	0.85
Copper	0.1	0.009	0.009
Lead	0.4	0.28	0.28
Mercury	0.002	0.001	0.001
Nickel	N/A	1.25	1.25
Silver	N/A	0.001	0.001
Zinc	1.0	0.020	0.020
Cyanide	0.02	†	0.02
pH	6 to 9	N/A	6 to 9

*40 Fed. Reg. 51722 (Nov. 6, 1975).

†"Quality Criteria for Water," United States Environmental Protection Agency (July 1976), indicated that an instream value of 0.005 mg/l total cyanide would be necessary to protect fresh water aquatic life. With the available dilution ratio, this would require an effluent limitation of approximately 0.017 mg/l.

All parties originally recognized that Homestake's effluent limitations were very stringent. Such stringent limits are often necessary on water quality limited streams. However, the relatively high quality of Homestake's untreated waste stream initially appeared to offer an advantage in designing a conventional treatment system using settling, ozonation (oxidation), and carbon adsorption.

When Homestake's ozonation system resulted in high cyanide levels in the effluent, it was discovered that the untreated wastewater actually included heavy metals, cyanide, metal-cyanide complexes, and thiocyanate (sulfur bound to a cyanogen group, SCN). It became clear that a system designed for heavy metals alone and cyanide alone was not going to effec-

treatment system to treat heavy metals and total cyanide in its effluent. The Decree contained no specific effluent limit goals because it was implicit that the system constructed would have to enhance the state-of-the-art even to approach permit limits. Under the Decree Homestake would provide monthly progress reports to EPA and the state, and technical representatives of both agencies would attend quarterly meetings with Homestake to discuss and evaluate the results of the company's research. This was to be a completely open development process.

Although the Decree contained a target date for construction of a treatment system, the critical path approach also necessitated provisions for intermediate decision points to allow for additional time and investigation of promising alternatives. Paragraph III, 4.(e) of the Decree provided:

> Compliance dates for construction of a treatment system may be extended if, by March 1, 1980, Homestake's research has identified a promising technology that is mutually determined to be worth pursuing, or if additional time is then mutually agreed to be necessary before process design can begin. In the event the process developed is mutually judged to be of sufficient complexity that the listed times are insufficient for adequate engineering, pilot plant testing, detailed process design, construction and operational startup, an additional mutually agreed upon extension may be granted.

For this Decree to work, the candid exchange of information among the parties would be essential. Reliance on such cooperation was a gamble but all parties agreed it was worth the effort. The Decree was approved and entered by the court on February 12, 1980.

VI. PROGRESS UNDER THE DECREE

Homestake's initial research effort involved numerous consultants, Homestake's corporate and local staff, Environment Canada, South Dakota, and EPA. The focus of its research included every known cyanide destruction technique and evaluated the potential application of those techniques to Homestake's effluent. The following technologies were evaluated in detail:

- Ozonation
- Air Sparging/Acidification/Volitization
- Ion Exchange
- Alkaline Chlorination
- Prussian Blue Precipitation
- Hydrogen Peroxide:
  - a. followed by lime precipitation
  - b. followed by ion exchange
  - c. followed by ferric ion addition
- Biodegradation

Simultaneously, analytic methodologies were developed that would accurately measure the cyanide in Homestake's effluent.

tively treat a waste stream that contained significant amounts of metal-cyanide complexes and thiocyanate. To further complicate the situation, Homestake also discovered that the EPA-approved analytic method for measurement of total cyanide was inaccurate at the levels contained in the permit because of the complex chemistry of the effluent. Homestake was thus faced with both a major treatment problem and an analytic problem.

V. THE LEGAL PROBLEM, DRAFTING AN "ENGINEER'S" CONSENT DECREE

The technical problems posed by the chemistry of Homestake's effluent also created some difficult regulatory problems. Since Homestake would be researching and attempting to develop a system that was beyond the current state-of-the-art, any workable agreement among the parties had to recognize the uncertainties inherent in the scientific process and provide for engineering flexibility. At the same time it was essential that the regulatory agencies be plugged into the process to assure themselves of the integrity of the research and development effort. The lawyers, therefore, agreed to draft the Consent Decree to reflect engineering objectives and a critical path approach.

From EPA's perspective, however, the legal problem in adhering to the engineering objective was that the uncertainty of engineering reality in this case ran square against EPA's policy requiring that Consent Decrees always specify the ultimate numerical standard or level of performance that a source must meet.[11] This EPA policy is based on a premise that Consent Decrees should not be used, or appear to be used, as a legal substitute for regulatory or statutory change. Nevertheless, EPA recognized after much internal debate that the environmental objective for purposes of this Consent Decree was to have Homestake design, build, and operate the best state-of-the-art treatment system possible, and that no one could realistically predict what level of effluent that system would ultimately produce. In other words, while no one could anticipate whether Homestake's system would ultimately meet the stringent numeric water quality limitations contained in its NPDES permit, from the standpoint of environmental results it was preferable to reach agreement on constructing the system and evaluating its performance capability. The complex legal issues of enforcing or modifying Homestake's permit could then be dealt with after the Consent Decree terminated, when an operational system would be on line and actual performance data available.

With the environmental results objective in mind, the lawyers defined the ultimate goal of the Decree simply as construction by Homestake of a

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[11] The EPA policy requiring that Consent Decrees specify ultimate standards or levels of performance was reaffirmed in EPA's "Guidance for Drafting Judicial Consent Decrees" May 12, 1983.

Detailed process development focused on a chemical system based on hydrogen peroxide. The chemical system looked as though it would produce a reasonably good effluent, but it would be very costly to operate and would not remove the thiocyanate. Almost as an incidental part of its research, however, Homestake was looking at biological pretreatment as a possibility for reducing operating costs of the chemical system in the future. During this program, Homestake discovered that certain bacteria from the mine have an affinity for cyanide. Further investigations showed that these bacteria could actually be seeded on rotating biological discs similar to those employed in treatment of municipal wastewater, and a highly promising and efficient form of biological cyanide destruction could be achieved. This process would also remove thiocyanate and a substantial portion of the remaining heavy metals.

Since EPA and South Dakota technical staff had been active participants in the Homestake treatment process development, they were well aware of the significance of Homestake's preliminary tests using bacterial treatment.

In June 1981 Homestake presented a proposed engineering/construction schedule premised on the lead times necessary for development of a biological treatment system. The proposal also stated that the chemical system that had been developed would still be implemented if further development of the biological system should run into serious problems. The schedule projected a mid-1984 completion date. While the 1984 date would entail a substantial extension of the original September 1981 compliance date in the Consent Decree, the technical staffs of all parties unanimously agreed that the extension was warranted under paragraph III, 4. of the Decree. The Decree was, therefore, modified and approved by the court on January 24, 1983.

To date Homestake had authorized nearly $7 million for biological treatment plant construction and equipment purchases. The results of continued pilot testing look highly promising.

With the elimination of Homestake's tailings and the untreated municipal sewage from Lead/Deadwood, Whitewood Creek today runs clear and supports basic aquatic plants and insects. But the final chapter in the stream's recovery is yet to be written. If Homestake's biological treatment system is completed on schedule and proves effective, Whitewood Creek may, after one hundred years of sterility, once again support a fishery. Whether this goal is attained remains to be seen, but without the cessation of legal confrontation and the resulting cooperative effort by EPA, Homestake, and South Dakota, the current prospect for recovery of Whitewood Creek would not be nearly as likely. Given the progress that has been demonstrated to date, there is certainly room for optimism. There is a great deal at stake in the continued success of this cooperative approach to environmental regulation that may go beyond Whitewood Creek to serve as a model for resolution of complex environmental problems in the future.

CHAPTER 9

KEY CONTACTS AND EXPERTS ON REGULATIONS CONCERNING EFFLUENTS AND SOLID WASTE DISPOSAL

It is not always easy to determine the status of environmental protection regulations for a particular proposed mining operation as these pertain to effluents, mine and mill waste disposal, etc.

The following list of names and addresses is a long way from complete, nor has it set out to be complete. What is is is a list of those people who came to the attention of RANDOL INTERNATIONAL LTD. during the course of this investigation.

Starting with these contacts, it should be possible to auger into further contacts.

One source of information is, of course, the regulatory authority involved. However, it was the author's experience that sometimes just finding out what state department has jurisdiction over a particular water quality aspect is a time-consuming undertaking in the U.S.A.

In South Africa and Canada, it is a much more straightforward matter to find the appropriate government contact, and one is certainly dealing with fewer of them to achieve a given goal.

Miss Penelope Hansen	Manager, Analysis Assessment Program Solid Waste Division Office of Solid Waste U.S. Environmental Protection Agency Washington, DC	(202) 382-7917
S. Jackson Hubbard	Resource Extraction and Handling Division Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	
William Telliard	Chief, Energy and Mining U.S. Environmental Protection Agency Washington, DC	(202) 382-7131
Geoffrey Bennett	Director Effluent Guideline Division U.S. Environmental Protection Agency Washington, DC	

Rod Dwyer	Solid Waste Disposal American Mining Congress #300, 1920 N Street NW Washington, DC 20036	(202) 861-7530
John Austin	Vice President American Mining Congress #300, 1920 N Street NW Washington, DC	
Doug McAllister	Water Quality Issues American Mining Congress #300, 1920 N Street NW Washington, DC	(202) 861-2878
James R. Walpole	Partner Holland & Hart #1200, 1875 I Street NW Washington, DC 20006	(202) 466-7340
	Division of Health, Siting, & Waste Management U.S. Nuclear Regulatory Commission Washington, DC 20555	

California:

Jim Pappas	Senior Engineer California Dept. of Health Services Hazardous Waste Management Branch 4250 Power Inn Road Sacramento, CA 95826	(916) 739-3141
Ray Hunter	Director California Mining Association Post Office Box 3 Jackson, CA 95642	(209) 223-1129
Roger E. Nelson	Utah International, Inc. 550 California Street San Francisco, CA 94104	(415) 981-1515

James Good	Attorney and Chairman Committee on Hazardous Wastes California Mining Association c/o Grisham, Barnard, Savage, Knowlen & Tilden 398 West Fourth Street San Bernardino, CA 92401	(714) 884-2171
	The Chairman Water Resources Control Board 1416 Knight Street Sacramento, CA	(916) 322-8353
Ray Walsh	Chief Division of Water Rights 1416 Knight Street Sacramento, CA	(916) 324-5619
	Dept. of Conservation 1416 Knight Street Sacramento, CA	(916) 322-7683
John Hannum	North Coast Water Quality Control Board Santa Rosa, CA	(707) 576-2220
Dennis Goldstein	Attorney Homestake Mining Company 650 California Street San Francisco, CA 94108	(415) 981-8150
David B. Crouch	Director of Environmental Control Homestake Mining Company 650 California Street San Francisco, CA 94108	(415) 981-8150
Jim Petrie Dennis Herman	State of California Regional Water Quality Control Board Redding, CA	(916) 246-6376
Craig M. Wilson	Staff Counsel III State Water Resources Control Board Post Office Box 100 Sacramento, CA 95801	(916) 322-3580

Colorado:

	Colorado Dept. of Health 4210 East 11th Avenue Denver, CO 80220	(303) 320-8333
Ken Weaver	Chief, Radiation Control Division	
Ken Waesche	Division Chief, Waste Management Division	
Randy Jones	Section Chief, Waste Management Division	
Bob Shukle	Mining Water Quality	
Robert E. Walline	Chairman, Mine Waste Committee U.S. Environmental Protection Service Compliance Branch Region VIII 1860 Lincoln Street Denver, CO 80295	(303) 293-1589
Phil DeDycker	Steffen Robertson & Kirsten #210, 7510 West Mississippi Avenue Lakewood, CO 80226	(303) 936-8254
Jim V. Rouse	Envirologic Services International 2425 South Colorado Blvd. Denver, CO 80222	(303) 759-2611
Roger Olsen	IT Corporation 7400 South Alton Court Englewood, CO 80112	(303) 694-0044
A. O. Courtney	Director of Environmental Affairs #301, 9305 West Alameda Parkway Lakewood, CO 80226	(303) 232-8218
James Gilliland	Director of Environmental Control Climax Molybdenum Division AMAX, Inc. 1707 Cole Blvd. Golden, CO 80401	(303) 234-9020
Jim Kerrigan	AMAX Environmental Services, Inc. 1707 Cole Blvd. Golden, CO 80401	(303) 234-9020

Colleen D. Kelly Lynn Trozzoli	Environmental Supervisor Hecla Mining Company Post Office Box 320 Wallace, ID 83873	(208) 752-1251

Wisconsin:

Susanne Bangert	Review Engineer Bureau of Wastewater Industrial Wastewater Section Madison, WI	
Barry Hansen	Permitting Engineer Exxon Minerals Corp. Rhinelander, WI	

South Africa:

Dr. J. J. (Koos) Barnard	Directorate of Water Affairs on CSP Committee Office 614, Eloff Building 339 Paul Kruger Street Pretoria 0001 South Africa	(012) 269 208
A. Lewis, Inspector D. Cousins, Inspector Mr. Young, Inspector Mr. Neethling, Inspector	Mining and Metallurgical Dept. Dept. of the Environment Private Bag X4000 Germiston South 1411 South Africa	(011) [illegible] 47/8
Hendrik J. Best M. Erasmus	Director of Water Pollution Control The Dept. of the Environment Private Bag X313 Pretoria 0001 South Africa	(012) 299-9111
	S.A. Bureau of Standards Private Bag 191 Pretoria 0001 SABS-241-1971 Water for Domestic Supplies	

Danie J. Bosman	Anglo American Research Laboratories Post Office Box 106 Crown Mines 2025 South Africa	(011)
Johan Wagner	Rand Mines (Mining & Services) Ltd. Post Office Box 62370 Marshalltown 2107 South Africa	(011) 833-0611
A. W. Pullen	Gold Fields of South Africa Ltd. Post Office Box 1167 Johannesburg 2000	(011) 639-9111
Dr. Ron Squires	Binnie & Partners, Inc. Box 23040 Joubert Park Johannesburg South Africa	(011) 802-4230
A. T. Alexander	Environment & Services Research Dept. AECI Ltd. P.O. Northrand 1645	(011) 608-1201
Dr. Ravenscroft	Dept. of Water Affairs Windhoek South West Africa - Namibia	
Piet E. Odendaal	Senior Advisor Water Research Commission Post Office Box 824 Pretoria 0001 South Africa	(012) 28-5461
Okkert Fourie	Deputy Director of Hazardous Substances Dept. of Health & Welfare Private Bag X63 Pretoria 0001 South Africa	(012) 28-2851

John Fitzgerald	Environmental Attorney Gold Fields Mining Company #500, 200 Union Blvd. Lakewood, CO 80226	

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George M. Obeldobel	Manager, Projects Development St. Joe International Corp. 250 Park Avenue New York, NY 10017	

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Bruce Leavitt Donald Ross Baker	Consolidation Coal Company 1800 Washington Road Pittsburgh, PA 15241	

Arizona:

Brad Mueller	Bureau of Water Quality Control Arizona Dept. of Health Services 1740 Adams Street Phoenix, AZ 85007	(602) 255-1172

Idaho:

Dr. John R. Moeller	Source Control Field Office Dept. of Environment State of Idaho 1118 F Street Lewiston, ID 83501	(208) 799-3430

Canada:

James S. Scott	Chief Water Pollution Control Directorate Environment Canada Place Vincent Massey Hull, Quebec K1A 1C8	(819) 997-2270
John Hawley	Head, Mining & Metallurgy Water Resources Branch Ontario Ministry of the Environment 135 St. Clair Avenue West Toronto, Ontario	(416) 965-6954
Dr. Frank Frantisak	Noranda Mines Ltd. Post Office Box 45 Commerce Court West Toronto, Ontario Canada M5L 1B6	(416) 867-7111
Hennie Veldhuizen	Noranda Mines Ltd. Post Office Box 45 Commerce Court West Toronto, Ontario Canada M5L 1B6	(416) 867-7111
John K. Weglo	Falconbridge Nickel Mines Ltd. Falconbridge, Ontario Canada P0M 1S0	(705) 693-2761
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John Halton Rick Besner Gordon Miller	Ontario Ministry of the Environment 83 Algonquin Street West Timmins, Ontario Canada p4N 2R4	(705) 264-9474
Joe Anderson	Head - Environment Key Lake Mines Ltd. Saskatoon, SK	(306) 665-7000

Al Vivyurka	Chief Environmental Engineer Rio Algom Mines Ltd. Post Office Box 1500 Elliot Lake, Ontario Canada P5A 2K1	(705) 461-1800
Dr. Stewart Warner	Vice President, Environment Ince Ltd. Toronto, Ontario	(416) 361-7511

England:

A. K. Barbour	Environmental Scientist RTZ Services Ltd. York House Bond Street Bristol BS1 3PE	(0272) 428809

Australia:

Barry T. Hart	Dept. of the Environment Water Research Council Canberra Australia	

Brazil:

Dr. Mario Beer	Natron Consultoria e Projetos S.A. Environmental Control Dept. Rua Teofilio Otoni 63-11 Andar 20090 - Rio de Janeiro RJ	Telex: 021-23510
Dr. Paulo Campos Gimenez	Natron Consultoria e Projetos S.A. Environmental Control Dept. Rua Teofilio Otoni 63-11 Andar 20090 - Rio de Janeiro RJ	Telex: 021-23510
	Secretaria Especial do Meio Ambiente Av. W-3 Norte Quadra 510 70.570 Brasilia DF	(061) 1429

	Departamento Nacional de Producao Mineral Setor de Autarquias Norte Q-01, Bloco B - 2 Andar 70.040 Brasilia DF	(061) 1116 (061) 1545

Sweden:

Torbj RN G. Ranssont	Boliden Mineral AB S-93600 Boliden Sweden	(0910) 60600
	Koncessionsnamden for Miljoskydd Box 34067 S-10026 Stockholm Sweden	
	Stockholms Tingsratt Vattendomstolen Box 510 S-10126 Stockholm Sweden	

CHAPTER 10

COMPUTING WATER AND SALT BALANCES

Water balance modeling in mine-mill complexes would be easy were it not for problems relating to salt or contaminant buildup to levels that either present an effluent discharge problem (i.e., because they do not meet effluent discharge permit requirements) or because they cause interferences when the water is recycled to certain parts of the mineral processing sequence. Water quality effects are also important factors in corrosion and scaling phenomena.

Consequently, in solving problems in existing plants or in designing a new operation, it has become essential in many cases to carry out salt balance modelling to examine various process and water management alternatives. Modelling salt balances represents a much bigger challenge than does water balance modelling but, of course, the two go hand in hand.

One of the problems is that when complex solutions are mixed, i.e., solutions containing a range of cations, anions, and suspended solids, and a variety of residual organic reagents, oils and greases, and surfactants, as well as dissolved gases, it is not possible to predict reliability from theoretical or classical chemistry exactly what the resulting solution composition will be; that is, unless the solutions involved are all so dilute that all the species remain in solution. However, when solutions are cascaded and recycled repeatedly as is necessary in most mine-mill complexes, salt levels in solution build up until some become saturated or even supersaturated.

When dealing with a new process, it is usually recycled water rather than fresh water that comes in contact with the ore. Of concern is the chemistry of mill solutions after they have been in contact, not only with the ore particles, but also the gangue. Ions may precipitate from solution as well as be dissolved.

To accurately predict what recycle solution chemistry at various steps in a mine-mill complex will look like with respect to both major and trace element constituents requires a huge body of empirical data on actual cases. Unfortunately, no such data bank exists, and the cost of collecting one would be beyond the means of most companies, let alone their mineral processing departments.

The closest that industry has come to being able to model salt and water balances to predict the dynamic composition changes in water management systems is the Calgon Corp.'s calgard program for power plant water recycling. Based on many hundreds of thousands of solution analyses in actual power plants around the world, Calgon has built a program on this empirical data which can predict solution compositions, their scaling

and corrosion characteristics with respect to different materials, and the dosage of various water treatment chemicals required to avoid scale or corrosion. This phenomenonally useful program and data base was developed at a cost of $6-8 million over several years, but it is not designed for mine-mill water systems.

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Frank Danihar
Bennett P. Boffardi

Amongst the companies that are working on water and salt balance modelling, two stand out as having experience in mine-mill systems:

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Russell Vandenberg

CH2M HILL
Post Office Box 91500
Bellevue, WA 98009-2050
(206) 453-5000
Jim Mavis

CH2M HILL
Post Office Box 2090
Milwaukee, WI 53201
(414) 272-2426
Michael Harris

A short description by CH2M Hill on water balance modelling approaches is inserted below.

From a more physical point of view, it has become necessary to model water balances where purely the volumes of water gained by precipitation, lost by evaporation, or with tailings in the impoundment. This is necessary to compute the amount of new water that will be needed for an operation in the dry season or in areas where there is a net evaporation, and to compute whether impoundments, runoff diversion measures, water treatment facilities, etc. are adequate for the volumes of water generated either during temporary wet seasons or from year to year as impounded water volume grows.

Many companies have the capability to compute water balance models of this sort. A schematic illustration of some of the parameters to be taken into account is provided below.

Recently, a major long-term water balance simulation was undertaken for the new McLaughlin project of the Homestake Mining Company in California. It was designed to compute the water balance and impoundment needs as well as the requirement for the

operation over a twenty-year period using various climatic assumptions--e.g., several years of drought, or several wet years with high precipitation. This useful program was developed by:

STEFFEN ROBERTSON AND KIRSTEN
7510 West Mississippi Avenue, #20
Lakewood, CO 80226
(303) 936-8254
Ian P. G. Hutchison

Dr. Ian Hutchison presented an interesting description of how this type of water balance modelling is undertaken for heap leaching operations as well as to be used as a tool in designing civil engineering aspects and tailings impoundments for conventional mine-mill complexes.

Randol International Ltd. has borrowed a water balance diagram from a tailings impoundment and drafted a table for computation of a water balance for this case as an example of how such a balance is computed for a tailings impoundment.

This table was carried around on several plant visits in the hope of collecting data to show a few examples, but it appears that this kind of data is not routinely monitored at most mine-mill sites. This type of data is used, it seems, primarily in the tailings design and permitting phases of operations.

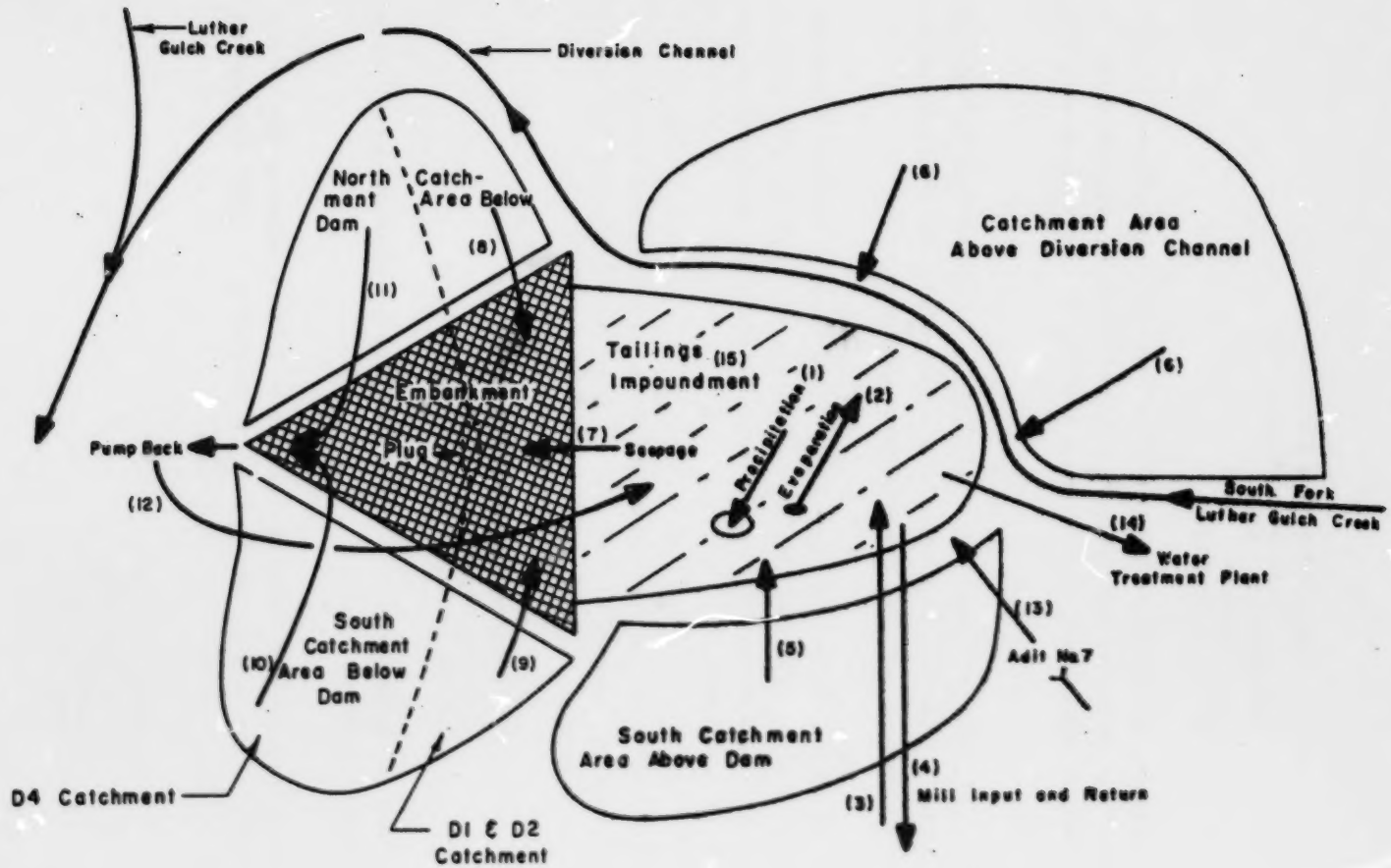
FRITZ (1984) described some practical applications in mining hydrology and howed how a desktop PC can be used as a powerful tool for water balance computing for mining operations. He can be reached at:

WESTERN WATER CONSULTANTS, INC.
Sheridan, Wyoming
Doyl M. Fritz

FRITZ (1984) Some Practical Applications of Computers in Mining Hydrology. AIME Local Chapter Meeting, Rapid City, South Dakota.

Another world leader in groundwater hydrology and water balance modeling for tailings impoundments is Dames & Moore who, in 1984, were completing a water balance for Rossing Uranium Ltd.

DAMES & MOORE
1626 Cole Blvd.
Golden, CO 8401
(303) 232-6262



NOTE: See Table 4-2 For Quantitive Values For Components.

Water Balance Data

1) Total water consumption by mill

Total tonnage of ore milled

Water consumption per tone ore milled

2) Water Balance at Tailings Impoundment

Water Balance Component	Component Number see figure	Mean annual water balance flow (gpm)	10-year recurrence wet year flow (gpm)	Comments
Inflows:				
Precipitation	(1)			
Runoff	(5)			
Tailings slurry	(3)			
Pumpback	(12)			
Other				
TOTAL				
Outflows				
Gross Evaporation	(2)			
Mill return	(4)			
Water Treatment Plant	(14)			
Seepage	(7)			
Trapped in Tailings	(15)			
TOTAL				

Notes:
1: Flow components of diverted streams are not shown in the balance. List these separately.
2: Flow component (12) is the sum of (7), (8), (9), (10) & (11) in the example diagram.
3: Typical assumed dry density of Tailings of around 65 lb/cu ft. is between initial settled density 40-50 lb/cu ft and final settled density 75-90 lb/cu ft for Grey Eagle example.

Additional Notes and Comments:

WATER BALANCE MODELING

OVERVIEW

Water and wastewater management in mine-mill complexes has become more complicated over the past two decades with the enactment of environmental regulations and conflicting demands for available water resources. Water which might previously have been discarded after limited use (for example, once-through cooling water) is now recirculated or is used as feed to another water-consuming process in the plant. Water is now discarded as wastewater only after its quality has degraded beyond the point where further use is infeasible (or the volume is too great such as in high precipitation areas).

Water recycle and cascade water reuse is generally limited by the buildup of dissolved solids or an accumulation of some troublesome constituent. For this reason, it is useful to define water management objectives in terms of both water balance and salt balance components. Consequently, the "product" of a computerized water balance modeling exercise is a forecast of the water and salt distribution at discrete points throughout a mine-mill complex, including composition-based process performance predictions (e.g., precipitation or scale formation).

PURPOSES OF WATER BALANCE MODELS

There are several common reasons for performing a water balance modeling study. The usefulness of such modeling can extend to planned and existing facilities.

Modeling is commonly used to identify water and salt related process problems during design. These problems can include scale formation, precipitation upstream of or inside sensitive process equipment, leaching or other chemical changes. Similarly, wastewater quality and quantity estimates can be made for permitting of new facilities, and the effects of process changes on wastewater quality in existing plants can be assessed when selecting among various regulatory compliance options.

A flexible model is invaluable when assessing how much water quality parameters may change with various process, meteorological, or ore grade changes (sensitivity analysis). This is important when it is necessary to minimize raw water intake or eliminate wastewater discharge.

APPROACH

Water balance modeling consists of describing the water flow diagram and salt components (ion by ion) in a "link-node" format on a computer. The nodes represent the various unit operations which in some way modify the composition or quantity of the water (and salt), and links represent flow paths (pipes) between the unit operations.

The steps involved in setting up the computer program and running it are summarized in the following basic sequence.

- Define the objective(s)--evaluate reuse options, meet pollutant discharge limits, look for potential heat exchanger scaling, or other objectives.

- Identify constraints--regulations, water quality requirements for sensitive equipment, costs, existing problems, schedule, etc.

- Prepare a process diagram indicating major piping and the unit operations. This flow diagram is then introduced into the computer in link-node format.

- Prepare a water balance by identifying sources and sinks of water, assigning flowrates to the links, describing the water balance relationship around each node (unit operation), and finally, setting conditions for water balance closure around the mine-mill complex.

- Prepare a salt balance by selecting the important dissolved species, choosing "sampling" locations in the link-node diagram that permit salt balance closure, and using experimental data bases (<u>not</u> theoretical simulations). Enter into the computer program the effect that each unit operation has on each constituent in the water, set criteria for calling out special attention such as scale formation, and impose the requirement of electroneutrality (equivalence of positive and negative ions).

- Compute stream compositions by iterating the program until convergence is attained.

This necessarily abbreviated description suggests a fairly complicated sequence of steps leading up to the actual computation of a water and salt balance. However, many of these steps have been completed for previous modeling efforts and need not be repeated. This results in considerable ease in applying the model to new systems. Most importantly, the extensive compilation of available experimental information on how a wide variety of ionic species behaves provides the basis for producing more realistic simulations than would be possible with the more common theoretical models.

Computer modeling as described above has been used extensively for evaluating water management options in mine-mill projects, and the techniques are readily adaptable for use with a wide range of water management configurations. Further details can be provided by Mike Harris (414/272-2426) or Jim Mavis (206/453-5000).

1983 Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation
(University of Kentucky, Lexington, Kentucky 40506-0046 – November 27-December 2, 1983)

Integrated Water Supply and Quality Control Analysis of the McLaughlin Gold Mine Project, Lake County, California

by

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Lakewood, Colorado

and

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Lakewood, Colorado

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Abstract. A generalized network flow computer model called MODSIM, has been successfully applied to integrated water supply and quality control analyses for a planned gold mining project in California. The program has proven to be particularly well suited for design and operational studies for the various facilities associated with the project. The results of the study have demonstrated the usefulness of integrated water balance evaluations in the designs for complex mining and civil engineering projects.

Introduction

The planned McLaughlin Gold Mine Project, located in Napa and Lake County, California (Figure 1) includes a system of interrelated water supply and water control facilities that must be designed and operated in an integrated fashion. During design studies for several of the facilities, including the tailings impoundment grinding and low grade ore stockpile areas, it was noted that the wide range of potential hydrologic conditions at the site had a significant effect upon the overall project water balance considerations. The water balance for such facilities had a direct influence upon water supply and quality control aspects of the project. The water balance for the individual facilities was particularly sensitive to the rate of water use from other project water sources. For these reasons, integrated water balance studies utilizing a generalized network flow computer model using the out-of-kilter algorithm, were initiated for the entire project.

Project and Site Description

The McLaughlin Project will be an open-pit mine, processing up to 3,000 tons per day of gold bearing ore. The mine will operate for 24 years producing an estimated 26 million tons of ore. The ore will be crushed at the mine site and slurried to processing facilities. Process tailings will be disposed of in an impoundment adjacent to the process facilities. A layout of the various project facilities is shown in Figure 2. A summary listing of the various project facilities considered in the integrated water balance studies is given in Table 1.

Figure 1. Project Location Map

Table 1. Summary of Project Facilities Considered in the Integrated Water Balance Studies

Facility	Design Storage Capacity (acre-ft)	Comments
1) Water Storage Dam	6,000	
2) Tailings Impoundment	22,000	Zero discharge system. 1,000-year, 24-hour flood event freeboard required
3) Mine Pit	--	Specified maximum allowable pit water buildup.
4) Water Quality Control	310	Zero discharge system. 100-year, 24-hour flood event freeboard required.
5) Grinding Facilities	--	Average water demand = 480 gpm for ore slurry production (minimum clean water required = 107 gpm)
6) Process Facilities	--	Average water demand = 1,050 gpm for tailings slurry and 207 gpm for evaporative losses (minimum clean water required = 200 gpm)

The climate in the vicinity of the project is dry summer subtropical. It is characterized by warm summers and mild winters. More than 90 percent of the annual precipitation occurs during the six month period between October and March. Most precipitation occurs as rainfall. Some snow may fall during the winter months, but snowpack is not formed.

The recorded precipitation ranges from a low of 9.1 inches to a high of 55 inches, with a mean annual precipitation of 33.5 inches. The mean annual evaporation in the area is approximately 48 inches. A total of 51 years of site specific hydrologic data has been developed for the various project design studies.

Description of MODSIM

MODSIM is a water management computer model originally developed by the Texas Water Development Board in 1972, and subsequently modified at Colorado State University (CSU).[1] It was selected for use with this project because of its generalized structure and capability of modeling water allocation in a system under policies and priorities as specified by the user. Although it was originally developed as a river basin model, it has proved adaptable to water systems at a much smaller scale.

In MODSIM, the water system is defined as a series of nodes and links. The nonstorage nodes represent points of inflow or diversion, and consumptive or flow-through demands. Storage nodes corresponding to reservoirs have user specified area-capacity tables, monthly target operating levels, and net evaporation, precipitation and seepage losses. Each water use is assigned a priority number, which translates into a nega-

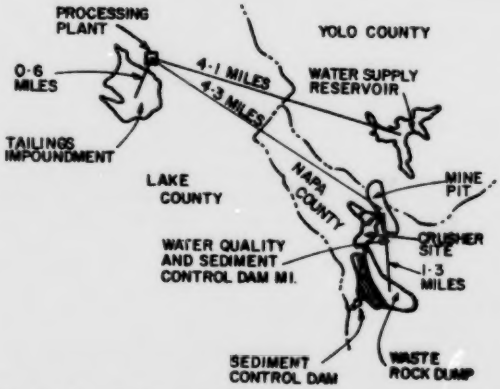


Figure 2. Project Facilities Layout

tive cost. The nodes are connected by a series of one-way links, which may represent river reaches, canals, or pipes. Each link is given maximum and minimum capacities and and an associated transport cost. These costs may reflect actual costs, e.g. pumping; or they may be manipulated to favor certain flow paths.

Flows in the system are analyzed on a monthly basis. Inflows are added to the water currently stored in the system, and the water is routed to meet demands or reservoir storage goals, so as to minimize the overall systemwide cost. Spilling from the system is allowed if no other destination is possible, and is avoided by assigning to it, the high cost. MODSIM uses the out-of-kilter algorithm to calculate the most favorable routing, subject to flow and storage capacities. This algorithm iteratively determines the least-cost solution for any configuration of a circulating network.

The CSU version of MODSIM has been modified for use with the McLaughlin analysis. Some changes

[1] Shafer, John M., An Interactive River basin Model: Synthesis and Application, Technical Report No. 18, Colorado Water Resources Research Institute, Colorado State University, Ft. Collins, Colorado 1979

were required to fit the model on an IBM Series I, while others were made to tailor the output to the needs of this project. The present model is able to write over fifty years of results to disk storage. An auxiliary program, MODSUM, has been written to allow selective printing of results and statistatical summaries.

Description of Project Model

The objective is setting up a model was to develop a tool which would assist in sizing the water storage and control facilities and to develop operating procedures that would maximize use of available storage during dry years and minimize the potential for spillage during wet years. The system of links and nodes used for modeling the McLaughlin Gold Mine Project are shown in Figure 3. Twelve nodes have been created to represent six physical areas; the extra nodes are used to simulate special usage conditions. The nineteen links correspond to planned or potential connections.

1. Davis Creek Reservoir. The 6,000 acre-foot reservoir is supplied by the runoff from a 10.16 square mile natural basin. The reservoir is the only source for the clean water demands at the grinding and processing facilities. It also serves as a backup for other water needs at the mine, but pumping costs make it less desirable than more proximate, alternative sources. A synthetic node downstream from the reservoir allows overflow of the good quality water without the penalty normally attached to spilling from the remainder of the system.

2. The Mine Pit. The pit requires 136 gpm during the winter months and 272 gpm during the summer for dust suppression. When this water is not available from its own inflow or storage, it must come from Davis Creek Reservoir. Inflows consist of groundwater seepage and runoff from the pit area. The pit is modeled as two nodes, one which must be kept relatively dry for mining, and the other which may temporarily store up to 200 acre-feet. The capacity of the pit will vary with time, especially during the first ten years of operation. Excess water from the pit may be pumped to the grinding facility or to Pond M1. Other alternatives considered for the management of excess pit waters included pumping to the tailings impoundment, or water quality control Pond W1. Since discharge of this water is undesirable, a high penalty is attached to spilling.

3. The Tailings Impoundment. The tailings impoundment has a maximum capacity of 22,000 acre-feet. It receives the runoff from a catchment of 315 acres, but its major source of inflow is 1050 gpm of slurry from the processing facilities. Depending on the scenario, it may occasionally receive excess water from the mine pit. Consumption of water includes that which is retained in the tailings and surface evaporation. The pond

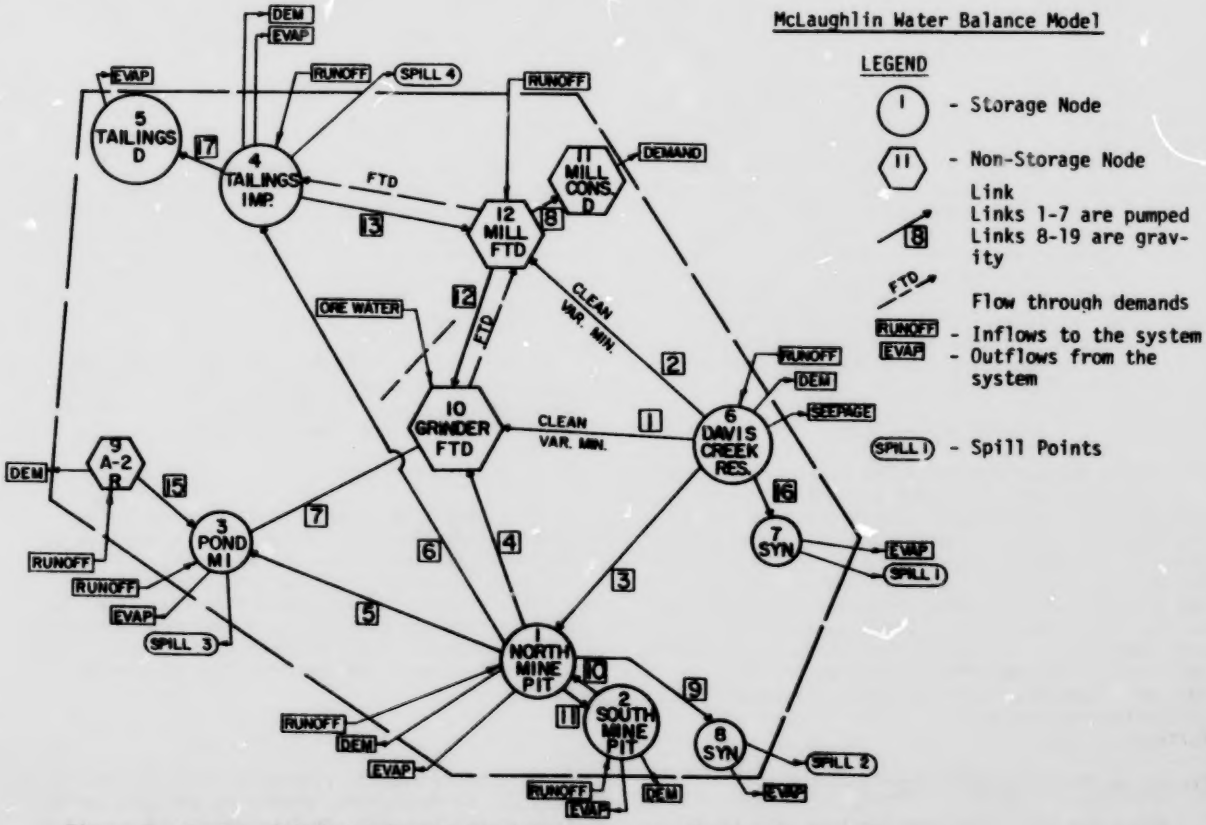


Figure 3. System of Nodes and Lines Established For the McLaughlin Project

has been divided into two nodes to represent the main pond and a synthetic pond which represents accelerated evaporation due to tailings management techniques. Water from the tailings is recycled to the processing facility to meet its water demands and as a water balance consideration for the tailings impoundment.

4. The Grinding Facility. This facility grinds the ore and pumps it in slurry form to the processing facility. It requires 480 gpm, of which 60 gpm is the minimum clean water requirement. A small supply of water is derived from the incoming ore, but most of the demand is met from outside sources. These sources, in order of preference are the mine pit, Pond M1, the tailings and Davis Creek reservoir.

5. The Processing Facility. This facility is represented as two nodes to model its demand for 207 gpm for consumption, and 1,050 gpm for slurry flow-through to the tailings pond. Of this, there is a minimum clean water (i.e. non-recycle) requirement of 200 gpm. It has a small inflow of runoff from a 20.5 acre basin, but receives most of its water from the ore slurry. The remainder of its water is supplied from the tailings impoundment or from Davis Creek Reservoir.

6. Pond M1 has a dual function as a water quality control structure and as a water supply for the grinding facility. Its major source of inflow is runoff from 178 acres. Since 80% of this area will be disturbed by mining, the water may be of poor quality and should be consumed either at the grinding facility or by evaporation. When the pond is below its operating capacity, it is also used to store excess water. The pond's function as a water supply for the grinding facility is important during the dry seasons. Its supply of runoff may be enhanced by collection of waters from a 54.9 acre natural drainage basin. This runoff is diverted from the site unless Pond M1 is below its optimum operating level. Since the two functions of supply and spill prevention are potentially in conflict, the model is particularly important for testing the operating rules for this pond.

Results of the Study

The model was run for a ten year period which included sequences of extreme wet and dry years. Operating procedures were established to minimize the potential for spillage during wet years and to maximize the use of water from all sources during dry years. The model runs were used to evaluate the effectiveness of these operating procedures and the designs of the various water storage and conveyance facilities. Iterative runs were carried out to refine both the operating procedures and the designs. Some highlights of the study results illustrating the versatility of the program are as follows.

Processing Facility Water Supply

Water for the processing facility will be derived from four sources: 1) Ore slurry water (from the grinding facilities) 2) tailings recycle water 3) clean water from the water supply reservoir, and 4) runoff from the process facilities area (requiring containment for water quality purposes). The integrated study results indicated that all water demands of this facility above the minimum clean water flow requirements (see Table 1) can be provided by runoff waters from the mine pit and water quality control pond M1 (utilized in ore slurry production) and recycled water from the tailings impoundment. A typical summary of these results are presented in Table 2.

Grinding Facility Water Supply

Water for the grinding facility will be derived from four sources: 1) Runoff and groundwater accumulation in the Mine Pit, 2) runoff contained in Pond M1, 3) clean water from the water supply reservoir, and 4) when necessary, recycled water from the tailings impoundment. The results indicate that all water demands of this facility above the minimum clean water flow requirements (see Table 1) can be provided by waters collected in the Mine Pit and Pond M1, and, during extreme dry years, with minimal recycle from mine pit water stored in the tailings impoundment.

Mine Pit

The results indicate the potential for significant buildup of water in the mine pit. The management of the pit waters will be critical for efficient mine operation. Use of the program has provided the basis for establishing pit water management schemes and operating rules. Storage of pit waters in the tailings impoundment have a significant design impact which was predicted and available for inclusion in the overall impoundment design.

Water Quality Control Pond M1

The results indicate that Pond M1 can be successfully operated as a water quality control structure. Operating rules developed as part of these studies are successful at maintaining acceptable water levels in the pond. The typical set of results for water levels are shown in Figure 4.

Tailings Impoundment

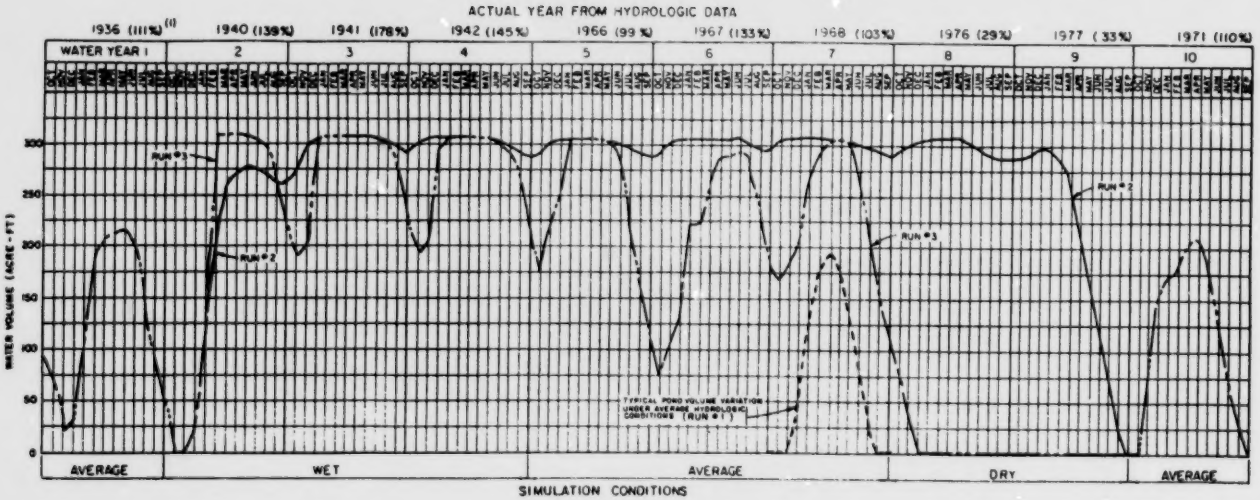
The results indicate that the tailings impoundment can be operated as part of the integrated water management system and that it would meet the required design criteria of zero discharge.

Water Supply Reservoir

The sizing of a water storage reservoir for projects of this type are typically based upon operational studies without consideration of potenial water contribution from other sources. The results of these studies indicated that water availability from the mine pit, the tailings impoundment and runoff water quality control ponds has a significant effect upon the required size of the reservoir.

Conclusions

The study results provide a basis for design of many of the facilities, pipelines and pumping systems associated with the McLaughlin Project. Spe-



NOTES

(1) FOR THE YEAR SHOWN, THESE VALUES REPRESENT THE PERCENTAGE OF THE AVERAGE ANNUAL PRECIPITATION (31 inches). FOR EXAMPLE; IN 1936, THE TOTAL PRECIPITATION WAS 34.4." 34.4/31 = 111%

(2) OPERATING RULES ASSUMED FOR RUN #3 UNDER AVERAGE ANNUAL CONDITIONS

MONTH	DESIRED STORAGE LEVEL (ACRE-FT)
OCT	105
NOV	84
DEC	92
JAN	115
FEB — AUG	175
SEPT	147

Run Number	Hydrologic Regime	Mine Pit Water Considerations	Evaporation (inches/yr)	Comments
1	10-year sequence, average conditions only	Max allowable pit volume = 200 ac-ft	48	Primary purpose of run is to define steady-state conditions and seasonal variations in storage facilities under average conditions. Excess pit water diversion to tailings impoundment considered.
2	10-year sequence of dry, average, and wet conditions as described in Section 3.1	No max allowable pit water volume	48	Determination of maximum water volumes in pit if no diversion to tailings impoundment provided.
3	10-year sequence of dry, average, and wet conditions as described in Section 3.1	Max allowable pit volume = 200 ac-ft	48	Base Case. Diversion of excess pit water to tailings impoundment considered. Spillage of pit water allowed under extreme wet conditions when tailings impoundment water reach maximum allowable. Return of tailings impoundment water to grinding facility during dry conditions allowed.

Figure 4. Results for Water Quality Control Pond M1

Table 2. Typical Computer Output for Process Facilities

SIMULATION YEAR 1 CALENDAR YEAR 1932 MONTHLY FLOWS IN GPM

FLOW TYPE	CT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	TOTAL
UREG INFLOW	7	7	58	36	32	14	15	14	15	7	7	7	18
FROM DAVIS CR	196	203	196	196	201	196	203	196	203	590	590	587	297
FROM TAILINGS	1254	1296	999	1021	1025	1042	1032	1254	1085	656	656	655	997
TOTAL FLOWS	1458	1507	1254	1254	1259	1254	1250	1465	1303	1254	1254	1250	1314

SIMULATION YEAR 2 CALENDAR YEAR 1933 MONTHLY FLOWS IN GPM

FLOW TYPE	CT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	TOTAL
UREG INFLOW	7	7	14	29	24	36	22	14	15	7	7	7	16
FROM DAVIS CR	583	580	474	211	339	196	361	444	474	590	590	587	453
FROM TAILINGS	663	663	765	1013	896	1021	866	794	761	656	656	655	784
TOTAL FLOWS	1254	1250	1254	1254	1259	1254	1250	1254	1250	1254	1254	1250	1253

SIMULATION YEAR 3 CALENDAR YEAR 1934 MONTHLY FLOWS IN GPM

FLOW TYPE	CT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	TOTAL
UREG INFLOW	7	7	43	29	40	21	15	14	7	7	7	7	17
FROM DAVIS CR	583	580	196	196	201	196	361	491	587	590	590	587	430
FROM TAILINGS	663	663	1013	1028	1017	1035	874	758	655	656	656	655	805
TOTAL FLOWS	1254	1250	1254	1254	1259	1254	1250	1254	1250	1254	1254	1250	1253

SIMULATION YEAR 4 CALENDAR YEAR 1935 MONTHLY FLOWS IN GPM

FLOW TYPE	CT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	TOTAL
UREG INFLOW	7	22	14	58	32	51	45	21	15	7	7	7	24
FROM DAVIS CR	583	384	437	196	201	196	203	196	203	249	590	587	338
FROM TAILINGS	663	844	802	999	1025	1006	1002	1035	1032	977	656	655	890
TOTAL FLOWS	1254	1250	1254	1254	1259	1254	1250	1254	1250	1254	1254	1250	1253

SIMULATION YEAR 5 CALENDAR YEAR 1936 MONTHLY FLOWS IN GPM

FLOW TYPE	CT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	TOTAL
UREG INFLOW	7	7	7	51	104	29	30	14	15	7	7	7	23
FROM DAVIS CR	583	580	583	196	201	196	203	196	203	196	430	587	347
FROM TAILINGS	663	663	663	1006	952	1028	1017	1042	1032	1050	816	655	882
TOTAL FLOWS	1254	1250	1254	1254	1259	1254	1250	1254	1250	1254	1254	1250	1253

cific conclusions regarding the designs have been omitted for purposes of brevity. General conclusions reached during these studies are as follows:

1) Integrated water balance studies conducted for the McLaughlin Project have indicated sensitivities which would have remained unknown if the facilities had been designed on an individual basis only.

2) Integrated studies should be employed whenever possible for the sizing of water supply reservoirs and tailings impoundments for mining projects. Such studies can be particularly beneficial when water balance considerations are critical.

3) Operation guidelines and water management alternatives for water quality control structures and mine planning can be easily evaluated with computer models such as MODSIM. The particular advantages of MODSIM over many other similar types of models is that it allows the system configuration and all operating procedures to be input as data. The program then determines the flow regime which best suits the system constraints, and cost and operational guidelines

4) The computer program MODSIM also shows promise as an operational and forecasting tool for the mine. On a regular basis, the model could be used to forecast water storage conditions in the various facilities for a range of projected hydrologic conditions. These results could then be used to further refine the day-to-day operating procedures and to plan the provision of any emergency measures that may be required.

CHAPTER 11

REDUCING WATER CONSUMPTION IN MINERAL PROCESSING
WATER EFFICIENT METALLURGICAL FLOWSHEETS AND EQUIPMENT

Chapter 3 reviewed water use in mineral processing operations. It was observed that water consumption varies from operation to operation depending largely on the amount of water available and the traditional approach to water use in the mill.

Reduction of water consumption is likely to be of interest mainly to those operations where water is not abundantly available or where it is very expensive.

Again, it is pointed out that the water consumed in a metallurgical or mineral recovery process is not the only water required for an operation. The total water requirement varies tremendously, too, depending on what infrastructure must be provided for a mine-mill complex. If a townsite and accommodation must be provided for staff and mine labor, then a significant additional amount of water will be needed, possibly even exceeding that used in the mill. Here too, the degree of labor intensiveness of the operation will also have an influence on the water demand for the townsite. In South African gold mines, the rule of thumb is 0.4-0.8 m^3/d per man employed. Clearly, one way to save water is through savings at the townsite. These aspects are not discussed here. Also, one of the most effective ways of reducing water consumption is through tight housekeeping and operator education.

This chapter identifies and briefly describes some of the more water efficient metallurgical flowsheets and equipment items encountered.

WATER EFFICIENT FLOWSHEETS

Rössing Uranium

Water efficient aspects of the Rossing Uranium flowsheet are listed below. Details are provided in the Appendix 1 trip report.

- Greater use of recycled tailings return solution. This was made possible by acid-proofing the CCD thickener rakes using a polyurethane coating to prevent corrosion of the rakes made of stainless steel 316L.

- Use of tailings return solution as glandwater for pumps which was made possible by modifying the bearings and pump shaft to overcome what would otherwise be a corrosion problem.

- Leaching ore at 75% solids in the pulp.

- Collection of seepage from the tailings dam for recycle. Seepage quality is significantly improved over decant from tailings due to reaction with calcerous strata through which the solution seeps, precipitating many undesirable contaminants.

- Living with a slightly reduced efficiency of recovery by ion exchange adsorption due to higher salt load in the process solution.

- Drawing down the tailings pond water level so that a smaller surface area of pond is presented for evaporation.

- Careful scale and corrosion control measures due to the greater use of recycled solution.

- Choice of eluant allowing eluant and yellowcake decant solution to be recycled.

Apart from the above measures, the actual metallurgical flowsheet employed at Rössing is standard for a low-grade uranium ore by sulfuric acid leach. RÖSSING URANIUM LTD. reduced their net water consumption from 30,000 m^3/d to 14,000 m^3/d in 1984 which worked out to 0.39 m^3/t ore treated. This is an exceptional achievement. In due course, their consumption will increase again once their tailings pond level has been reduced to the level they desire, but it will still be around 0.5 m^3/t which is exemplary considering their flowsheet.

An important contribution to Rössing's water savings is certainly due to the excellent training programs provided by the company for operators. These are ongoing programs, and every operator is aware of his contribution to the water conservation program. Water to each section of the plant is metered, and operators and their foremen are called to account when their water consumption increases.

The correct channel through which technical information on Rossing Uranium can be requested is:

RÖSSING URANIUM LTD.
Post Office Box 22391
Windhoek 9000
South West Africa/Namibia
(061) 36760
Telex: 908-3104
Peter N. Vernon
Technical Controller

UNC, Morton Ranch Project, Wyoming

The Nuclear Regulatory Commission, during the late 1970's, insisted that every new uranium mill should evaluate the alternative of dry tailings disposal. Burns & Roe, in conjunction with Pechiney, was the first in North America to demonstrate that the efficient use of belt filtration could first save water and (more importantly as far as the NRC was concerned) offer the possibility of being able to dispose of dry tailings. The idea was that dry tailings containing less moisture could be disposed of in trenches in a way that would allow the tailings to be stabilized on a continuous basis thereby, hopefully, reducing the impact on the environment. Every new mill proposed at the time in the U.S.A. examined this alternative as a requirement for their NRC permit application. Unfortunately, the uranium boom was dead before the NRC got around to issuing permits, and no mills using dry tailings were constructed in the U.S.A.

The Morton Ranch project in Wyoming of United Nuclear Corporation examined the possibility of belt filtration followed by dry tailings disposal via conveyor belts to the tailings area. It was concluded that this procedure would not be practical in Wyoming due to the risk of the tailings freezing on the belt in winter and the likelihood of windblown losses from the conveyor in summer. Adequate water was available for the operation using CCD for solid-liquid separation, and the Wyoming climate made it possible for the plant to achieve zero discharge with the use of evaporation ponds. This project was anticipated to draw only 5.0 gpm fresh water from ground or surface sources, all process water requirements (683 U.S. gpm, 3,750 m^3/d) being provided by evaporation pond recycle and water pumped from the open pit mines. Of course, seepage into the mine pit really would be a draw on groundwater from the area.

The Morton Ranch environmental impact statement showed a net minewater consumption of 2,140 m^3/d to treat 1,800 mt/d ore or 1.19 m^3/t ore treated with an additional 1,580 m^3/d (0.88 m^3/t ore) recycle water from the tailings pond (i.e., via the evaporation pond).

In this case, clearly there is no need to conserve water as the mine pits need to be dewatered anyway, and this water would otherwise have to be treated and discharged if it were not to be used in the mill.

The Morton Ranch project is an appropriate example of a uranium mill where dry tailings disposal was seriously considered and evaluated but where it proved neither practical nor cost effective within the Wyoming climate and water balance constraints for the project.

NRC (1978) pointed out that solvent extraction was selected for uranium recovery from solution because it uses less water than resin exchange processes.

Compagnie Miniere Dong-Trieu, France

This operation, which belongs to the Empain-Schneider Group, is located about 70 km from Limoges, France. It is a small operation which, when visited by Randol in 1980, treated 200 tpd with a grade of 0.5% U_3O_5. The plant, designed and engineered by Spechim, Paris, practiced dry tailings disposal in open pits. The tailings dewatering and washing was achieved using two (70 m^2 and 25 m^2) Philippe belt filters. This volume of solids applied to a 70 m^2 filter at 10 cm cake thickness means that the belt would be advanced at 1.4 m/minute which allowed time for five counter-current washes. The operation was described in greater detail by RANDOL (1979), and more information could be obtained from:

COMPAGNIE MINIERE DONG-TRIEU
Le Cherbois
87890 Jouac
France
(55) 68-21-09
Telex: 580-796
Christina Duchamp
Mill Manager

STEFFEN ROBERTSON & KIRSTEN
#801, 1030 West Georgia
Vancouver, B.C. V6E 2Y3
(604) 681-4196
Andrew McG. Robertson

The purpose of using belt filtration was to achieve optimum washing and a concentrated preg solution as well as compact dry tailings for below ground disposal at the location which is amidst a productive farm community. It was not established what the CM Dong-Trieu net water consumption is or what their motivation was for the installation of belt filters. This operation does serve to demonstrate that belt filtration and dry tailings disposal can be applied, bearing in mind that this is a small tonnage, high grade operation, yet they installed a 70 m^3 filter for 200 tpd of solids treated.

Rudnik Urana Zirovsky VRH, Yugoslavia

A Yugoslavia uranium mill, Rudnik Urana Zirovsky, which was commissioned in 1980, employs two 50 m^2 belt filters in parallel and disposes of dry tailings. RANDOL INTERNATIONAL LTD. did not visit this operation, but it has been learned that their motivation for using belt filtration was to reduce capital costs to achieve superior wash efficiencies and a degree of simplicity while also disposing of dry tailings allowing a greater degree of solution recycle, reduced water consumption, and minimized pollution of a local river by liquid effluents. The operation treats about 600 tpd. Names of contacts at the operation include Dusn Pensa and Smargo Logar, and the operation is located 12 km from the town of Skofja Loca Slovenia. Information can be requested from:

FLUOR MINING AND METALS, INC.
Redwood City, CA
(415) 595-6000
Don Skufka

More details can be requested from an engineer who visited this operation and is very familiar with some of the tradeoffs that must be made when water recycling is enhanced in metallurgical plants.

THE RALPH M. PARSONS COMPANY
100 West Walnut Street
Pasadena, CA 91124
(213) 440-4085
Telex: 677-336
Brian C. Haydon

Pioneer Uravan, Colorado

Uranium circuits can be designed to be still more water efficient by incorporating the following innovations which were proposed for use at a uranium mill in Colorado at a site where water availability was a major problem:

1) The Use of Counter-Current Leaching
2) The Use of Belt Filtration as Opposed to CCD for Solid Liquid Separation
3) The Use of Solvent Extraction Rather than CIX
4) Disposal of Dry Tailings

The use of counter-current leaching makes it possible to achieve a more concentrated pregnant solution. Two stages of counter-current leaching were proposed and tested for the Pioneer Uravan project. Testwork was performed at the Colorado School of Mines Research Institute. The project was ultimately shelved because the economics of uranium recovery changed, and the company was unsuccessful in finding adequate water for the project.

Counter-current leach results in a lower water consumption inventory need with a corresponding lower evaporation loss in the circuit. The greatest benefit is the higher solution tenor which allows solvent extraction to be employed rather than ion exchange. The greater selectivity of SX compared with CIX allows more extensive recycling of solution recovered from the tailings.

Belt filtration, if skillfully applied, allows counter-current washing of the leached pulp employing only 1.0 m^3/t ore washwater as opposed to 3 m^3/t required in a CCD circuit with an equivalent wash efficiency,

Solvent extraction is much more selective than resin ion exchange and does a better job of uranium recovery in the presence of competing ions which, due to the recycling of

solution to the degree planned for this project, would be a necessary process selection. The higher the tenor of the pregnant solution, the more efficient the solvent extraction step and the more cost effective as well.

Belt filtration is ideal for washing and dewatering the coarsely ground sandstone ore pulp because of its top-loading feature. In the CSMRI pilot plant, moisture content could not be reduced below around 30% which was higher than expected. Possibly on production scale units, the edge effects would be less of a factor, and mosture content of the tailings could be reduced closer to the 20% target.

The belt filters were planned to provide dry tailings for disposal with a minimum water content which would provide a major water savings.

In the pilot plant operations, TDS built up rapidly in the process solutions until eventually they reached a density of 1.2. In the filtration step, alum crystallized out in the filtrate receiver and the vacuum box, which presented a problem. Salt balance considerations are critical if water is to be recycled to this extent. Needless to say, special materials or coating would be needed to prevent equipment from being corroded by solutions with such high TDS levels.

In pilot plant belt filter tests at the Colorado School of Mines Research Institute, Golden, Colorado, it was found that in the counter current leaching step, that alum would crystalize in the vacuum box of the filter which ultimately interferred with the filter operation. Also, for an effective counter-current leach, it was found that a repulping step was needed between leaches. In the final design, the use of a thickener instead of a belt filter was found to be more cost effective.

Robert J. Polak was the project manager for Pioneer Uravan, and Daniel Blakeman supervised the CSMRI testwork during the final stages of the program. He and a senior metallurgist involved in the project can be reached as follows:

SUMMITVILLE CONSOLIDATED MINING CO.
Post Office Box 2G
Del Norte, CO 81132
(303) 657-2741
Daniel Blakeman
Roger Leonard

Belt Filtration in French Uranium Mills

In France, belt filtration was pioneered and successfully applied for uranium recovery circuits.

According to COGEMA, belt filtration of French uranium leach pulps provides successful washing when 2.0 to 2.2 m^3 solution is recovered per ton of solids as compared with 3.5 m^3/t ore for CCD pregnant solution.

Recycle water is used to supplement fresh water used to wash the filter cake.

A paper by BODU, et al. (1982) provided a comparison of CCD versus belt filtration for uranium ore processing.

Depending on the dissolved salt concentrations in solvent extraction raffinate, part of the raffinate can be recycled in the plant. However, appropriate settler capacity must be provided to remove solvent droplets. Somair in Niger uses a safety settler with a residence time of over one hour. Solvent droplets could damage rubber components (linings, belts, etc.) which are made of natural rubber. This danger is greater the higher the aromatic content of diluents used.

One comment made is that the best way to reduce water consumption in a plant is probably to fit a large number of recording flowmeters at appropriate places in the circuit.

In France, a COGEMA plant of LODEVE operated by SIMO and the SIMO plant of Bessines (after 1986) will dispose of dry tailings.

In Niger, the SOMAIR plant in Arlit uses belt filters and also disposes of dry tailings.

Information can be requested from:

COGEMA
2 Rue Paul Dautier
BP 4
78141 Velizy-Villacoublay Cedex
France
(3) 946 96 41
Telex: 697833 COGEM
Robert Baschivitz

Belt Filtration: Rand Mines Ltd., Harmony

At the Merriesprut uranium plant in the Orange Free State, Rand Mines Ltd. installed belt filters with a view to conserving water. Their original plan was to apply multiple counter-current washes on the same filters. This proved impractical and, in the end, two co-current washes were applied. It is not known how much wash solution was applied, but it is expected that around 2.5 m^3 of pregnant filtrate is recovered per ton ore treated. According to C. E. Fivaz, former consulting metallurgist of Rand Mines Ltd., the soluble losses of uranium in the belt filter tailings amounts to about 4% which is very much more than was expected.

THE STRONG ACID AGGLOMERATION PROCESS

Ranchers, Naturita, Colorado

The Rangers Exploration Co. was the the first in the U.S.A. to use concentrated sulfuric acid agglomeration of uranium ore (actually roasted tailings) followed by curing and heap leaching in an impermeable pad. This was carried out at Naturita, Colorado. A process based on similar principles has been employed by COGEMA/PECHINEY at Arlit in Niger, Africa, and the British Atomic Energy Agency has patented a similar process.

The Ranchers operation treated 1,500 st per day (1,350 mt/d) and required only about 40 gpm net water or 229 m^3/d which works out to 0.17 m^3/t. Water was pumped from the adjacent river in summer and hauled to the site in winter. The acid cure released adequate heat to avoid freezing--also, the high concentration of acid lowered the solution freezing temperature.

The sandy, minus 48 mesh tailings contained 6-7% H_2O to start. During the saturated leaching step, they contained around 18% H_2O and then drained to 11-12%. Consequently, only about 0.05 m^3 new water was lost to entrainment per ton of tailings.

Because water recycle was so tightly controlled, dissolved salts built up in concentration, and the salt load was not balanced by entrainment in tailings. NaCl was used to strip the loaded organic phase in the SX plant. This resulted in chloride buildup which had to be controlled below 3 g/l in the recycled water. This necessitated about 30 gpm (165 m^3/d = 0.12 m^3/ton feed) bleed.

The Naturita operation worked with a very small water inventory and is possibly the most water-efficient metallurgical process identified to date. The concentrated acid cure served to "open up" the ore for good extractions despite the coarse grind. Concentrated acid mixed into the ore comes into contact with interstitial moisture in the ore grains and through the exothermic reaction of H_2SO_4-H_2O mixing, resulted in a good leach recovery in advance of the subsequent washing step.

Although the original Ranchers team has disbanded, the engineer who installed and operated the Naturita project can be reached:

RANDOLPH E. SCHEFFEL
9204 Avenida de la Luna NE
Alburquerque, NM 87111
(505) 821-9462

Pechiney, Arlit Project, Strong Acid Leach

The Arlit strong acid leach project in Africa was described in RANDOL (1979), Appendix V. Information on this process would be available from:

URANIUM PECHINEY UGINE KUHLMANN
6 Avenue Bertie Albrecht
75008 Paris
France
(1) 766-52-00
Mr. Guy Boutonnet
Directeur de l'hydrometallurgie

Holmes and Narver Thin Layer Leach

The Holmes and Narver thin layer leach process, employed in oxide ore treatment, works on the same principles as the strong acid leach process for uranium described above. It would be expected to be equally water efficient. More details could be requested from:

HOLMES AND NARVER, INC.
4704 Harlan Street, Suite 515
Denver, CO 80212
(303) 458-8181
Paul E. Thompson

GOLD AND SILVER HEAP LEACHING VS. AGITATION LEACH

At first glance, one might expect heap leaching, which employs spray irrigation and multiple pass solution applications for many days, weeks, and even months, to be inefficient with respect to water consumption compared with agitation leaching which takes hours.

It, in fact, turns out that heap leaching is very water efficient. Data gathered as part of this investigation and shown in Chapter 3 indicates that heap leaching in the western U.S.A. typically consumes only 0.2-0.3 m^3 new water per ton ore and, if need be, this can be reduced to 0.2 m^3/t ore average for the year. This compares with 0.7-1.5 m^3 water/ton ore used in conventional circuits. In both cases, precipitation adds water to the system, and evaporation results in solution losses. It is important to note that the 0.2 m^3/t rule of thumb is an average water requirement over the whole year. In colder months and during the spring melt, water needs will be very much less than this. In the hotter summer months, the water consumed per ton ore will be very much higher than the average.

Experiments in Arizona showed that when wobbler sprinklers are used for heap leaching, evaporation losses work out to 10-15% of the solution irrigated during summer daytime periods. By changing the droplet size of the spray, the rate of evaporation can be

modified as a means of adjusting the water balance as needed. There are innovative desert drip irrigation techniques which hold promise when water consumption has to be minimized.

There are four possible reasons that heap leaching requires less water than agitation leaching:

1) Ore is crushed and not ground. Consequently, tailings are disposed of with a much lower moisture content, say 10%, compared with 50% or so for milled tailings. This factor alone would account for a water savings of 0.40 m^3/ton ore.

2) Tailings ponds and recycle solution reservoirs in conventional leach operations are often not designed to be impervious, and considerable losses of water occur from some due to seepage. In heap leaching, solution ponds are plastic-lined, and water has already been recovered from the heap material by the time it is disposed of as tailings.

3) Heap leaching presents smaller surfaces of water for evaporation, i.e., it uses no tailings ponds.

4) In most cases, heap leaching does not need to bleed barrens. It appears that the heap material in many cases prevents buildup of metals such as Zn, Cu, etc. in solution. This observation requires confirmation, however.

The addition of concentrated cyanide solution during an ore agglomeration pretreatment followed by curing also saves water. The water recycling potential is enhanced by the addition of scale inhibitors.

MERRILL-CROWE VS. CIP FOR GOLD RECOVERY

The Merrill-Crowe (zinc precipitation) circuit arrangement which uses solid-liquid separation after leaching offers an opportunity, if need be, to recover solutions from tailings before they are discarded. This would be the case if a dry tailings disposal technique were to be used. So far, no gold or silver operation has been identified which uses this technique, although uranium operations in France and Yugoslavia do use dry tailings disposal. The Mahad adh Dhahab operation in Saudi Arabia plans to employ CIP followed by filtration for solution recovery to conserve water in this extremely arid part of the Arabian desert. It will be very interesting to learn what the net water consumption of this operation proves to be. In their case, the ore contains cyanide-soluble copper which will require a barren bleed unless some form of cyanide recovery/copper removal process in employed. Information on Mahad adh Dhahab was provided by LEWIS (1984), and further inquiries may be directed to:

CONSOLIDATED GOLD FIELDS LTD.
49 Moorgate
London
England EC2R6BQ
(01) 606-1020
Peter J. Lewis
Group Metallurgist

Normally, there is a tradeoff between CIP and Merrill-Crowe. CIP achieves a slightly better gold recovery, especially when the ore contains small quantities of cyanide-soluble base metals, but cyanide losses through the inability to recycle barren solutions are higher. Merrill-Crowe, because of the solid-liquid separation step, allows greater flexibility in water management. For example, reusable barrens can be returned to the plant, while water that is not so suitable for metallurgical use can be used for filtercake repulping and transport to the tailings pond, or dry tailings can be disposed of by conveyor belt. The Mahad adh Dhahab project will be combining both.

FOSTER WHEELER DRY CYANIDATION

The Foster Wheeler "dry" cyanidation process involves agglomerating a very coarsely-ground gold ore with concentrated alkaline cyanide solution and allowing the agglomerate to cure in vats in contact with an oxygen enriched atmosphere.

After essentially leaching gold values in the ore during the curing stage, values are next washed from the ore for recovery.

It is known that Noranda Research in Montreal evaluated the "dry" cyanidation process, but they have not used it at either of the gold plants that they installed since then. The engineer at Foster Wheeler who was involved in the development of the process, Dr. R. Balakrishnan, has left that company. Information about this process, which is not without promising features, particularly from a water conservation standpoint, could be requested from:

FOSTER WHEELER COMPANY
Station Road
Reading, Berks
England RG1 1LX
(0734) 585211

NORANDA RESEARCH CENTRE
240 Hymus Blvd.
Pointe Claire, Quebec
Canada H9R 1G5
(514) 697-6640
Dr. G. B. Harris

REFRACTORY GOLD ORE TREATMENT

The Homestake Mining Company at their McLaughlin project will use pressure oxidation to make their refractory gold ore amenable to cyanidation. This operation, which is now in a startup phase, is summarized in Appendix I. Sulfides and sulfosalts that encapsulate gold are oxidized and washed from the ore together with heavy and base metals. By keeping the wash solutions segregated from the cyanide leach circuit, the formation of metal cyanide complexes can be avoided which otherwise would result in metallurgical interferences and the need for more difficult cyanide complex treatment or disposal of a bleed.

By washing the oxidized ore and keeping the wash solutions separate, the base metals in solution can be removed by simple neutralization with lime and settling, allowing it to be reused in washing more oxidized ore.

A similar step can be used as effectively to remove soluble base metals from calcined concentrates prior to cyanidation with the same advantage of reducing the volume of barren bleed.

WITWATERSRAND GOLD-URANIUM CONCEPT

Witwatersrand ore is treated by alkaline cyanidation for gold recovery followed by sulfuric acid leaching for uranium recovery, or vice versa. This two-step process involves the addition of lime to get the high pH needed for cyanidation followed by acidification for uranium leaching and a final neutralization of uranium leach tailings in the "forward-leach" process and just as wide a swing in pH for the "reverse leach" process. In each step, large quantities of water are involved.

If both gold and uranium could be leached in either an acid or an alkaline pH and extracted together, a significant water savings would potentially be possible as well as a potential reagent savings. Cyanidation does not work at a low pH, and Witwatersrand gold ores do not leach well in carbonate or alkaline solutions.

One possible way is to leach gold in an acidified thiourea solution which would also leach uranium. It is believed that an improved thiourea leaching technology has been developed by SKW in Germany which involves the stabilization of thiourea using SO_2 or sodium sulfite addition. This is merely a concept at this stage demonstrating how a systems approach can be used to potentially improve water management, i.e., reduce water consumption in metallurgical processing.

COPPER-LEAD-ZINC FLOTATION

Conventional conditioning of pulps for the separation and recovery of copper, lead, and zinc concentrates from complex sulfide ores involves aeration and conditioning with SO_2. Various activators, frothers, collectors, and depressants are used. The presence of some of these and also of oxidation products due to partial oxidation of reactive sulfides in the ore or metals, e.g., Cu that may leach from oxidized fragments in the ore, can put constraints on the amount of water that can be recycled without interferring with the process. Similarly, the discharge of effluents may cause a problem in the receiving waters due to oxidation of thiosulfate which results in a drop in pH.

One plant that is wellknown for thiosalt generation is Brunswick Mining near Bathurst, New Brunswick. There was a limit to the amount of water that can be recycled due to metallurgical interference in some circuits, e.g., the Pb-Cu separation step; thiosalts in mill tailing solutions cause pH problems in the receiving waters. Numerous ways have been investigated to treat effluents to remove metals and thiosalts prior to discharge without finding an economical way. It is believed that BM&S, in conjunction with Lakefield Research, has developed a processing sequence that reduces the use of SO_2 as a conditioning reagent and which promises to allow 100% recycle of mill tailings decant solution reducing the amount of thiosalts discharged in effluents. The processing sequence is said to be simpler than the previous arrangement.

The implementation of the new process arrangement has just begun, and it is premature to seek out details. At some future date, these may become available from:

BRUNSWICK MINING AND SMELTING
CORP. LTD.
Post Office Box 3000
Bathurst, N.B.
Canada E2A 3Z8
(506) 546-6671
John Martin
Concentrator Superintendent

LAKEFIELD RESEARCH OF CANADA LTD.
Post Office Box 430
Lakefield, Ontario
Canada K0L 2H0
(705) 652-3341
A. M. Wyslowzil
Manager

If successful, the BM&S mill hopes to reduce fresh water intake to an extent that effluent discharge from mill tailings can be greatly reduced.

BELT PRESS WATER RECOVERY FROM TAILINGS

Residual water content in some tailings never drops below say 60-65% H_2O because of the nature of the solids material. This not only means that 2 m^3 (tons) of water are tied up in the tailings pond for each ton of ore treated, but also that an expensive tailings impoundment will be needed because of the extra volume of water to be contained.

One alternative way in which, in some cases, water can be recovered and a more stable form of tailings produced that is suitable for "dry" tailings disposal is by squeezing the tailings. Innovative belt press devices have been installed for this purpose. The major market for belt presses is in dewatering sewage sludges, but they are also used for dewatering metal precipitates and in at least once case (WIDCO, Washington), for dewatering a clay-rich fine coal plant refuse.

LAROS, et al. (1985) will describe the use of the EIMCO belt press for cyanide and water recovery from a silver mill tailings material.

EIMCO PROCESS EQUIPMENT COMPANY
Post Office Box 300
Salt Lake City, UT 84110-0300
(801) 526-2000
Telex: 388-320
Tim Laros
Product Marketing Engineering

REFERENCES

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CHAPTER 12

REMOVAL OF SUSPENDED SOLIDS

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MOTIVATION

Motivation for the removal of suspended solids is generally one of the following:

- To meet effluent permit limits for suspended solids.
- To meet effluent premit limits for total metal values.
- The treatment of pregnant liquors prior to metal value recovery by solvent extraction, zinc precipitation, or crystallization.
- To avoid abrasion of water-powered hydraulic tools.
- To avoid abrasion wear on pumps used to dewater mines.
- Recovery of reusable values.

TECHNOLOGY GOALS

The technology goals and process selection criteria for suspended solids removal are:

- The removal of S/S from water to as low a level as possible.
- To produce a sludge with a high solids denisty.
- To yield a "non-hazardous" sludge which can be disposed of in a routine manner.

TECHNOLOGIES

Several technologies, some innovative, others costly but good, and others very simple have been identified for the removal of suspended solids. As solution recycling is required to an ever-increasing extent in mineral processing with resultant TDS buildup, such solutions can become highly scaling which present a downstream problem when polishing is required for the removal of suspended solids.

- Coagulation and Flocculation
- Hopper Clarifier - The Claricone
- AARL-CSIR Cylindro-Conical Settler
- Platepack Clarifiers, Lamella Settlers
- Dispersed and Dissolved Air Flotation
- Lectroclear Clarifier
- Settling Ponds/Polishing Ponds
- Biological Systems
- Multi-Media and Deep-Bed Filtration
- Conventional Clarifiers
- Magnetic Processes
- Cross-Flow Filtration
- Ultrafiltration and Reverse Osmosis

COAGULATION AND FLOCCULATION

Coagulation and flocculation are required to separate suspended solids from water whenever their natural settling rates are to slow to provide clarification. Water clarification, lime softening, sludge thickening, and dewatering and removal of trace quantities of suspended metal precipitates all depend on the correct application of the theories of coagulation and flocculation for their success.

NALCO (1979) includes the following table showing the settling rate of silica at different particle sizes which illustrates the effect of size.

Sedimentation of Small Particles of Silica of 2.65 Sp. Gr.

Typical	mm	Micron	Surface area (total)	Settling time, 1 m fall
Gravel	10.	10,000	3.14 cm^2	1 sec
Coarse sand	1.	1,000	31.4 cm^2	10 sec
Fine sand	0.1	100	314 cm^2	125 sec
Silt	0.01	10	0.314 m^2	108 min
Bacteria	0.001	1	3.14 m^2	180 hr
Colloidal matter	0.0001	0.1	31.4 m^2	755 days

NOTE: Particles larger than 100 microns are visible to the naked eye and are considered to be settleable solids. In the range of 10–100 microns, they are considered to be turbidity. Below 10 microns they are considered colloidal. Particles larger than 0.1 micron are visible by light microscope; below 0.1 micron, the electron microscope is used for detection.

It is fair to point out that the municipal water treatment industry is far ahead of the mining and mineral processing industry in their understanding and application of coagulation and flocculation technology. In the mining industry, the operator's concept of coagulation and flocculation does not go much beyond the hassles of making up and ageing flocculant solutions and dosing it somewhere--usually by injection into a pipeline or channel carrying solution ahead of a clarifier, thickener, or filter.

The water treatment industry employs separate equipment units for coagulation using high-energy flash mixers followed by low-energy mixing to allow the growth of the floccules formed in the first step to take place which is called flocculation.

A good understanding of the basic principles of coagulation and flocculation is provided by NALCO (1979) and in NALCO Bulletin 40, "Water Clarification: Questions and Answers," available from:

NALCO CHEMICAL COMPANY
2901 Butterfield Road
Oak Brook, IL 60521
(312) 887-7500
Robert E. Finch
Corporate Sales

The terms coagulation and flocculation are often used interchangeably; however, when seen as two different mechanisms, they can provide a better understanding of clarification and dewatering.

WHAT IS COAGULATION, AND WHAT IS FLOCCULATION?

COAGULATION

Coagulation is a chemical or physical process wherein the negative charge on colloidal turbidity particles is neutralized by a positively charged (cationic) chemical permitting them to collide and eventually to settle. This phenomenon is known as colloid destabilization or coagulation.

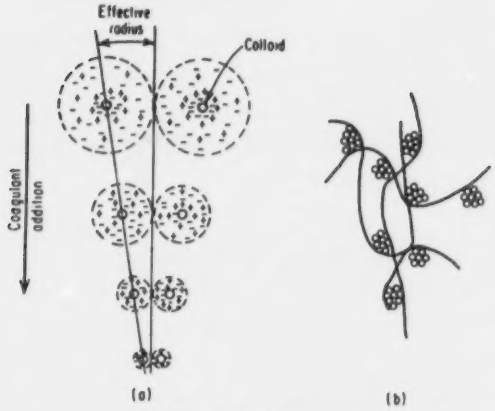
Coagulation is achieved in three steps:

1. Initial rapid mixing of coagulation chemicals with the water or solution to be treated.

2. Neutralization of particle surface charges.

3. Collisions between electrically neutralized particles caused by "rapid mix" energy input allowing the neutralized particles to coagulate into "floccules."

A coagulant is a chemical which, in solution, furnishes ionic charges opposite to those of colloidal turbidity particles in the water. Generally, coagulants are positively charged (cationic) and react with negatively charged clay particles which are a common cause of turbidity. Colloidal metal precipitates are usually hydrated or surrounded by OH^- ions and, therefore, also present a negatively charged surface. The cationic coagulants may be inorganic, e.g., alum, iron, or inorganic as well as organic polymers with cationic groups. The primary function of a coagulant is to neutralize charge.



(a) Coagulation: The addition of a coagulant neutralizes charges, collapsing the "cloud" surrounding the colloids so they can agglomerate. *(b) Flocculation:* The bridging of the flocculant chemical between agglomerated colloidal particles forms large settleable flocs.

Colloids are catagorized as hydrophobic or hydrophilic. Hydrophobic colloids do not react with water; most natural clays are hydrophobic. Hydrophilic colloids react with water and organic colloids which cause color are usually of this type. Hydrophilic colloids react chemically with coagulants and, therefore, require larger doses than are required for hydrophobic colloid coagulation.

Zeta Potential

The zeta potential is a measurement of the force which prevents colloidal particles from approaching close to each other or colliding, and this is determined by the charge of the ion layer surrounding the colloid.

For colloids in natural water sources in a pH range 5-8, the zeta potential is generally -14 to -30 millivolts; the more negative the number, the stronger the particle charge. As the zeta potential diminishes, the particles can approach one another closely, increasing the likelihood of colliding. Coagulation usually occurs at a zeta potential that is still slightly negative, so the coagulant addition need not completely neutralize the colloid charge. If the particles are all given a positive charge, they will redisperse.

Coagulants may be required at high pH as in lime softening or lime precipitation. Calcium carbonate carries a negative charge, and cationic coagulants may be needed to enhance their settling rates.

Magnesium hydroxide, on the other hand, has a positive charge until the pH exceeds 11, so in lime or lime-soda softening processes where $CaCO_3$ and $Mg(OH)_2$ precipitate, the oppositely charged particles co-precipitate.

Zeta potential is determined directly from data obtained in observing particle motion under a microscope. Zeta potential measurements have been used successfully to control plant coagulant dosages. However, for selecting the best coagulant, zeta potential readings alone are not reliable. The NALCO Water Treatment Handbook points out that for coagulant selection, the jar test remains the best.

Zeta potential is measured using a zeta meter available from:

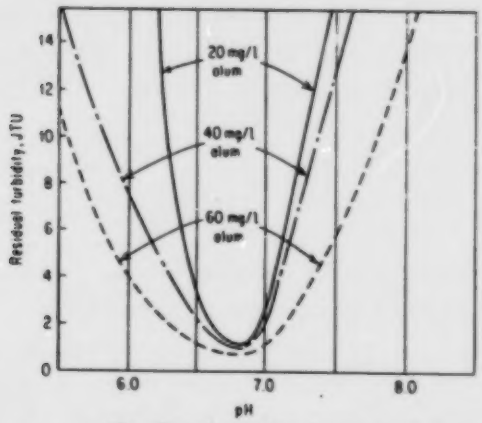
KOMLINE-SANDERSON ENGINEERING CORP.
Holland Avenue
Peapack, NJ 07977
(201) 234-1000
Telex: 136-328
Eric Jannelli
Sales Engineer

One of the most challenging colloidal suspension problems in mineral processing is encountered in diamond recovery operations in which oxidized kimberlite ore is crushed and washed. Suspended colloids up to 10-12μ or more are encountered in thickener overflow water as described in Appendix I in the trip report on the Premier Diamond Mine. More germain to sponsors of this study, however, are the effects of colloidal adsorption from pulp solutions onto activated carbon, which requires more research, and the use of engineered coagulation for removal of metal contaminant precipitate colloid from treated effluent solutions.

COAGULATION AND FLOCCULATION CHEMICALS

Historically, metal coagulants (alum and iron salts) have been most widely used in water clarification. These products function both as coagulants and flocculants. When added to water, they form positively charged species in a typical pH range for clarification of 6-7. Hydrolysis, however, yields an insoluble gelatinous aluminum or ferric hydroxide. Even if there are no suspended solids in the feedwater, the metal coagulants form flocs which enmesh destabilized colloids. However, the voluminous sludges produced by the addition of metal coagulants create disposal problems because they are difficult to dewater. This is the reason alum and iron salts are not often used to improve the efficiency of centrifuges, filter presses, and other dewatering devices.

Metal coagulants are particularly pH sensitive. If pH is not in the proper range, clarification is poor, and the iron or aluminum may be solubilized. The lower the coagulant dose, the more sensitive the floc is to pH changes as shown in the following diagram borrowed from NALCO (1979).



The effect of coagulant dosage on pH range limitations. The optimum pH remains almost constant, but the pH range becomes less restrictive as coagulant dosage increases.

In the 1940's, activated silica was introduced, and it improved the performance of alum and iron salts as coagulants and flocculants in water clarification. During the 1950's, the development of a range of organic flocculants called polyelectrolytes revolutionized water treatment technology. Polyelectrolytes are large water-soluble organic molecules. They usually incorporate ion exchange sites which give the molecular chains an ionic charge. Those having a positive charge, e.g., polyakrylamides, are cationic, and those with a negative charge are anionic. These polyelectrolyte molecules react with colloidal material in water by neutralizing charges or by bridging (tying together) individual particles to form a visible, insoluble precipitate or floc.

Cationic polyelectrolytes are designed to work at lower pH and anionics at higher pH. Nonionic and quaternary flocculants are only slightly influenced by pH. This general rule should not be interpreted to mean that anionic polymers do not work at low pH--it simply means that they are no longer ionic. They produce good results in flocculating solids at low pH simply because of their nonionic bonds. The same applies to cationics; even though they are not charged at a high pH, they may well be equally as effective because of their polar groups.

Organic polymers used in water treatment are of two major types, coagulants and flocculants. Coagulants are positively charged molecules of low molecular weight. Flocculant polymers have much higher molecular weights providing long bridges between small flocs to inhance particle growth. Flocculants are either cationic, anionic, or nonionic. Polymer flocculants, unlike coagulants, are not selected for neutralization.

Unlike inorganic salts, polymers do not produce voluminous gelatinous flocs. In applications where additional solids improve results, inorganic coagulants or clay may be required to supplement the use of polymers. Polymers do not affect pH, nor is their performance as sensitive to pH as initial coagulants.

ACTIVATED SILICA

Some inorganic compounds can be polymerized in water to form inorganic polymer flocculants. Activated silica is one example. When sodium siliute is diluted to 1.5-2% and then partially neutralized by the addition of Cl_2 or Na_2CO_3, the silica becomes colloidal and then begins to slowly polymerize. After aging for 15-30 minutes, the solution is diluted to 0.5-1.0% SiO_2 arresting further polymerization and producing activated silica. Although this preparation procedure is complicated, this is a very effective flocculant for applications such as alum treatment for color removal and improving the softening of organic containing waters.

COAGULANT AIDS

A coagulant aid is an additive which aids the coagulation process. It is finely divided colloid which may be surface modified which, when added to raw water, provides increased and more effective particle collisions during the initial neutralization step. Although these inorganic colloids (e.g., activated bentonite clay) may be compared with inorganic metal salt addition, they provide a different function, and they do not have the same disadvantages, such as the formation of hydrous polymerized floc structures which can give rise to dewatering difficulties in later sludge handling. These coagulant aids provide an effective means of building a sludge bed (where turbidity of the feed is low) and providing the additional turbidity needed to enhance the clarification process.

Several most innovative applications of this sort tailored specifically to the mineral processing and effluent treatment needs of mines and mills are demonstrated for an activated bentonite product by:

DRILLCHEM (PTY) LTD.
Post Office Box 78642
Sandton 2146
South Africa
(011) 783-4456
Telex: 4-24529
John Dent
Ian B. Jackman

FLOCCULATION

Flocculation is the entrapment of neutralized particles into a larger solids network or floc. Although coagulation is a chemical reaction, the flocculation process in which floccules are adsorbed together to form larger flocs is mainly a mechanical process. In addition, molecular bridging may be enhanced by the use of flocculants. Flocculation results in a considerable increase in the size and density of coagulated particles resulting in a faster rate of settling of the flocs.

Flocculants are often "ionic," but their function is not to neutralize charged particles. The charge of the flocculant is primarily an indication of how it will uncoil in a given situation. The primary function of a flocculant is to provide a bridge between previously neutralized particles. These chemical sform larger floc particles that are dense enough to settle and which, in the process, also adsorb other coagulated particles, thereby enhancing the rate and efficiency of clarification processes.

FLOCCULATION IN PLACER MINING

Placer gold mining operations more often than not are located alongside or in a streambed or creek. Water requirements are nearly always drawn from the creek. Placer mining uses a large volume of water per ton of ore (1 yd^3 = about 2 t) for washing. Often, clay minerals are "scrubbed" from the ore in a trommel. Water containing suspended solids cannot legally be returned to the stream within permit rrequirements in North America and several other countries. This means that water is settled in a series of ponds before being returned to the process and/or decanted and discharged. The area of settling pond required can be extensive. Operating a flocculant makeup and dosing system to enhance settling rates and to reduce the size of the pond needed is possible but expensive to build and maintain. It also needs a power supply and a source of clean, fresh water with which to make up the polymer solution.

Hercules, Inc. has developed a new way of dosing flocculants using gel logs which are placed in the water stream and which dose according to the flow rate that comes into contact with the log. The application of gel flocculant to remote impoundment ponds has been described by MOORE (1982) in a technical report brochure titled "Treatment of Remote Impoundment Ponds with Gel Flocculants." This is probably not the ideal way to dose a flocculant to a system, but it is very simple and convenient and certainly would beat no flocculant at all. Information can be requested from:

HERCULES INCORPORATED
Water Management Chemicals
33092 Highway 550 North
Durango, CO 81301
(303) 247-0335
Perry J. Hensley
Area Manager

HERCULES, INC.
Water Management Chemicals
910 Market Street
Wilmington, DE 19899
(302) 575-6500
T. Davis
K. Fletcher

It is believed that CALGON CORP. may also offer a similar product, but this has not been convirmed.

COAGULANTS AND FLOCCULANTS IN MINERAL PROCESSING

Most texts on coagulation and flocculation deal with municipal water and wastewater treatment. Flocculation has been intensively used since the 1960's for enhanced settling of solids in CCD circuits and for improved filtration performance in metallurgical circuits.

Flocculants have also found application in solution clarificaton and polishing although examples have also been encountered where better overall extraction results are achieved by not adding coagulants or flocculants. One example of this was in the cone clarifier installed at Vaal Reefs South ahead of Stellar filter clarification before zinc precipitation as described by KUN, et al. (1979). Installation of the "Hopper Clarifier" using 5 mg/l $FeCl_3$ and an organic polymer alone resulted in an increase of the Stellar filter cycle from 4 to 40 hours. When $FeCl_3$ addition was discontinued, the cycle of the Stellar filter clarifier was increased to 170-200 hours. In this case, the shape of the suspended solids particle is such that it forms an accumulating "precoat" layer on the Stellar filter surface which enhanced the cycle time when particles of a particular species were not removed.

Chapter 4 refers to underground sludge removal from minewater in which the organic flocculant PERCOL is used to advantage in the AARL-CSIR cylindro-conical clarifier. Appendix I includes a trip report on the Mount Emmons water treatment plant installed by AMAX, Inc., which employs the DRAVO Lectrocoagulation process which works well for solutions with a low solids load. More information can be obtained from:

DRAVO RECOVERY SYSTEMS
222 Third Street
Neville Island
Pittsburgh, PA 15225
(412) 777-5241
O. A. Clemens

In the treatment of minewater and mill tailings decant effluents for discharge, often it is necessary to use flocculants and coagulants to enhance precipitate settling characteristics. The use of polyelectrolytes in settling of sewage sludges in municipal waste water treatment plants is also standard practice, and it is suspected by some that residual amounts of polyakrylamides may be one cause of interference in flotation processes when

treated sewage water is used in flotation circuits, but this has by no means been firmly established.

Coagulant and flocculant technology is largely based on empirical experience, and water treatment suppliers are usually the best source of information, e.g.:

CALGON CORPORATION
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Dr. Frank Daniher

ALLIED COLLOIDS, INC. (Percol Products)
Post Office Box 820
Suffolk, VA 23435

ALLID COLLOIDS (SA) PTY LTD. (Percol)
Post Office Box 48775
Roosevelt Park 2129
South Africa
(011) 782-5335
R. J. Daly

AMERICAN CYANAMID CORP.
859 Berdan Avenue
Wayne, NJ 07470
(602) 624-0496
Arnold Day

ANIKEM (PTY) LTD. (Nalco in RSA)
Post Office Box 67817
Bryanston 2021
(011) 706-6106
Mervyn S. C. Wilson

FLOCCOTAN (PTY) LTD.
Post Office Box 39
Pietermaritzburg 3200
South Africa
(011) 429001
(0331) 33265

NALCO CHEMICAL COMPANY
2901 Butterfield Road
Oak Brook, IL 60521
(312) 887-7500
Robert E. Finch

Of all the flocculants tested, a modifid polysaccharide guar gum product seems to provide the best initial clarification rate for pregnant acid uranium solutions in CCD solid/liquid separation section of a uranium plant. This was reported as far back as 1967 by GREIG (1967). Suppliers of guar gum flocculants in South Africa are:

TROCHEM LTD.
Post Office Box 14032
Waderville, Transvaal
South Africa
(011) 34-2457
Murdock McKenzie

STEIN HALL S.A. (PTY) LTD.
Post Office Box 520
Meyerton 1960
South Africa
(01612) 22340
Telex: 83167
Martin Hattingh
Managing Director

ROSEN, et al. (1980) described an analytical method for rating flocculant performance. This is a simple technique for characterization of the performance of flocculants in various mining applications. The method utilizes three key parameters obtained from raw settling data and combines them into a single mathematical parameter called the desirability coefficient. The first two parameters are the times required for the slurry supernatant interface to fall to two selected fractions of the starting height, and the third is the clarity of the supernatant liquid. The relative values of the three parameters may be assigned different weights in order to make them correspond with laboratory and field performance requirements of a particular industry. Provision is also made of an internal comparison of test flocculant data with that of a control. This method was developed and described by development scientists of the UNION CARBIDE CORP.:

UNION CARBIDE CORPORATION
Chemical and Plastics Division
Tarrytown, NY
Meyer R. Rosen
David B. Braun

NATURE OF PRECIPITATES

The nature of precipitates is, of course, an important factor in determing the degree of clarification achievable by settling. This not only is affected by the precipitant used, but also by conditions under which precipitation occurs, e.g., temperature and the presence of other species. For example:

- When zinc is precipitated at pH 10 or above, the flocs are said to be fluffy and difficult to settle. See Mine-Mill M in Appendix I.

- Cadmium hydroxide flocs are notoriously difficult to settle, and usually a polishing process must be employed (e.g., deep-bed sand filtration) to achieve very low levels. See Lead Smelter B and AMAX Mount Emmons trip reports in Appendix I.

- MgO added as a powder to an effluent is said to precipitate metals effectively and yield a dense, easy to settle precipitate not requiring further clarification.

MIKHNEV, et al. (1978) describe the use of a sulfide solution in $Ca(OH)_2$ to precipitate heavy metals from metallurgical plant effluent. The Cu, Ni, and Fe were precipitated at

pH 5.2, 7, and 7-9 respectively. The degree of removal depended on pH and the composition and dosage of the added $Ca(OH)_2$- $S^=$ solution, and to a very limited extent, on temperature (20-80°C). The treatment at final pH 7.5-8 decreased the metal concentrations as follows:

	Inflow	Outflow
Cu (mg/l)	70	0.1
Ni (mg/l)	80	0.01
Fe (mg/l	10	0.01

The precipitate contained about 12% Cu, 12% Ni, and 20% CaO as CuS, NiS, and $CaSO_4$.

Importantly, the use of $Ca(OH)_2$- $S^=$ solution increased the clarification rate by 50-100%.

CLARIFIERS

Numerous devices are used to clarify solutions. The NALCO (1979) Water Treatment Handbook, Chapter 8, describes several versions typical in the municipal treatment industry where huge volumes of water are treated using very large-scale equipment for coagulation and flocculation which is accomplished in separate operating units, flash mixing for coagulation followed by gentle flocculation mixing. In municipal treatment plants, flocculation is followed by settling and sand filtration.

NALCO (1979) makes the point that the lower the suspended solids content in the process stream or the higher the required effluent clarity, the more critical is mixing to the final results.

There are several clarifier types and approaches to choose from:

- Cylindrical Clarifiers
- Slurry Recirculation Cylindrical Clarifiers
- Hopper Clarifier
- CBI Claricone Clarifier
- AARL-CSIR Cylindro-Conical Clarifier
- Lamella Clarifiers

LAMELLA CLARIFIERS

The capacity of a clarifier is a function of the settling area provided. In this respect, the lamella clarifiers can offer a very much greater effective settling area for a given

floorspace and, except where water is very scaling in nature, this type of clarifier is gaining in popularity.

Lamella or plate-type clarifiers with extensive internal surfaces are less suitable when the solutions are highly scaling. Lamella clarifiers are used in Canada for clarification of effluents after lime precipitation of metals from acid mine drainage and tailings pond decant solution by NORANDA MINES LTD. at Mattabi, Waite-Amulet, and elsewhere. Platepacks are inserted into cylindrical clarifier tanks. The reason platepack lamella clarifiers are preferred be cause of the cold climate making the compactness of lamella clarifiers desirable as the clarifier can then be housed indoors. At two operations, Brunswick Mining at Bathurst, N.B., and the GECO effluent water treatment plant in Ontario,the solutions caused such bad scale that the lamella clarifier proved impractical.

A platepack lamella clarifier that is popular and well backed up in Canada is the PARKSON or AXEL JOHNSON unit offered by:

AXEL JOHNSON
Division of Brian Engineering Ltd.
25 Shaft Road
Rexdale, Ontario M9W 4M3
(416) 249-7961
Telex: 06-989331
Maurice L. Leblanc

SERPAC platepack clarifiers have also been tested for minewater clarification underground on Witwatersrand Mines at the Blyvooruitzicht Gold Mining Company (Rand Mines) and at the Harmony Gold Mine (Rand Mines) near Welkom. It is not known how well these clarifiers have performed for the underground application, but inquiries could be made through:

RAND MINES SERVICES (MINING & MILLING) LTD.
Post Office Box 62370
Marshalltown 2107
South Africa
(011) 836-1166
Johan Wagner
Consulting Civil Engineer

The SERPAC plate clarifier is designed and fabricated by the French firm ERPAC. In South Africa, they are offered through R. J. SPARGO LTD., and in North American by LINATEX.

ERPAC
85 rue Carpeaux
59290 Wasquehal
France
(20) 26 95 05
Telex: 132 658F

R. J. SPARGO LIMITED
Post Office Box 3793
Alrode 1451
South Africa
(011) 864-2744
Telex: 4-20365
Jimmy Van der Bergh
C. B. Parker
Company Metallurgist

LINATEX CORP. OF AMERICA
Box 65
Stafford Springs, CT 06076
(203) 684-2756

Lamella clarifiers which work on similar principles are also offered by:

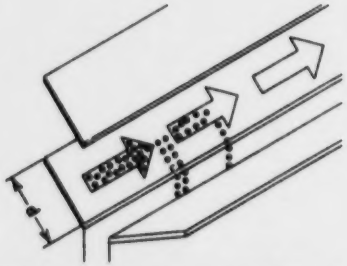
PASSAVANT
Passavant-Werke
6206 Aarbergen 7
Holland
(06120) 281
Telex: 4186596

PARKSON CORP.
Box 408399
Fort Lauderdale, FL 33340
(305) 974-6610
Mike Miller

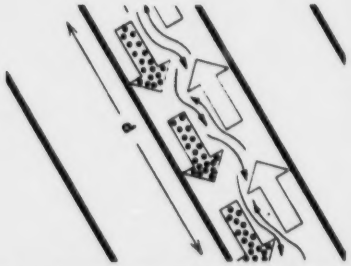
Neptune Microfloc, Inc., a division of Signal Companies, offers an inclined tube settler which performs along similar principles to the inclined plate clarifier. Information can be requested from:

NEPTUNE MICROFLOC, INC.
Box 612
Corvallis, OR 97339
(503) 754-7654
Steve Urban

1

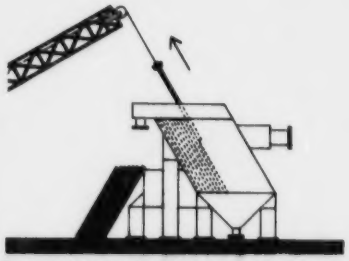


Unobstructed, cross flow characteristic of LINATEX-SERPAC gravity settler. In the patented SERPAC cell suspended solids have, at the very most, only 3.75 cm) to settle before they are out of the primary flow and falling in an isolated sludge chimney zone. This beneficial characteristic of the SERPAC design promotes rapid reduction in the level of suspended solids within the liquid medium as the flow progresses across the cell, creating an optimum condition for settling out of remaining solids. SERPAC design results in more efficient clarification.

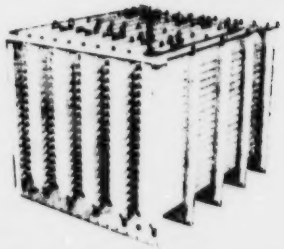


Hindered settling characteristic of conventional counter current plate/gravity settler design. Conventional plate (and tube) type "counter current" gravity settlers are not designed for maximum efficiency. Typically, solid particles travel downward through a somewhat turbulent "teeter column" (dimension 'd') during which particles settling out on the plates must travel 183 cm to 305 cm in a downward flow, which is in opposition to the upward rising clarified effluent. Resulting interference and turbulence impede efficiency of clarification process.

2

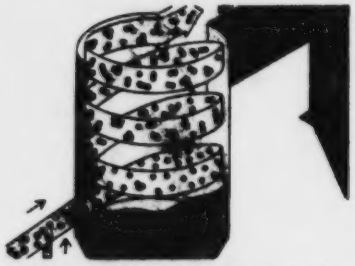


Removal of metal plates from conventional plate type gravity settler. Other designs of gravity settlers are such that large metal plates and elements must be removed one by one using cranes or other heavy equipment. Moreover, metal components are subject to corrosive attack unless costly stainless steel construction is used.

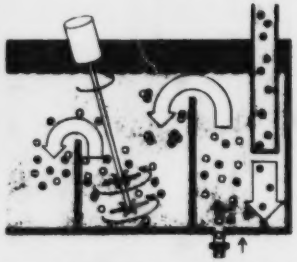


LINATEX-SERPAC cell is removed as single lightweight assembly. Periodically, it may be desirable to inspect the inside of any gravity settler, and its interior components, to determine their condition. The LINATEX-SERPAC cell construction permits rapid withdrawal of complete cell units from the settling chamber, using a small, inexpensive overhead hoist which can be furnished with the original equipment. Settling chamber interiors are epoxy coated for long service life. For highly corrosive applications, settling chambers can be LINATEX-rubber lined.

3

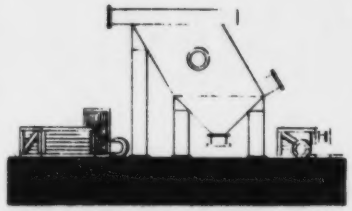


LINATEX-SERPAC reaction chamber. Flocculent solution is uniformly introduced into feed. Floc formation is promoted and enhanced by controlled centrifugal action and long retention time in large SERPAC reaction chamber. There are no mechanical stirring mechanisms, therefore shear forces are minimized and consumption of flocculent solution is reduced.

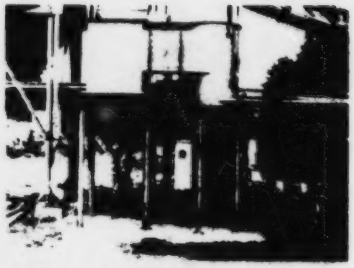


Conventional mechanical mixing of flocculating solution and influent. Flocculating tanks, provided with certain other types of gravity settlers, employ mechanical mixing apparatus for the purpose of promoting rapid polymer disbursement and floc formation in relatively small flocculating chambers. Experience has shown that the action of the mechanical mixer blades can break up partially formed flocs, resulting in abnormally high rates of flocculent consumption.

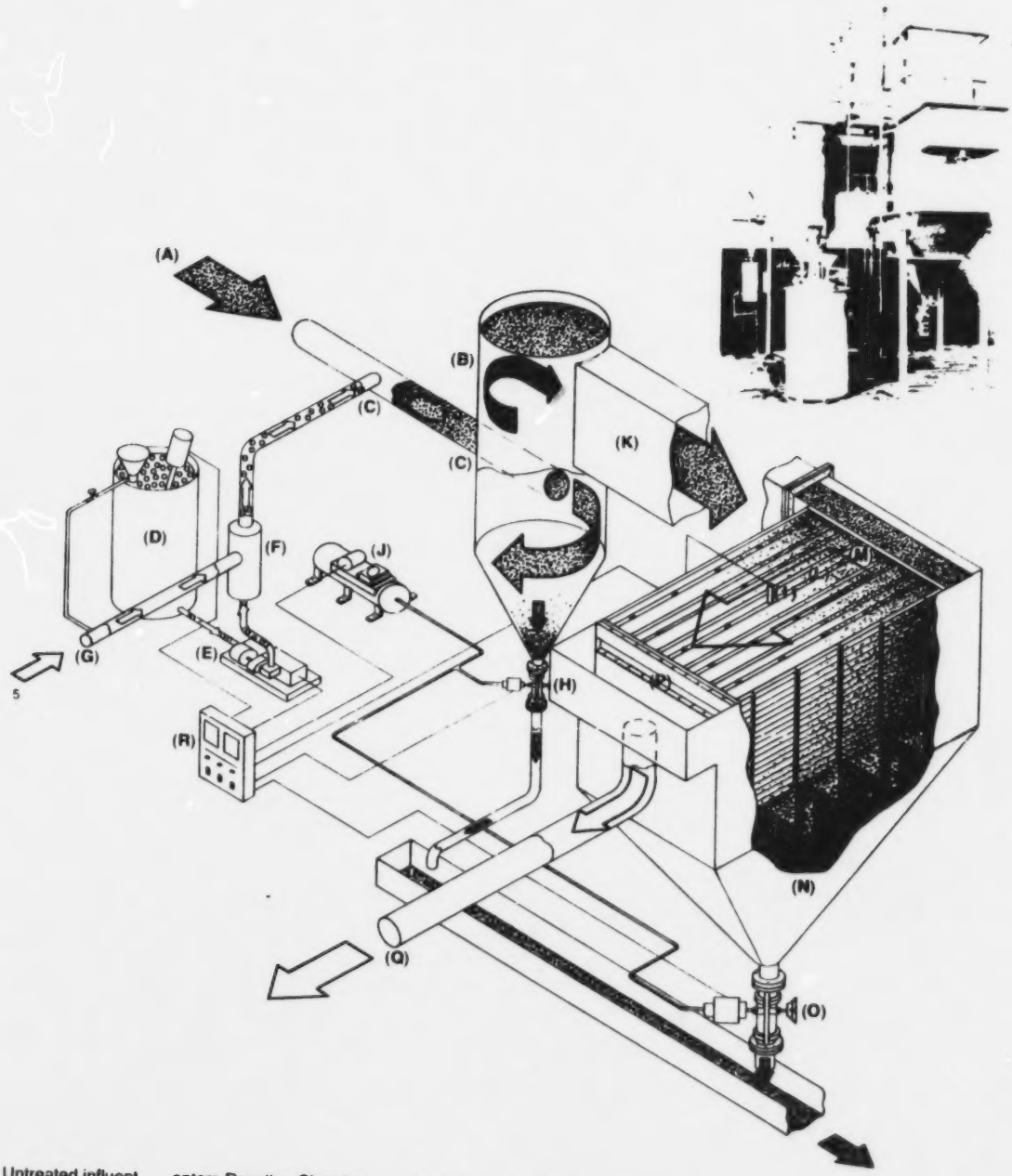
4



Other "package" systems. Some manufacturers sell only a clarifier or gravity settler. The purchaser must determine requirements for all accessory equipment, purchase same from a variety of vendors who assume no unified responsibility for an integrated, functional system. If problems occur, the purchaser must deal with a number of parties, each with limited responsibility and no tie-in to overall system requirements.



LINATEX-SERPAC package system. Each LINATEX-SERPAC water treatment system includes *all* key components required for a fully compatible and functional system. Items normally supplied, in addition to the basic SERPAC cell tank and reaction chamber, include: flocculent mixing and dispensing apparatus, pumps, valves, piping, automatic controls, control panel. All items are selected and manufactured or supplied by Linatex, providing the purchaser with *single source responsibility* for a system to meet proposal specifications.



Untreated influent enters Reaction Chamber at point . Premixed flocculent solution is dispensed from polymer mixing station by metering pump to polymer dilution vessel . Dilution water is introduced to vessel through line . Properly diluted flocculent solution flows from vessel and is injected into influent pipe at . Reagentized influent gently rises in upward spiraling flow within Reaction Chamber, permitting optimum flocculation. Coarser solids present in influent rapidly settle, collecting at lower apex to be periodically discharged by valve , controlled by pneumatic actuator activated by density sensor and powered by compressor . Flocculated influent flows from Reaction Chamber across connector section and enters SERPAC cell(s) through distribution baffle . Suspended solids settle within cell (see page 5 for details), collecting in sludge hopper . Periodically, when sludge is at optimum density, electronic sensor signals air control valve causing the valve to open, thereby discharging sludge into collecting trough below. Clarified effluent discharges from cell through distribution plate exiting via pipe . Control panel provides single point control of all system equipment.

THE SERPAC CLARIFIER

by C.B. PARKER
R.J. Spargo Limited

SYNOPSIS

The Serpac Clarifier is a further development of the thin plate type thickeners and should be considered as tertiary settlers, at the end of the line when clean water is required.

The Serpac system is modular in construction, the flocculent is injected into the feed pipe ahead of the reaction chamber where floc formation is enhanced by gentle centrifugal action and desanding occurs.

A connecting channel to the Serpac settling chamber allows for a non-turbulent stabilised pulp flow. The thin blade settling cell completes the settling of suspended flocs and the water is clarified by a regulating control unit at the discharge end of this cell.

Each Serpac unit has an equivalent of $10m^2$ of settling area and can settle a nominal one ton per hour of solids per module. For efficient clarification suspended solids are limited to ± 3,0% by mass. By using small plastic plates, similar to those used in venetian blinds, a large settling area is generated which is suitable for small flocs containing colloidal and near colloidal solids. The settled sludge is extracted on a timed cycle and the cycle can be controlled by density probes.

Capital cost will vary from ± R600,00 m^3/hr for a single module reducing to ± R215,00 for larger volumes of up to $780m^3$/hr.

Operating costs are in the region of 2,0 cents/m^3.

2. INTRODUCTION

Water is the most commonly used raw material in any industrial process. Upstream it is used as a product constituant, a materials carrier, for washing etc. Downstream it is inevitably a vehicle of industrial refuse; it is this product which is considered in this paper.

Water has mistakenly been considered a cheap material, with rising populations increasing usage, the variability of supply and the rising cost of both for the raw material and sewage surcharges for the treatment of difficult industrial wastes, it becomes more necessary to clean and re-use this water within industrial plants. Considerable water re-use is already practiced and as water reclaimation eventually becomes a cost exercise, the market for reclaimation systems is very cost competitive.

The most common impurity to be removed from water is suspended solids, both non-colloidal and colloidal.

The three important methods are:

i) gravity settling

ii) flotation

iii) filtration

These suspended particles, either in simple or in colloidal suspension, mostly carry a negative surface charge which makes them repulse each other. It is thus necessary to remove or reduce these repulsion charges by the addition

...../2

of positive charged particles using Fe, Aℓ metal hydroxides etc. The second stage is to increase the size of the particles into flocs by agglomeration using long chain high mollecular weight polyelectrolytes.

A third stage comes in with the Serpac, this is artificially multiplying the settling surface by introducing parallel thin bladed plates in order to reduce the floor surface required by the system. The water movement in the Serpac is crosscurrent (see Figure 3).

3. THE MAKEUP OF A SERPAC MODULE

The installation principle is based on an association of components, whose role is clearly defined and optimised, (Figure 1).

3.1. The reaction chamber: Providing -

- the eventual desanding and even some deoiling.
- the coagulation - flocculation reaction with a sludge bed, fluidised at the optimum concentration by the flow of water which leads to a reduction of consumption of flocculating agents.
- an extremely short retention period, 0,5 - 1 minute for quarry muddy water, 1 - 3 minutes for clarification of surface water, whereas 10 - 30 minutes is usually needed.

3.2. A connecting channel between the reaction chamber and the settling tank enabling -

- predecantation without turbulence of the water which comes out of the reaction chamber with up to 50% of the sludge carried by the incoming water already deposited.
- a very stabilised supply adapted specifically to the problem to be solved.

3.3. A thin blade settling cell that -

- completes the settling of the agglomerated suspended microparticles.
- clarifies the water which has been moved by settling and thickening of the sludge. (Figure 2).

3.4. A regulating control unit that -

- regulates the water flow within the cell. The settling is done on clarified water and unlike other thin blade settling modules there is no need for equal distribution of the rate of flow. The pre-settling channel clarifies the upper flow of water very quickly, this arrangement enables the acceleration of the rate of flow in the upper part of the cell, unlike the lower part which works at the normal rate of flow of the thin blade settling tank. (Figure 4).

To enlarge in the principles of the Serpac Cell there are three elements, each making separation easier and more efficient.

1) An upstream reaction chamber for removing the coarser particles.

2) A cell, made up of vertical elements with a certain number of inclined plates, each of the elements being hung on a frame which can support the weight of a man and serve as a grating. Particles slide on the upper side of the thin blade which is at an angle of 60°; when they reach the blade edge they fall into a vertical channel in which the flow of water is stilled by appropriate screens. The particles can therefore, by their density, sink down into the sludge thickener section of the tank, this section will normally be pyramidal. Under the cell vertical baffles are placed in the downhill section to prevent water from running directly under the cell and thus disturb the settlement on the thin blades.

3) A device for recovery of the treated water. This is a perforated tubular spillway which controls the flow of water that can be treated in the cell and is one of the most important elements of the Serpac unit.

It is possible, by increasing the number of stacked blades, to multiply the equivalent surface area of the cell and thus it's capacity for very difficult settling slimes. With the standard 18 blades an equivalent surface of $13m^3$ is obtained (CI Cells). With 27 blades (C2 Cells) an

equivalent surface of $18m^3$ is now available.

The floor area of a cell is approximately $1m^2$.

Advantages of the Serpac

i) Control and optimisation of all the stages in the process.

ii) Reduction of consumption of floculating agents by -

- maximum utilisation of the reaction time
- existance of a fluidised floc forming bed
- smooth transfer of the obtained flocs to the sedimentation zone.

iii) Reduction of floor space occupied by the settling basin as detailed above.

iv) Reduction of the total cell height and thus of the settling tank height compared to other types of thin blade settlers due to the use of cross current flow.

Disadvantages of the Serpac

i) Due to having a low volume ratio to the actual settling area available Serpac is sensitive to changes in the loading rate. It can be advantageous to fit an automatic level/discharge system, especially if the influent solids concentration varies.

ii) Solids content by mass should not exceed 3% for a clean water overflow.

4. COSTS

i) Capital cost can best be expressed for a volume throughput. As the units are modular (each equivalent to $10m^2$ of settling area), a single unit is the most expensive, one would be looking at ± R600,00/m^3/h of flow capacity.

Going up to a 12 cell unit, with a throughput of up to 480 m^3/h then the cost per m^3/h flow drops to R215,00. This is not expensive considering local water costs 23,7 cents/m^3. Using a 4 cell unit, with a 90% recovery and operating 23 hours/day, the payback time is ±714 days.

ii) Reagent costs are difficult to quantify as this depends on the difficulty or ease of flocculation, we have found costs from 0,4 to 5,1 cents/m^3 with 1,8 c/m^3 being a conservative guide figure.

iii) Maintenance costs. These are very low and mainly concern the dosing pump and reagent mixing plus the sludge extraction system. This maintenance cost is likely to be about 20% of the reagent cost.

5. USES

Clarification of industrial waste water from factories, sand washing operations, quarry water, recirculation and cleaning of process water, mill scale separation, separation of metal hydroxides from rinse water in pickling and galvanising plants and final clarification of domestic water.

In the event of the solids content of the influent being too high this can often be sufficiently reduced by using a cluster of hydrocyclones ahead of the Serpac Unit.

Organic materials usually require a completely different treatment.

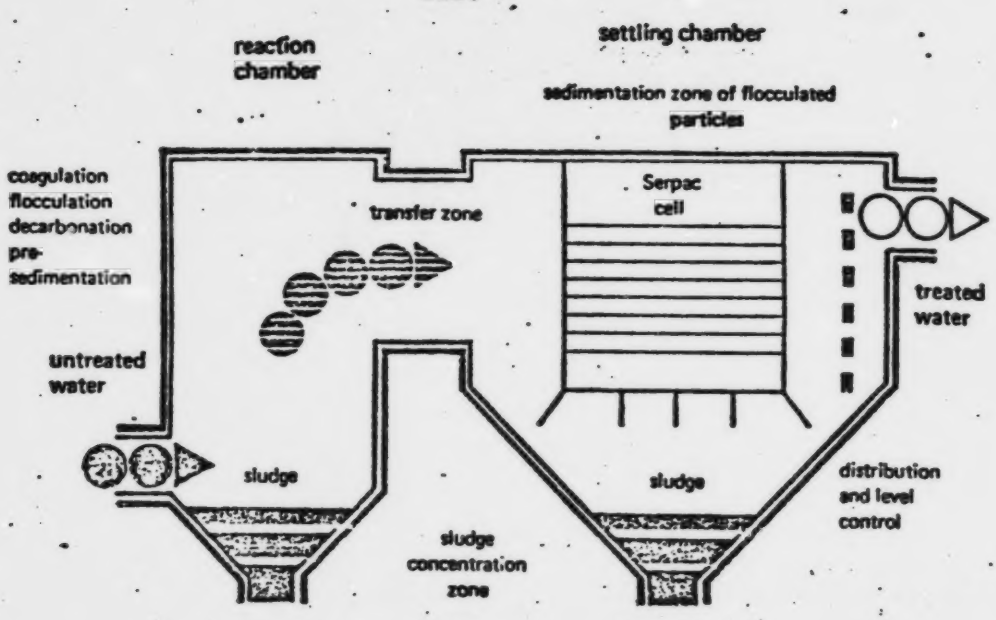
CONCLUSIONS

Thin plate clarifiers of the Serpac type will have an increasing use in the last stages of reclaiming industrial and mining waters for reuse. As industry expands along with the population growth the demand for water increases, this demand can best be provided by recycling as much water as possible, especially so within the Republic of South Africa where we rely on rainfall to fill manmade storage dams which are subject to high evapourative losses.

ACKNOWLEDGEMENTS

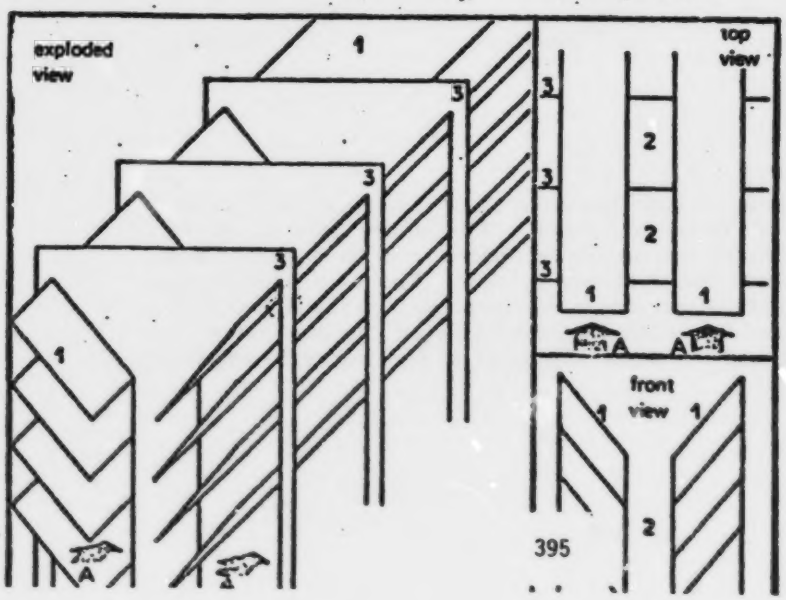
This paper is presented with the permission of Mr. S.H. Spargo, Chairman of R.J. Spargo Limited. The author thanks ERPAC of Wasquehal, France for their technical assistance.

FIG. 1



The Serpac Cell

FIG. 2



The Serpac Cell (Erpac patent

Flowing in the direction of th arrow (A) the water to be treat ed runs horizontally throug the cell. Under separation for ces, the particles move ver tically in the water flow unti they touch the cell blades (1 then they slide along the blade and are drained away throug the sludge collecting funnels (2 where transverse baffles (3 prevent internal circulation.

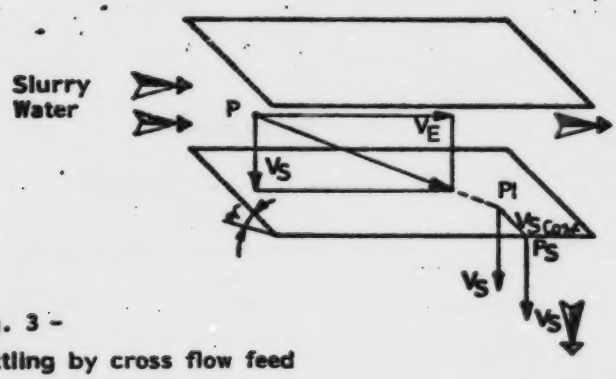


Fig. 3 -
Settling by cross flow feed

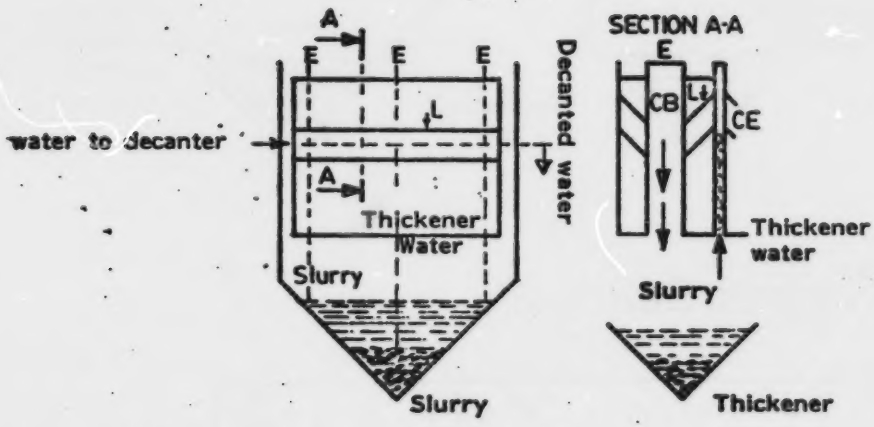


Fig. 4

Crossflow decanters - Type Serpac

The water circulates in each decanter element between two parallel blades with angle to the horizontal. The slurry decants on the lower blade and slides due to the inclination and then falls into the passage CB to enter the thickener section. The water displaced by the slurry in the thickener comes up through a passage and is clarified in channel CE. The filters E obstruct the raw water circulation and cause the water displaced in the slurry to ascent vertically.

APPENDIX 1

The three types of settling process on thin blades

The HAZEN formula defines the climbing velocity as the quotient of the rate of flow treated on the mirror surface : Q/S. The equivalent surface of separation S is the product of the projected surface of the rectangular blade L.I. on a horizontal plane by the number of blades N in service; it formulates itself:

$$S = N\ (L.I.\ \cos.\alpha) \qquad \text{(Fig. 1)}$$

Co-current supply, supply by reversed current, these devices suffer from inadequacies. They led the test department ERPAC to experiment and improve the third type of supply known as "cross currents". With this system, the effluent must not pass once again through the sludge screen and particles can be eliminated from the plates and will settle out according to an oblique trajectory. Moreover, this choice is justified by the useful length of the plates. The theoretic calculation of the length of the necessary distance between two plates for a same space e, a same length l, a settling velocity Vs and a laminar flow Ve shows the advantage of the supply by cross currents (Fig. 2b).

By reversed current, the time needed to cover $P_E P_S$ is equivalent to:

$$t = \frac{e}{V_S \cos \alpha}$$

The length L will then have to be:

$$L = (VE - V_S \sin \alpha) \frac{e}{V_S \cos \alpha}$$

.....cont

By co-current under the same conditions, we obtain:

$$t = \frac{e}{V_S \cos \alpha}$$

relative to a distance :

$$L = (VE + V_S \sin \alpha) \frac{e}{V_S \cos \alpha}$$

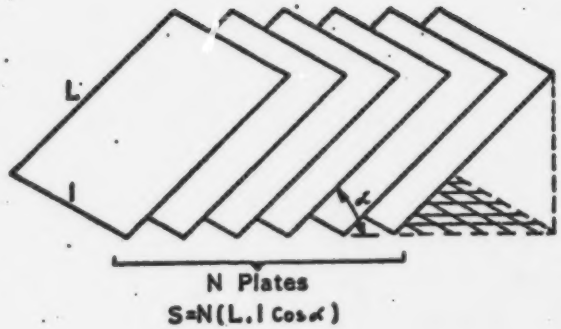
Whereas by cross currents, we have :

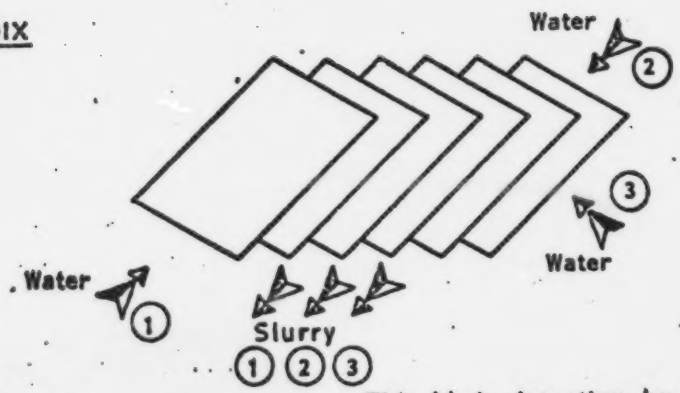
$$t = \frac{e}{V_S} \quad \text{et} \quad L = \frac{VEe}{V_S}$$

As a consequence, the length L will be shorter in a thin plate settling basin with cross currents because α and $\sin \alpha = 0$, $\cos \alpha = 1$.

The thin plate settling tank by counter current would have to be slightly shorter than the system by co-current for a same value of α but in practice, the difference affects only by a few percentages the value of L. Ve ranging between 30 and 100 m/h, V_S varying between 0,5 and 5 m/h.

APPENDIX





Thin blade decanting by reversed current (1)
" " " with current (2)
" " " by cross-current (3)

Fig. 2 - Methods of sedimentation by thin blade decanters. Slurry and water circuits.

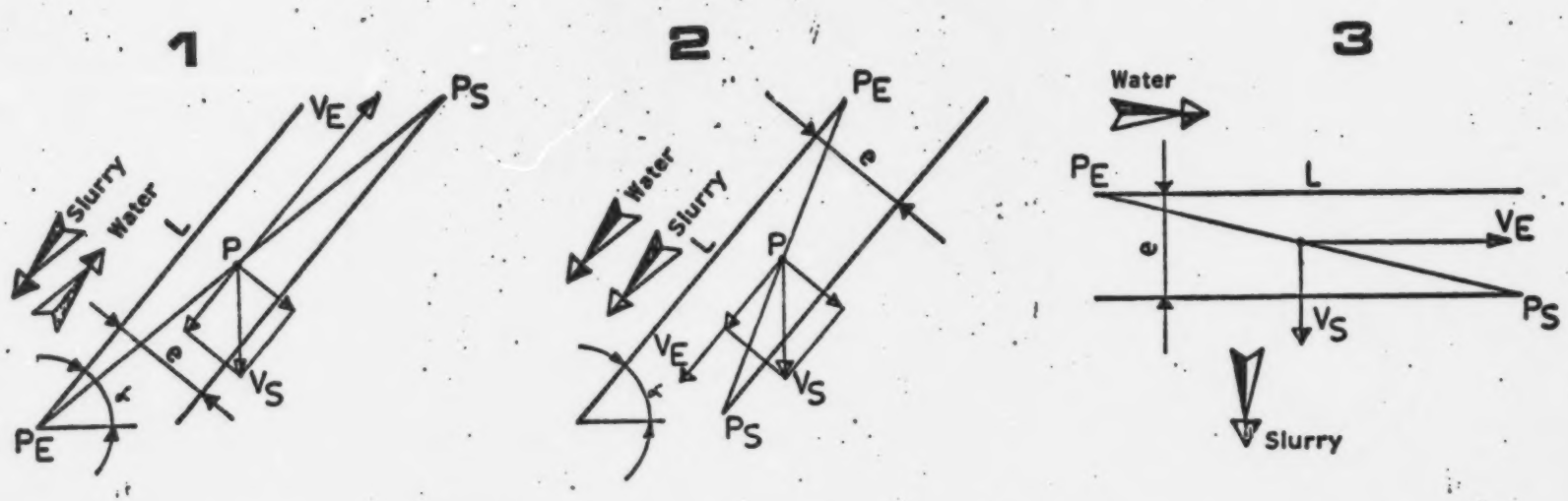


Fig. 2b - Length of plates

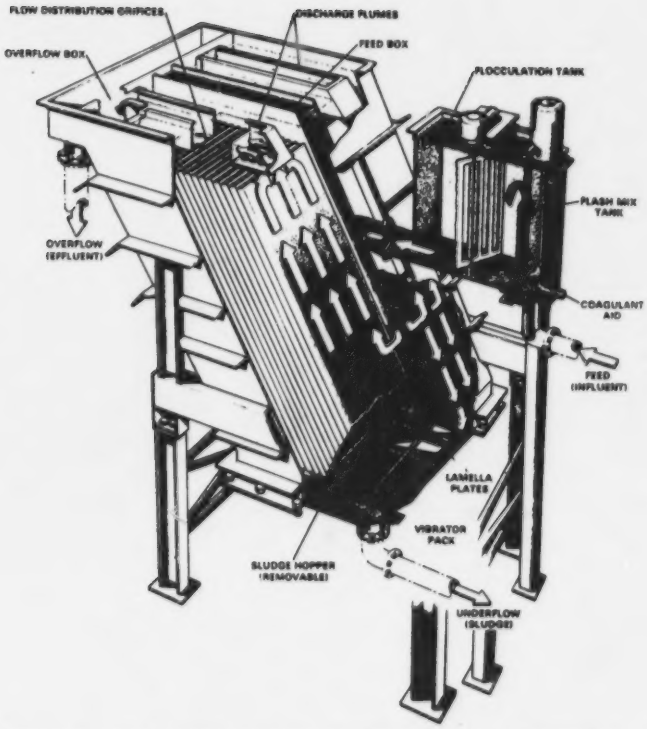
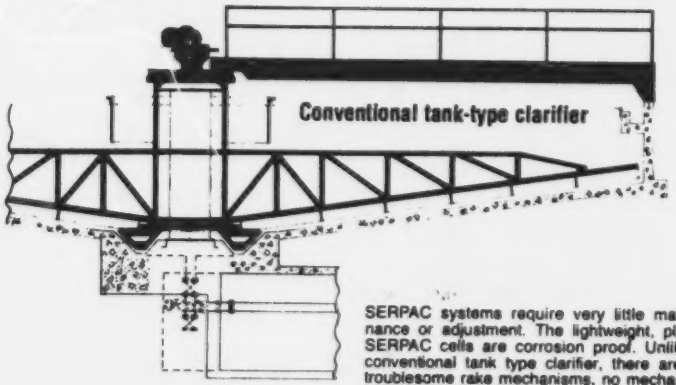


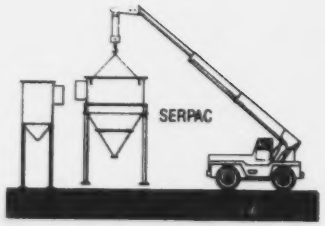
Figure 9.17 Closely spaced inclined plates (lamella) multiply the available settling surface in a small volume and reduce installation space. *(Courtesy of Parkson Corporation.)*

advantages when compared to conventional clarifiers

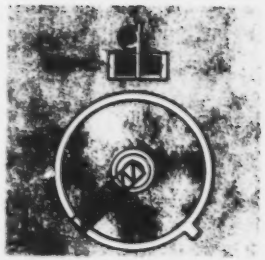
A LINATEX-SERPAC system usually offers a number of significant advantages without sacrifice of efficiency when compared to conventional tank type thickeners. These are:



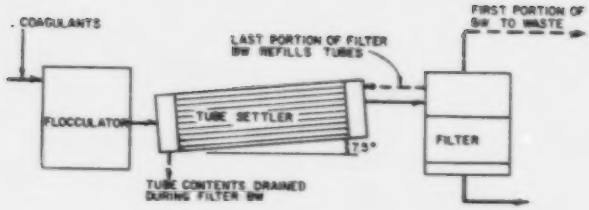
SERPAC systems require very little maintenance or adjustment. The lightweight, plastic SERPAC cells are corrosion proof. Unlike a conventional tank type clarifier, there are no troublesome rake mechanisms, no mechanical drives to maintain, no moving bridge-work. There are *no* moving parts in the SERPAC settler.



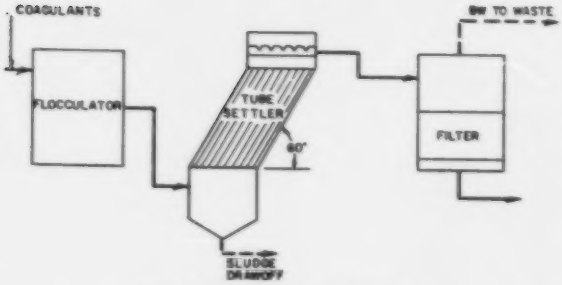
The installed cost of a SERPAC system is, in almost every case, considerably lower than the cost for a conventional thickener-clarifier. Installation of a SERPAC system requires only simple foundations: no expensive excavation, no underground sludge pumps and tunnels, no complex erection stages. Units are shipped semi-assembled from our factory and erection can be accomplished in a matter of days, not several months as is commonly the case with conventional tank type clarifiers.



SERPAC plants occupy only a fraction of the space required for the installation of a conventional circular tank thickener-clarifier. In many cases the space requirement can be reduced by as much as 90%. Such a consideration may be very important if the clarifier is to be installed in mountainous terrain or housed in a building.



ESSENTIALLY HORIZONTAL TUBE SETTLER

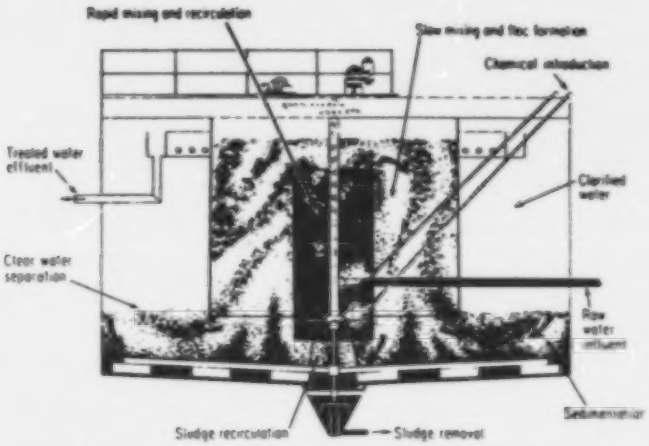


STEEPLY INCLINED TUBE SETTLER

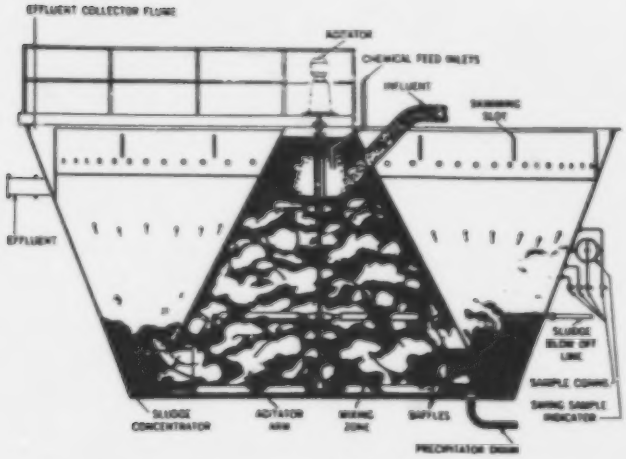
The basic tube settler configurations used with flocculation and filtration. *Neptune Microflloc, Inc.)*

CYLINDRICAL CLARIFIERS

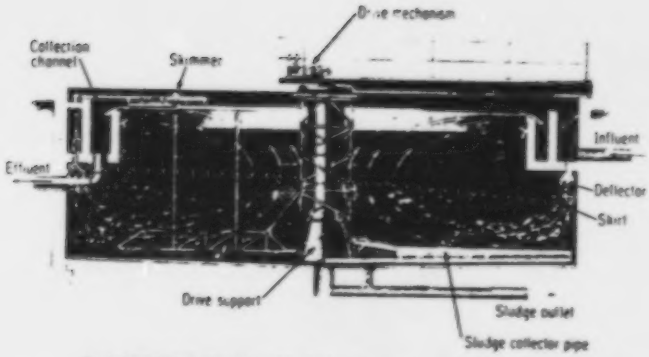
Various configurations of cylindrical clarifiers as illustrated in NALCO (1979) are shown below. There are numerous suppliers of cylindrical clarifiers serving each industry center.



Slurry recirculation design clarifier. *(Courtesy of Ecodyne Corporation.)*



Sludge blanket clarifier providing increasing area for the water rising in th outer annulus, resulting in reducing velocity to match sludge settling rate. *(Courtesy of Th Permutit Company.)*



Peripheral feed clarifier with sludge pipe and scum removal device. *(Courtesy of Envirex, a Rexnord Company.)*

Degremont, a wellknown French water treatment company, is known for its innovative clarification systems:

DEGREMONT
183 Av. dei 18 Jun 1940
92500 Rueil Mal Maison
Paris, France
Jacques le Febeve

CYLINDRO CONICAL SETTLERS

In the U.S.A., CHICAGO BRIDGE AND IRON, Walker Process Division, offers a cone settler which they call a claricone clarifier. This is no more than a conical tank into which feedwater is introduced tangentially with flocculant addition allowing a sludge banket to build up. There are also internal skirts and baffling. The claricone clarifier is said to be an expensive version of the "Hopper Clarifier" of which several versions are installed on Witwatersrand gold and uranium mills where they are constructed by the mine maintenance staff using the basic Pachuca design as the shell.

"Hopper Clarifier"

The first "Hopper Clarifier" on the Witwatersrand was installed at Vaal Reefs South to preclarify pregnant gold solution ahead of a Stellar filter in the Merrill-Crowe Zinc precipitation section of the gold mill. This described by KUN, et al. (1979). More information is included in trip reports on Vaal Reefs in RANDOL (1982, 1983). A critical feature of the operation of the Hopper clarifier is that an adequate flow velocity must be maintained to keep the sludge bed suspended. The minimum flow velocity is 7 m/h and, at Vaal Reefs, it is maintained at 7-9 m/h and a pH of 10.8-11.2. CYANAMID Superfloc N100 non-ionic flocculant at 0.1% concentration is dosed to the bottom of the conical bottomed clarifier at 0.2 g/t through a separate feed line by a mono pump.

The required energy for coagulation is supplied by the feed velocity into the apex of the cone at 1.8 m/s flow velocity in the feed pipe.

The advantages of the Hopper Clarifier are several:

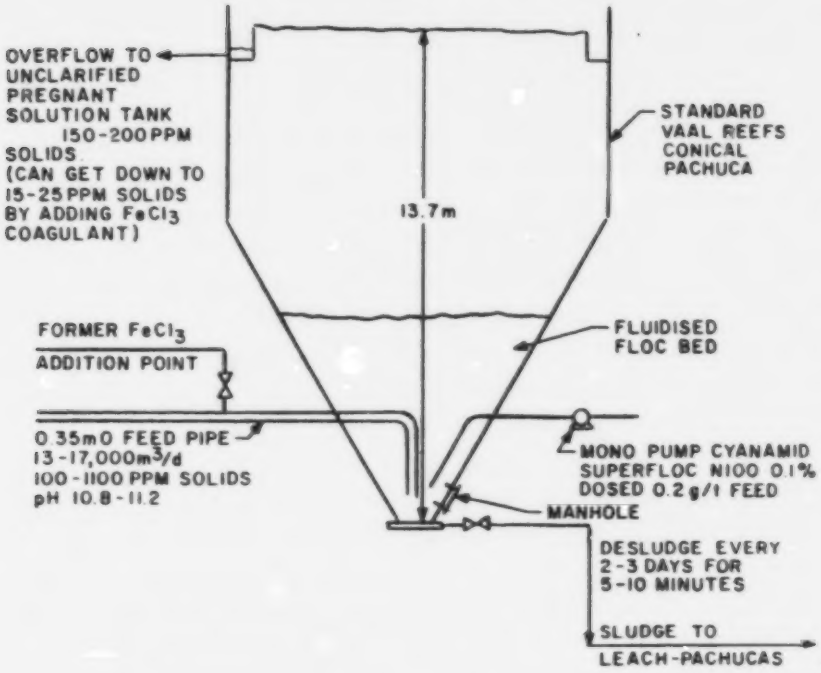
1. Trouble-Free Operation
2. Easy to Operate Requiring Almost No Operator Attention
3. Very Inexpensive
4. Simple Design, Easy to Install at a Low Capital Cost

More information can be obtained about the Hopper Clarifier through:

W. A. KRETSCHMER
Manager Metallurgical
Vaal Reefs Exploration and Mining Co. Ltd.
Post Office Box 5010
Vaal Reefs 2621
South Africa
(018) 7141

Eddie Van Vuuren, a former metallurgical manager of Vaal Reefs who was actively involved in the development and installation of the Hopper Clarifier at Vaal Reefs South may also be able to provide an insight into its design and operation as a consulting service:

HOPPER CLARIFIER VAAL REEFS



E. J. J. VAN VUUREN
Metropolitan Rand Projects (Pty) Ltd.
Post Office Box 32068
Braamfontein 2017
South Africa
(011) 836-2075

Variations of the "Hopper Clarifier" have subsequently been installed on several gold and uranium mills on the Witwatersrand. These include GOLD FIELDS OF SOUTH AFRICA LTD., at Deelkraal, RANDFONTEIN ESTATES G.M. CO. LTD. (JCI) at Cooke Plant, and GENCOR LTD. at Buffelsfontein, where a REUNERT & LENZ deep cone circulator clarifier has been installed.

At RANDFONTEIN ESTATES, a Vaal Reefs-type Hopper Clarifier has been installed to clarify acid uranium leach filtrates with excellent results--apparently, it works so well that no further polishing of the solution is needed before it can be sent to the solvent extraction step for uranium recovery. More information can be requested through:

JOHANNESBURG CONSOLIDATED
INVESTMENT CO. LTD.
Post Office Box 231
Johannesburg 2000
J. David Parker
Consulting Engineer (Metallurgical)
(011) 836-2571

At BUFFELSFONTEIN GOLD MINING CO. LTD., the REUNERT & LENZ deep cone hopper clarifier reduces suspended solids from 500 mg/l in the feed to 10 mg/l in a single stage. It is said to differ slightly from the ANGLO AMERICAN hopper clarifier in that its internals are not quite the same. The The unit tested at BUFFELSFONTEIN G.M. CO. LTD. was a pilot unit which treats 10 m^3/hr. Also, REUNERT & LENZ are said to have an excellent lab scale demonstration of the system. The person to contact from which to find out about this unit is:

PIETER VAN ASWEGEN
Gencor Ltd.
Box 1820
Marshalltown 2107
(011) 836-1121

HUNTER & EMERE (1977) described the use of cylindro-conical settlers for underground minewater clarification at the Harmony Gold Mine, but this would refer to data prior to the Anglo American Research Laboratory improvements to the system.

DISPERSED AND DISSOLVED AIR FLOTATION

For acid mine drainage and metallurgical solutions containing very small suspended solids loadings and also for solutions or wastewater containing oils and grease (often in

saponified colloidal suspension), cutting oils, or emulsified solvent extraction organics, DAF may well prove to be the most practical and effective approach. DAF can refer to dissolved air flotation or dispersed air flotation.

DAF: REXNORD ENVIREX DIVISION

Dispersed air flotation was tested, reputedly with excellent results, alongside the DRAVO electroclear coagulation and flotation system installed at AMAX's Climax Molybdenum Mine effluent treatment plant and at their Mount Emmons water treatment plant, Crested Butte, both in Colorado. The Mount Emmons facility is described in Appendix I.

Because both AMAX plants are already running well using the DRAVO Lectroclear process for metal precipitate sludge recovery, it is not likely that it would be cost effective to replace a system that already works well with another that works marginally better. However, AMAX is said to have found the ENVIREX DAF system as being one of the best they could find from among DAF equipment suppliers.

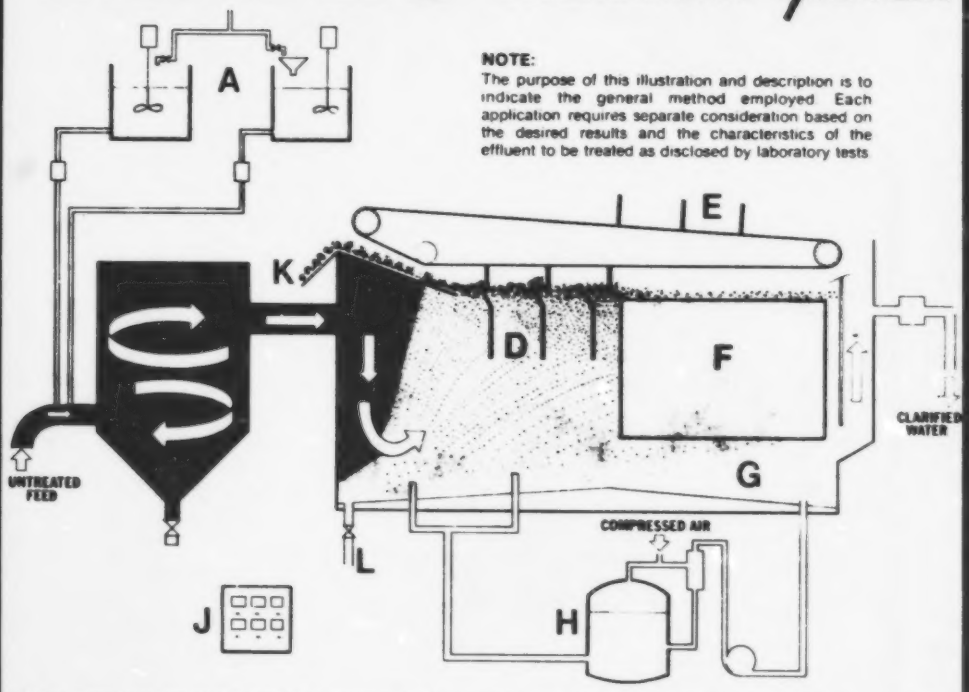
Rexnord DAF systems are available from:

ENVIREX WATER POLLUTION CONTROL DIV.
Rexnord
1901 South Prairie Avenue
Waukesha, WI 53186

TED MILLER ASSOCIATES, INC.
2140 South Ivanhoe
Denver, CO 80222
(303) 758-3912
Debbie Miller

SERFLO EFFLUENT WATER TREATMENT SYSTEM

NOTE:
The purpose of this illustration and description is to indicate the general method employed. Each application requires separate consideration based on the desired results and the characteristics of the effluent to be treated as disclosed by laboratory tests.



Numerous features of the SERFLO System are covered by patents in Great Britain and other countries.

A. The flocculating reagent is prepared and metered into the untreated feed by a dosing pump. A coagulant or other reagent is also added if required.

B. The treated feed is conditioned in a reaction chamber the purpose of which is to encourage the formation of stable and well formed flocs. At the base of the reaction chamber a drain is provided to enable any heavy solids present to be removed.

C. From the reaction chamber the flocs in suspension pass to the entry chamber of the Serflo Tank.

D. In the main section of the tank the introduction of dissolved air causes the flocs to float to the surface. The dissolved air stream is dispersed over the complete width of the tank and moves in a horizontal direction. This forms a parallel layer below the floc laden material being treated.

E. As the solids reach the surface they are removed by the slow moving chain driven scraper gear.

F. The efficiency of flotation is improved by means of the patented Serflo cell.

Table of Capacities and Dimensions Height required 2,3 metres. For servicing allow 3 metres.

Standard Modules	Capacity m³/hr	Floor Space Dimensions
Serflo 1.	20 to 40	4,0 x 5,2
Serflo 2.	40 to 60	5,5 x 5,5
Serflo 3.	[illegible] 120	6,7 x 6,2
Serflo 4.	80 to 160	8,5 x 7,9
Serflo 5.	100 to 200	10,0 x 6,3
Serflo 6A.	120 to 240	10,0 x 7,2
Serflo 6B.	120 to 240	9,0 x 8,5

G. Clarified water passes a specially designed weir plate to be discharged.

H. Clarified water, drawn from the tank adjacent to the point of discharge, is pumped to the pressurisation unit where air is dissolved under pressure and later released at three separate points in the Serflo tank to form curtains of minute air bubbles.

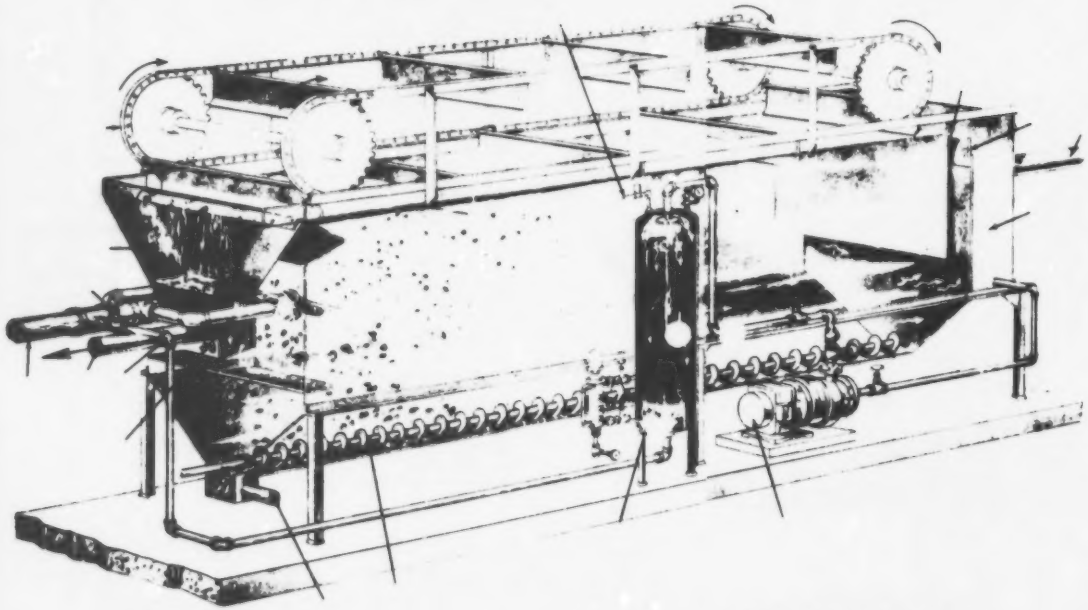
J. A control panel is provided which incorporates control gear for the mixing of the reagents, the scraper gear, the pressurisation unit and in most instances, the pump feeding the system but not shown in the illustration.

K. The scraper gear conveys the recovered solids up a ramp and discharges them from the system.

R. J. SPARGO Ltd.

228 Fuchs Street, Alrode, Tvl.
P.O. Box 3793, Alrode 1451
Tel. (011) 864-2744 Telex 4-20365

FLOAT-TREAT SEPARATOR

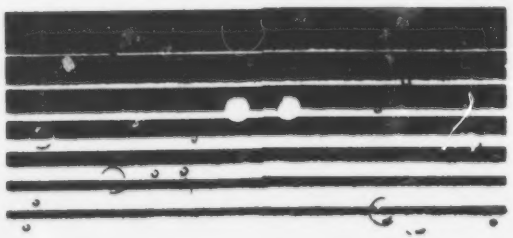


FOR STEEL OR CONCRETE TANKS

Rex Float-Treat Tanks employ proven principles of tank design assuring optimum use of tank volume. Inlet piping, reaction jets, inlet and effluent baffles provide positive, thorough distribution and dispersion with carefully controlled flow patterns for maximum clarification, flotation and settling.

The many advantages of Rex Float-Treat Separators may be obtained with either steel or concrete tanks, in single or multiple units. Steel tanks are available as "packaged duty" units shipped complete, ready for simple piping and wiring on installation.

Existing gravity settling tanks can often be converted economically to Float-Treat. Existing sludge-handling equipment may also be used with slight modifications.



Correct pressure is maintained by either automatic or manual controls to assure efficient operations under all flow conditions.

with accurately formed beach assures a relatively dry scum and clean discharge.

Rex Scum Removers are available in a wide variety of types and sizes. Proper materials are available for unusual corrosive conditions, explosive atmospheres, etc.

Proper amount of air is fed directly into the pressure tank for optimum saturation. Air feed is regulated by the pressure tank liquid level controller and a solenoid valve in the air line.

prevents floatable solids from passing out of tank . . . directs clarified effluent to outfall weir.

assures uniform discharge and controls water level in tank for optimum skimming conditions.

integral with Float-Treat tank, provides a continuous supply of treated effluent for recycle system even though raw flow may be interrupted.

withdraws portion of effluent and pumps it to pressure tank. Because only a small portion of effluent is recycled, pump size and pumping costs are held to the minimum.

is designed and tested to conform to rigid code requirements. Positive liquid level control assures maximum saturation of pressurized flow. Tank may be supplied with or without packing as conditions warrant.

is obtained by any of several types of conveyors . . . from screw conveyors in smaller tanks up to heavy-duty conveyor sludge collectors for the larger projects.

Raw flow and recycle stream enter the Float-Treat Tank through the inlet manifold. As the blended stream enters, it impinges on concave reaction baffles for thorough diffusion throughout width and depth of tank. Inlet piping and reaction jets are carefully sized and located for correct velocities, proper bubble formation and thorough blending.

Pressurized recycle liquid is introduced into raw flow line immediately downstream from pressure reduction valve.

TRICELLERATOR DAF FOR LOW-DENSITY ACID MINE DRAINAGE PRECIPITATE REMOVAL

BOSMAN (1983) demonstrated that dissolved air flotation is an attractive alternative means of solids/liquid separation to gravity settling for water producing relatively small amounts of sludge on lime precipitation (100 to 200 mg solids per litre). At hydraulic loadings of 7 m^3/m^2 h (seven times higher than gravity settling), the flotation process produced an effluent containing less than 15 mg/l suspended matter and a sludge with a density of 50 g/l (5% solids). The case that was tested was neutralized acid mine drainage from a coal mine at Vryheid Coronation Ltd. in Natal, South Africa, one of the mines in the ANGLO AMERICAN CORPORATION GROUP.

Based on these tests completed in 1981, a plant to remove precipitate from 1,200 m^3/day of neutralized acid mine drainage was estimated to cost about R90,000 ($45,000).

Normal operating pressures in the vessels used to supersaturate feed solution with air for the DAF process is around 400 kPa. Once saturated with air under pressure, the water is fed into the inlet stream of the flotation unit, and the air comes out of solution as a cloud of minute bubbles. These bubbles then lift suspended solids in the form of a sludge to the water surface where it is scraped off mechanically. DAF can also be performed in a somewhat simplified version of the process. Instead of using an air compressor and pressure vessel, the "Tricellerator" uses high pressure water pumps to dissolve air in water. The pumps, usually three per unit, draw water from the bottom of a cylindrical cell, entraining air into the stream by means of a hydraulic ejector. Under the turbulent and pressurized conditions in the pump, the entrained air becomes dissolved in the water and, on being discharged into the cell and consequent release of pressure, comes out of solution as fine bubbles.

The concentration of air dissolved in the water is not as high in this system as in systems using optimum saturation conditions. However, the process achieves similar air to solids ratios by operating at larger recycle ratios.

When laboratory-scale DAF tests indicated benefits in effluent clarity, sludge density and possibly plant capital costs over gravity settling of solids for treating Coronation Vryheid mine drainage, pilot tests were conducted with the smallest size of "Tricellerator" available. The unit was rated by its suppliers at 11 m^3/h. The results of the tests showed that consistent with acceptable sludge density and effluent clarity, the plant was capable of athroughput of 18 m^3/h which is 160% of the supplier's design capacity and which represents a hydraulic loading of about 7 $m^3/m^2/h$. Since gravity settling can seldom be conducted at loadings of more than 1 $m^3/m^2/h$, the flotation cell may be substantially more compact than a settler for gravity settling for treatment of the same water. The sludge density of 50 g/l produced in this test means that the DAF sludge volume would be only 20% of that obtained by gravity settling and 2.5 times more than the

volume generated by the HDS process. However, since the amount of solids in this water is so low to begin with, the 2.5 l of sludge per m^3 water treated would not present a major disposal problem.

The brief ANGLO AMERICAN RESEARCH LABORATORIES' tests at Coronation Vryheid revealed that proper flocculation of the suspended solids was the key to successful operation of the plant. The flocculation stage of the pilot plant consisted of the addition of lime to the acid water under conditions of vigorous stirring to pH 9 (the same coagulation may have been achieved at pH 7 with the aid of alum, but the former method was chosen for simplicity). The water was then passed through a pipe with a retention time of 4 minutes at a velocity of about 0.3 m/s followed by a dosage of polyelectrolyte (0.5 mg/l of nonionic polyacrylamide proved optimal) injected directly into the inlet to the "tricellerator."

In the pilot test, the best sludge density was achieved by allowing a float to build up undisturbed for 25-30 minutes before removing it during a 2-5 minute period of scraping with the scraper arm rotating at about 2 rpm.

The following results were achieved in the pilot test:

	Raw Water	Effluent Water	Sludge
pH	6.7	9.0	
Total Iron	30 mg/l	LT 1 mg/l	
Suspended Solids	46 mg/l	LT 15 mg/l	5.3%

The approximate 1981 cost of a tricellerator clarification unit treating 1,200 m^3/d was 20% less than a comparable gravity settling plant.

Mechanical Equipment Including Electrical Controls, pH Control, Steelwork, etc.	R75,000
Civil Engineering:	
12 m x 6 m x 200 mm Slab (Reinforced)	R4,000
Room 4 m x 5 m Chemical Storage and Makeup	R5,000
Contingencies	R6,000
	$90,000

In the end, it was found that a waste treatment plant was not required because the flow of acid mine drainage stopped before the plant could be constructed.

Further information on the test and on the equipment may be available from:

ANGLO AMERICAN RESEARCH LABORATORIES
Post Office Box 106
Crown Mines 2025
South Africa
(011) 835-3251
Danie J. Bosman
Head, Water and Air Treatment Services

POLLUTION CONTROL ENGINEERING, INC.
10751 Lakewood Blvd.
Downey, CA 90241
(213) 861-1297
Telex: 910-583-5718
George E. Hurst
President

PURIFICATION SYSTEMS (PTY) LTD.
Post Office Box 7731
Johannesburg 2000
South Africa
(011) 674-1960
R. P. Woosman-Tavage

BLUEBIRD MINE, ARIZONA - SX REAGENT RECOVERY

Dissolved air flotation was tested for a copper in situ leach project at the Bluebird Mine, Arizona, for entrained solvent recovery from aqueous solutions. The circumstances, aims, or motivation of these tests are not known and have not been published. These tests were completed years ago by Ranchers Exploration when they were still based in Albuquerque. It is understood that the solvent recovery tests were successful.

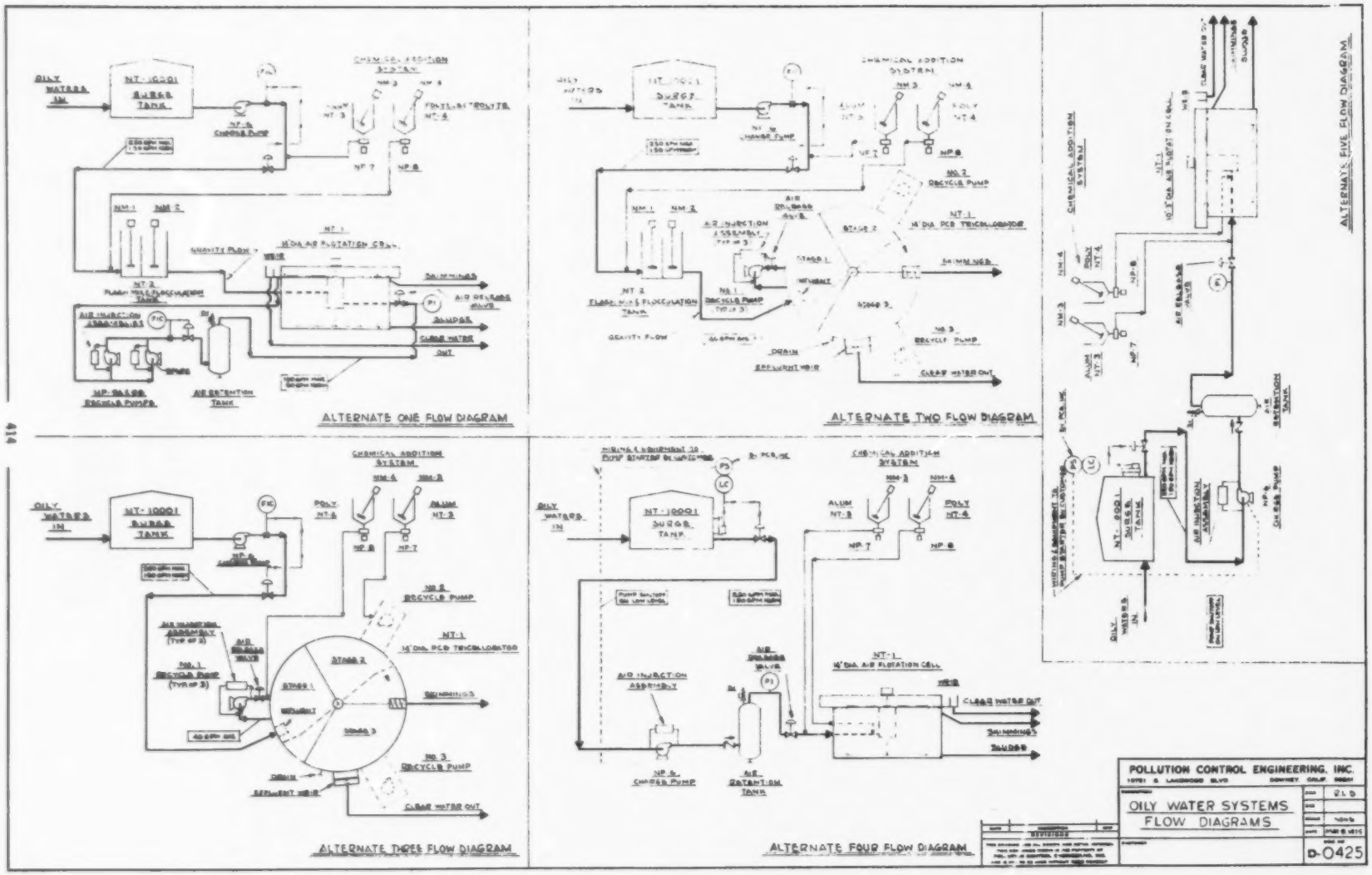
More information could possibly be obtained from:

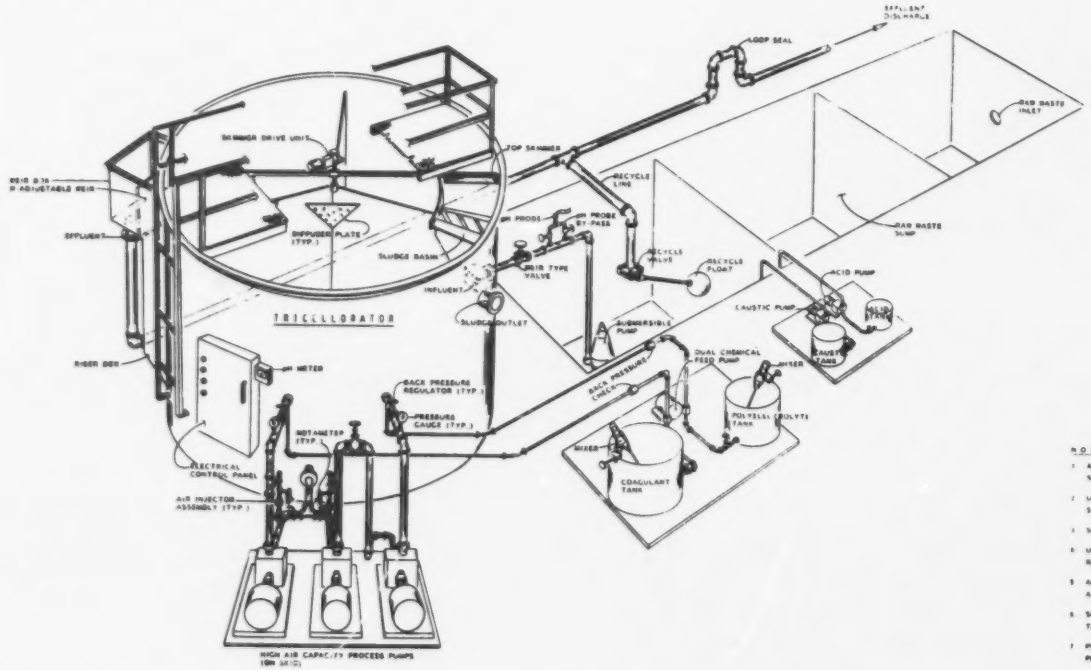
RANDY E. SCHEFFEL
9204 Avenida de la Luna NE
Albuquerque, NM 87111
(505) 821-9462

GEORGE E. HURST
Pollution Control Engineering, Inc.
10751 Lakewood Blvd.
Downey, CA 90241
(213) 861-1297
Telex: 910-583-5718

PCE Tricellerators are used on numerous installations for oil removal/recovery from water. Dispersed or dissolved air flotation systems are available from several suppliers. Lurgi has supplied many such systems, especially for oil recovery:

LURGI APPARATE-TECHNIK GmbH
Berrich Chemotechnik
Gervinusstrasse 17-19
Postfach 119181
D-6000 Frankfurt (Main)
West Germany


ALTERNATE ONE FLOW DIAGRAM
ALTERNATE TWO FLOW DIAGRAM
ALTERNATE THREE FLOW DIAGRAM
ALTERNATE FOUR FLOW DIAGRAM
ALTERNATE FIVE FLOW DIAGRAM
OILY WATERS IN
SURGE TANK
CHEMICAL ADDITION SYSTEM
SKIMMINGS
SLUDGE
CLEAR WATER OUT
AIR RETENTION TANK
RECYCLE PUMP
AIR INJECTION ASSEMBLY
POLLUTION CONTROL ENGINEERING, INC.
OILY WATER SYSTEMS
FLOW DIAGRAMS
D-0425



NOTES

1. ALL MODELS FURNISHED WITH ONE COAT PRIMER AND ONE FINISH COAT SPECIAL PROTECTIVE COATINGS ARE AVAILABLE AT EXTRA COST
2. UNITS SHIPPED FULLY ASSEMBLED OR KNOCKED DOWN DEPENDENT ON SITE LOCATION ETC
3. SOME PIPING ORIENTATION MAY BE ARRANGED TO SUIT JOB SITE
4. UNITS SUPPLIED WITH STANDARD BRIDGEWALK & ACCESS LADDER AS REQUIRED
5. ALL MODELS MAY BE SUPPLIED WITH GAS TIGHT DECK AND CONE BOTTOM AT EXTRA COST
6. SPECIALLY DESIGNED RECTANGULAR UNITS AVAILABLE WHERE DICTATED BY SPACE LIMITATIONS
7. PUMPS AND OTHER EQUIPMENT DEPICTED HERE ARE FOR ILLUSTRATIVE PURPOSES ONLY

DATE	DESCRIPTION	BY
	REVISIONS	

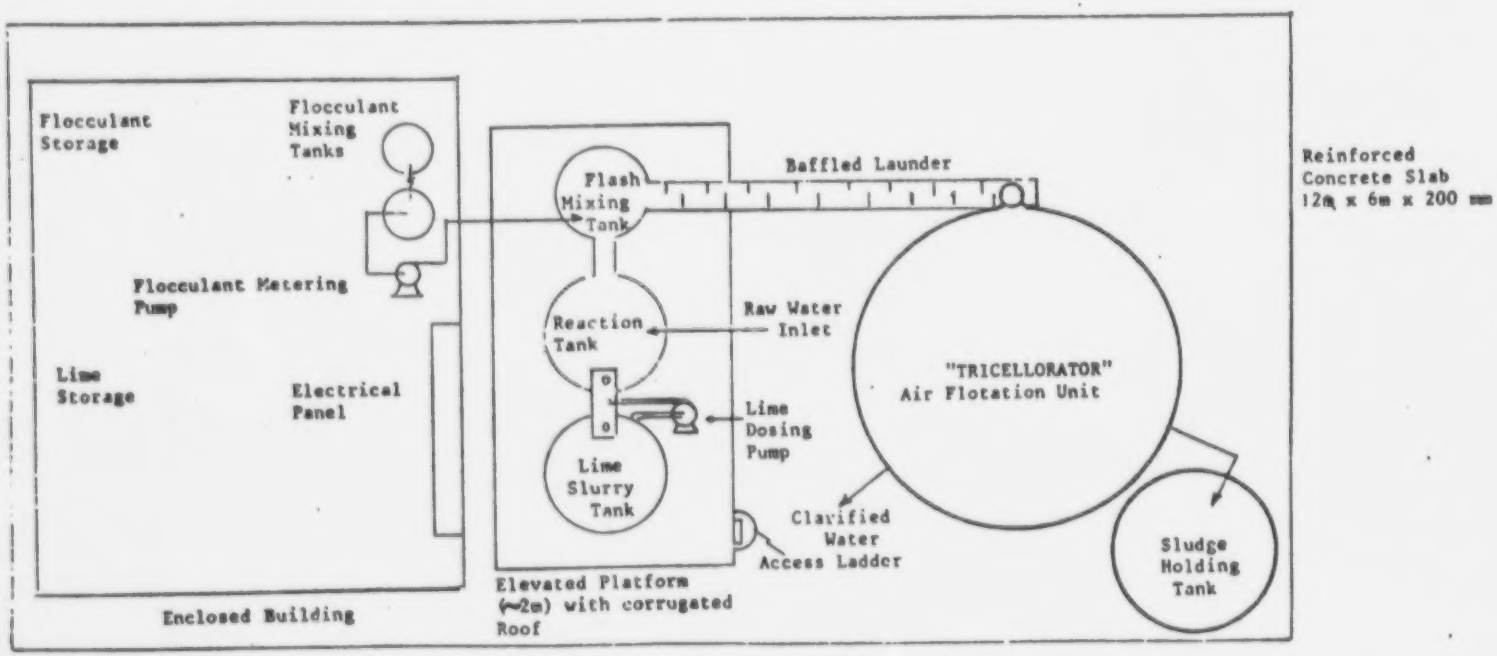
THIS DRAWING AND ALL DESIGN AND DETAIL INFORMATION THEREIN CONTAINED REMAIN IN THE PROPERTY OF POLLUTION CONTROL ENGINEERING, INC. AND IS NOT TO BE USED WITHOUT THEIR CONSENT

POLLUTION CONTROL ENGINEERING, INC
10701 S. LAKEWOOD BLVD. DOWNEY, CALIF. 90241

TRICELLORATOR
WITH CHEMICAL FEED SYSTEM

DRN. MORALA
CHK. NO. 0157
SCALE NONE
DATE 11 / 8 / 81
DWG. NO. D-1176

FIGURE III. SUGGESTED LAYOUT OF PROPOSED FULL SCALE PLANT



SCALE: APPROXIMATELY 1:50

TRICELLORATOR

The Tricellorator operates on the principle of dissolving gas in a liquid under pressure, but not with the use of a gas contacting tower. This device takes advantage of high speed pumps to disperse the gas and collapse the bubbles by pressure on the discharge side of the pump. The water or liquid is pumped three times and unlike conventional flotation cells the discharge is confined to a relatively small area. This is accomplished by dividing the tank into three equal parts or four in the design of larger systems. Each section confines the gas rise so that a scrubbing action is achieved. This action accounts for the high percentage removal of both oil and solids. Tests show residual oil less than 10 PPM without chemical dosage.

Incoming water may be pumped or it may flow into the Tricellorator by gravity. In any event the incoming liquid is not pressurized beyond normal pumping practice. The first stage only takes suction from itself and returns water to itself. Number two and three pumps take suction from the preceeding stages. Clarified water is removed from the last stage by a riser tube connected to an adjustable weir box.

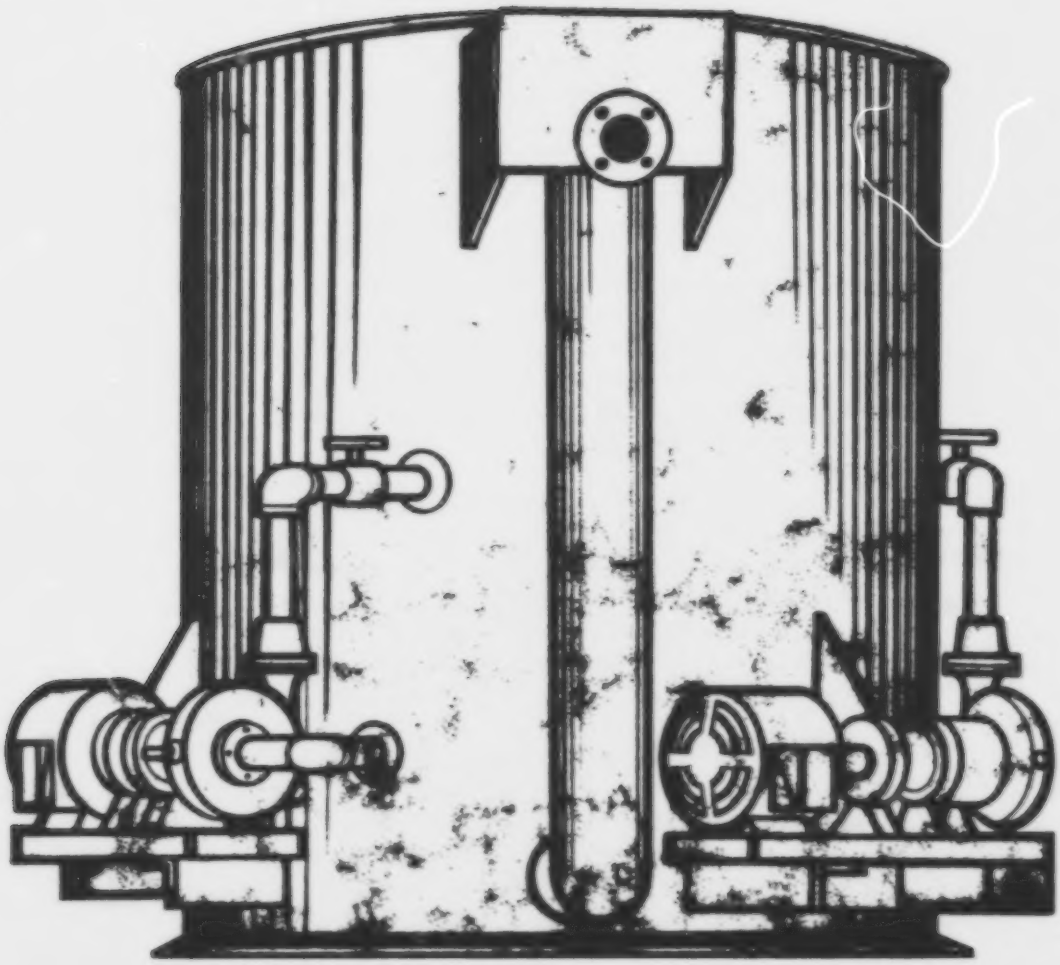
The surface of the Tricellorator may be skimmed in a conventional manner with a single paddle discharging recovered float into a recovery chute. Where water may be tolerated with the recovered oil, skimming may be by gravity with adjustable weirs in each sector. The Tricellorator may also be skimmed by a Continuous Belt Skimmer where it is desired to have minimum water in the recovered oil.

Gas or air may be used as a flotation media. Where it is desired to maintain anaerobic conditions than Methane should be injected. In all cases the gas (air) must be injected on the suction side of the pumps and through a premixing system that reduces the possibility of gas locking. Units are available in sizes from 50 GPM through 2,000 GPM. Please see drawing D-406. Patent applied for.

Pollution Control Engineering, Inc.

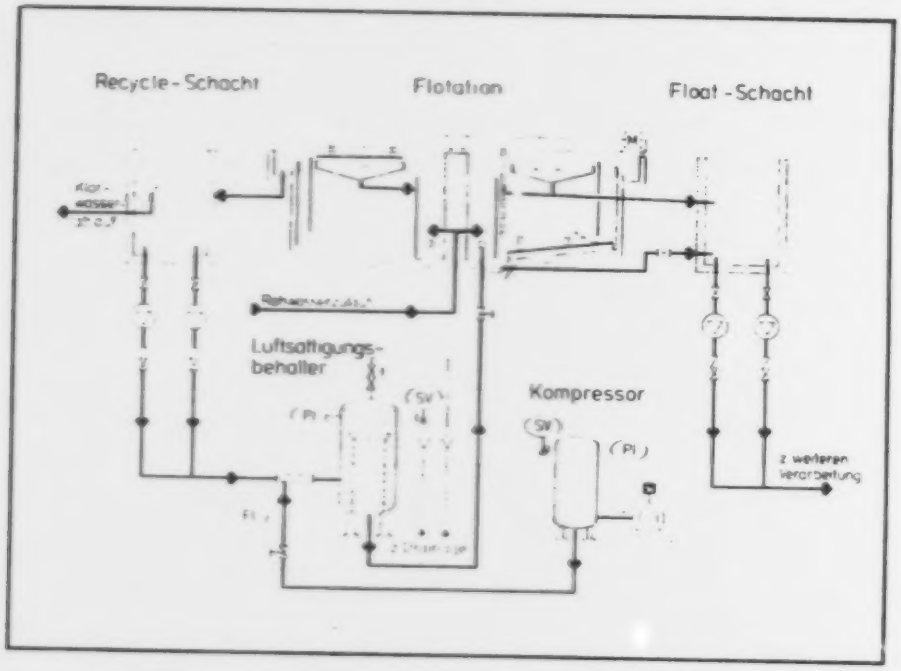
10751 S. LAKEWOOD BOULEVARD • DOWNEY, CALIFORNIA 90241 • PHONE: (213) 861-1297

TRICELLORATOR



POLLUTION CONTROL ENGINEERING, INC.

A schematic diagram of a Lurgi system is shown below. LURGI estimates that their systems work best at a hydraulic load of 3 $m^3/m^2/h$.



PRECIPITATE FLOTATION OF IRON-CYANIDE COMPLEXES

According to BUSCH, et al. (1980), ion precipitate flotation was tested as a means of removing cyanide in the form $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{3-}$ from wastewater from plating and mineral processing. Preliminary tests indicated that this process has good potential for the removal of ferrocyanide and ferricyanide complex ions. Free ions are extracted but do not float as well as the Fe-cyanide complexes. The removal of Fe-cyanide complexes increases with addition of a surfactant, i.e., tricaprylmethylammonium chloride in a dose of no more than 1.25 times the stoichiometric amount and decreases with increased surfactant dose. The removal of these complexes is satisfactory at the air flow rate of 3 l/mm and pH 4-10. After the Fe-cyanide complexes have combined with the surfactant, they float equally well.

More information could be requested from:

DAVID J. SPOTTISWOOD
Dept. of Metallurgy
Colorado School of Mines
Golden, CO 80401

DAF GENERAL

1. In Japan, the use of dissolved air flotation is believed to be used for the recovery of ultrafine materials from water suspensions--e.g., chemical precipitates. Reference has been made to the Nagom cell which is believed to be cylindrical.

2. Tolltreck Ltd. in Droitwich, England, has developed a way of controling the bubble size in bubble generators. Their process is known as KONTAX. They can be contacted at:

   TOLLTRECK LTD.
   Priory House
   Friar Street
   Droitwich, Worcs.
   England WR9 8ED
   Droitwich 5661
   Michael C. S. Gardiner

   TOLLTRECK INTERNATIONAL LTD.
   7108-M South Alton Way
   Englewood, CO 80112
   (303) 779-5331
   John Whellock
   Dave Robinson

3. SHIMOIIZAKA and MATSOUKA (1976) reported the use of dissolved air flotation for removal and recovery of Cu and Cd precipitated by lime or sulfide ions from solution.

4. KAIDA, et al. (1978) reported the use of air oxidation of Fe^{2+} catalyzed by $NaNO_2$ fractional precipitation of $Fe(OH)_3$, neutralizing coagulation, and sedimentation followed by flotation separation and sludge treatment The concentration of heavy metals in the effluent was reduced from 549 ppm to 0.91 ppm to 0.91 ppm for Zn, and 4.92 to 0.04 ppm Cd. Fe and Cu were not detected in the treated effluent.

5. In Bulgaria, the selective recovery of cobalt from aqueous sulfuric acid solution was tested by selective solvent extraction followed by flotation of the organic phase. Zn, As, and Pb ions in the clear aqueous solution were then precipitated as hydroxides by lime addition. This was tested on waste water from the wet scrubbers at the G. Dimitrov Mining and Metallurgical Plant in the city of Eliseina.

6. BENCKE, et al. (1981) showed that Cr^{3+} can be effectively removed from metallurgical wastewaters by coagulation and dissolved air flotation. DAF resulted in more effective and faster clarification and a greater solids content in the sludge than could be achieved by settling. pH of the solution, formation of $Cr(OH)_3$ flocs, and the type of wastewater influenced the degree of clarification. Although $Cr^{3=}$ can be removed from suspension, it is not clear to what levels the precipitate can be

removed. The authors can be tracked down through the following incomplete address:

SONIA BENCKE
Dept. Eng. Quimica
P.U.C.
Porto Alegre
Brazil

7. Dissolved air flotation is also offered by the French water treatment firm ERPAC:

ERPAC
85, rue Carpeaux
59290 Wasquehal
France
(02) 26.95.05
Telex: 132 658

ELECTROFLOTATION OF PRECIPITATES

Electroflotation is identical to DAF in principle, except that in electroflotation, gas bubbles are generated electrolytically. The disadvantages are that hydrogen gas is generated and secondly, unless the electrodes are made from expensive alloys, they tend to be corroded and require periodic replacement. In oil flotation, electrodes tend to become coated and passivated.

The only commercial units known for electroflotation are those offered by Dravo, known as Lectroclear. These have been installed in numerous meat packing operations for water treatment where the process was known as the SWIFT Lectroclear process until it was acquired by DRAVO CORPORATION.

Although several Lectroclear flotation units are installed for a variety of clarification purposes--e.g., recovery of suspensions of drilling muds in wastewater--only two are known in a minewater-mill effluent environment. These are at the Mount Emmons water treatment plant of AMAX, Inc., near Crested Butte and at the mill tailings effluent treatment plant of CLIMAX MOLYBDENUM, INC. at Climax, Colorado.

The two Colorado clarification systems remove base metal and iron hydroxide precipitates from an effluent stream located at high altitudes where water temperatures are at or close to 4°C' for much of the year. The systems are described in a trip report on Mount Emmons in Appendix I. They were selected because at the time, Lectroclear was the only system that had been demonstrated to work well on cold, high viscosity water. In the meantime, other methods of removing suspended precipitates have been demonstrated at these sites--namely, dissolved air flotation.

The Mount Emmons treatment plant treats an average flow of 400 U.S. gpm (2,200 m^3/d) but is designed to treat up to 11,000 m^3/d during the spring runoff. The plant cost around $10.9 million to install, and annual operating costs are around $750,000.

After electrocoagulation and Lectroclear flotation of suspended precipitates, the water is filtered through two Dravo deep-beed sand filters to achieve very clean water with very low base metal contaminant levels and 5 mg/l suspended solids. The Lectroclear flotation units remove 98% of the suspended solids at 700 ppm solids feed level. Allied Colloids' Percol 728 (a cationic polymer) is used for final sludge dewatering ahead of the belt presses, but Nalco 8815 at 1.5-3.5 ppm is used for coagulation and 1-3 ppm Percol 278 cationic polymer is added ahead of the flotation cells. The sludge as skimmed from the cells contains 2-3% solids, but this is increased to 12% using belt presses.

RAMIREZ (1981) described the use of electroflotation for removal of Group IV-A heavy metals from mine tailings wastewater.

Details on the Dravo Lectroclear Flotation System is available from:

DRAVO RECOVERY SYSTEMS
222 Third Street
Neville Island
Pittsburgh, PA 15225
(412) 777-5241
O. A. Clemens

SETTLINC AND POLISHING PONDS

Settling and polishing ponds are generally more effective for the removal of coarser suspended solids and denser materials than base metal precipitate sludges.

Onaping

In the trip report on Falconbridge's Onaping mine-mill complex in Ontario in Appendix II, it is noted that a large lake is effectively used to polish solutions after addition of a ground limestone slurry for pH adjustment of tailings decant solutions. This works effectively. There apears also to be some kind of biological nickel removal effect in the pond, but this has not been defined.

Also, in the same trip report, reference is made to the treatment of minewater from the Onaping Mine by addition of sodium hydroxide solution to the feedline to precipitate nickel as nickel hydroxide. The neutralized minewater representing a small flow is settled in a small pond which is fitted with a berm baffle to discourage short circuited flow and allow longer residence time for settling. The $Ni(OH)_2$ precipitate settles effectively in

this arrangement forming a sludge on the bottom of the pond containing 5-10% Ni. This is where a problem arises.

Mine sewage in small volumes is also dumped into the same pond. Due to biological degradation of sewage, much of which settles to the bottom of the pond, methane gas is generated which in turn attaches itself as bubbles to the precipitate. The result is that 5% Ni precipitate particles are being floated, and these escape with the pond overflow to the main solution polishing lake. Even though the floating precipitate is diluted in the main pond, it certainly would not take much to give a high reading if it happened to be collected in a final effluent sample.

Settling ponds are in standard use in placer gold recovery operations. As mentioned above, these streamside ponds lend themselves to the use of Hercofloc gel flocculant logs to make them more efficient.

It is common practice to compute a nominal residence time in such ponds by dividing the total volume by the influent flow rate. This has often been found to be an overestimate of actual residence time because where a pond has an inlet and an outlet, there will almost certainly be short circuiting. First, surface waters do not mix with deeper waters which may be stratified due to temperature or concentration effects. Second, channelling of surface water flow from the inlet to the outlet does typically occur. Actual residence time of water in a pond may be as low as 10% of that calculated by dividing total volume by flow rate.

An important application for settling ponds is, for example, as a primary treatment in plant runoff water to settle out concentrate particles. These particles are dense and settle readily but if not removed, will settle elsewhere in the system where they oxidize over a period of time and add metal ions to solution. At Falconbridge's Falconbridge operation, plant runoff water was collected in a small lake and decanted. Over the years, the oxidizing mineral particles generated soluble metals which started contaminating local wellwater used as potable water in the plant. The problem was solved by dredging the lakebed and processing the material through the mill to recover values worth $1.5 million. Another example is at St. Joe Minerals' Edwards Mill at Balmat, New York, where runoff water was allowed to settle in a shallow pond, and significant quantities of mineral value were trapped over a period of time. This pond, now dry, is illustrated below.

SETTLING POND TRAPS CONCENTRATE IN MILLSITE RUN-OFF

BIOLOGICAL POLISHING POND - FALCONBRIDGE, ONTARIO

BIOLOGICAL SYSTEMS

Biologically active ponds can be very effective at removing suspended particles from effluents. They can also have the reverse effect. It was shown above how, in a small pond at the Onaping Mine, biological degradation of sewage resulted in the flotation of a nickel hydroxide sludge from the pond bottom which was then discharging at the pond outlet.

At Falconbridge's operation at Falconbridge, Ontario, mill tailings decant solution containing metals is neutralized, and metals are precipitated by lime addition. The neutralized solution discharges from the aeration/lime addition plant to a settling basin and from there into a huge swamp area covering 2-3,000 acres which supports a prolific growth of cattails and a host of other species including large underwater algae populations. The algae and plants offer a huge surface area onto which the precipitate particles can and do attach themselves. Water discharging from the far end of the pond has a low suspended solids content. If the pond is large enough and if the biomass is great enough, the suspended metal precipitate load will be "metabolized" by such ponds. Decaying biomass at deeper levels on the pond bottom release enough marshgas H_2S to convert the hydroxides to sulfides which will then settle to the bottom of the marsh and accumulate. This phenomenon has been observed by Dr. R. L. Kleinman at the Bureau of Mines in his studies of acid mine drainage abatement.

DR. R. L. P. KLEINMAN
Bureau of Mines
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422

Biological ponds have also been observed by Jennet as reported in WIXSON (1977) to reduce organics contained in mine-mill effluents. Presumably, much of the organics measured are colloidal oil and grease from the mining operation and possibly some flotation reagents. Algae in the meander system installed at a lead-zinc mine in Missouri resulted in a marked decrease in the levels of organics in water that passed through the ponds.

Further information on this phenomenon as well as metals polishing in the meander system containing algae could be discussed with:

DR. CHARLES JENNETT
109 Riggs Hall
College of Engineering
Clemson University
Clemson, SC 29631

DR. BOBBY G. WIXSON
Center for International Programs
University of Missouri - Rolla
321 Engineering Research Lab
Rolla, MO 65401-0249
(314) 341-4208
Telex: 883633

MICHAEL KEARNE
Director, Safety, Health, and
Environmental Services
AMAX Lead Company of Missouri
Route KK
Boss, MO 65440
(314) 626-4211

An interesting phenomenon pointed out by Dr. Wixson is that when metal precipitates or organics from flotation plants are present in a pond, algal mats are likely to form due to enhanced growth of algae (perhaps stimulated by the contaminants?). During periods of flooding, these can break loose and become distributed downstream and, in that way, also distributing metal values. For this reason, both the mine-mill complexes in Missouri that installed meander systems for algae growth also installed final polishing ponds to trap any algae that break loose.

In New York state, St. Joe Resources at their Pierrepont mine have constructed a meander pond to encourage plant and algae growth as a means of polishing minewater before final discharge. At the time of the Randol 1984 visit, this system had just been constructed, and the plants had not yet properly established themselves, so it was too soon for performance data. More information could be requested from:

ST. JOE RESOURCES COMPANY
Mining Division
Balmat, NY 13609
(315) 287-2500
J. G. (Mike) Reilly

MULTI-MEDIA AND DEEP-BED FILTERS

Low suspended solids (say, 1-8 ppm) can be achieved using multi-media or deep-bed filtration. This type of equipment is generally required to meet permit requirements for effluent discharge, not only with respect to suspended solids, but also heavy metals. Even if base and heavy metals, arsenic, etc. have been precipitated, they are unlikely to have been removed to the levels required by typical U.S. effluent discharge permits in the primary settling or flotation process. This is where a polishing filter is required. Usually, the solids load in the precipitated effluent is too high for a sand filter to be used as a primary sludge removal process, but these filters do work well as a polishing step.

Several types of polishing filters were observed in various water treatment plants at mines and mills visited.

AMAX, Mount Emmons

Four 12' 6" Ø 16' 4" deep Dravo multi-media sand filters are installed as a polishing step at the Mount Emmons water treatment plant, Crested Butte, Colorado. Several grades of sand and gravel are loaded into these downflow filters as described in the trip report in Appendix I. The bulk of the media is made up of 1-2 mm graded silica filter media. The other fractions are gravel in various sizes grading from 1 1/2" x 3/4" to 1/4" x 1/8" silica gel. Since startup in 1980/1981, the media has never had to be replaced although, occasionally, mudballs are removed from the surface of the filters.

DRAVO CORP. markets an innovative and effective deep-bed sand filter system. The units at Mount Emmons are open gravity flow units, but Dravo also offers a pressurized system. Advantages calimed for the DRAVO deep-bed system are:

- High Filtration Efficiency
- High Specific Loadings; from 1.0-10.0 lbs. of suspended solids removed per ft^2 of filter area (time?).
- Heavy Duty Backwash
- Compactness; it requires 50% or less of the area needed for other types of clarification processes.
- Simplicity of Operation; usually no pumps are required for pressure operation.
- Easily Designed for Fully Automatic Operation
- Low Backwash Water Requirements
- Low Media Attrition - Less than 1% per Year
- Low Operating Costs

The vendor claims that suspended solids can be reduced to 1.0 ppm or less using these filters.

Information on Dravo deep-bed filters can be obatined from:

DRAVO RECOVERY SYSTEMS
Manufacturing Development Center
222 Third Street
Neville Island, PA 15225
(412) 777-5241

Other locations where deep-bed sand filters or multi-media filters are installed for final polishing of effluents after precipitated metals have been removed by conventional settler-clarifiers are at INCO LTD.'s Copper Cliff water treatment plant, Sudbury, Ontario, and at ST. JOE RESOURCES CORP. at Monaca, Pennsylvania, where effluents from their zinc smelter/refinery are treated for discharge. In Appendix I, a lead smelter is described where an attempt to remove metal precipitates from an effluent by a clarifier alone does not produce final effluent that meets their discharge criteria for much of the time.

Deep-bed sand filters are standard items in water treatment, and there are numerous suppliers to choose from. One supplier who believes he has developed an improved system is:

NEPTUNE MICROFLOC, INC.
Box 612
Corvallis, OR 97339
(503) 754-7654
Steve Uban

In South Africa, a water treatment engineer, John A. Buchanan, has considerable experience in the application of deep-bed filtration and has achieved some remarkable results. A copy of his paper has been inserted to provide further insight. He may be reached as follows:

PRENTEC PTY LTD.
Post Office Box 1433
Edenvale 1610
(011) 609-5216
John A. Buchanan
Managing Director

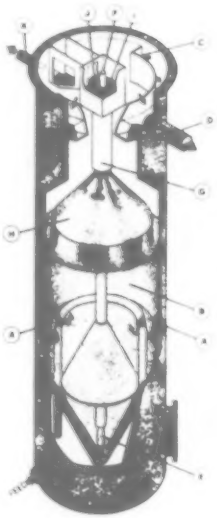
DYNASAND FILTER

A brochure describing the DYNASAND filter made by AXEL JOHNSON is inserted below. This device is very practical because it continuously recirculates the sand media to remove particles of suspended solids that would otherwise clog the surface. More details on this most innovative device can be obtained from:

A NEW Concept In Sand Filtration

Continuous Sand Filtration

The DynaSand Filter is a continuous backwash, upflow, deep bed granular media filter. The filter media is continuously cleaned by recycling the sand internally through an airlift pipe and sand washer. The regenerated sand is redistributed (right) on top of the sand bed allowing for a continuous uninterrupted flow of filtrate and reject water.



Feed is introduced into the bottom of the filter, then flows upward through a series of riser tubes and is evenly distributed into the sand bed through the open bottom of an inlet distribution hood (A) (Fig. 1). The influent flows upward through the downward moving sand bed (B) with the solids being removed. The clean filtrate exits from the sand bed, overflows a weir (C) and is discharged from the filter (D). Simultaneously, the sand bed, along with the accumulated solids, is drawn downward into the suction of an airlift pipe (see Fig. 2) which is positioned in the center of the filter. A small volume of compressed air is introduced into the bottom of the airlift (E). The sand, dirt, and water are transported upward through the pipe at a rate of about 200 gpm/ft². The impurities are scoured loose from the sand during this violently turbulent upward flow. Upon reaching the top of the airlift (F), the dirty slurry spills over into the central reject compartment (I). The sand is returned to the sand bed through the gravity washer/separator (G) which allows the fast settling sand to penetrate, but not the dirty liquid. The washer/separator is placed concentrically around the upper part of the airlift and consists of several stages to prevent short circuiting (Fig. 3). By setting the filtrate weir (C) above the reject weir (J) a steady stream of clean filtrate flows upward, countercurrent to the sand, through this washer section and acts as a liquid barrier that carries away the dirt and reject water (K). Since the sand has a higher settling velocity than the dirt particles, it is not carried out of the filter. The sand is redistributed by the means of a sand distribution cone (H). The sand bed is continuously cleaned while both a continuous filtrate and a continuous reject stream are produced.

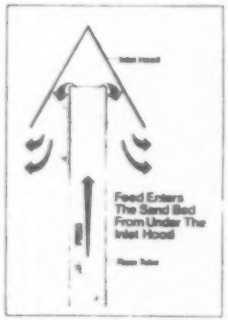


Fig. 1

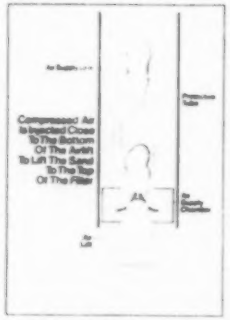


Fig. 2

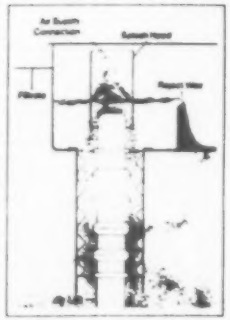


Fig. 3

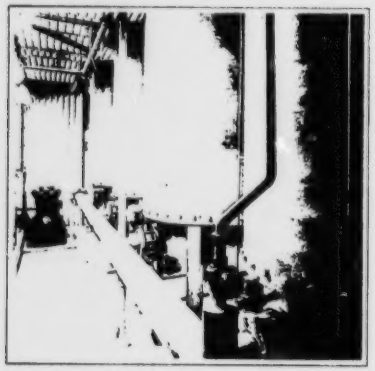
Applications: Typical Data.

	Loading Rates (gpm/ft²)	[illegible]
Metal Finishing	4-6	[illegible]
Tertiary Filtration	3-10	[illegible]
Surface Water (Direct Filtration)	4-8	[illegible]
P Removal	4-6	[illegible]
Mill Scale	8-12	[illegible]
Algae Wastewater	3-4	[illegible]
City Wastewaters	2-6	[illegible]

[illegible]

- Brine Filtration
- Laundry [illegible]
- Black Liquor [illegible]
- Pigment [illegible]
- Coating [illegible]
- Various OPA [illegible]

DYNASAND® FILTER



Multiple units can be installed and still maintain system simplicity (top photo). The pressure drop across the sand bed insures an even feed to each filter without the need for splitter boxes. A header pipe with the appropriate number of Tee Connections is all that is required.

For large flow applications, our concrete basin design consisting of multiple cells is available. Cells can be custom arranged to fit individual plant configurations. The concrete designs are particularly well suited for large flow surface water and tertiary filtration applications. (Bottom photo).

Other Axel Johnson Inc. Products

Lamella® Gravity Settler/Thickener – a compact inclined plate separator

Aqua Guard™ – a self cleaning bar/filter screen

AXEL JOHNSON INC.

AXEL JOHNSON INC.

10161 Côte de Liesse
Montreal, Quebec H9P 1A3
Tel. (514) 636-8712
Telex: 05-824088

All equipment described in this brochure is protected by patents, and additional patents may be pending.

Advantages: DynaSand® Filter Vs. Conventional Filtration Designs

Continuous Operation
No need to shut down filters for backwash cycles

Elimination of Auxiliary Equipment
There is no need for backwash tanks, pumps, valves, instrumentation, etc.

Simplicity
No moving parts — no operator attention required.

High Solids Capability
Can handle up to 800 ppm solids in the influent for some applications

Low Pressure Drop
Less than 24" pressure drop — easy to gravity feed

Low Power Consumption
Gravity feed or low pressure feed pump and small air compressor are all that is required.

Single Media
No need for internal screens, grids, underdrains, etc.

Continuously Cleaned Sand Bed
No mudball formation

No need for Continuous Chlorination

Improved surface loading rates where the loading rates are limited by solids capacity.

No requirement for flow control valves or splitter box arrangements

	DSF	Downflow Gravity Filters	Upflow Filters	ABW
Backwash Pumps, Valves, Storage Tanks	No	Yes	Yes	Yes
Standby Filter (Cell) for Backwash Cycles	No	Yes	Yes	No
High Solids Capacity	Yes	No	Medium	No
Continuous Operation	Yes	No	No	Yes
Low Pressure Drop	Yes	No	No	Yes
Power Consumption	Low	Low-Moderate	High	Low
Internal Screens, Underdrains	No	Yes	Yes	Yes
Deep Bed Filtration	Yes	Yes	Yes	No
Air Scouring of Filter Media	Yes	Yes	Yes	No

Standard Features

- Epoxy Painted Carbon Steel or FRP Tanks
- All Stainless & FRP Internals
- Air Control Panel
- No Moving Parts
- Fully Assembled – Ready to Install Upon Arrival
- Seismic 2 Design
- Deep Bed Filtration

Optional Features

- Access Platforms & Ladders
- Tank Covers or Screens
- Seismic 4 Design

Typical Data

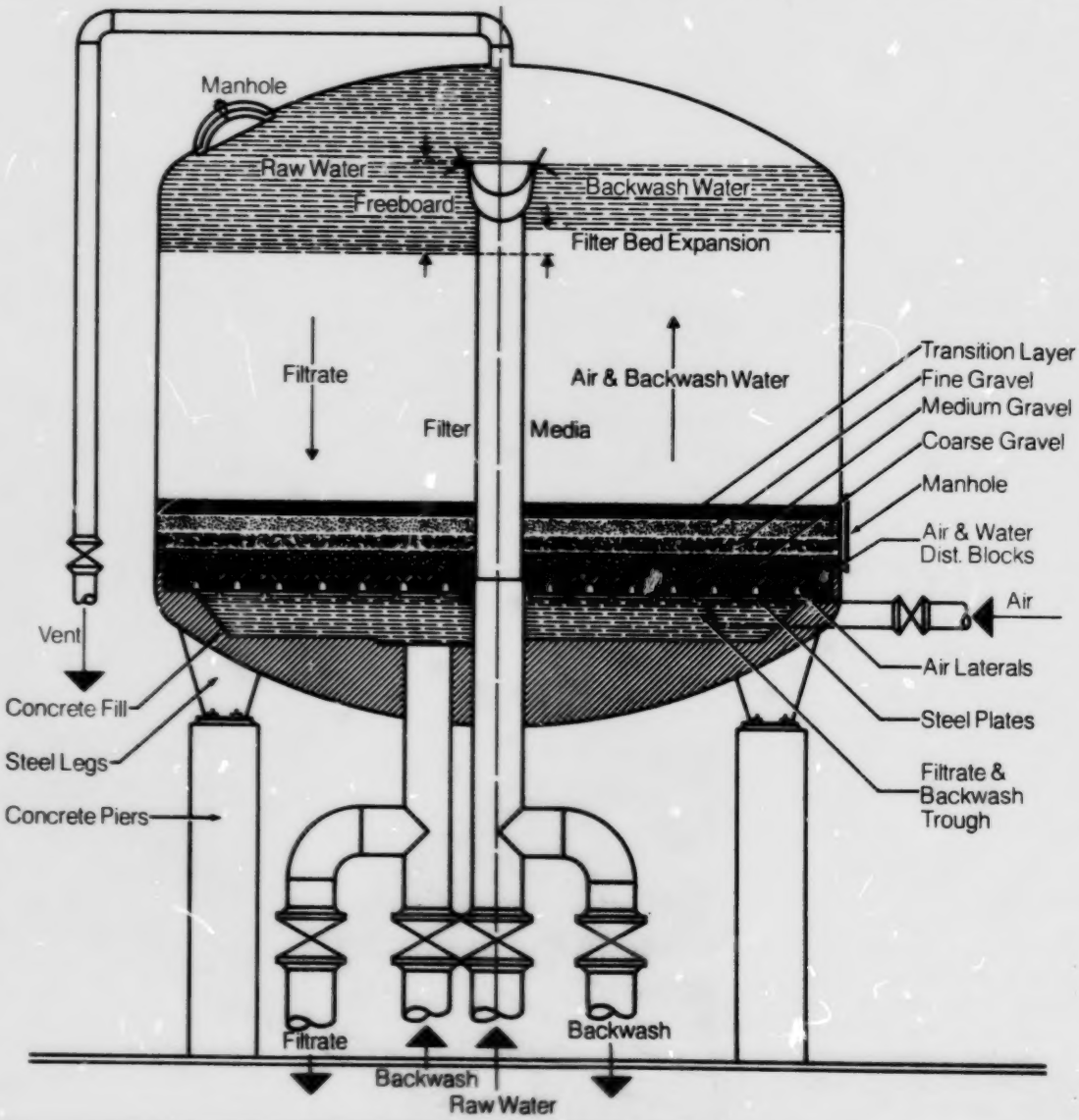
Model	DSF-7	DSF-12	DSF-19	DSF-38	DSF-64	DSF-100
Filtration area (Ft²)	7	12	19	38	64	100
Inside Diameter	3'0"	4'0"	5'0"	7'0"	9'0"	10 x 10
Height	9'6"	12'0"	12'6"	17'11"*	23'3"*	12'0"
Feed Rates (gpm)	28-56	48-96	76-152	152-304	250-500	400-800
Reject Rate (gpm)	1.5-4	2-8	2-10	3-15	5-25	12-40
Sand Required (tons)	1.6	3.3	6	11	20	21
Sand Bed Depth	30"	40"	40"	40"	40"	40"
Air Consumption (SCFM @ 15-25 psi)	0.5-1	0.5-1.5	1-2	1-3	1.5-4	2-5
Pressure Drop	15"-20"	18"-24"	18"-24"	18"-24"	18"-24"	18"-24"

* Includes handrail and platform

High Efficiency/Low Energy—Because of the efficiency of this backwash system, air and water requirements are low, usually about 6 scfm of air and 6-8 gpm of water per square foot of filter surface area. Total backwash water consumption usually is about 150 gallons per square foot of filter surface area for each backwash cycle. This small requirement allows backwash to be supplied from a standpipe in the filtrate header on pressure plants. In all cases, the size of pumps, piping, valves and storage tanks in the backwash water supply system and in the dirty backwash water disposal system can be smaller with the Dravo Filter system than with other types.

Instrumentation— The standard instrumentation for Dravo Deep-Bed Filters incorporates the latest Programmable Logic Control for unattended automatic operation. Primary backwash initiation is based on time, with system differential pressure and operator manual initiation overriding.

In addition to a main control panel, local panels are provided on large installations allowing the operator to monitor, inspect and maintain the filters from the filter plant floor.



Pressure or Gravity Operation— The Dravo Deep-Bed Filter System is available for pressure or gravity operation. The proper selection depends upon hydraulics, economics, available space and energy requirements of the total system.

Media Selection— The Dravo Filter can accommodate a variety of media types, sizes and depths. Each application is analyzed carefully and the proper media is selected to optimize the system's design.

Flow Rate— For industrial wastewater applications, a deep bed of specially selected filter media which permits high filter flow rates in a range of 8 to 20 gpm per square foot is used. For applications such as algae removal, bio-clarifier effluent polishing and river water treatment, flow rates between 2 and 8 gpm per square foot are used.

Flow Control— Each filtration application is analyzed to determine which of the following flow control methods is best suited:

- Influent Flow Splitting
- Effluent Rate-of-Flow Control
- Variable Flow Declining Rate

Dravo has experience in all of the above methods as well as other control variations.

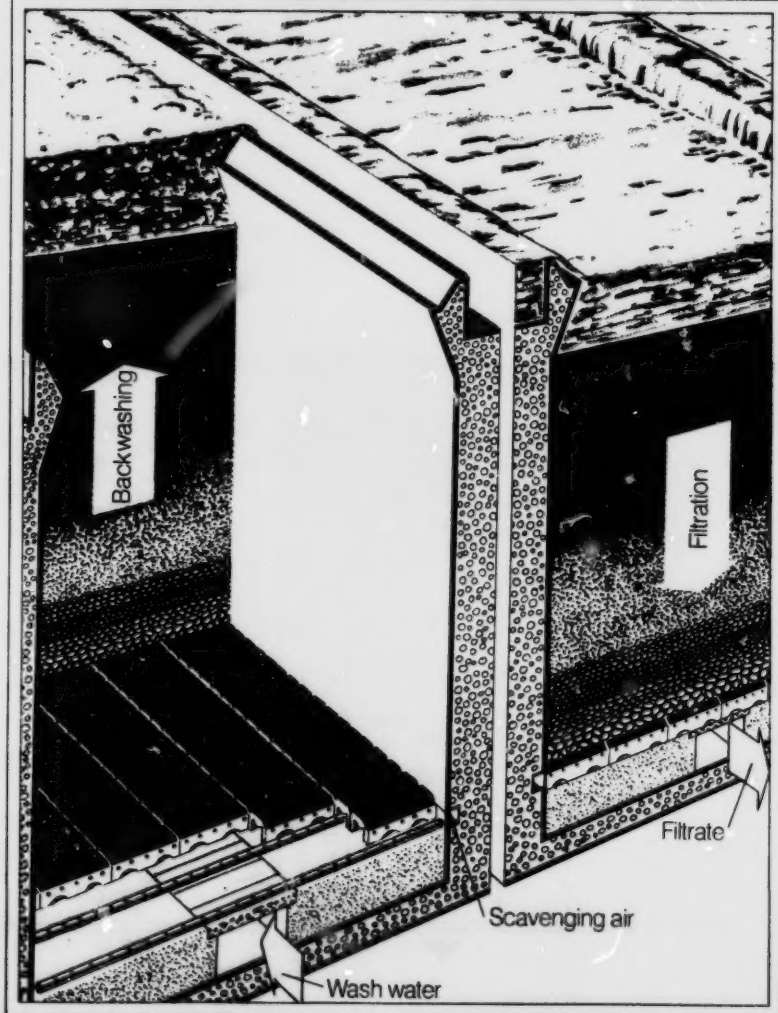
Underdrain Design— A unique design feature is the nozzleless filter bottom, which is made of domed-shaped, high-strength concrete air/water distribution blocks. These blocks are hollow with open bottoms and are arranged in rows on the level floor of the filter compartment. The correct spacing of the rows is assured by lugs cast on the sides of each block. (See illustration.)

The bottoms of the air/water distribution blocks are arched to permit free passage of the filtrate through open slots in the floor to the filtrate channel. The openings are carefully designed to maintain low water velocity and pressure drop. The head loss through the air/water distribution system is measured in inches rather than pounds due to this unique nozzleless design.

Backwash— The effectiveness of the deep-bed filtration concept is dependent upon complete removal of retained material at every backwashing. Therefore, the success or failure of any filter system is dependent upon the efficiency of the backwash technique employed.

Effective Air/Water Scrubbing— The Dravo Deep-Bed Filter uses an air and water backwash with a water rinse. The backwash air is introduced via a distribution system installed under the rows of air/water distribution blocks. The blocks are equipped with large ports formed into the sides at the highest point. As the air passes upward through the supporting layers of graded gravel, it is dispersed uniformly over the entire filter bottom in a pattern of coarse bubbles. Backwash water is usually supplied from the same system used for filtrate collection. Nozzles are not used. Consequently, the major maintenance problem of plugged nozzles and media removal usually associated with nozzles is eliminated.

The air and water are introduced simultaneously. This allows the air bubbles to provide the needed scouring action and an airlift pump effect to carry the loosened solids to the surface for removal. Chemical cleaning is not required to remove the oily films retained during filtering.



BACKWASH RATES Total backwash water required is the same for the 3- and 4-component Mixed Media beds (100 gallons per square foot), but backwash rates can vary. A comparison of backwash requirements is shown below (in gpm per square foot):

Temperature	(4-component) MF 196	(3-component) MF 196
90° F.	22 gpm/ft²	21 gpm/ft²
70° F.	19 gpm/ft²	17 gpm/ft²
60° F.	18 gpm/ft²	15 gpm/ft²

INITIAL HEADLOSS Typical starting headlosses for a Mixed Media filter are 1.25 to 1.5 feet at a five gpm per square foot filter flow rate.

ACTUAL APPLICATIONS Microfloc filtration technology is at work today in a wide range of applications—from small 10 gallon per minute self-contained water treatment plants to large industrial and municipal water and waste treatment installations. Some examples:

COAL RIVER, W. VA.—0.8 MGD Microfloc Modular Aquarius plant provides municipal water treatment.

PHARR YARNS, McADENVILLE, N. C.—Three 8-foot skid mounted vertical pressure filters provide tertiary filtration for a 0.7 MGD flow of textile dye waste.

HATFIELD TOWNSHIP, PA.—Tertiary treatment system, including Microfloc Mixed Media pressure filters, reclaims 3.6 MGD of municipal waste water.

CLACKAMAS WATER DISTRICT, OREGON—20 MGD water treatment plant uses four 20 x 22 foot Microfloc Mixed Media gravity filters and polishes unsettled water to consistently less than 0.2 JTU.

GEORGIA-PACIFIC, SAMOA, CALIFORNIA—Industrial plant uses Mixed Media pressure filters to provide process water at the rate of 30 MGD.

WINNETKA, ILLINOIS—11 MGD municipal plant expanded capacity by converting to Mixed Media beds in existing filters.

Current Microfloc Mixed Media filtration is extensive. Total installed capacity, including industrial and municipal systems for both water and waste treatment, exceeds 2.5 billion gallons per day.

Neptune Microfloc, Incorporated
P.O. Box 612
Corvallis, Oregon 97339
Telephone: 503-754-7664

neptune microflox

One of The Dexter Companies

Regional offices located in Boston, Massachusetts • Chicago, Illinois • Dallas, Texas • Corvallis, Oregon • Representatives located in major cities of the U.S. and Canada • Licensed manufacturers in Australia • Europe • Far East • South America •

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Litho in U.S.A.

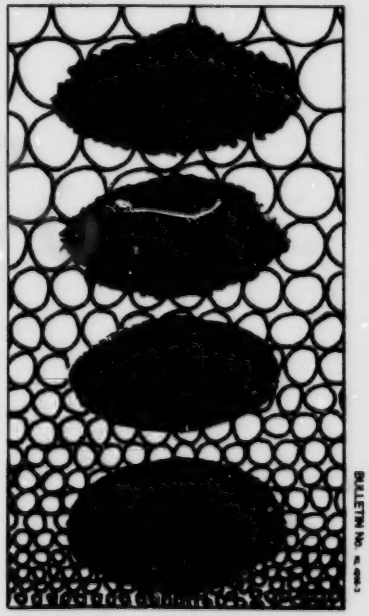
FILTER EVOLUTION Mixed Media filtration has become widely accepted as the standard in high-rate, high-performance filtration technology. Mixed Media uses a combination of three or more materials to approach the coarse-to-fine grain configuration of the ideal filter. This significant development by Neptune Microfloc research makes possible safe, reliable filtration at advanced filter rates. The practical application of this technology arose from a continuing evolution in filter design.

Development of high-rate filtration began in the 1940's with work aimed at overcoming the disadvantages of rapid sand filter beds. Rapid sand filters were plagued by fast headloss buildup and a tendency to blind. Hydraulic grading during backwash would shift the finest sand grains to the top of the bed causing most of the filtration to be done in the top few inches of the bed and thus creating the headloss and blinding problems.

Preliminary research resulted in the 2-media filter—a layer of coal over a layer of sand. The layer of coal opened up the top of the bed, extending the effective filtration depth. This configuration offered more acceptable headloss characteristics, but presented other problems. Replacement of the finer sand with coarse coal reduced overall media surface area in the filter, lowering the filter's stability and filtering efficiency. The sand could not be graded finer to restore stability and efficiency because it would regrade above the coal upon backwash. As a result, the coal-sand filter proved to be susceptible to breakthrough when surged, and had difficulty producing satisfactory effluent and long filter runs under high solids loading conditions.

The 3-component Mixed Media filter developed in 1962 by Neptune Microfloc research under the direction of Walter R. Conley solved the problems of the coal-sand filter while retaining its improved headloss characteristics. The 3-component filter, through its unique inverse void graduation, provided for higher filtration rates, long filter runs and consistently higher effluent quality than had been possible before. Materials of differing size and specific gravity were intermixed coarse to fine in the filter bed, providing superior performance while maintaining a stable configuration even after long periods of use and backwash. Introduction of a very fine high-density media restored the stability and efficiency lost in the coal-sand filter by increasing the total media surface area in the bed.

Four-component Mixed Media is the latest Microfloc development. Formulated for the tougher filtration jobs—municipal secondary effluent, industrial wastes, or unsettled water—the 4-component filter adds a layer of special



Mixed Media filter materials shown are, from top: low density anthracite, regular anthracite, silica and garnet. These materials intermix in the filter bed, forming an inverse-void gradation.

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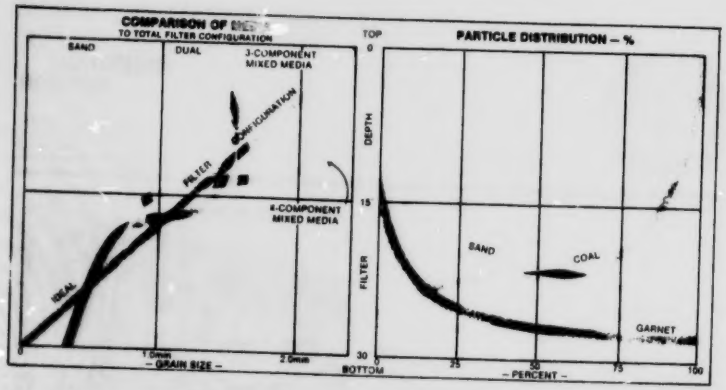


Three and four-component Mixed Media filter beds closely approach the ideal configuration as shown on the media comparison chart above. Graph at right provides media particle distribution percentages showing typical Mixed Media filter bed composition.

light coal to the top of the filter bed, extending Mixed Media's traditional coarse-to-fine gradation. Storage capacity is increased so the filter can accept even higher influent solids loadings, provide longer filter runs, or operate at higher rates. Filter runs are 25 to 50 percent longer at the same solids loading or are the same length at a 25 to 50 percent higher solids loading.

THE IDEAL FILTER Theory states that in the ideal filter, media grain size should decrease uniformly in the direction of flow. This configuration provides an infinite series of progressively finer "screens" which remove increasingly smaller particles and distribute the captured solids throughout the entire depth of the bed. Slow headloss buildup, ability to accept higher solids loadings, and longer filter runs result; and consistent filtered water quality is maintained. The removal of fine suspended solids is assured by the fine final grains in the filter.

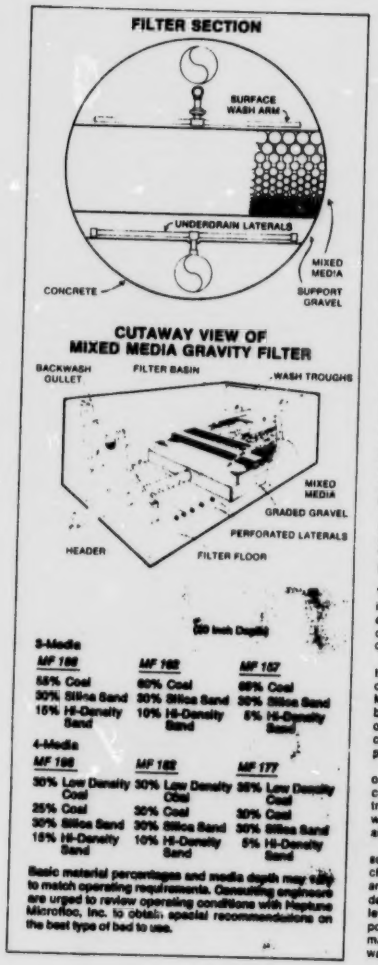
Maintaining coarse grains above finer ones and achieving the important intermixing needed to produce a nearly uniform decrease in grain size requires the use of materials of different sizes and specific gravities. Neptune Microfloc's 3-component Mixed Media was developed using materials ranging in size from 1.5 mm to 0.15 mm and in specific gravities from 1.6 to 4. These materials intermix, with particles distributed in the bed as shown in the graph at top right. 3-component Mixed Media filters can run at higher

filtration rates, obtain longer filter runs, handle solids loadings and produce higher quality effluent than either the rapid sand or coal-sand filters.

For some filtration jobs—municipal, secondary, effluent, industrial wastes, or unsettled water—theory suggests that addition of a coarser, fourth component to the top of the filter would provide additional improvement in headloss characteristics and filter run length, producing a filter more closely approaching the ideal configuration (see comparison graph above left).

This fourth component, a low specific gravity coal, makes it possible to change the top grain size of the filter from a mean of 1.4 mm to 2.4 mm without changing the grain size of the other three components. The larger grain size at the top of the filter significantly increases solids holding capacity. This increase can vary from 15 to 100 percent depending on the nature of the material being filtered.

IN THE FILTER BED Mixed Media has been effective in a wide range of filtration applications and readily adapts to most filtering equipment. The filter box schematic at middle left, opposite page, illustrates a gravity filter configuration typical of package and modular treatment systems and of larger municipal facilities. A pipe lateral underdrain system rests on the floor of the filter, collecting filtered water and introducing backwash water. Over this is placed a supportive layer of silica gravel and a second supportive layer of high-density gravel. The high-density gravel is used to prevent the fine high-density media from sifting down into the support gravel and to evenly distribute backwash water: Microfloc has support gravel configurations designed to cover most common underdrain systems. The Mixed Media filter bed is installed on top of the support gravel under the supervision of highly trained Neptune Microfloc technical directors. The media is carefully placed and hydraulically graded to insure the proper configuration for optimum performance. Above the Mixed Media surface are the surface wash arms and backwash troughs.



Vertical and horizontal pressure filters (horizontal shown at top left) also effectively utilize Mixed Media. Mixed Media and supportive gravel are installed in the same manner as in gravity filters, and the underdrain system operates similarly. Microfloc prefers pipe lateral underdrains with pressure filter systems.

Water depth in gravity filters ranges from 7 to 14 feet; and in pressure filters from 8 to 10 feet. Mixed Media beds for either filter type are normally 30 inches deep, variable to 36 inches when required; and support gravel layers range from 10 to 16 inches deep, depending on the underdrain system utilized.

WATER AND WASTE TREATMENT Mixed Media filtration technology is applicable to both water and waste treatment.

The Mixed Media filter design used in potable water treatment utilizes larger proportions of finer filtration materials to insure safe, reliable production of the highest quality filtered water. The large surface area of the finer materials provides the filtration capability needed for producing high clarity water and the stability against solids or hydraulic surges needed for safe operation. Coarser materials in the top of the bed assure adequate filter runs, but the key is the safety provided by the lower portion of the Mixed Media filter.

In advanced waste treatment, the criteria for efficient filtration are longer filter runs and satisfactory effluent quality. A coarser filter is required to satisfactorily remove the chemical and biological solids generated in secondary and tertiary treatment processes. The Mixed Media filter is opened up by increasing the proportion of coarser materials. A coarser, light anthracite is used to replace a portion of the regular coal, thus increasing storage capacity in the top of the filter. This reduces headloss, extending filter runs. Fine materials in the lower part of the Mixed Media bed polish the effluent to produce the tertiary quality desired. Satisfactory quality and operation efficiency are balanced.

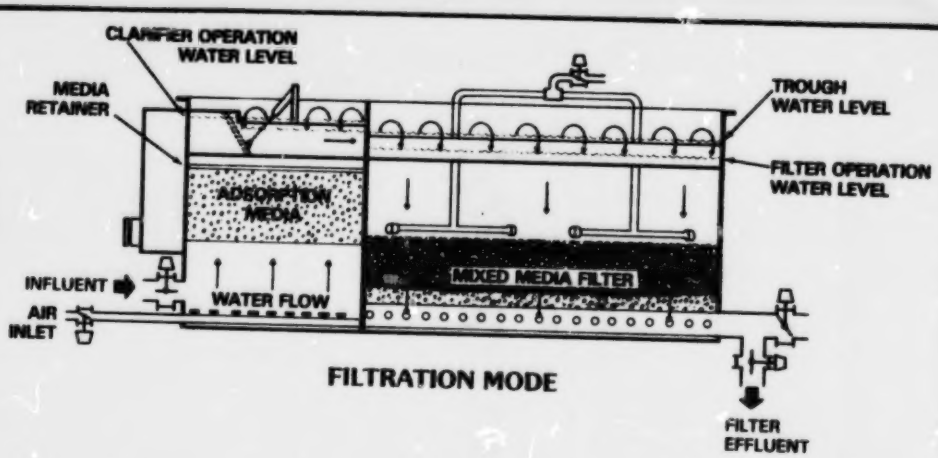
Typical flow rates for Microfloc Mixed Media filters are 5 to 10 gpm per square foot for municipal water and waste treatment applications and 5 to 20 for industrial applications. These rates are variable depending on the nature of the filtration problem.

TAILORED FILTERS The versatility of Mixed Media makes it possible to vary filter bed configuration to meet specific client needs. Grain size, filter depth, and media quantities can be altered to meet the desired balance of filtered water quality and filter run length.

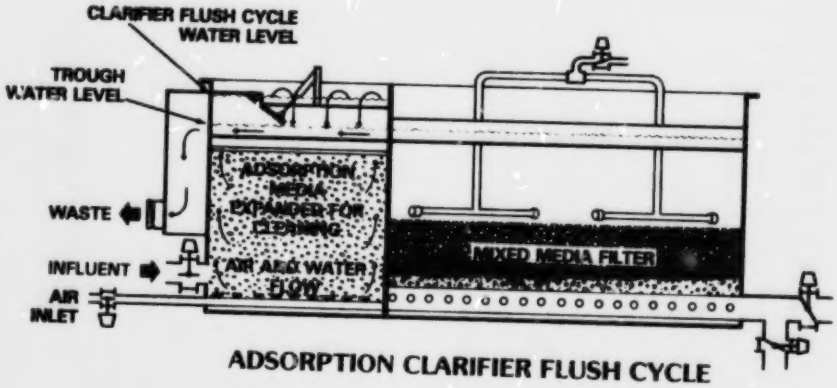
Microfloc starts with standard bed designs, then tailors these designs to fit individual applications. For the majority of municipal and industrial water supply applications, the MF 188 filter bed is recommended. This bed provides the balance of filter run length and filtered water quality most often required in water treatment. It is composed of 55 percent low density material, 30 percent medium density, and 15 percent high density.

MF 198, a 4-component Mixed Media bed, is generally recommended for most of the tougher filtration jobs. The extra capacity of this bed design makes it ideal for filtering industrial waste, municipal wastes, and unsettled or flashy raw water. The 4-component bed is also ideal for handling heavy algal loading and high solids surges.

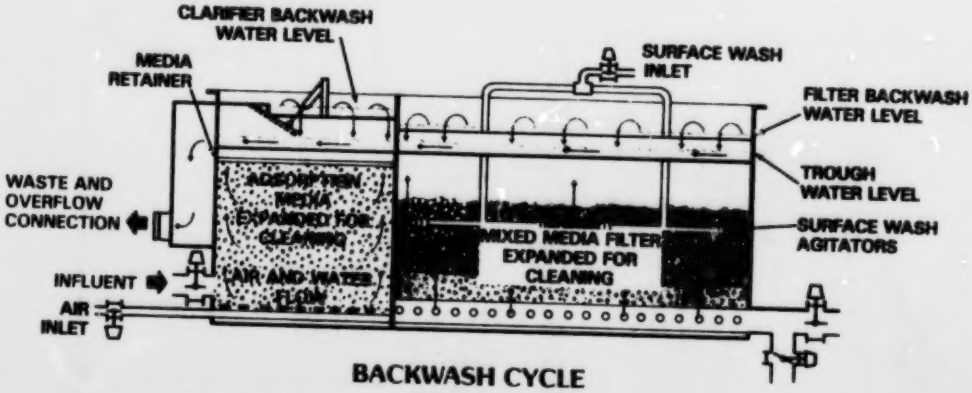
The MF 188 and MF 198 bed designs can be varied to suit specific application requirements. Raw water or waste characteristics, required effluent quality, rate of filtration, and desired filter run length can all be balanced by custom designing the composition of the filter bed. The chart at the left illustrates the most common variations of 3- and 4-component Mixed Media. Variation of filter media materials also makes possible the control of starting headlosses and backwash rates.



FILTRATION MODE



ADSORPTION CLARIFIER FLUSH CYCLE



BACKWASH CYCLE

Neptune Microfloc, Inc. P.O. Box 612 Corvallis, OR 97339 (503) 754-7654	neptune microfloc	DRAWN DATE COORDINATOR DATE CHECKED DATE APPROVED DATE	FLOW DIAGRAM TRIDENT™ WATER SYSTEMS	DRAWING NO. M2181 REV 1 SHEET OF

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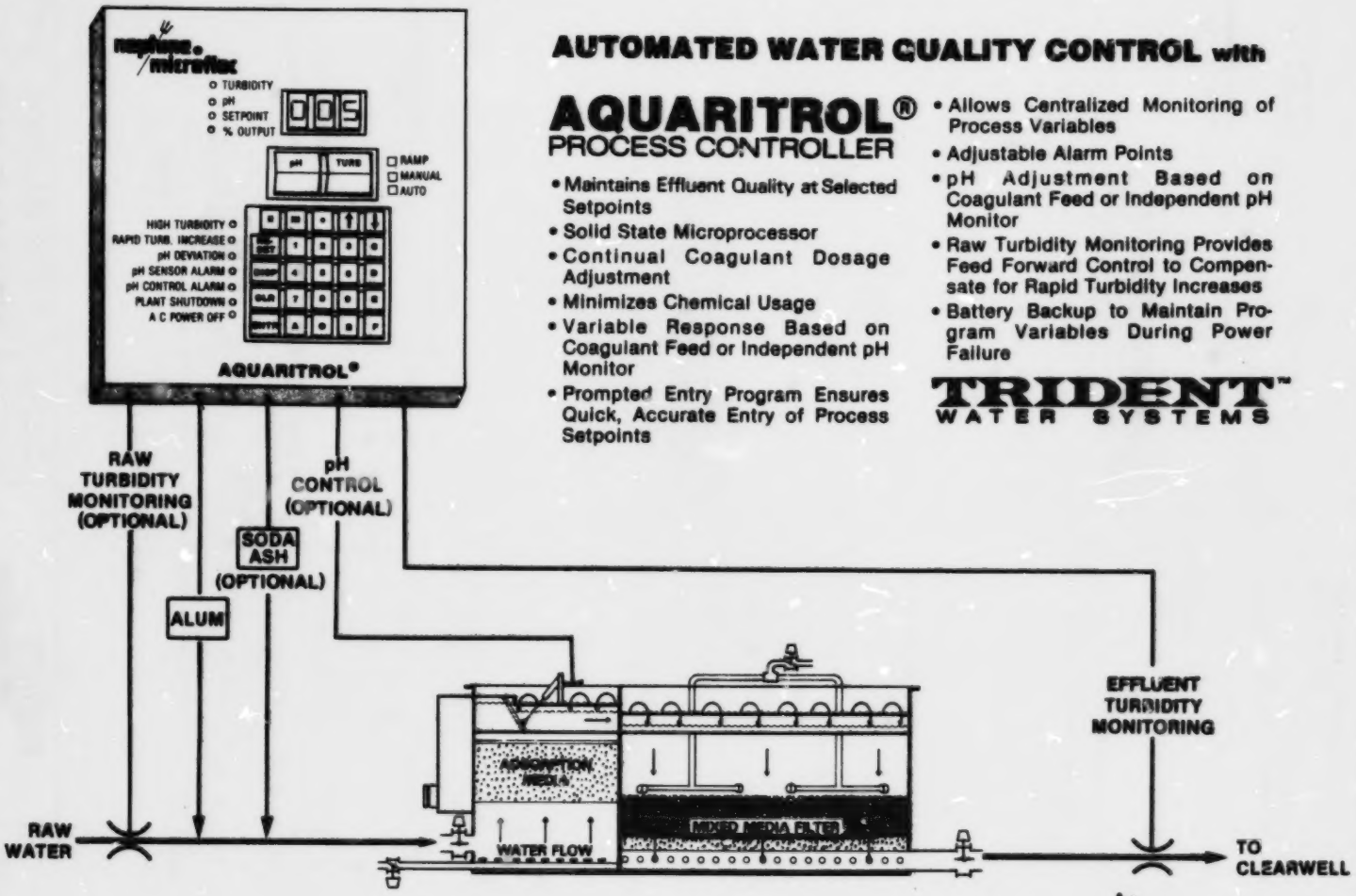

neptune microflox
P.O. Box 512 Corvallis, C 10

KS 8.55 Rev. 1 (7/84)

Application and results of deep bed filtration

by JOHN A BUCHANAN, Pr. Eng, B.Sc, A.P.T.C, M.I. Chem.E, A.M.I.W.P.C.

Mr Buchanan, who is managing director of Prentec (Pty) Ltd, has had more than 25 years experience in constructing, research and development, and production. For the past 10 years he has worked exclusively on water and effluent treatment both as a consultant and contractor.

INTRODUCTION

Filtration of a liquid may be defined as the passage of the liquid through a porous medium whereby the matter held in suspension in the liquid is removed.

In the field of water and effluent treatment, the most common type of filtration equipment employed is the rapid gravity filter in which the porous filtering media is a fixed bed of carefully screened sand. The liquid flows vertically downwards. In the rapid gravity filter, in common with most types of downflow filters, the majority of the filtered-out suspended matter is collected in the upper part of filtering media and the full dirt holding capacity of the filter is not realised. Deep bed filters are a development to enable almost 100% utilisation of the filtering media dirt holding capacity, with progressive filtering from coarse to fine layers of media in some cases.

Deep bed filtration is better defined as in-depth filtration since it is the in-depth filtering process which is more important than the depth of the filter bed.

Several types of deep bed filters are available on the market, e.g. mixed media, anthracite/sand, biflow, contact, etc, but none has been as successful as the Immediumfilter which is an upflow sand filter developed and patented worldwide by Imacti, Holland (South Africa patent number 60/1283).

In this paper, the Immediumfilter is employed to illustrate the principle advantages and applications of deep bed filtration.

PRINCIPLE OF THE IMMEDIUMFILTER (Dual Filter)

Figure 1 illustrates a typical cross-section of the downflow gravity or pressure type filter and the upflow sand Immediumfilter. Structurally the filters are very similar; both have a retaining wall and filter bed support plate provided with nozzles, with the various grades of media placed on top of one another.

In the conventional downflow filter, the unfiltered liquid passes through the sand, gravel and stone layers in that order, and leaves the filter from the bottom. This results in the top part of the sand layer collecting the majority of the suspended matter with little penetration of the matter into the filtering media. The dirt penetration can be increased by applying high pressure/flow to the filtering media. However, this causes an increase in pumping costs, a lowering of the filtered water quality and possible declassification of the filtering media.

Figure 1. Typical section through a sand filter

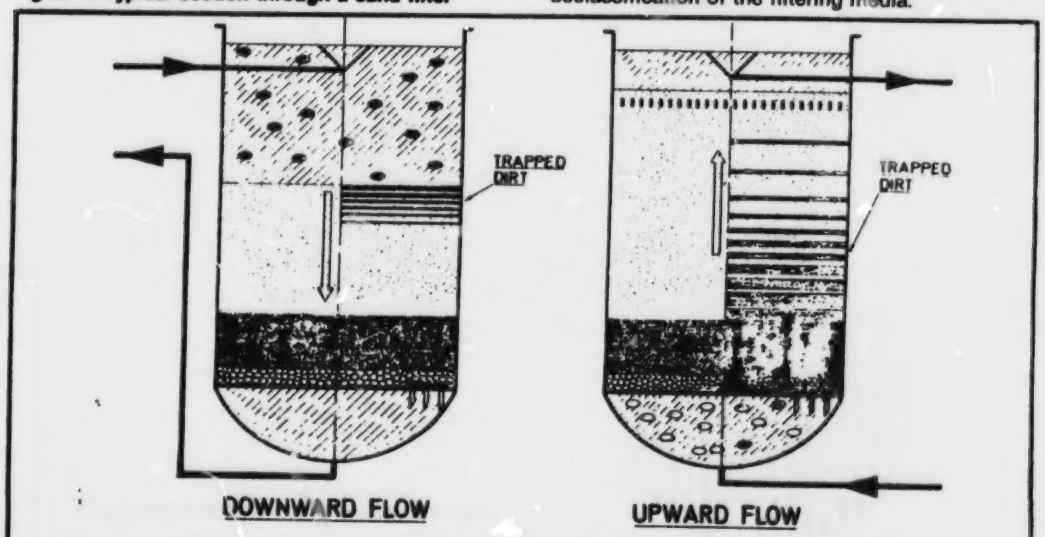

FIGURE 1. TYPICAL SECTION THROUGH A SAND FILTER

Common sense suggests that the filter should be fed from the bottom, thus allowing the flow to pass through the media layers progressively from the coarse stone to the fine sand. If the upflow principle is applied to the conventional sand filter, the filter run would be very short and the filtrate quality poor due to spasmodic breakthrough of the filter bed. To completely eliminate this breakthrough, the Immediumfilter is provided with a grid as shown in *Figure 2*. During filtration, a natural arching arrangement is formed between the sand grains and the grid bars, thus ensuring that the filtering media is held rigidly in position. The unfiltered liquid enters from the bottom and passes through the stone, gravel, coarse sand and fine sand layers, in that order, and leaves the filter from the top. The lower part of the filter containing the coarser media thus acts as a prefilter, the upper part as a polisher, and the intermediate section, because it contains coarse sand grains, provides the dirt holding capacity for the suspended matter being removed.

Cleaning of the Immediumfilter is achieved by first air scouring the media with low pressure air and then fluidising the media through the grid, thus releasing the collected dirt in the normal way to the backwash collecting launder or pipe.

ADVANTAGES OF THE IMMEDIUMFILTER (Dual Filter)

The upflow sand Immediumfilter has, in thousands of installations, clearly demonstrated the many advantages over the more conventional downflow sand gravity or pressure filter. *(Table 1)*.

APPLICATIONS OF THE IMMEDIUMFILTER (Dual Filter)

The Immediumfilter has been successfully applied in all filtration processes where the fixed filter media bed technique is employed. Some of the more common applications are shown in *Table 2*.

The performance and advantages of the Immediumfilter have been well proven in practice and, in order to illustrate its flexibility and reliability, two installations are described which vary greatly in capacity and duty. The Immediumfilter can be con-

Table 1

Advantages	Effects
Larger dirt holding capacity	longer service cycle. higher water efficiency. reduced labour requirements.
Higher service velocity	less filtration area required. large saving in capital cost. less overall plant area required.
Filter cleaned with feed water	no separate washwater storage required. large saving in capital cost. greater flexibility in plant design.
Simpler to operate	reduced labour cost. reduced maintenance cost.
Lower headloss experience	reduced operating power cost. more positive control.
No blinding or mudballing of media experienced	reduced labour and maintenance costs. greater plant efficiency.
Ideal for in-line flocculation or contact filtration.	large saving in capital cost. immediate and positive treatment. simplifies plant operation.

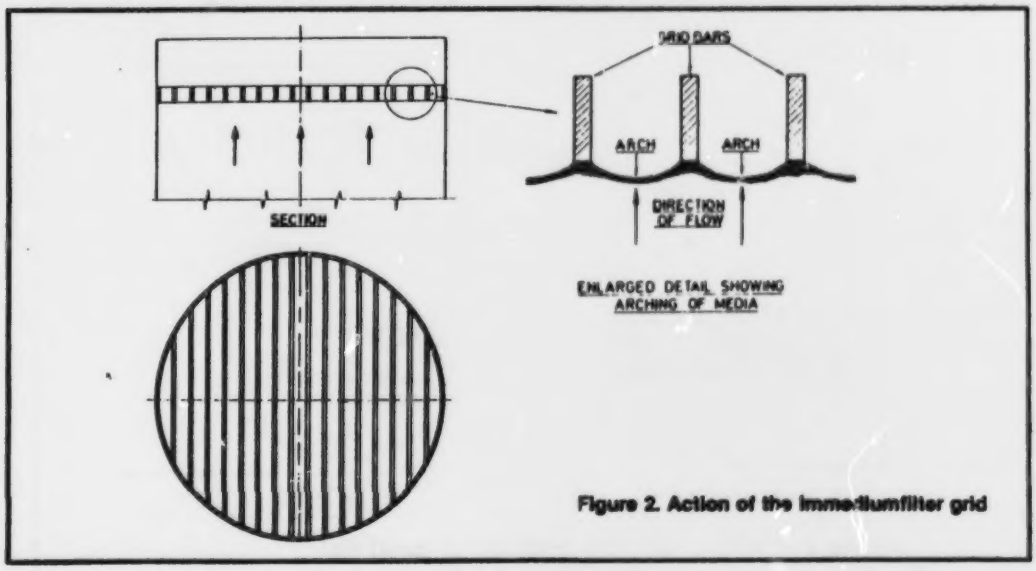

Figure 2. Action of the Immediumfilter grid

Table 2

a. Potable water and industrial process waters	- filtration of flocculated and settled water. - complete treatment by in-line flocculation i.e. without sedimentation.
b. Cooling water	- Slipstream filtration of circulating cooling water.
c. Sea water	- filtration of flocculated and settled sea water.
d. Effluent treatment	- removal of oil and scale from iron and steel industry effluents. - removal of solids from industrial effluents.
e. Colour removal	- in-line flocculation to remove colour from potable and industrial process water.
f. Electrolytic solutions	- polishing of electrolyte feeds to electrolysis plants.
g. Pregnant solution	- polishing of pregnant solution prior to further treatment.
h. Miscellaneous solutions	- polishing of starch, brine, oil, sodium hypochlorite, etc.
i. Swimming pool filtration plants	- maintaining ultra-clean water to international olympic standards.
j. Final sewage effluent	- tertiary treatment of sewage effluent to meet rigid standards.

structed in concrete when the design filtering area becomes too great to make it viable to fabricate the plant in steel.

POTABLE WATER PLANT

At the Drakensberg Pumped Storage Scheme near Bergville, Natal, the Electricity Supply Commission produced up to 90 m³/h of potable water by treating raw water from the pump station forebay.

The treatment plant consists of 5 pyramidal bottomed settling tanks followed by 3 Immediumfilters (*Figure 3*). The water is chemicated with aluminium sulphate and soda ash solutions, mixed by means of an in-line mixer and the bulk of the floc produced settled out in the settling tanks. Because of the relatively high upflow velocity of 2,0 m/h in the settling tanks, the carry-over of floc to the filtration section varies between 5-20 ppm. This solids loading would prove excessive for conventional downflow filters, but the Immediumfilter readily handles the load.

If required, the plant can be operated with the settling tanks bypassed. This involves rendering the raw water potable by employing the technique of in-

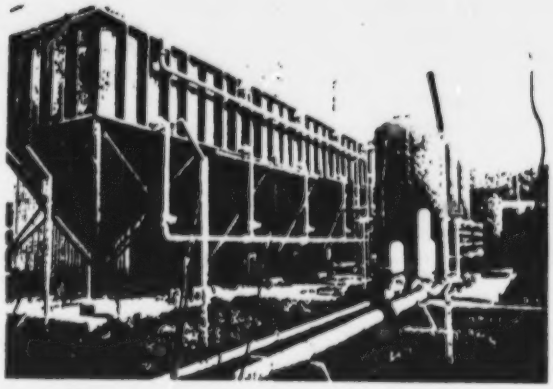

Figure 3

line flocculation into the immediumfilter

Turbidities of over 200 ppm have been successfully removed in the plant, and a consistently very high clarity of water produced. Therefore, when the raw water has a turbidity of less than 200 ppm, this technique can almost halve the capital cost of a water treatment plant.

Figure 4

In both applications, dirt holding capacities of 3 kg/m³ were obtained by the Immediumfilter, which is approximately 10 times greater than that expected by a rapid gravity sand filter.

EFFLUENT TREATMENT PLANT

At ISCOR's Vanderbijlpark Works, the effluent arising from the steel works is handled by the terminal effluent treatment plant. The basic steps of treatment are:

- descalping in scale pits;
- oil skimming;
- settling in horizontal flow settlers;
- low lift pumping;
- filtration by Immediumfilter.

The total capacity of the plant is 5 500 m^3/h and the prime objective of the filters is to render the effluent acceptable for recycling to the works, and/or for discharging into the River Vaal, by removing the suspended matter and oil to the desired levels.

The filtration section of the plant (*Figure 4*) consists of a block of 18 Immediumfilters constructed in concrete. The feed to each filter is kept constant irrespective of the solids loading in the filter, by means of equilibrium control chimneys. A summary of the operating results are shown in *Table 3*. Dirt holding capacities well in excess of 7 kg/m^3 have been achieved but, in order to maintain a high degree of filter cleanliness, the operating dirt holding capacity employed is 5 kg/m^3.

The removal of oil from effluents by means of sand filtration is considered by many to be non-viable. However, the above results clearly show that the sand Immediumfilter, with its in-depth filtration action, performs well in this difficult operation.

Table 3

	Influent		Filtered	Removal
	Average	Peak	Water	efficiency
Total suspended solids (ppm)	40	1 000	2	95-99%
Total oil content (ppm)	10	50	1	90-98%

CONCLUSION

Immediumfilter installations have clearly proved that deep bed filtration is an important tool in the field of filtration and it is the author's opinion that this tool is not exploited fully in South Africa.

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Maurice L. Leblanc

CROSS-FLOW FILTRATION/ULTRAFILTRATION

For suspended solids removal from water, the new technologies employing cross-flow filtration and ultrafiltration (incorporating cross-flow filtration principles) are believed to offer significant advantages. These systems will no doubt play greatly increased roles in the years to come in the removal of suspended solids from water.

The principle on which this technology is based is to use a dynamic membrane built up from the material that is being filtered from a recirculating slurry of the solids fraction which is mixed back into the feedwater. There are three main untrafiltration/cross-flow filtration system vendors.

NEPTUNE MICROFLOC, INC.
Post Office Box 612
Corvallis, OR 97339-0612
Steve Uban

MEMTEK, INC.
42 Cummings Park
Woburn, MA 01801
(617) 935-7840
Telex: 979-829

MEMTEK, INC.
25652 Taladro Circle, #D
Mission Viejo, CA 92691
Albert G. Anderson
Western Regional Manager
(714) 586-8691

ROMICON, INC.
100 Cummings Park
Woburn, MA 01801
(617) 935-7840
Telex: 94-9333

Romicon, Inc. supplies potential users with an excellent booklet entitled, "Ultrafiltration Handbook," which explains the principles of cross-flow filtration and ultrafiltration and its applications. Another description of the process by COMSTOCK, et al. (1983) describing the cross-flow microfiltration process is inserted below. Remarkable solution fluxes are achieved with even small cross-flow filtration units.

One other version of cross-flow filtration and its application in minewater treatment was demonstrated at the ARGO Tunnel and described by HOLM and SIMPSON (1981). A copy

of their paper is inserted in Chapter 24 on acid mine drainage treatment. The Wannamaker continuous concentrator is said to function best in removing crystalline particles 1-10 microns in size. The portable test unit treated about 80 gpm of feedwater.

The simple cross-flow filtration system employed used a porous fabric media which looked similar to a porous firehose. The precipitate was recirculated and allowed to build up until there was enough of it that a bleed became necessary. The experiment was conducted by:

COLORADO DEPT. OF NATURAL RESOURCES
Mine Land Reclamation Dept.
1313 Sherman Street
Denver, CO 80203-2273
(303) 866-3567
J. David Holm

The Wannamaker continuous concentrator was invented by:

W. W. (BILL) WANNAMAKER
Post Office Box 1121
Camden, SC 29020
(800) 845-2202

and supplied by:

COLORADO MINERALS AND CHEMICAL CO. LTD.
2885 Mount Herman Road
Monument, CO 80132
(303) 481-3710
George M. Morris

Excerpt from:

Removal of Trace Elements and Acidity from the ARGO Mine Tunnel Drainage. J. DAVID HOLM and DONALD H. SIMPSON, April, 1981.

A precipitate concentration and filtration device was tested at the Argo Mine Tunnel. The system used was a Wannamaker Continuous Concentrator furnished by Colorado Minerals & Chemicals Ltd. with a capacity of 57,600 gpd product flow.

This particular continuous concentrator apparatus is a relatively simple device designed to fractionally remove solids from liquid-solid suspensions or slurrys. The continuous concentrator is essentially portable and employs a modular design so that a wide range of flows can be treated. The system uses relatively little floor space and was installed inside a building near the portal of the Argo Mine Tunnel.

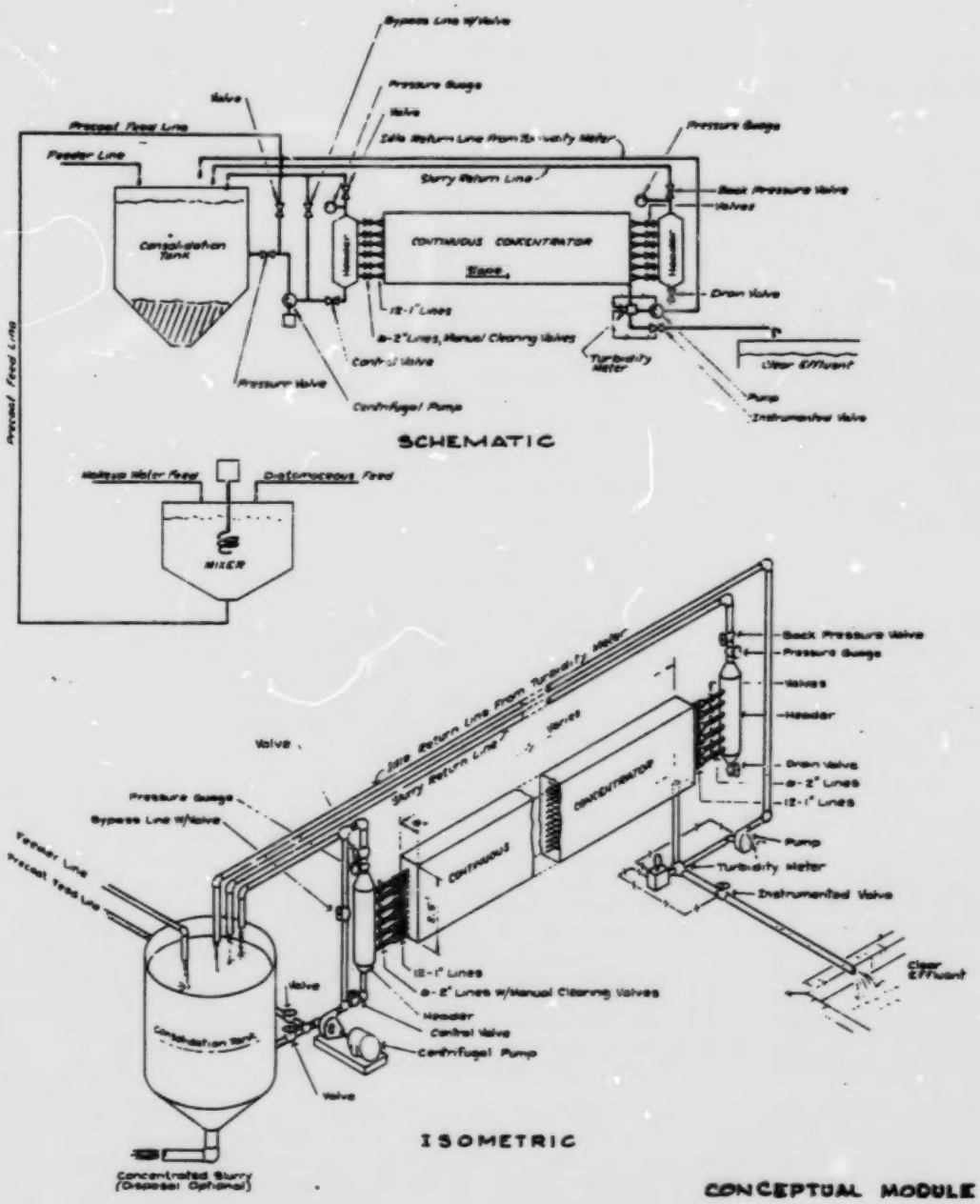
The device was used simply to remove minerals from mine water using a precipitation and filtration process. A schematic of the continuous concentrator apparatus is presented in Figure 1.

Continuous Concentrator System Evaluation

Sampling of the effluent from the continuous concentrator water treatment/minerals recovery system at the Argo Tunnel was performed on October 15, 1980. The test unit was operated as a single stage multipass concentrator with an intermittent feed of raw mine water and a continuous product flow of clear effluent water. The concentrated sludge was discharged from the tank following the experiment. The sludge has not yet been assayed for mineral content.

Samples of processed water or effluent were taken as the system was operated at various pH values. The objective of the sampling program was to determine the optimum pH range which provided maximum precipitation of dissolved metals in the Argo Mine drainage and produced an effluent of acceptable quality. Approximately 450 gallons of raw water draining from the Argo Mine Tunnel was pumped into the concentration consolidation tank and sampled for pH and baseline metal concentrations. Industrial Grade Caustic Soda (NaOH) was then added to the tank in measured increments until the pH of the mine water was raised to 11.5. The mine water and sodium hydroxide were thoroughly mixed using the centrifugal pump and a return line to the consolidation tank. After complete mixing this water was then pumped into the continuous concentrator and the system was operated for 5 minutes and allowed to reach equilibrium. An effluent sample was obtained and analyzed for pH and metal concentrations.

The system was operated continuously and effluent samples were obtained at pH 11.5, 10.5, 9.8, 8.3, 7.2, 6.6, 6.0 and 5.6. The pH was lowered gradually by simply adding raw mine water to the consolidation tank (which had originally been spiked with NaOH). At each desired pH level the system was allowed to equilibrate prior to extracting effluent samples. The pH of all effluent samples was measured immediately with a pH meter. All samples were acidified with HNO_3 and analyzed on an atomic absorption spectrophotometer by the Industrial Laboratories Company. The following parameters were analyzed: Total dissolved solids, sulfate, sodium, arsenic, cadmium, chromium^{+3}, chromium^{+6}, copper, iron, manganese, lead and zinc. The results of the examination of the effect of increasing pH on removal of trace elements from the Argo Mine drainage using the continuous concentrator system are presented below.



WANNAMAKER CONTINUOUS CONCENTRATOR

(Paper No.) IWC-83-5

44TH ANNUAL MEETING
INTERNATIONAL WATER CONFERENCE
PITTSBURGH, PENNSYLVANIA
OCTOBER 24, 25, 26, 1983

HYDROPERM™ CROSS FLOW MICROFILTRATION
A NEW PROCESS FOR THE LIQUID PROCESS INDUSTRY

BY
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ANDREW K. HSIUNG
JOSEPH A. MILLEN
OF
NEPTUNE MICROFLOC, INCORPORATED

Introduction

Cross flow microfiltration is a new solids/liquid separation process that has grown out of microfiltration technology.

The objective of this paper is to highlight the factors that govern the theory and practice of this intriguing new process and to present lime softening and seawater reverse osmosis pretreatment pilot study data. Lastly, the benefits of HYDROPERM™ Cross Flow Microfiltration will be presented for these applications.

Through Flow Vs. Cross Flow Microfiltration

Commercial through flow microfilters consist of flat sheets or discs and cartridge filters which are commonly used for laboratory and industrial separations. In both cases, feedwater is introduced at right angles to the membrane surface.

Cross flow microfiltration is a generic description of a category of processes that combine microfilters and tangential feedwater flow. Figure 1 illustrates through flow and cross flow microfiltration concepts.

Included in the cross flow microfiltration category are ultrafilters and reverse osmosis unit processes. In both reverse osmosis and ultrafilter processes, a thin solids rejecting membrane is deposited over a microporous support structure.

One subcategory of cross flow microfiltration includes microfilter elements that do not have a fixed rejecting membrane and do not reject dissolved (ionic) solids or macromolecules. HYDROPERM™ Cross Flow Microfiltration falls into this category. Instead of requiring a fixed, solids rejecting membrane, a dynamic membrane is formed on the inner surface of the filter element by the material being filtered. Figure 2 is an electron photomicrograph of a single HYDROPERM™ filter element. Each filtration tube has an inside diameter of 6 mm and contains pores that average 2 microns in diameter. The pores comprise 65 percent of the tube wall volume. HYDROPERM™ modules are made up of many such tubes. Module construction is illustrated in Figure 3.

The HYDROPERM™ Cross Flow Microfiltration Process

To best describe the HYDROPERM™ Cross Flow Microfiltration process, it is instructive to compare and contrast it to a tubular ultrafilter device. Typically, ultrafilters operate on feedwater that contains relatively low levels of suspended solids. Feedwater flows through the lumen of the tubular elements with the filtrate permeating outward through the walls. A typical feedwater suspended solids concentration is about 15 mg/L. The reject suspended solids concentration might be on the order of 150 mg/L. Pretreatment chemicals are not employed, and feedwater velocity through the ultrafilter elements is typically in the laminar to low turbulent range depending upon the application and type of ultrafilter.

Ultrafilters depend upon a thin, fixed, surface membrane for particulate rejection. Pore sizes may be engineered to reject macromolecules as well as larger particulate material. System pressures generally fall into the 25-35 psig range. At this pressure, distilled water fluxes are on the order of 150 gpd/sq.ft. of membrane area. Distilled water flux to module volume ratio is about 45,000 gpd/cu.ft. Operating flux rates are generally in the 25 gpd/sq.ft. range, giving a flux to module volume ratio of 7,500 gpd/cu.ft.

HYDROPERM™ filtration tubes do not use a fixed rejecting membrane but rather a dynamic membrane formed from the material that is being filtered, Figure 4. It is this membrane that actually rejects particulates. Feedwater velocity within the filter elements is within the turbulent regime (Reynolds number of 18,000). System pressures are similar to ultrafiltration and fall into the range of 25-35 psig. Distilled water flux is on the order of 3,000 gpd/sq.ft., giving a flux/module volume ratio of over 200,000 gpd/cu.ft. Operating flux rates in the 1,000 gpd/sq.ft. range are typical, resulting in a flux/volume ratio of 66,000 gpd/cu.ft.

HYDROPERM™ Cross Flow Microfiltration may also operate on feedwater containing very high levels of suspended solids. For example, flux rates of 1,000 gpd/sq.ft. have been achieved at suspended solids levels as high as 5-8 weight percent through the HYDROPERM™ tubes.

Pretreatment chemicals are often employed to improve the rheology of the filtered solids. Table 1 compares the physical and process capabilities of the two unit processes.

In terms of solids loading, HYDROPERM™ Cross Flow Microfiltration overlaps and even surpasses the capabilities of clarifiers and thickeners. Clarifiers can generally operate to a solids loading limit of 20-40 lbs/day/ sq.ft. of clarification area. Granular media filters can tolerate about 0.2 lb. solids/day/sq.ft. A typical HYDROPERM™ module solids loading rate is 150 lbs/ day/sq.ft. of tube area.

Figure 5 illustrates how cross flow microfiltration relates to other unit processes with respect to filtrate quality. Reverse osmosis rejects dissolved (ionic) solids as well as macromolecules and colloids. Ultrafilters overlap reverse osmosis with respect to rejection of macromolecules and colloids. HYDROPERM™ Cross Flow Microfiltration has demonstrated particle size removal down to 0.5 micron.

HYDROPERM™ Cross Flow Microfiltration System Operation

At this time, three specific commercial applications for cross flow microfiltration have been studied. These include metal plating waste treatment and recovery, lime softening of municipal and industrial waters, and seawater reverse osmosis pretreatment.

A description of the HYDROPERM™ lime softener will best serve to illustrate the system concepts. Raw water to be treated enters the system through a small reaction tank with approximately 4 minutes of detention time. The reaction tank is only required when a chemical reaction must take place ahead

of the HYDROPERM™ Cross Flow Microfiltration unit. Lime and sometimes a rheology aid (metal salt or polymer) are added directly to the reaction tank. Solids concentration is maintained at about 2 weight percent within the tank to accelerate the softening reactions and to retard scale formation. The slurry is pumped into the filtration loop by a makeup pump which maintains pressure within the loop at about 35 psig, and a second recycle pump moves slurry through the HYDROPERM™ tubes at a constant velocity. Filtration takes place through the porous tubes in a direction perpendicular to the slurry flow. Product water is collected from around the outside of the tubes and flows to storage. A portion of the concentrated slurry (5-7 weight percent) is recycled back to the reaction tank as a moving sludge blanket. A small portion of the thickened sludge is also wasted from the filtration loop as blowdown. Generally, the blowdown flowrate represents about 0.5 percent of the raw water makeup flowrate.

After a period ranging from 12 hours to several days, the filtration run must be terminated due to high differential pressure across the HYDROPERM™ module. The system is then flushed with raw water, and a cleaning solution is recycled through the filtration loop for about 5 minutes. Following a second brief raw water flush, the unit is brought back on-line in the filtration mode. All cycles are initiated automatically. Figure 6 illustrates these operational modes. Figure 7 is a system drawing.

The reverse osmosis pretreatment system is very similar to the lime softener except that a reaction tank is not needed and sludge recycle is not required.

Nonequilibrium Operation

State of the art cross flow microfilters such as reverse osmosis and ultrafilters operate in an equilibrium filtration mode. That is, differential pressure across the microfilter remains constant while the flux or filtration rate is allowed to decline to a lower equilibrium value, Figure 8. During the initial declining or nonequilibrium phase, the dynamic membrane is deposited. Also during this phase, flux rate is directly proportional to recycle velocity and differential pressure, and flux is inversely proportional to slurry concentration and time as indicated by the following formula:[1]

$$F = K\, V^{a}\, \Delta P^{b}\, C^{-c}\, t^{-d}$$

Where, F = flux rate
V = recycle velocity
ΔP = differential pressure
C = slurry concentration
t = time
a,b,c and d are filtration exponents

When the dynamic membrane is fully formed, flux rate reaches a plateau. At this stage, differential pressure drops out of the equation and flux rate

[1]Marshall Tulin, NSF Proposal, 1980.

is only a function of velocity, slurry concentration, time, and the filtration constant.

By contrast, HYDROPERM™ Cross Flow Microfiltration is operated in the nonequilibrium phase which is characterized by higher flux rates created by partially throttling the product valve and providing an intermittent product water backflush through the tube walls. Flux rate can therefore be held constant while differential pressure is allowed to increase as illustrated by Figure 9.

By rearranging the equation for nonequilibrium operation, one obtains:

$$\Delta P = \frac{K F^{\frac{1}{b}} C^{\frac{c}{b}} t^{\frac{d}{b}}}{V^{\frac{a}{b}}}$$

This equation best describes the nonequilibrium, constant flux mode of HYDROPERM™ Cross Flow Microfiltration operation.

Differential pressure increases as the flux rate, solids concentration and time increase. Differential pressure decreases with increased recycle velocity. Improvements in solids rheology have the effect of decreasing the exponents of flux, solids concentration, and time. The exponent for velocity is increased and the filtration constant (K) is decreased.

Rheology Considerations

Control of the dynamic membrane is a key to successful cross flow microfilter operation. By proper chemical pretreatment, the erosion characteristics of the dynamic membrane can be improved markedly. This allows operation of the cross flow filter at significantly higher flux rates for longer periods of time. As an example, Figure 10 plots the development of differential pressure with time for two lime softening runs. The upper curve is from a run that employed lime only. The lower curve was obtained from a run that was made with lime and a small quantity of an organic polymer. The flux rate was 1,000 gpd/sq.ft. in each case.

Lime Softening Applications

A number of lime softening pilot studies have been conducted. Data from the pilot study at Nanton, Alberta, Canada, is presented below.

The water source for the town of Nanton is a meandering prairie stream that is high in hardness and also contains silt, clay, algae, and some iron. Table 2 tabulates raw and HYDROPERM™ Cross Flow Microfilter softened water quality parameters. Figure 11 plots differential pressure and blowdown suspended solids concentration as a function of time. Excellent quality softened and filtered water was produced, and HYDROPERM™ Cross Flow Microfilter run times were in excess of several days. A constant flux rate of 1,000 gpd/sq.ft. was maintained. Product water recovery in excess of 99% was achieved. Weight percent suspended solids in the blowdown averaged 5 percent.

An on-going lime softening study is being conducted in Corvallis, Oregon, on hard well water. This water is low in turbidity but contains moderately high levels of carbonate hardness.

Figure 12 plots softened water quality parameters. Run times average 12 hours or more at a flux rate of 1,000 gpd/sq.ft. of tube area. Product water recovery is greater than 99 percent.

Seawater Filtration

Table 3 tabulates seawater pretreatment data from a pilot study run at the Oregon Coast. Ferric sulfate was added to the raw seawater as a rheology aid at a dosage of 20 mg/L. Filter run times were equal to or greater than 12 hours at a flux rate of 1,000 gpd/sq.ft. of tube area. Silt Density Indexes[2] were always below 1.5 percent/minute regardless of the changing quality of the raw seawater. While not a reliable predictor of reverse osmosis feedwater quality, filtered water turbidities were always less than 0.2 NTU.

Advantages of HYDROPERM™ Cross Flow Softening

Conventional lime softeners have been used successfully for over 40 years. Any new process or technology must offer some attractive alternatives in order to warrant consideration as a replacement. HYDROPERM™ Cross Flow Lime Softening does this. The advantages begin with low installed cost and continue with features such as compact equipment size, simplified operation and improved product quality. The major benefits are numerous:

Low installed cost. HYDROPERM™ softeners provide a significant installed cost advantage over conventional softeners. Installed cost is comprised of three major factors: process equipment, floor space, and installation. HYDROPERM™ Cross Flow softeners provide a savings in all three categories. The compact HYDROPERM™ Microfilter systems have a lower process equipment cost, and installation of a skid-mounted process provides savings in labor.

The installed cost savings offered by HYDROPERM™ softeners has been shown to range from 30 to 50 percent over a wide range of flows.

Ease of operation. Unlike conventional softener-filters, cross flow softeners may be turned off and on without a lengthy restabilization period. In addition, filter breakthroughs cannot occur and there are no sludge blanket control problems. This feature is especially important when softened water is needed only intermittently or when water demand is tied to process needs, shift operations or peaking cycles.

[2] Silt Density Index is the standard test used to characterize reverse osmosis feedwater quality. The test is performed by forcing filtered water through a 0.45 micron pore size Millipore microfilter. The decay in flowrate at the end of 15 minutes of flowing is an index of the quantity and quality of colloidal material present in the raw water.

Recarbonation not specifically required. Recarbonation is not specifically required for operation of the HYDROPERM™ Cross Flow softener. Recarbonation can be included if stabilized water at a lower pH is desired in the distribution system. Conventional systems require recarbonation prior to filtration to prevent incrustation of the media or underdrain.

Convenient sizes. Modular construction using one, two or three module systems is available that gives a broad range of flow rate options. System capacity can also be increased at a later date by simply adding another skid.

Superior effluent quality. Water quality in terms of particulate removal rivals that of ultrafilters. Virtually complete bacterial removal has been demonstrated, and extremely low silt density index values are always achieved.

Power consumed by the HYDROPERM™ softener average 1 kw-hr/1,000 gal. of softened water produced. Chemical consumption is the same as for conventional softeners.

Advantages of Reverse Osmosis Pretreatment by HYDROPERM™ Cross Flow Microfilters

Granular media filters have traditionally been used for reverse osmosis pretreatment. The major disadvantage of granular media filters for seawater pretreatment is that they cannot reliably and consistently produce low SDI feedwater. Cyclical changes in the raw water quality and the complex nature of seawater can make the process chemistry required for good granular media filter operation too complex for plant operators to handle. HYDROPERM™ Cross Flow Microfilters always produce a superior product water regardless of the raw water quality. In addition, filtered water quality is independent of the rheology aid added to the HYDROPERM™ Cross Flow Microfilter system.

The cost of a HYDROPERM™ system parallels that of a good automatically controlled granular media pressure filter system. HYDROPERM™ Cross Flow filters are also skid mounted for easy installation and they occupy a minimum of floor space.

Power consumption for the RO pretreatment units is 0.8 kw-hr/1,000 gallons of filtered water. Chemical consumption is equal to or less than for granular media filters.

Conclusions

HYDROPERM™ Cross Flow microfilters make use of a dynamically formed membrane for solids rejection. The dynamic membrane may be controlled by chemical addition and by controlling the operational variables such as recycle velocity, flux rate, differential pressure and solids concentration.

HYDROPERM™ Cross Flow Microfilters offer significant technical and economic benefits for a variety of water, wastewater, and process stream treatment applications. Commercialized applications for metal finishing waste treatment, lime softening, and seawater reverse osmosis pretreatment have been

demonstrated. In the years to come, it is expected that cross flow microfiltration will be used for hundreds of applications that range from process stream solids/liquid separations to secondary wastewater pretreatment for reverse osmosis.

TABLE 1
Unit Process Comparison

Process	Solids Loading lb/day/sq.ft.	Flux/Volume Ratio gpd/cu.ft.	Flux gpd/sq.ft.
Ultrafiltration	0.45	7,500	25
HYDROPERM™ Cross Flow Microfiltration	150	66,000	1,000
Granular Media Filtration	0.2	720	7,200
Clarification	20-40	360	3,600

TABLE 2
Water Quality Parameters
Nanton, Alberta

Component	Raw	Softened
Ca (as $CaCO_3$)	160 mg/L	40 mg/L
Mg (as $CaCO_3$)	165 mg/L	74 mg/L
Hardness (as $CaCO_3$)	325 mg/L	114 mg/L
Alkalinity (as $CaCO_3$)	330 mg/L	106 mg/L
pH (Units)	8.5	11.2
Iron (as Fe)	0.25 mg/L	0.04 mg/L
Color (Units)	30.0	0
Turbidity (NTU)	20	0.14
Recovery		99%

TABLE 3
Seawater Pretreatment Data

	Raw Water Quality				Filtered Water Quality				
Run Number	TSS, mg/L	Turbidity, NTU	SDI, %/Min.	Bacteriological Count #/ml	Turbidity NTU	SDI %/Min.	Bact. Count #/ml.	Flux Rate, gpd/sq.ft.	Run Time hrs.
14	130[a]	110	Too high to Measure	1,600[b]	0.11	1.2	1[b]	1,000	12
19		3.0			0.07	1.4		1,000	> 12
20		3.4			0.09	1.5		1,000	> 12
22	8.45	2.7	54		0.07	1.4		1,000	> 18
23	6.60	2.5	64	869[b]	0.07	1.2	1[b]	1,000	> 23
24		2.5	53		0.07	1.0		1,000	> 12

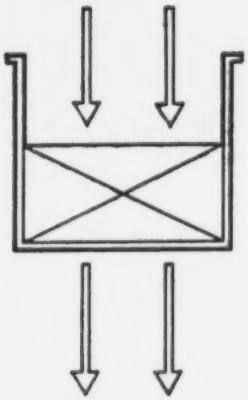
Notes:

a. Kaolin clay added to artifically increase the raw water turbidity.

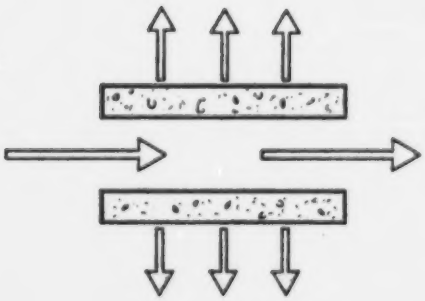
b. Total bacteriological counts were made on nutrient agar that contained sodium chloride.

FIGURE 1

THROUGHFLOW MICROFILTRATION
VS.
CROSSFLOW MICROFILTRATION



THROUGHFLOW MICROFILTRATION



CROSSFLOW MICROFILTRATION

FIGURE 2

ELECTRON PHOTOMICROGRAPH OF A SINGLE HYDROPERM TUBE

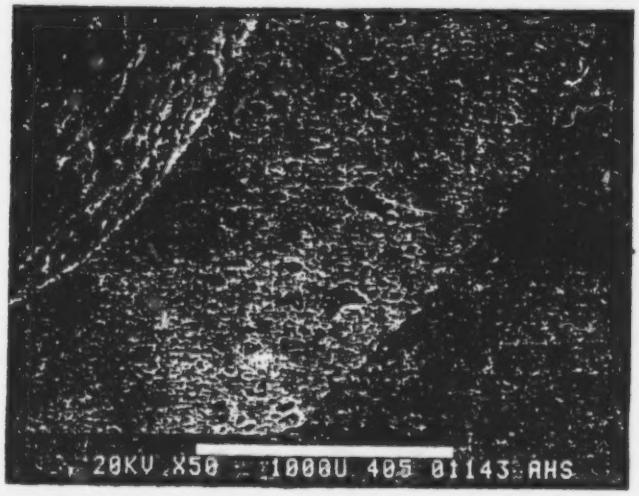


FIGURE 3

HYDROPERM MODULE

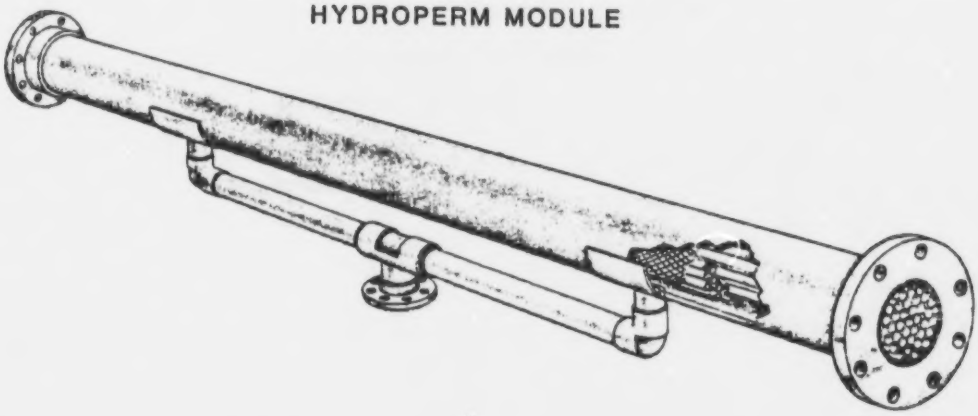


FIGURE 4

DYNAMIC MEMBRANE CONCEPT

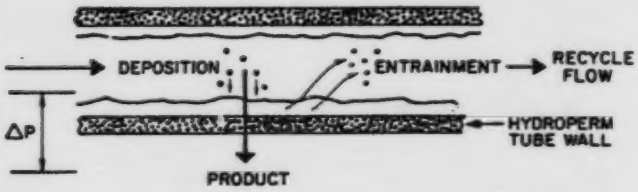


FIGURE 5

WATER QUALITY FOR SEVERAL UNIT PROCESSES

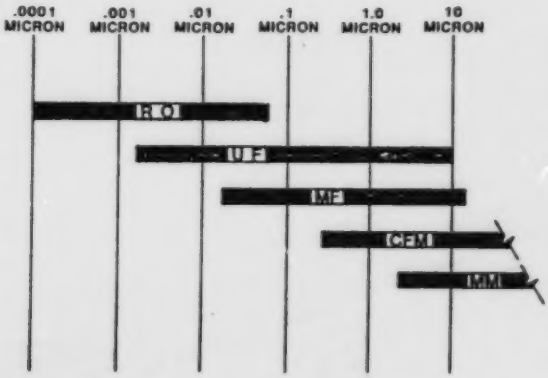
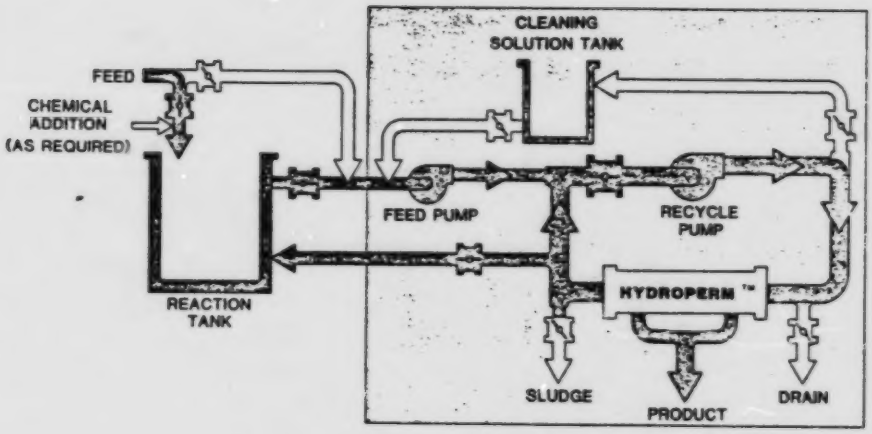
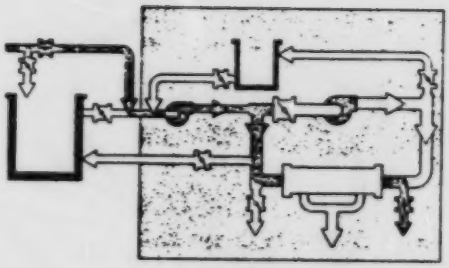


FIGURE 6

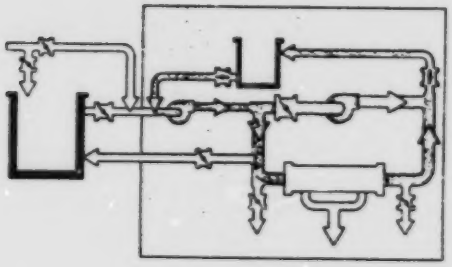
HYDROPERM SOFTENING OPERATIONAL MODE



SOFTENING CYCLE



FLUSHING CYCLE



CLEANING CYCLE

FIGURE 7

HYDROPERM LIME SOFTENER

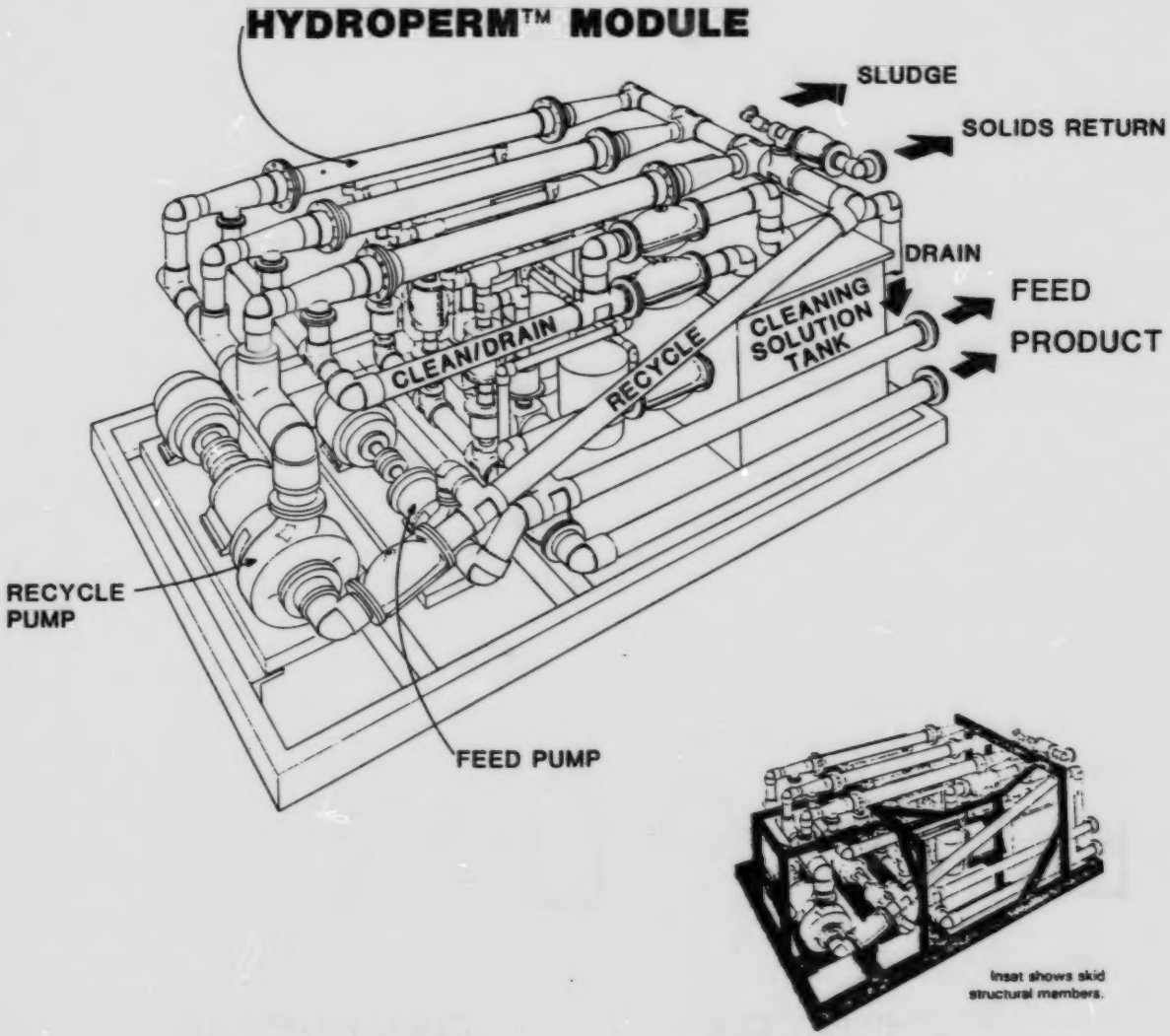


FIGURE 8

CONVENTIONAL CROSSFLOW MICROFILTRATION

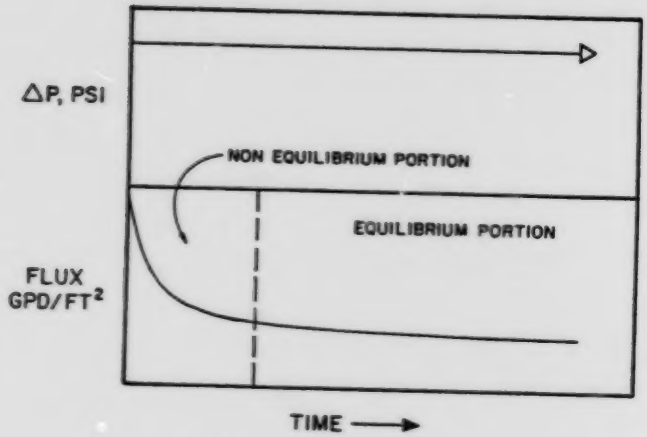


FIGURE 9

NONEQUILIBRIUM HYDROPERM OPERATION

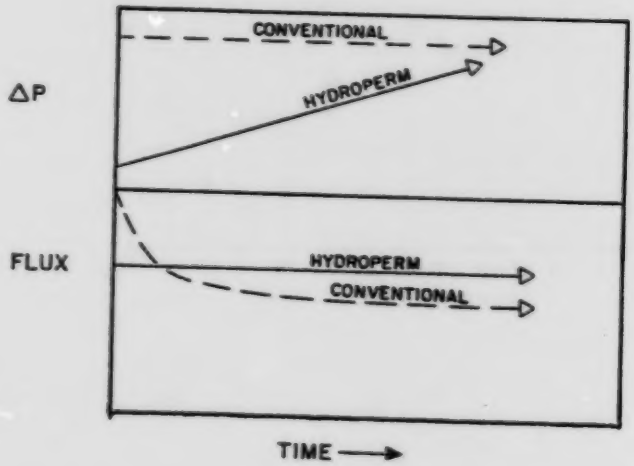


FIGURE 10

THE EFFECT OF RHEOLOGY AIDS

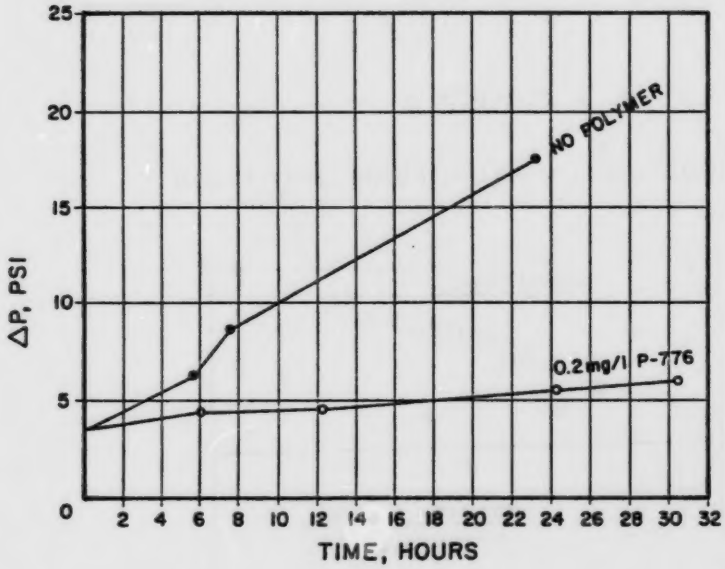


FIGURE 11

NANTON HYDROPERM SOFTENING STUDY
DIFFERENTIAL PRESSURE-TIME CURVE

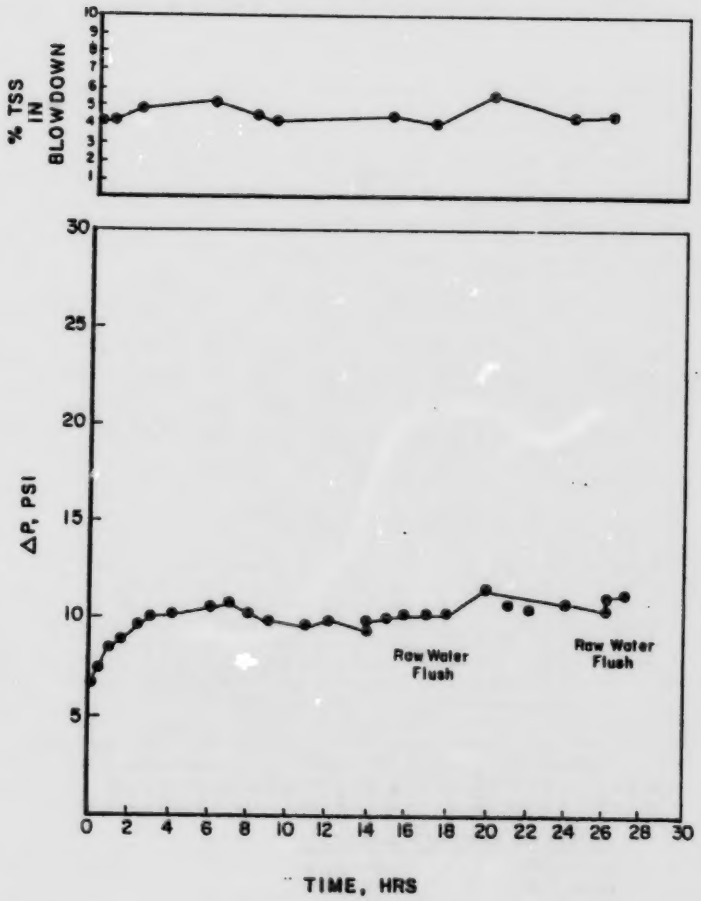
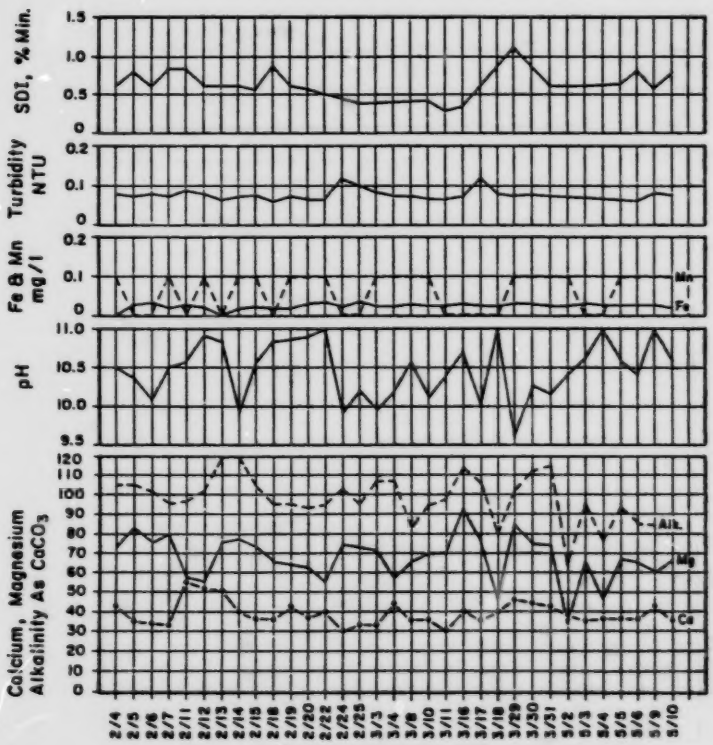


FIGURE 12

SOFTENED WATER QUALITY PARAMETERS FOR CORVALLIS WELL WATER



AVERAGE RAW WATER QUALITY

Ca — 137	Fe — 0.04
Mg — 87	Mn — 0.31
Alk. — 223	Turb. — 0.43
	SDI — 5.0

neptune microflor

HYDRO

CROSS FLOW MICROFILTRATION

TECHNOLOGY

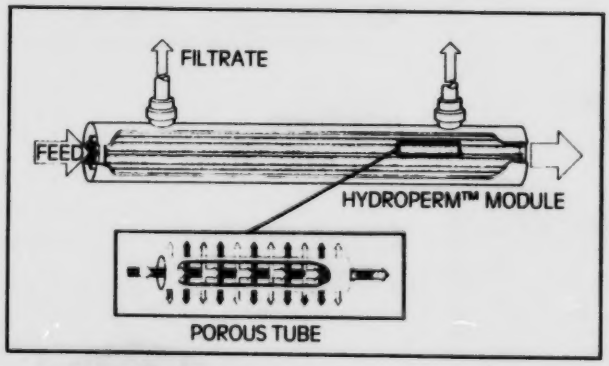
HYDROPERM™ cross flow microfiltration is a new solids liquid separation technology which substitutes a single process unit for clarification, filtration and thickening.

HYDROPERM™ combines the high flux rates of granular media filters with the thin-skin surface filtration aspects of membrane ultrafilters. Micron sized particles and colloids can be easily removed.

CROSS FLOW MICROFILTRATION (CFM)

Filtration processes can be divided into two general categories: **cross flow** and **through-flow.** In through-flow filtration, the flow of both influent and product water is perpendicular to the surface of the filter media; thus filtered particles continuously accumulate on and within the filter. As a result, filtrate flux steadily decreases with time due to particle build up. Periodic backwashing is necessary to remove accumulated solids from the filter.

In cross flow filtration, the direction of the feed flow is parallel to the filter surface, and filtration occurs through the porous tube wall in a direction perpendicular to the flow. Steady-state operation exists because the continuous buildup of solids on the filter surface is prevented by the hydrodynamic shear exerted by the cross flow.

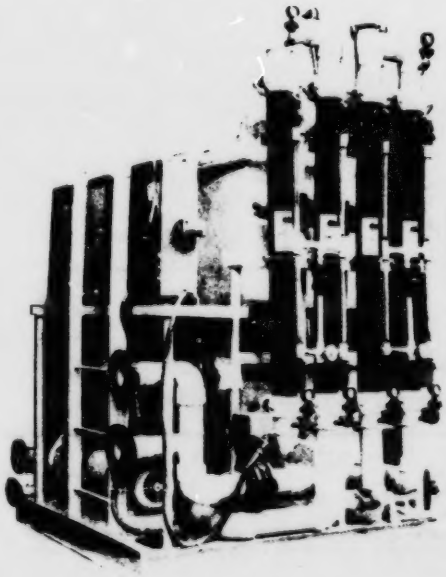


- Steady state operation.
- Product flow direction is perpendicular to that of the feed flow.
- Particle build up is prevented by the shear induced by the feed flow.

ADVANTAGES

HYDROPERM™ systems have many advantages over conventional systems:

- **Low Cost.** HYDROPERM™ combines low capital and operating cost to provide a true, cost-effective process.
- **Ease of Operation.** HYDROPERM™ is simple; does not involve complex controls and requires no in-depth process knowledge.
- **Continuous Product Water Quality.** Regardless of raw water characteristics, chemical requirements or operator control, there will be no solids breakthrough.
- **High Filtrate Quality.** Product water quality rivals that of ultrafiltration at greater than 20 times the flux rate of ultrafiltration.
- **Reduced Chemical Usage.** Treatment chemicals are continuously recycled, resulting in substantially lower treatment costs.
- **Reduced Sludge Volume.** Solids thickening capabilities have been demonstrated up to 25 percent by weight.



BULLETIN KL 4560

Type		TS (mg/L)	SS (mg/L)	Pb (mg/L)	Cu (mg/L)	Zn (mg/L)	Ni (mg/L)	Sb (mg/L)	As (mg/L)	Cr (mg/L)	Cd (mg/L)
Battery Waste	Feed	27,260	24,600	54.2	0.330	0.880	0.400	1.350	0.172	NA	NA
	Filtrate	2960	0.6	0.04	0.015	0.037	[illegible]	[illegible]	[illegible]	—	—
Plating Waste	Feed	5940	4010	NA	3.85	800.0	120.0	NA	NA	90.0	11.50
	Filtrate	2750	2	—	0.42	1.4	[illegible]	[illegible]	[illegible]	[illegible]	0.0[illegible]

HYDROPERM™ MODULES

HYDROPERM™ by Neptune Microfloc, Inc., utilizes thick walled, microporous plastic tubes. Pore structure is carefully controlled during manufacturing to obtain the performance desired. HYDROPERM™ tubes are:

- RUGGED
- INERT TO CHEMICAL ATTACK
- INERT TO BIOLOGICAL ATTACK
- NOT SUSCEPTIBLE TO THE HANDLING, FOULING AND CLEANING PROBLEMS OF MEMBRANE SYSTEMS.

HYDROPERM™ modules are assembled from microporous, plastic tubes. Individual tubes are bundled into modules and assembled into process units. HYDROPERM™ modules are available in various diameters and lengths for a wide range of process applications.

HYDROPERM™ SYSTEMS

The operation of a HYDROPERM™ system is shown below. Raw feed enters the HYDROPERM™ system at the recycle tank. Flow is continuously pumped from the recycle tank through the inside of the HYDROPERM™ tubes at relatively low pressure, typically 15 to 30 psi. Product water passes through the HYDROPERM™ tubes and is withdrawn through ports on the sides of the modules. The concentrated stream leaving the end of the modules returns to the recycle tank to be again concentrated by flowing through the module. Periodic or continuous blowdown of sludge from the recycle tank controls sludge concentration.

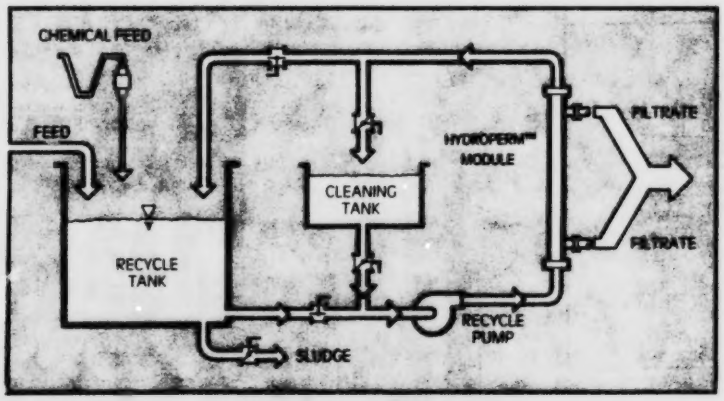
HYDROPERM™ EXPERIENCE

Extensive tests have been conducted on a variety of water and waste streams. Application has been demonstrated for both domestic and industrial streams including: acid battery wastes, metal finishing wastes, laundry wastewater, sewage, explosives wastewaters, seawater, estuary waters, turbid waters, and many other streams.

Reliable performance has been achieved at product fluxes of greater than 400 gallon/ft²/day at full scale commercial installations. Sludge dewatering capabilities have been demonstrated up to 25 percent by weight. Operating results at two installations are shown above.

HYDROPERM™ technology provides a new, more efficient means of simultaneously solving many clarification, filtration, liquid/solids separation and solids concentration problems. HYDROPERM™ cross flow microfiltration systems are perhaps the most cost-effective treatment alternative available today for jobs involving:

- FILTRATION OF TURBIDITY AND OTHER COAGULABLE SUSPENSIONS FROM POTABLE AND INDUSTRIAL PROCESS WATER.
- FILTRATION AND CONCENTRATION OF MANY SUBMICRON PARTICLES INCLUDING SILICA AND OTHER COLLOIDAL SUSPENSIONS.
- REMOVAL OF SUSPENDED SOLIDS FROM BOTH DOMESTIC AND INDUSTRIAL WASTE STREAMS.
- REMOVAL OR RECOVERY OF METAL HYDROXIDES FROM METAL PLATING WASTES.
- PRETREATMENT FOR REVERSE OSMOSIS AND DEMINERALIZATION.
- SOLIDS-LIQUID SEPARATION IN MANUFACTURING PROCESSES.



neptune microfloc.

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HYDROPERM™ CROSS FLOW MICROFILTRATION

CASE HISTORY NO. 72

CRAFTSMAN PLATING AND TINNING CORPORATION CHICAGO, ILLINOIS

ELECTROPLATING WASTE TREATMENT

Under EPA Grant No. R-807503-01-0, Design, Construction and Field Testing of a full scale HYDROPERM™ cross flow microfiltration system was conducted at an electroplating shop. The product from the demonstration unit was required to meet the standards set forth by the Metropolitan Sanitary District of Greater Chicago.

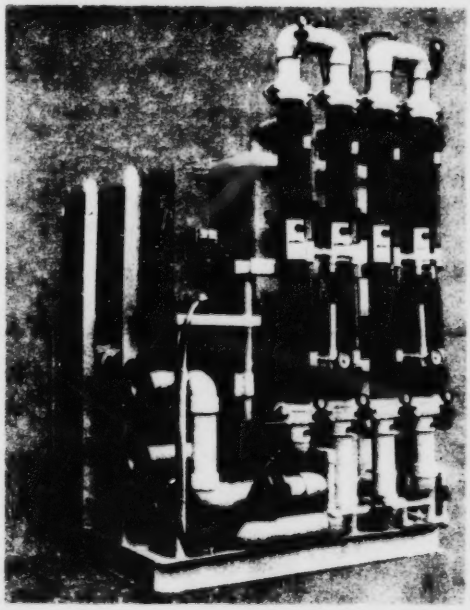
The HYDROPERM™ system was installed at the Craftsman Plating and Tinning Corporation in Chicago. CP&T's metal plating lines include cadmium, copper, tin, tin-lead, and zinc. Special treatment in the shop includes chromate conversion coating, etching, passivating pickling, hot solder dipping, and organic coating. All wastewaters flow to a common sump at 2,000 gallon/hour. From this point, CP&T was treating the wastewater by conventional processes using cyanide destruction, neutralization, suspended solids removal by clarification and centrifugal sludge thickening. The HYDROPERM™ system was placed in parallel with the existing clarifier for comparative performance tests.

A HYDROPERM™ system with 100 square feet of tube area was installed. Average flux values experienced in this demonstration were approximately 200 gallons per day per square foot (gf^2d) of HYDROPERM™ module area, with values as high as 600 gf^2d HYDROPERM™ module surface area being achieved. Talbe I presents the average results obtained at this full scale installation.

	TSS	Cd	Cu	Zn
Feed (mg/L)	6547	982	581	117
HYDROPERM Product (mg/L)	6	0.87	0.71	0.1
Sludge (mg/L)	approx. 12,000			

TABLE I

The CP&T field demonstration unit showed that HYDROPERM™ is an effective technology for removal of suspended solids in electroplating wastewater. Proper pretreatment is required to convert soluble constituents to suspended solids. In comparing the performance of the HYDROPERM™ system to a conventional system, the HYDROPERM™ system provides greater consistency in effluent quality with less operator attention.



neptune microflex

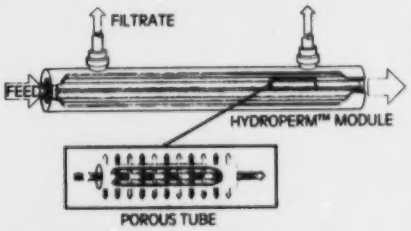
HYDROPERM™ CROSS FLOW MICROFILTRATION CASE HISTORY NO. 70

GENERAL BATTERY CORPORATION
HAMBURG, PENNSYLVANIA

LEAD-ACID BATTERY WASTE

General Battery Corporation has over two years of operating experience using HYDROPERM™ technology to treat neutralized wastewater from a lead-acid battery manufacturing plant. The wastewater is generated from the manufacture of industrial and automobile batteries, and after neutralization has the characteristics shown in the table below. High suspended solids and lead concentrations are the major concerns at this plant, but significant levels of copper, zinc, nickel, arsenic and antimony must also be reduced to meet State and EPA standards.

The Hamburg plant is located where stream discharge is convenient and acceptable providing all Pennsylvania NPDES permit requirements are met. In all cases, the final filtrate produced by the HYDROPERM™ cross flow microfiltration system has substantially surpassed even the strictest limits, as indicated in the table of Treatment Results.

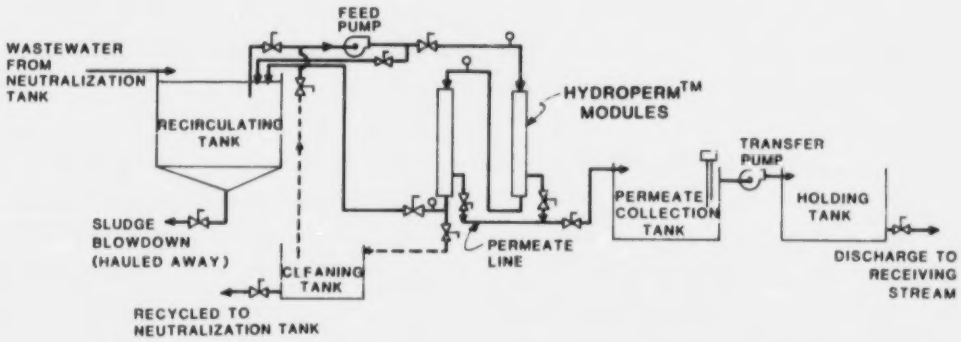


- Steady state operation.
- Product flow direction is perpendicular to that of the feed flow.
- Particle build up is prevented by the shear induced by the feed flow.

HYDROPERM™ Treatment Results

	Effluent From Neutralization Tank	HYDROPERM™ Filtrate To Receiving Stream	Percent Removal	Pennsylvania NPDES Permit Requirements Daily Average
pH	9.8	8-9	NA	6-9
SS	24,600 mg/L	0.6 mg/L	99+%	20 mg/L
Pb	54.2 mg/L	0.04 mg/L	99+%	0.14 mg/L
Cu	0.33 mg/L	0.015 mg/L	95.5%	0.04 mg/L
Ni	0.40 mg/L	0.032 mg/L	92%	0.07 mg/L
Zn	0.88 mg/L	0.007 mg/L	99+%	0.03 mg/L
As	0.17 mg/L	0.002 mg/L	99+%	0.01 mg/L
Sb	1.35 mg/L	0.292 mg/L	78.4%	0.97 mg/L

neptune microflox



At General Battery the treatment system includes a neutralization reaction tank for lime addition to raise the pH to a range of 8-9, a recirculation tank which acts as a sludge thickener and feed tank for the HYDROPERM™ system, two independent HYDROPERM™ treatment systems each containing 180 square feet of HYDROPERM™ tubes, a permeate holding tank and a cleaning tank. The HYDROPERM™ systems are skid-mounted and include feed pumps, valves and associated instrumentation for immediate field startup.

Flux rates of over 400 gallons per day per square foot of tube area are easily attained in the HYDROPERM™ unit. Normally only one system is on-line at any point in time to treat the wastewater at the plant. Operation is straight forward and plant maintenance personnel are used to run the facility. Solids content of the sludge withdrawn from the system has been in excess of 25% by weight. Module cleaning is practiced using a dilute HCl solution of approximately 2 percent. The filtrate is discharged directly to a small receiving stream.

neptune/microflot
P.O. Box 612
Corvallis, Oregon 97339
Telephone: (503) 754-7654
A WHEELABRATOR-FRYE CO.

REVERSE OSMOSIS (SEEDED SLURRY R.O.)

Reverse osmosis is not the category of process that would normally be considered as a candidate for suspended solids removal. Indeed, most forms of revese osmosis require some form of pretreatment of feed to deep suspended solids out of the system.

During 1983/1984, a new approach to reverse osmosis was demonstrated on minewater from the East Rand Proprietory Mines Ltd., as described in a trip report in Appendix I, in a test program undertaken jointly by the Water Research Commission, the Chamber of Mines of South Africa, equipment vendors, and Rand Mines.

Normally, when using holofine-fibre or spiral-would R.O. membrane systems, various solution pretreatment systems are required. When gypsum-containing minewater is to treated, then a very large pretreatment may be needed ahead of a small R.O. Plant. The new technology employs a tubular R.O. system which is considerably more bulky for the same job than the more sophisticated types of R.O., but it avoids, altogether, the need for water pretreatment.

By recycling precipitated sludges consisting mainly of gypsum, SiO_2, and alumina through the tubular R.O. system in much the way way as for cross-flow filtration (as described above), a high yield of product water can be obtained. Suspended solids in this particular test case where dropped from 50 mg/l to less than 1 mg/l in the permeate (product) water. Precipitate solids content of the sludge in the recirculating stream of concentrate was 4.5%, but this would be increased perhaps tenfold by allowing the concentrate solids to settle out.

Seeded slurry R.O., therefore, demonstrates a highly efficient means of removing not only dissolved solids, but also suspended solids.

Not for one minute would a relatively capital intensive process such as R.O. be recommended for removal of suspended solids, but this aspect is one more plus factor favoring its use in dissolved contaminant removal.

The seeded slurry reverse osmosis process is patented and under further development by:

RESOURCE CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 824-2400
Telex: 350160 RCC SEA
Russell Vandenberg
Tom Wolfe
Reams Goodloe

RESOURCES CONSERVATION COMPANY
INTERNATIONAL
Post Office Box 784561
Sandton 2146
(011) 783-7121
Pat di Benedetto

Additional information on seeded slurry R.O. generally may be available from the Resource Conservation Company or from the following:

CHAMBER OF MINES RESEARCH LABORATORIES
Post office Box 91230
Auckland Park
(011) 726-3020
Don Hebden
Project Coordinator

RAND MINES (MINING AND SERVICES) LTD.
Post Office Box 62370
Marshalltown 2107
South Africa
(011) 833-0611
Telex: 4-89671
John Wagner

MAGNETIC FILTERS

Magnetic filters as a means of removing very minute suspended particles from treated effluents have been discussed and researched for several years. To date, no commercial installations using magnetic filters for this application have been identified. However, considering the tremendous progress made in ultra high strength magnetic fields, as well as very much stronger permanent magnets, the possibility of magnetic separation of suspended precipitates from effluents should be considered a potential future development.

ALLEN, et al. (1976) discussed the use of SALA-HGMS magnetic filters for the treatment of combined sewer overflow water. Suspended solids in steelmaking effluents were reduced from, in some cases, 4,500 mg/l to less than 10 mg/l through the use of 5-10 kG magnetic fields at flow velocities of 2.5-5 m/min. in single pass applications. Removal of zinc, chromium, and lead precipitates from a solution containing very low levels of each to begin with also yielded promising results and, clearly, this process has some future merit.

Information on further developments may be available from:

SALA MAGNETICS, INC.
Cambridge, Massachusetts
D. Allen

KARELIN, et al. (1975) described Russian experiments in which sludges contatining 15-20% Cr, 30-40% Fe, and Ni were recovered from wastewater using a magnetic concentrating device. Chem. Abstracts contains little detail except that the maximum effectiveness was achieved at 200-250 rpm. The addition of tall oil improved the separation 2-3% for Fe and 1.0-1.5% for Cr and Ni."

COARSE PARTICLE SEPARATION

The processes discussed above concentrate on the problem of removing fine particles from water. Sometimes it is necessary to remove coarse grit and other debris from solutions or water as a means of preventing downstream clogging of screens or abbrasion effects. These can be removed by open screen decks or sievebends, but what of particles too small to be removed by such devices.

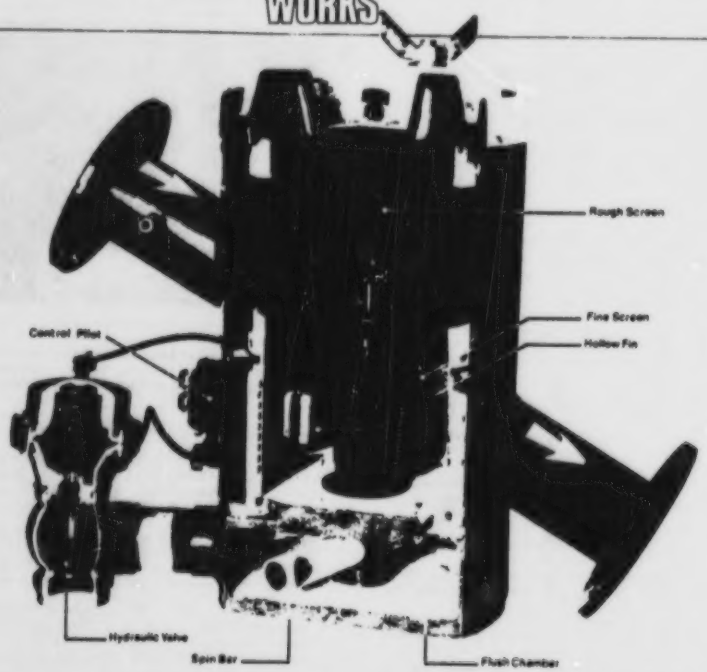
Usually with such devices, the problem arises in determining how and when to cycle the backflush. If carried out using a timer on a timed interval, if it backflushes too often then efficiency is lost, and if it backflushes too seldom, the filter may be clogged and ineffective for part of the time.

An innovative device was designed to overcome these proglems by automatically backflushing itself on demand whenever it senses that the pressure drop across the screen has built up too high. The Filtomat device is described in the following brochure and paper by PATZ and BARNEA (1984).

In the trip report on ZINCOR in Appendix 1, one user's opinion was canvassed. They found that the Filtomat rejected too much water during the backflush step in the cycle. Other users are reputedly very pleased with their Filtomats.

There are, of course, several other ways in which grit can be removed from feedwater, process solution, and effluents.

HOW THE FILTOMAT SELF-CLEANING WATER FILTER WORKS



The filter is flanged in-line. On entering the filter, water passes through a rough screen which traps any oversized particles that might clog the workings. The water then flows to the lower section which is enclosed by a fine screen mounted on a perforated cylinder. This screen size is chosen to suit the desired degree of filtration. As dirt builds up on the screen it gives partial filtration for smaller particles as well. The bed of solids which forms increases the difference between the inlet and outlet pressure.

At a predetermined pressure difference the control pilot opens the hydraulic valve. When this happens the pressure in the flush chamber falls to atmospheric pressure. Some of the filtered water is sucked into this low pressure chamber via the hollow fin. Holes in the spin bar cause the fin to spin allowing it to clean the entire fine screen.

The dirty water is discharged through the hydraulic valve to the drain, while the main flow is uninterrupted. The cleaning cycle stops when the filter screen is clean.

The length of the cleaning cycle is about 10 seconds, the frequency depending on the nature and quantity of suspended solids being removed.

Sole agents for South Africa

EDWARD L. BATEMAN LIMITED

P.O. Box 968 Boksburg 1460. Republic of South Africa.
Tel: (011) 899-9111. Telex: S-7880 SA
Cables and Telex address: "Founders", Boksburg, Transvaal.

FILTOMAT

THE FILTER THAT WORKS ON WATER

FILTOMAT | THE REVOLUTIONARY AUTOMATIC SELF-CLEANING WATER FILTER FOR INDUSTRY AND MINING

The **Filtomat** embodies a new concept in water filters that has numerous advantages over presently available solutions. It offers new opportunities for removing suspended solids which up to now may have been impractical or uneconomical. These uncomplicated units are installed and function with the minimum of fuss and attention.

Filtomat filters have proved their efficacy overseas where more than 7 000 units have been installed since 1975. Local engineers have been quick to see the opportunities and in the first ten months in South Africa more than 100 units were successfully commissioned in a variety of applications. These include bottle washing, citrus packing, steel, textiles, fish growing, golf courses, plastic and rubberware manufacture and mine applications both above and below the surface.

One of the most successful applications has been in cooling towers and condensers, giving dramatic reductions in suspended solids at a fraction of the price of sand filters.

An engineer's delight - the principle of operation is ingeniously simple - and it works! The kind of obvious solution to an age-old problem that makes you wish you had thought of it yourself.

If you feel you may have an application - contact us without obligation - if your application is right, the **Filtomat** will sell itself. Where we cannot show you a successful installation, we will arrange a trial.

We believe in back-up service and offer the following guarantee:

Any customer disappointed with his Filtomat can return it during the first month for an unconditional refund of the purchase price.

We won't have an unsuccessful Filtomat in operation!

12 inch Filtomat filtering water into the underground cooling system in a mine prevents clogging of the refrigeration plant saving over 8 000 man-hours in cleaning and maintenance per year.

Description	Model Designation						
	M 303	M 304	M 306	M 308	M 310	M 312	M 314
Inlet and outlet flanges	3"	4"	6"	8"	10"	12"	14"
Installation length	604mm	748mm	910mm	1176mm	1340mm	1450mm	1532mm
Nominal flow capacity [m³/h]	40	80	150	300	400	600	900
Weight of unit	30kg	40kg	80kg	150kg	250kg	350kg	500kg

- Normal design pressure is 10 bar (150 psi) (1).
- Clear screen pressure drop at nominal flow = 0.2 bar (3 psi).
- Maximum temperature 65°C (1).

(1) Special applications may be catered for with alternate materials of construction.

LONG UNITS

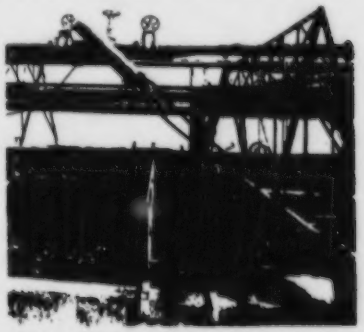
For heavy dirt-loads or fine filtration special long units are available for 3", 4" and 6" pipelines. These units have larger bodies that offer between 2 to 4 times the screening area of the regular units.

FILTOMAT SELF-CLEANING WATER FILTERS OFFER ALL THESE ADVANTAGES

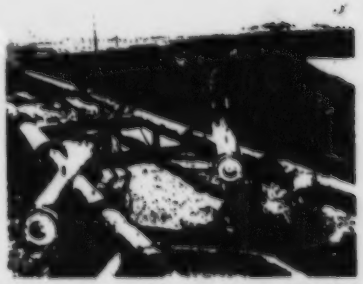
- **In-line** - flanges straight into the main pipeline. No support structures are needed.
- **Automatic operation** - self-flushing is automatically triggered by pressure differential.
- **No external power**- operates on water pressure only.
- **Attention-free**- requires little attention and only needs checking semi-annually.
- **Uninterrupted flow** - no interruption on the line flow during cleaning process.
- **Compact** - sturdy construction. Easy installation.
- **Positioning** - does not rely on gravity and can be installed in any position; horizontal, vertical, sloped or even upside-down.
- **Low pressure drop** - maximum pressure drop is adjustable.
- **Removes algae and organic matter** - is not contaminated by oil and other impurities.
- **Positive filtration** - can be controlled by the selected screen size.
- **High throughput** - the units can handle the full normal flow of the pipeline.
- **Competitive price** - a fraction of the price of equivalent sand filters.
- **Unaffected by fluctuating flows.**
- **Backed by the Bateman Organisation.**

FILTOMAT HAS MANY VARIED APPLICATIONS

COOLING WATER	Used in cooling towers, chiller water, heat exchangers, make-up water, to reduce the fine solids that would be deposited on heat transfer surfaces and reduce efficiency.
SAFEGUARDS EQUIPMENT	Prevents clogging of pipelines, valves and expensive equipment and reduces wear from abrasive particles.
PROTECTS NOZZLES	Keeps nozzles permanently open wherever water is sprayed even at high pressure. Removes particles that might damage the product being sprayed.
WATER RE-USE	Permits the re-use of factory water by removing contaminated particles.
PROCESS WATER	Removes undesirable solids from process water. Permits collection of desired particles as flush water can be collected.
IRRIGATION	Removes solids and sediments, clarifies supply water in drip, spray and sprinkler systems. Filters water from sewage farms.
WATER SUPPLY	Removes algae, dirt, sand and silt from boreholes, rivers and dams; removes sediments and rust and prevents the clogging of water meters and pipes. Reduces the quantity of chemicals required to treat potable water.



6 inch unit installed over sump in a cable factory filters PVC, rubber, grease oil and algae and prevents valves, nozzles and pipelines from blocking, saving thousands of Rands and man-hours in maintenance and downtime.



12 and 10 inch units used in agriculture remove sediment and solids and clarify the supply water for spraying and sprinkling.

APPLICATION OF AN IN-LINE SELF-CLEANING WATER FILTER IN THE MINING INDUSTRY

PATZ, ANTHONY JULIAN
B.Sc. I.E. B.Sc. (H)OR M.Sc. FIQA MSAIPE ASMORSSA

and

BARNEA, ELI
B.Sc. M.Sc. D.Sc. Tech

EDWARD L. BATEMAN LIMITED
P.O. BOX 565,
BOKSBURG 1460
SOUTH AFRICA

1. INTRODUCTION

Water is extensively used in the mining industry: for mining itself, as a medium for ore transportation and physical processing of the ore (wet milling etc)

- as a medium for chemical processing of the ore (whenever hydrometallurgy is involved),
- for cleaning (of spillages, machinery, belt conveyors etc.),
- for service to process (steam generation, liquid ring vacuum pumps, hydraulically operated valves and equipment, cooling of machinery and engines etc), and
- services to operating manpower (temperature conditioning in deep mines, air-conditioning of offices, washing, cooking, drinking etc.).

Part of the water will normally be kept in closed cycle, other parts will be consumed in the process and they will have to be supplied from primary sources like: wells, rivers, dams, national networks etc.

In nearly all cases, water will be contaminated by suspended solids to a larger or smaller extent. These may originate from the primary source of water (sand algae, large organisms like flies, small fish, mosquitoes, grass, woodchips, dust etc).

In recycled water solids may be present as a result of rust, scale, dust, finer fractions of ore etc. The presence of such suspended solids can seldom be considered desirable, however, in many cases the application as such and the problem associated with suspended solids is relatively small and not worth the cost of elimination.

In other cases, effort to eliminate or at least reduce the extent of the presence of these solids is justified or even imperative as the solids contribute to higher maintenance costs (e.g. by abrasion, fouling of heat transfer services, breakages of pipelines, nozzles etc., fouling the sealing action of valves etc.) and in certain cases, interferes with the process itself. (This occurs mainly whenever water is to be sprayed with relatively fine nozzles such as for instance, cake washing on filters, washing of conveyor belts and filter cloth etc.).

Further there are many cases where the reduction of the level of suspended solids would be desirable, were a convenient and economical means available. At present the problem is being lived with either because the decision-makers are unaware of a solution or because the direct and indirect costs of the problem are underestimated or not well-appreciated.

In this paper we shall introduce a new concept of elimination or reduction of suspended solids in water, which represents in many cases an ideal solution to the problem, and describe one such available system.

In order to clearly define the scope of problems that can be solved by the application of this new concept, it should be stated here that the upper level of suspended solids that can be economically treated by the Filtomat, is about 1000 ppm (it may be higher than that, say 3000 ppm in the case of relatively coarse solids to be eliminated) and the minimum particle size that can be eliminated is about 30 - 50 micron in the case of an open cycle (finer particles will also be eliminated or reduced in quantity, but 100% elimination is obviously determined by the size of the opening in the filter cloth or screen).

There is no lower limit in the case of water circulating in closed cycle as is described in the text.

Existing Technology

The simplest filters are of the disposable cartridge type where the filter elements are dispensed with when they become clogged. Also at the simple end of the scale are cartridge filters and hand strainers that are cleaned manually for reuse. While they are inexpensive to manufacture they demand constant attention and as such their operating cost is high. In the case of disposable cartridges, the cost of replacement cartridges also contributes to operating costs. As these units block up, they cause a growing pressure loss until they are cleaned. Thus the process downstream is subjected to variable pressure.

The so-called automatic strainers are operated by timers and auxilliary motors. These require a source of energy which adds to the complexity and expense of the installation. Such a source is also subject to failure. The timing device is unaware of the quantity of dirt in the strainer, and is set to flush the unit at regular intervals. The quantity and nature of solids in the water can vary, typically by orders of magnitude, and to cope, the timer must be set for the worst possible case. Therefore, the unit will flush in most cases well before it is necessary with an associated waste of flush water. Should an unusual quantity of solids come through the system, the unit is susceptible to being blocked.

Sand filters are capable of filtering suspended solids down to very fine sizes. However, they are large in size and expensive for large flows. For underground installations, the size becomes a problem. They also involve a relatively large indirect investment (civil and structural) to make the overall investment even higher.

They require attention as they have to be backwashed and they flush fairly large quantities of water. While they are being backwashed there is an interruption in the flow of water. Those that are automatic suffer from the same weak point with regard to the timer as described earlier. In addition sand filters are susceptible to contamination by oil and other chemicals.

The pressure drop across sand filters is considerable.

In contrast to strainers, there are cyclones. They are units that extract a portion of the solids by centrifugal force. They contain no moving parts, being operated by water pressure. These units have no positive straining so the filtration is of a statistical nature.

Therefore the unit does not provide a 100% protection for nozzles, but merely reduces the frequency with which they block up. Cyclones have a relatively large pressure drop especially if the removal of fine particles is required. They waste a lot of water in a continuous flow. If the units are adapted to collect the dirt, they require frequent manual cleaning. It is difficult to install cyclones for large applications as this requires many units in parallel. Cyclones are set to operate optimally at a specific pressure and any variation from this pressure will reduce the efficiency of the unit.

Requirements for an Ideal Strainer

From the above considerations, it can be seen that a strainer incorporation most of the advantages of the different systems described and avoiding most of the problems would be of great value to the mining industry.

What is ideally required is a unit with the following characteristics:

1. In-line - so that it can fit in as an intergral part of the process and not require water to be diverted. In-line filtration also implies low installation costs as no civil or structural work is involved;

2. Automatic operation activated by some feedback system which senses when the unit requires to be flushed. This not only eliminates unnecessary flushing, but ensures that the unit will react to sporadic high loads;

3. No power requirement - operating on water pressure alone;

4. Minimum maintenance and attention required;

5. Low pressure drop, thereby reducing energy requirements;

6. Positive straining - it is important that the unit be capable of giving 100% protection at a given cut-off point. The cut-off size itself should be as small as may be required for the particular application.

7. Uninterrupted flow - while the unit is flushing. It is desirable that the flow of water to the end use be uninterrupted. This would also reduce the necessity of having stand-by units or an automatic by-pass;

8. High throughput - Ideally a single in-line unit should be able to treat the throughput handled by the pipe.

9. Ability to be installed in any position to eliminate stereometrical constraints that are particularly severe in underground installations;

10. It would be desirable if the solids were ejected in concentrated form such as a wet-cake;

11. Relatively cheap - this is a self-evident advantage.

Some further advantages of the unit would be:

If the unit is triggered by the actual amount of dirt in the system, it is possible to ensure that the headloss due to the build-up of dirt never passes a maximum predetermined amount.

If the unit flushes itself, it can be made fairly compact as the screen can be cleaned at fairly frequent intervals and need be no longer than required to absorb dirt that would collect in less than an hour.

There are known in the art a great number of fluid cleaning devices which include one or more brushes which are adapted to scrape the surface of the filter member either manually or automatically by means of an auxilliary water motor pump. These devices suffer primarily from the drawback of poor cleaning since the brushes do not effectively loosen and free the dirt stuck in the filter's smaller holes. Moreover, such an arrangement calls for auxilliary driving motor which adds to the cost on the one hand and reduces the situations in which such a filter can operate on the other.

The objective of designing a self-cleaning filter would be to devise an effective method which overcomes the above and other disadvantages.

In order to free such a system from the requirement of external energy, it would be necessary to utilise the energy of the water flowing inside it to actuate the cleaning action and if required, this energy would be used for imparting motion to any cleaning body.

The unit would require some mechanism for sensing the load of dirt actually in the unit in order to trigger the flush and a separate flushing system that would not interfere with the main operation of the filter.

Description of the Filtomat Unit

Figure 1 illustrates one such embodiment of the above concepts - The Filtomat unit. In this particular example the unit has a steel cylinder housing (1) with flanged inlet (2) and outlet (3). A metal cover (4) is securely fastened to the housing by means of bolts and wing nuts, which allow easy removal when necessary.

It is necessary to protect the workings of the filter from outsized particles that could damage or jam them. Therefore, the raw water entering the filter under pressure is passed through a perforated plastic cylinder which acts as a coarse grid (5) and strains the large particles from the water. In order to prevent the water from flowing directly to the outlet, a steel ring (6) seals the raw water compartment from the strained water interior.

The water then enters the lower compartment which is enclosed by another perforated plastic cylinder, lined with a fine corrosion resistant screen (7), the size being chosen for the particular requirement (stainless steel screens are commercially available down to approx. 50 micron at this point in time.)

The screen is rigidly attached to the plastic cylinder. No particles larger than the screen openings can pass through the screen and reach the outlet of the unit.

The unit can be visualed as being divided into four chambers, as marked in Roman numerals on the diagram. The highest pressure is in Chamber I where the water enters. The water passes through the coarse grid (5) deposits any outsize bodies and enters the Central Chamber II. The pressure in Chamber II is virtually that of Chamber I as there is hardly any pressure drop across the coarse grid. Should a significant pressure difference be recorded between these two Chambers, this would indicate that the coarse grid had in fact become blocked and required cleaning.

After being filtered on the fine screen, the water passes to Chamber III which contains the clean water. The difference in pressure between Chambers II and III is equal to the pressure drop across the fine screen. Initially this is very low but as the solids accumulate they form a fine bed which increases the pressure difference.

The control unit can be set to flush at a specific difference in the range 0.2 to 0.7 bar. The control unit (Figure 2) contains a diaphragm with incoming and outgoing water below and above respectively. The clean water is assisted by a spring. At the predetermined pressure difference the equilibrium of the diaphgragm is upset and this activates the unit, causing the hydraulic flush valve to open.

Up to this point the pressure of the water in Chamber IV has been equal to that of Chamber II, to which it is connected solely via a hollow fin and shaft (10, 11). When the flush valve opens, the pressure in Chamber IV falls to atmospheric pressure. It is imperative for the good operation of the system that at this point the pressure in Chamber IV be much lower than those in Chambers II and III (about 40%). This requires that the minimum pressure in the main line be approximately 2 bar.

When this happens, some of the clean water from Chamber III is sucked into the fin (10) and evacuated out through the flush valve. In so doing it cleans a section of the fine screen. From the hollow fin (10) the suspension of dirt in the water flows through the hollow shaft and the spin bar (11). The positioning of the holes in the spin bar (11) directs the water to be ejected in a tangential direction which imparts rotational motion to the entire hollow fin, shaft and spin bar system (as in a rotary sprinkler). The rotating fins (10) thus cover the entire area of the fine screen. The duration of a flushing operation is approx. 5 seconds and while it is taking place the main flow is uninterrupted. On all the larger units, the screens are longer. In order to cover the screen area the fins require an axial movement in addition to rotation. This is provided by a piston that is also actuated and operated solely by the water pressure.

When the filter screen has been cleared, the cleaning cycle stops until the pressure difference between Chambers II and III again reaches the preset amount. The frequency of flush depends on the quantity of suspended solids and varies typically between minutes and days.

Initially the only filtering medium is the stainless steel fine screen. As the dirt collects on the fine screen a cake is slowly built up. This contributes to the filtering process and progressively finer particles are filtered out. Eventually towards the end of the cycle, just before flushing, very fine particles are taken out. A typical example is shown in Figure 3.

When the water is reticulated in a closed cycle operation (such as in a cooling water system) such a cake is capable of filtering down to a few micron in size. Fine solids that passed through the screen at an earlier cycle are trapped on a subsequent one.

The size of the fine screen will depend on the particle size distribution. It is sufficient that only a small percentage of the particles are larger than the screen size for a cake to be initiated. In order to allow a good cake to be built, one chooses the coarsest screen that will operate effectively.

In such a system very fine particles such as dust, slime and fine algae are separated from the water, safeguarding clean water in the tower and preventing sediments on the pipe walls.

When filters are initially installed into an existing closed circuit, they flush very frequently until the residual dirt is extracted. This may take one or two days of operation. The cycle slowly lengthens until equilibrium is reached, whereby the quantity of solids extracted per flush equals the quantity of dirt entering the system between flushes.

Technical data of the various models are given in Table 1.

To what degree does such a unit meet the abovementioned requirements:

1. In-line
   This configuration is flanged straight into the main pipe and requires no civil or structural supports;
2. Automatic Operation
   The unit operates automatically by its control unit which senses via the pressure drop that the unit requires flushing;
3. No Power Required
   The unit utilises the pressure of the water for all its operations and requires no external power. There is, however, a lower limit of about 2 bar and in systems with less than this, the units do not always operate satisfactorily. This should not be confused with the pressure drop which is low (see 5. below and also Table 1);
4. Maintenance Free
   The unit requires no attention and only needs checking on an annual basis;
5. The Pressure Drop across the screen depends primarily on the flow of water through it rather than on the screen size. At nominal capacity the pressure drop is relatively low (see Figure 4). The maximum pressure drop (across the screen plus the built-up cake just before flushing) is adjustable at will in the range of 0.2 to 0.7 bars).
6. Positive Straining
   The unit has positive straining for a given size of fine screen. In addition as dirt builds up on the screen, it gives partial filtration for smaller particles. A 100% retention of particles smaller than 30 micron in an open cycle is, however, currently impossible.
7. Uninterrupted Flow
   The unit has a separate flushing system and the main flow is left uninterrupted during flushing. During flushing, about 40m³/hr. of additonal flow is added.
8. High Throughput
   The largest unit currently available is capable of treating 1000m³/hr. on a 14" pipeline. Larger units of higher capacities are being developed.
9. Positioning
   As gravity does not play a role in the operating principle the unit can be installed in any position: horizontally, vertically, sloped or even upside-down.
10. The Filtomat cannot discharge the solids in the form of a cake, however, it does use less water than sand filters or simple cyclones.
11. Price
    Small units are expensive relative to hand cleaning and manual flushing systems, but large units are a fraction of the price of sand filters.

Practical experience in South Africa in the Mining Industry

As the unit is fairly new to South Africa, the number of operating units in the Mining Industry is relatively small while a number of units are in the process of being installed. The following two examples are quoted as they have been running for periods of 4 to 6 months which allow conclusions to be drawn.

Two 8" units were installed in an underground cooling system in February this year. The full throughflow was approximately 900m³/hr. The fine screen size was 400 micron with a small section of 200 micron. The suspended solids in the condensor water dropped from 45 ppm to less than the level of detection which was 2 ppm. On the first day, the filters flushed a few times per hour, settling down to an equilibrium flush of once per shift. With reference to the cleaning of the unit, the cost of manpower and material was also significantly reduced.

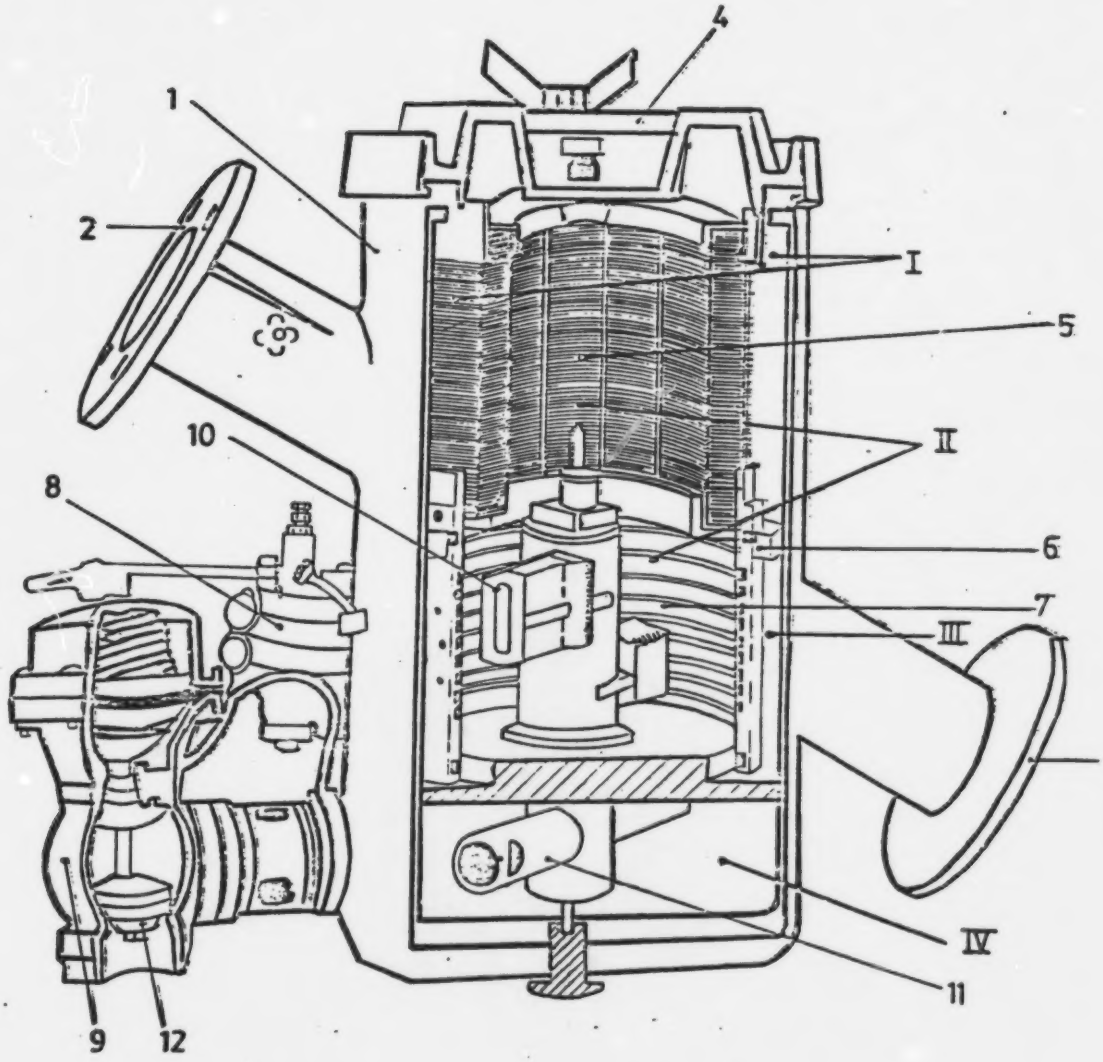
At Winklehaak Mine, initially a 12" to which was added a 10" unit were installed to protect the cooling plates of an on-surface cooling tower, the holes of which were being blocked by grass and flies. This necessitated daily cleaning of the plates. Subsequent to the installation, no cleaning was required.

TABLE 1

TECHNICAL DATA

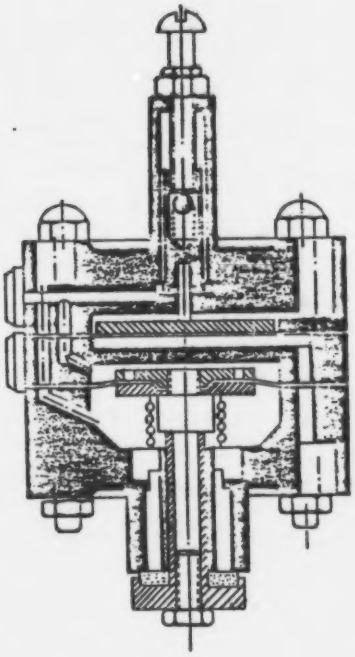
UNIT	2"	3"	4"	6"	8"	10"	12"	14"
1. Weight Kg	10	30	40	80	150	250	350	500
2. Inst. Length mm	--	600	750	910	1180	1340	1450	1530
3. Filter House mm	400	430	600	1000	1680	1850	2600	2600
4. Nominal Capacity m^3/hr.	25	40	80	150	300	400	600	1000
5. Pressure Drop in bar (Clean screen at Nominal Capacity)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

CUT OF FILTOMAT UNIT 3"



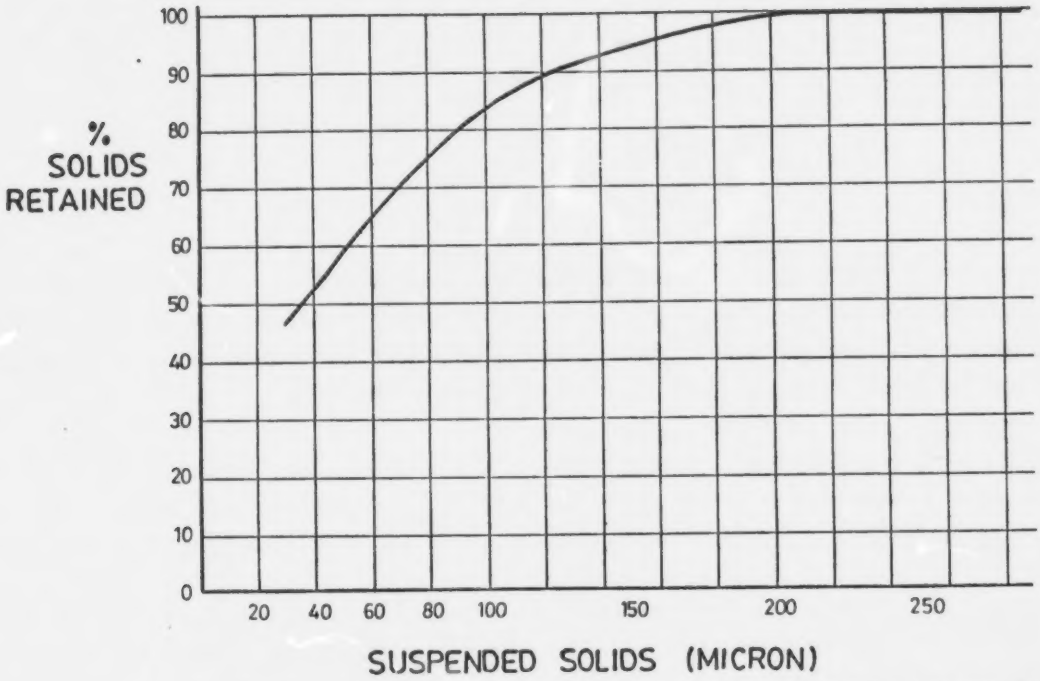
1. FILTER HOUSING
2. INLET
3. OUTLET
4. REMOVABLE COVER
5. COARSE GRID
6. STEEL RING (SEAL)
7. FINE SCREEN
8. RINSE CONTROL
9. HYDRAULIC VALVE
10. CLEANING FINS
11. SPIN BAR
12. DRAIN

FIGURE 1



CUT OF CONTROL UNIT

FIGURE 2



TYPICAL FILTRATION FOR 200 MICRON SCREEN (ONCE THROUGH)

FIGURE 3

PRESSURE LOSS CHART

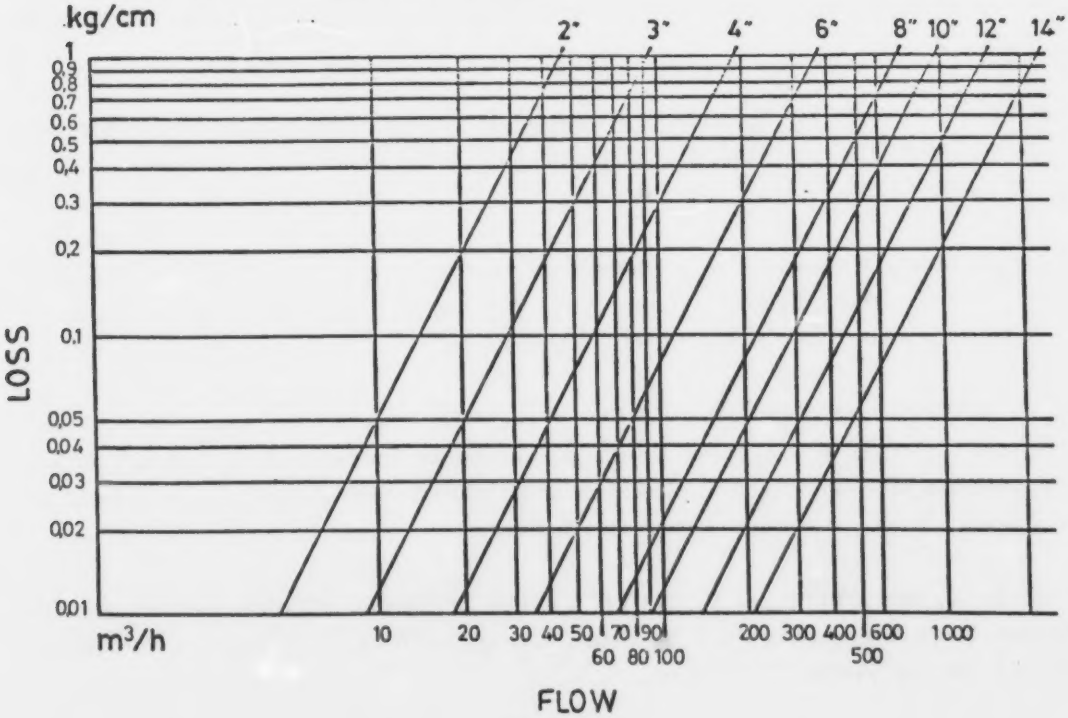


FIGURE 4

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CHAPTER 13

REMOVAL OF DISSOLVED SOLIDS

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There are numerous ways by which to remove or recover dissolved solids from aqueous solutions. Some of these are selective, while other are not.

MOTIVATION

Objectives in the removal of dissolved solids from solution include:

- Profitable recovery of an incremental, marketable resource. Here a selective way of concentrating a valuable species is needed.

- Removal of undesirable contaminants so that they can be discharged within effluent permit limits.

- Removal of undesirable contaminants allowing recycle solutions to be returned to the process without undesirable interferences.

- Desalination of water for use as boiler feedwater or in special processes requiring low salt levels.

TECHNOLOGIES

Several different technologies are available for the removal of dissolved salts from mine and mill effluent solutions. These are briefly reviewed by heading to illustrate the menu of tools available. In the chapters that follow, many of the most common contaminants are discussed one at a time, and the use of various processes is discussed for specific applications.

Precipitation -

Hydroxides:	Lime, Caustic Soda, Ammonia, Soda Ash
Sulfides:	
Carbonates:	CO_2, Na_2CO_3
Sulfates:	$BaSO_4$, $PbSO_4$, $CaSO_4$

Coprecipitation -

$$BaCl_2 + Ra + SO_4 = Ba\ Ra\ SO_4$$
$$Fe^{+3} + 5OH^- + M^{+2} = (M\ Fe)\ (OH)_5$$

Desalination -

Reverse Osmosis, Seeded Slurry R.O.
Electrodialysis Reversal
Evaporation
Ion Exchange

Specific Ion Removal -

Ion Exchange
Electrolysis
Biological Metal Removal
Insoluble Starch Xanthates
Cell Wall Adsorption Media
Devoe-Holbein Media

PRECIPITATION

- Precipitation processes are the most widely used for removing species from water.
- Precipitation as hydroxides is achieved by adding lime $Ca(OH)_2$, sodium hydroxide NaOH, ammonia NH_4OH, and soda ash Na_2CO_3.
- The lime-soda softening process uses precipitation to remove sulfate ions as a means of softening water.

- At very high pH values, i.e., high concentrations of hydroxide, some metal hydroxide solubilities increase again due to hydroxide complex formation, e.g., $[Al(OH)_4]^-$, $[Zn(OH)_3]^-$, $[Fe(OH)_4]^-$, $[Pb(OH)_4]^{-2}$, etc.

- Usually, more than one species must be removed by the treatment process. Various metal hydroxides have minimum solubilities at different pH values.

- At high pH in the presence of carbonate ions (atmospheric CO_2), some metals precipitate as insoluble carbonates, e.g., $PbCO_3$.

- Several metal sulfides are less soluble than their hydroxides. Addition of sulfide ions (Na_2S or NaHS) can achieve lower levels of these metals in effluents than is possible by hydroxide addition.

TABLE OF SOLUBILITIES
ppm in Pure Water

Metal	As Hydroxide	As Sulfide
Iron	5×10^{1}	1×19^{-4}
Zinc	3×10^{2}	1×10^{-6}
Cadmium	3×10^{0}	1×10^{-8}
Nickel	7×10^{-1}	6×10^{-8}
Copper	2×10^{-2}	2×10^{-13}
Lead	2×10^{0}	6×10^{-9}
Mercury	6×10^{-4}	1×10^{-21}
Silver	2×10^{1}	4×10^{-12}
Chromium	1×10^{-3}	(No Precipitate)

- In some cases, although sulfide is added, a metal hydroxide may be precipitated:

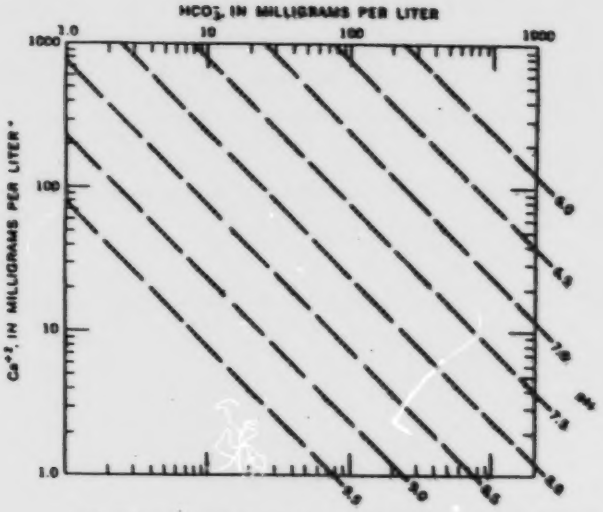
$$CrO_4^{=} + FeS + 4H_2O = Fe(OH)_3 + \underline{Cr(OH)_3} + S^0 + 2OH^-$$

- Effluent contaminant levels and flowrates vary. Since excess sulfide in treated effluent is undesirable, this process never became popular. Also, extremely low metal levels have only recently been required as effluent discharge criteria. The addition of FeS as a source of sulfide is a practical answer which is innovatively applied in the Sulfex process of Permutit Co., New Jersey, as described in EPA (1981) at the end of this chapter.

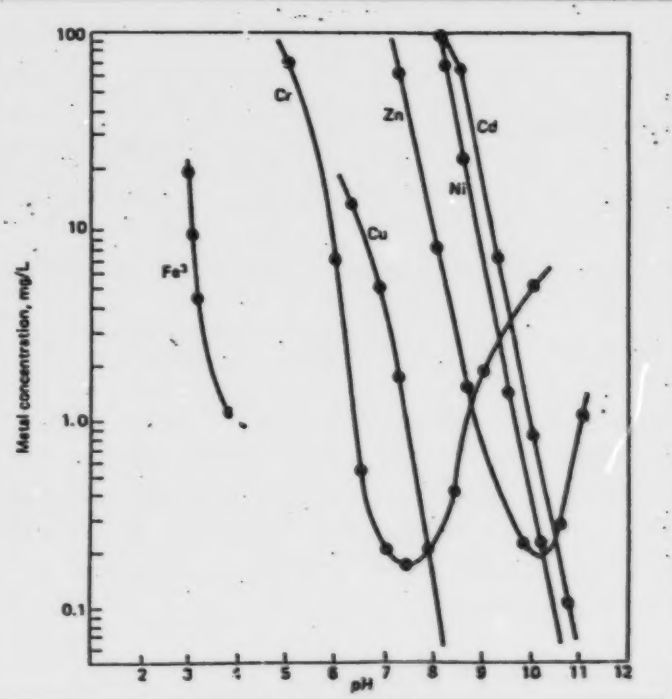
- Metal sulfide solubilities are pH dependent.

CALCIUM AND BICARBONATE SOLUBILITY VS pH

Source: HEM (1970)



—Equilibrium pH in relation to calcium and bicarbonate activity in solutions in contact with calcite. Total pressure 1 atmosphere; temperature 25°C.



Precipitation of heavy metals as hydroxides

Fig. 1

- Hydroxide precipitates are often gelatinous and difficult to filter or settle. Some sulfide precipitates are very finely divided and also difficult to filter or settle from solution.

- Metal hydroxide precipitates are amphoteric, i.e., if the pH is lowered again, they will go back into solution.

- Some metals from sulfide complexes which are less soluble than simple sulfide compounds--in the presence of excess sulfide, some metals go back into solution.

- $CaSO_4$ is soluble up to 2,000 mg/l beyond which it is likely to precipitate a scale unless the solution is stabilized by reagent addition. More often than not, gypsum precipitate as scale causes problems in metallurgical processes. Clever use of slurry seeding can made gypsum precipitate in a way that avoids scale formation.

- The eH of solutions and temperature affects precipitation processes as does the composition of the solution. $CaSO_4$ solubility and crystal structure are particularly temperature dependent.

- Co-precipitation is a powerful phenomenon used, for example, in the removal of radium which co-precipitates as $BaRaSO_4$ when $BaCl_2$ is added to solutions containing sulfate ions. Co-precipitation also occurs when ferric hydroxide is precipitated--for example, lead, arsnic, and selenite ions are amongst several that co-precipitate with iron. Manganese oxides and hydroxides co-precipitate radium and manganese from solution. In the seeded slurry process, gypsum co-precipitates silica and a host of other cations.

- Limestone has been used to precipitate silica from recycled solutions during which chloride levels are also reduced in a South American copper plant solution.

- Some precipitates are not stable when in contact with naturally occurring CO_2 (H_2CO_3) in water, e.g., $Ba_3(AsO_4)_2$ and $FeAsO_4$ convert to the $BaCO_3$ and $Fe_2(CO_3)_3$ when exposed over a long period of time to water in equilibrium with atmospheric CO_2. Possibly reduction of pH to 6.5 by H_2CO_3 plays a role here.

- Oxidation state of elements can have a profound effect on their solubilities, e.g., Fe^{2+} or Fe^{3+}, As^{+3} or As^{+5}, Cr^{+3} or Cr^{+6}, Se^{+4}, or Se^{+6}, etc.

- Complexing agents such as humic acids, cyanide, ammonia, etc. can interfere with hydroxide precipitation. Where precipitate compounds, e.g., sulfides, are more stable, then precipitation withdraws the metal ions from the less stable complexed form. For example, FeS added to copper cyanide precipitates <u>CuS</u> and ties the cyanide up as $[Fe(CN)_6]^{-4}$.

- Salt balance modelling, except in the simplest possible cases, is very complicated because of the many interrelated effects.

- In evaluating the cost of treating effluents by precipitation processes, the following items must be taken into account:

  1. pH adjustment reagents before, during, and after precipitation.
  2. Reagent costs, e.g., sulfide addition or oxidizing and reducing agents.
  3. Cost of recovering the precipitate, i.e., solid/liquid separation.
  4. Cost of precipitate sludge dewatering.
  5. Cost of disposing of the precipitate sludge safely and legally.
  6. Cost of polishing the solution after primary solid/liquid separation.

- The relative cost of various precipitation processes are so site specific that no generalizations can be made. A systems approach must be adopted to evaluate all alternatives.

- There are several highly innovative new techniques for reagent recycling, solid-liquid separation, enhanced precipitation techniques, etc., e.g.,

  - Jet Pump Oxidation and Precipitation
  - High Density Sludge Process
  - X-Flow Microfiltration

  These are discussed in Chapter 24 on Acid Mine Drainage treatment and Chapter 25. X-flow microfiltration is discussed in Chapter 12 on removal of suspended solids above.

DESALINATION

Desalination processes remove (or recover) all ionic and suspended species contained in feedwater to a concentrate, while producing water essentially free of dissolved or suspended solids. Several desalination processes involve membranes. Others involve ion exchange resins, while a third category of desalination is evaporation.

The RANDOL study concludes that desalination processes should, if at all possible, be avoided in mine-mill complexes. Desalination should be considered only when all else fails and even then, the simplest systems should be given priority. Some successful desalination plants are operating on metallurgical process effluents using R.O. followed by evaporation (distillation) for final water recovery from the R.O. concentrate stream.

Desalination (R.O. and evaporation) is employed for the recovery of potable water from seawater at large installation in the Middle East, Florida, and Malta, as well as in smaller installations on oil drilling platforms, trawlers, and naval vessels. Although these operations start with seawater containing over 30,000 mg/l TDS, in these installations recovery is inconsequential, and disposal of the concentrate is of no concern. The objectives of such systems are not comparable with those required to treat mine and mill effluents.

MORRIS (1982) compared the energy requirements for various desalination processes as follows:

Primary Energy Form	Process	Energy Required kWh/m³		
		Commercial	Demonstrated	Conceptual
Heat	Distillation	25	15(1)	15
	Freezing	--	27(2)	15
Electrical	Electrodialysis	--	13(3)	9
Mechanical	Distillation	20	15(4)	10
	Freezing	--	11(5)	8
	Reverse Osmosis	10	7(6)	5

Heat to kWh was converted at 33 1/3% conversion factor.

(1) 1 Mgd OSW test bed plant at San Diego, California, R&D Report 666.
(2) 15,000 gpd pilot plant, Wrightsville Beach, North Carolina, R&D Report 113.
(3) Projected value, plant under construction, Wrightsville Beach, North Carolina.
(4) 1 Mgrd OSW test bed plant, Roswell, New Mexico, R&D Report 170.
(5) 60,000 gpd pilot plant, OSW Wrightsville Beach, North Carolina, R&D Report 295.
(6) Small commercial units - Piston Pumps.

From the above, it is clear that from an energy efficiency standpoint, R.O. and electrodialysis are the most favorable of the commercially demonstrated desalination systems.

The 20,000 m³/d seawater desalination plant installed at Ghar Lapsi, Malta, using DuPont Permasep holofine fiber R.O. modules consumes 6 kWh/m³ energy. This plant was commissioned in 1983 showing how quickly the technology is developing. Only a year before, the U.S. OWRT reported 10 kWh/m³ as the best commercial performance, and 6 kWh/m³ as the conceptual optimum.

A potentially interesting source of information on reverse osmosis is an SRI multi-client study: Business Opportunities in Membrane Separation.

SRI INTERNATIONAL
333 Ravenswood Avenue
Menlo Park, CA 94025
(415) 859-3431
(315) 326-6200
Russ Phillips
Dr. Daryl L. Roberts

A useful source of information on desalination is the IDEA - Desalination Handbook prepared by CH2M Hill and available from:

IDEA PUBLICATIONS
Post Office Box 328
Englewood, NJ 07631

Preparation of this report was sponsored by the U.S. International Development Corporation, Office of Engineering.

An excellent review of "Desalination Processes from a South African Perspective," which includes desalination of acid mine drainage, is provided by SCHUTTE (1983) in a report available from:

WATER RESEARCH COMMISSION
Post Office Box 824
Pretoria 0001,
South Africa

C. F. (Frik) Schutte is a senior advisor to the Water Research Commission and is currently on sabatical in the U.S.A. The Water Research Commission and the South African mining industry are deeply involved in finding ways to avoid or treat acid mine drainage and today have access to the most comprehensive compilation of experience in desalination of mine-mill effluents, togethr with the vendors whose equipment was demonstrated. Of these, Resources Conservation Company whose address is shown below is probably the leader in this specialized application of desalination.

ANDREWS, et al. (1983) reported costs of the seawater reverse osmosis desalination facility installed by his company, Polymetrics, Inc., at Ghar Lapsi, Malta, which treats 20,000 m^3/d. Inquiries can be directed to:

POLYMETRICS, INC.
1005 Timothy Drive
San Jose, CA 95133

	Actual	Design
TDS in Feed (%)	3.65	3.95
Temperature	17°C'	21°C'
P	1,000 psig	1,000 psig
Recovery	35%	33%
SDI	2-4	LT 3
Product m^3/d	20,000	20,000 m^3/d
TDS Product (ppm)	500	380

Consumption Parameters

Electricity		
(Total) kWh/m^3	6.3	6.12
Cartridges/Year	12,000	6,000
Cl_2		
H_2SO_4		

Capital Costs

20,000 m^3/d	$17.5 mm	($3.75/gpd)

Operating Costs (U.S. $/m³)

Electricity	$0.43
Permeators	0.11
Labor/Overhead	0.05
Parts	0.04
Chemicals	0.01
Filters	0.01
	$0.65
Amortization	$0.43
Total	$1.08

Tom Sackinger at the Desalination Conference held in Florence, Italy, in 1983, estimated the cost of seawater desalination, based on a 12% per annum membrane replacement, as follows:

R.O. Costs: Seawater

Energy @ 7.4 kWh/m³	$1.80
Chemicals	0.14
Labor	0.19
Maintenance and Repairs	0.86
Amortization	1.75
Total	$4.96 per 1,000 U.S. Gallons

REED, S.A. (1982) and SCHUTTE (1983) report useful cost data and comparisons for various desalination processes. A further set of cost data was compiled by GLUECKSTERN (1982). Randol International Ltd. has a copy of each of these documents, and copies could be made available to sponsors on request. In addition, companies such as the RESOURCES CONSERVATION COMPANY and CH2M Hill also are continuously involved in updating costs of desalination. These contacts can be reached as follows, but it emphasized again that the real costs of desalination must include the cost of disposing of the concentrates produced which is not generally figured into desalination cost comparisons, and cost data for seawater desalination are not particularly applicable for acid minewater or metallurgical effluent treatment use of desalination processes.

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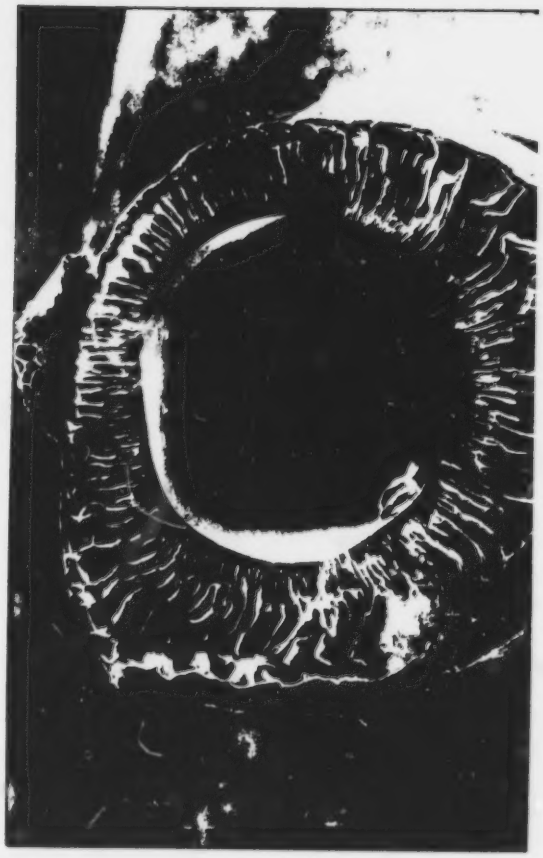

The latest theoretical developments in membrane and fluid transport and synthetic membrane treatment processes are analyzed in this well-designed work. Contributions by international experts consider the subject from the perspective of the chemical engineer and provide a valuable integration of theory and practical applications. The chapters review the fundamentals of hyperfiltration, ultrafiltration, and electrodialysis; summarize the experience with these processes in treating water and wastewater: examine the design and operation of membrane plants now established in the United States, Japan, and Europe; and analyze current economic considerations involved in the implementation of membrane processes. The volume also covers pretreatment, membrane cleaning, and fluid management for the reduction of the degradation effects of membrane fouling.

Synthetic Membrane Processes: Fundamentals and Water Applications will prove invaluable for those in the water and wastewater treatment fields, and for readers interested in the adaptation of membrane technology to new separation or concentration applications.

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GEORGES BELFORT, Membrane Methods in Water and Wastewater Treatment: An Overview. W. A. P. LUCK, Structure of Water and Aqueous Systems. DAVID C. SAMMON, Hyperfiltration Membranes, Their Stability and Life. C. E. BOESEN and G. JONSSON, Polarization Phenomena in Membrane Processes. C. KLEINSTREUER and GEORGES BELFORT, Mathematical Modeling of Fluid Flow and Solute Distribution in Pressure-Driven Membrane Modules. E. KORNGOLD, Electrodialysis Membranes and Mass Transport. GEORGES BELFORT, Desalting Experience by Hyperfiltration (Reverse Osmosis) in the USA. EBERHARD STAUDE, Desalting Experience Using Hyperfiltration in Europe and Japan. H. STRATHMANN, Water and Wastewater Treatment Experience in Europe and Japan Using Ultrafiltration. DAVID G. ARGO and I. NUSBAUM, Design, Operation, and Maintenance of a 5 MGD Wastewater Reclamation Reverse Osmosis Plant. ALFRED N. ROGERS, Design and Operation of Desalting Systems Based on Membrane Processes. PINHAS GLUECKSTERN and NATHAN ARAD, Economics of the Application of Membrane Processes. Part 1: Desalting Brackish and Sea Waters. A. N. ROGERS, Economics of the Application of Membrane Processes. Part 2: Wastewater Treatment. Each chapter contains references. Index.

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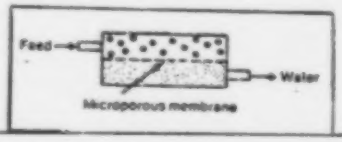
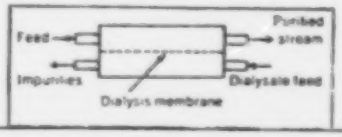
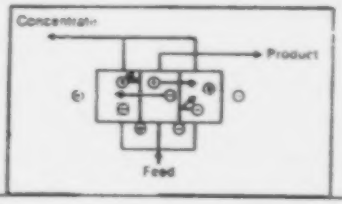
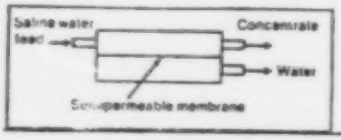
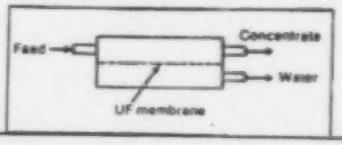
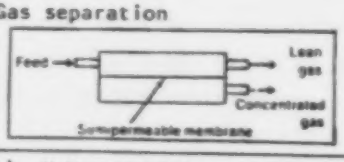
Table 1: Various membrane separation processes[a)]

Process/Concept	Materials passed	Driving force	Material retained
Microfiltration 	Water and dissolved species	Pressure difference, typically 10 psi	Suspended material (silica, bacteria, etc.). Variable particle-size cutoffs
Dialysis 	Ions and low-molecular weight organics (urea, etc.)	Concentration difference	Dissolved and suspended material with molecular weight > 1000
Electrodialysis 	Ions	Voltage, typically 1 to 2V/cell pair	All nonionic and macromolecular species
Reverse osmosis 	Water	Pressure difference, typically 100 to 800 psi	Virtually all suspended and dissolved material
Ultrafiltration 	Water and salts	Pressure, difference, typically 10 to 100 psi	Biologicals, colloids, and macromolecules. Variable molecular weight cutoffs
Gas separation 	Gases and vapors	Pressure difference, 1 to 100 atm	Membrane-impermeable gases and vapors

a) H.K. Lonsdale, J. Membrane Science, 10, April 1982, p. 81-181.

MEMBRANE SEPARATION TECHNIQUES

R.O., ED, and EDR processes all use membranes but in different ways. The table from LONSDALE (1982) summarizes the family of related membrane separation technologies. Between R.O. and ED/EDR, there is a very important difference. In R.O., water permeates the membrane; in ED/EDR, ions migrate through the membrane.

REVERSE OSMOSIS (R.O.)

- Water is forced under pressure through a membrane in a reversal of the natural osmotic migration of water across membranes from concentrated to less concentrated solutions on either side of the R.O. membrane. To achieve this, an external pressure is applied to the feedwater side of the membrane. This pressure must exceed the osmotic pressure for the given concentration difference.

- Osmotic pressure across a membrane is proportional to the concentration difference of the solutions on both sides of the membrane.

- Rate of solution transfer through R.O. membrane is proportional to the surface area of the membrane. To obtain a good flux rate for a R.O. module, designers have resorted to very high surface area systems such as spiral wound and holofine fiber systems. These large surface area systems can produce 80 m^3/d from a 1 m long module compared with only 1 m^3/d from a tubular membrane system of comparable size.

- Holofine fiber and spiral wound membranes are very sensitive to fouling by precipitates that form on the membrane surface from scaling solutions and/or organic fouling. This necessitates very extensive water pretreatment steps which may exceed the cost of the desalination equipment when this type of R.O. module is used. There is a limit to the recovery that is possible from scaling solutions using holofine fiber and spiral wound membrane modules due to $CaSO_4$ and $Fe(OH)_3$ fouling unless a multiple pass arrangement is used with pretreatment between each pass which would be most impractical and energy intensive.

- Th use of tubular R.O. systems, although many more modules may be needed for the same water production, saves the need for pretreatment and has been demonstrated to be capable of recovery in excess of 95% of the feedwater from a highly scaling $CaSO_4$ containing feed when the innovative new seeded slurry R.O. process is applied.

- There are several new membrane materials in addition to the original cellulose-acetate which is stable within limited pH and temperature ranges. Significantly improved membranes made from sulfonated poly sulfones, for example, and composite membranes containing polyamides are now becoming available.

- Reverse osmosis is an emerging technology, and there are steady improvements as well as more experience accumulating in its application.

- Reverse osmosis modules present a way of bringing water into contact with a membrane and of collecting a product and concentrate solution. R.O. systems, however, require a pump to deliver pressure, piping, valving, and a pretreatment system, as well as provision for recycling solutions in a R.O. water treatment system.

- Typical applications for reverse osmosis are:

  - Demineralization of boiler feedwater.

  - Providing potable water for mines and mills.

  - Desalination where species such as Na, $CaSO_4$, Cl^-, NO_3^-, etc. cannot be removed by conventional means.

  - There are some cases where reverse osmosis may be contemplated as a concentrating device, e.g., to preconcentrate effluent containing $[Cu(CN)_4]^=$ and other base metal cyanides, e.g. in foul liquors, ahead of cyanide recovery.

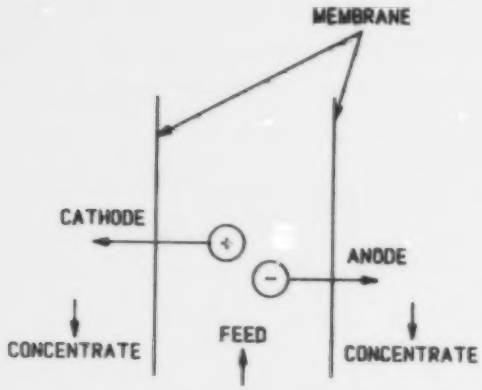
- The application of R.O. to mine and mill water recovery problems or purification for discharge is technically and economically feasible at a cost of around \$0.30-\$0.60/m^3 (including capital costs), but it is not a routine or easy technology. This is not yet available "off the shelf" as standard equipment.

- Reverse osmosis is installed in hundreds of operating plants for potable water recovery from seawater and brackish water in the Middle East, Malta, the Florida Keys, and on oil drilling platforms, as well as trawlers and naval vessels. In the case of seawater desalination, recovery is not a significant aspect, nor is the disposal of the resultant brines generated, even though the TDS of the feedwater is much higher than typical mine-mill effluents.

- Additional data on R.O. technology, membrane suppliers, and some cost data, as well as sources of expertise and examples of installations, are provided in Chapter 15.

ELECTRODIALYSIS (ED) AND ELECTRODIALYSIS REVERSAL (EDR)

- Electrodialysis and electrodialysis reversal differ from reverse osmosis in that in this case, ions are forced to migrate through a specially designed ion exchange-type membrane by applying an electric field across the compartment containing the feed solution. Cations migrate through the membrane on one side of the compartment to the cathode side, and anions migrate through the membrane on the opposite side, thereby deionizing the solution in the compartment between the membranes.



- In EDR, the polarity of the cell is reversed cyclically with the result that cations and anions migrate through both membranes.

- Gypsum, manganese, and iron cause fouling problems on EDR membranes. Iron and manganese cam be removed from recycled concentrate by precipitation. Gypsum must be sequestered using reagents but, because of limits in the concentration of gypsum that can be kept in solution (2-3x saturation), there is a limit to recovery of water from gypsum-containing solutions.

- A demonstration EDR plant was installed at the ERPM mine in South Africa to desalinate minewater. The EDR stack was compact, but it was hooked up to a large pretreatment plant, and there was evidence of a battle with gypsum problems.

- A very large ED plant was operated in the 1960's to treat mill tailings recycle water at one of the Orange Free States' gold mines near Welkom, South Africa. Problems and performance at this plant could prove useful if a source of information could be found, although EDR technology has made tremendous advances since then.

- There are two main suppliers of ED and EDR systems in the world, namely IONICS, U.S.A., and the ASAHI CHEMICAL CO., Japan. Their addresses are shown in Chapter 16 on EDR below.

DESALINATION: A SOUTH AFRICAN PERSPECTIVE

C.F. SCHUTTE

Senior Adviser:
Water Research Commission

PRETORIA
SEPTEMBER 1983

CHAPTER 11 ECONOMIC CONSIDERATIONS

11.1 Introduction

Numerous cost estimates, cost projections and cost comparisons for the desalination of seawater and brackish waters by the various desalination processes have been and are being prepared and published by various organizations and companies. One of the most authoritative of these is the "Desalting seawater and brackish waters : 1981 Cost Update" prepared by the Oak Ridge National Laboratory for the Office of Water Research and Technology, U S Department of the Interior. ORNL/TM 8191 (Reed 1982).

This cost update (and three earlier cost estimates) by the Oak Ridge National Laboratory operated by Union Carbide Corporation, has become the standard cost reference for cost projections and cost comparisons in the world desalination community. The discussion in this chapter and most of the cost figures are based on ORNL/TM 8191 unless otherwise stated.

No provision is made in these estimates for brine disposal costs other than for construction costs for brine outfalls. Any other disposal costs should be added to the figures presented herein.

11.2 Basis for cost estimates

(i) Costs are based on second quarter 1981 installed equipment costs in USA dollars for installation in the USA.

(ii) Plant load factors of 85% for seawater and 95% for brackish water systems have been assumed.

(iii) Membrane lifetime for reverse osmosis has been assumed to be 3 years and for electrodialysis membranes 7½ years.

(iv) Cost for electricity was taken as $0,05 per kWh.

(v) Capital costs include site development, civil work associated with the establishment of well fields and brine disposal, or installation of intakes and outfalls.

(vi) Indirect capital costs have been included :
11% interest rate on capital during construction
16% capital costs for contingency and engineering and architect fees.

(vii) Costs are based on commercially available desalination equipment with standard pretreatment equipment such as chemical dosing and cartridge filtration. No provision has been made for additional pretreatment such as clarification or filtration.

11.3 Conversion to South African conditions

Figures 11.1 to 11.4 reproduced from Reed (1982) give cost figures on the basis of the assumptions in paragraph 11.2. The same assumptions also apply to figures 11.5 and 11.6 reproduced from USAID (1980). To convert these to South African conditions the following factors should be taken into account :

(i) Transport costs USA to RSA and from the port of entry to the plant location must be added to capital costs.

(ii) Import duties, surcharges and other charges must be added to capital costs.

(iii) Appropriate escalation figures for the period second quarter 1981 to the present should be added to capital costs (USA inflation).

(iv) US dollars for capital equipment must be converted to SA rands.

(v) Any fees for local agents must be included in capital charges.

(vi) Local electricity rates must be used.

11.4 Costs for seawater desalination

Figures 11.1 and 11.2 give capital and total water costs respectively for desalination of seawater by distillation and reverse osmosis as a function of plant size.

Table 11.1 and 11.2 give examples of cost calculations for a 3800 m^3/d and a 19000 m^3/d plant respectively.

11.5 Costs for Brackish water desalination

Figures 11.3 and 11.4 give capital and total water costs respectively for desalination of brackish water by reverse osmosis and electrodialysis as a function of plant size.

Table 11.3 gives examples of cost calculations for a 3800 m^3/d and a 19000 m^3/d brackish water desalinating plant by reverse osmosis and electrodialysis reversal respectively.

The reverse osmosis energy costs have been determined for 80% recovery of a feed of 5 000 mg/l TDS. This means that the energy costs in table 11.3 for a reverse osmosis plant operating on a 2 000 mg/l TDS feed is conservative by about 20%.

TABLE 11.1

SEAWATER DESALINATION

Design capacity : 3 800 m^3/d

Multistage flash (MSF) : acid treated; performance ratio 12; concentration ratio 2.

Multiple Effect Distillation (MED) : Non-acid treatment, aluminium tube evaporator.

Reverse Osmosis (RO) : Water recovery 30%; membrane life 3 years; no energy recovery.

	MSF	MED	RO
Total capital cost $/$m^3$/d	2664	2110	1412
Installed equipment cost $/$m^3$/d	1444	1105	921
Water cost $ /m^3			
Fixed capital charges @ 18% per annum	1,55	1,22	0,82
Operation and maintenance	0,28	0,28	0,20
Membrane replacement	-	-	0,26
Energy (Coal)	0,32	0,34	-
Energy electricity $0,05/kwh			0,50
Total water cost $ /m^3	2,15	1,84	1,78

TABLE 11.2

SEAWATER DESALINATION

Design capacity : 19 000 m^3/d

Multistage Flash (MSF) : acid treated; performance ratio 12; concentration ratio 2

Multiple Effect Distillation (MED) : Non-acid treated, aluminium tube evaporator.

Reverse Osmosis (RO) : Water recovery 30%; membrane life 3 years; no energy recovery.

	MSF	MED	RO
Total capital cost $/$m^3$/d	1780	1318	1163
Installed equipment cost $/$m^3$/d	934	710	794
Water cost $ /m^3			
Fixed capital charges @ 18% per annum	1,00	0,76	0,67
Operation and maintenance	0,12	0,11	0,12
Membrane replacement	-	-	0,24
Energy (Coal)	0,32	0,34	-
Energy electricity $0,05/kwh			0,50*
Total water cost $ /m^3	1,44	1,21	1,53

*This figure may be reduced by about 30% if energy recovery is incorporated.

TABLE 11.3

BRACKISH WATER DESALINATION

Reverse osmosis (RO) : Feed 2000 - 5000 mg/l : 80% recovery,
Electrodialysis reversal (EDR) : Feed 1800 mg/l, 3 stages

Plant capacity	3 800 m^3/d		18 900 m^3/d	
	RO	EDR	RO	EDR
Installed equipment cost $/$m^3$/d	158	328	138	303
Total capital cost $/$m^3$/d	318	531	254	464
Water cost $/$m^3$				
Fixed capital charge @ 18%	0,16	0,26	0,12	0,23
Operation and maintenance	0,08	0,07	0,05	0,04
Membrane replacement	0,04	0,05	0,03	0,03
Electricity @ $0,05 kwh	0,10	0,05	0,10	0,05
Total water cost $/$m^3$	0,38	0,41	0,31	0,35

Total desalinated water costs for electrodialysis reversal for a 18 900 m^3/d plant vary from $0,31/$m^3$ to $0,42/$m^3$ depending on the chemical composition of the feedwater which in turn determines the water recovery possible (80-87%) and the number of stages required for a specific production and desalination duty. The figures given in table 11.3 are for one type of feedwater and a product quality of 500 mg/l TDS.

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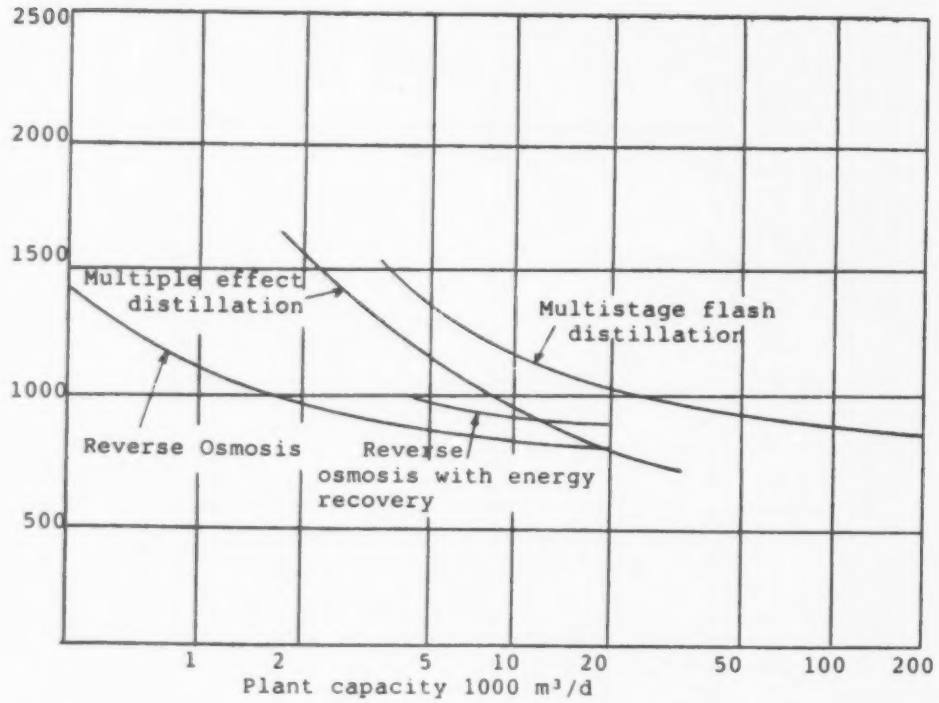

FIGURE 11.1 : CAPITAL EQUIPMENT COST - SEAWATER DESALTING (REED 1982)

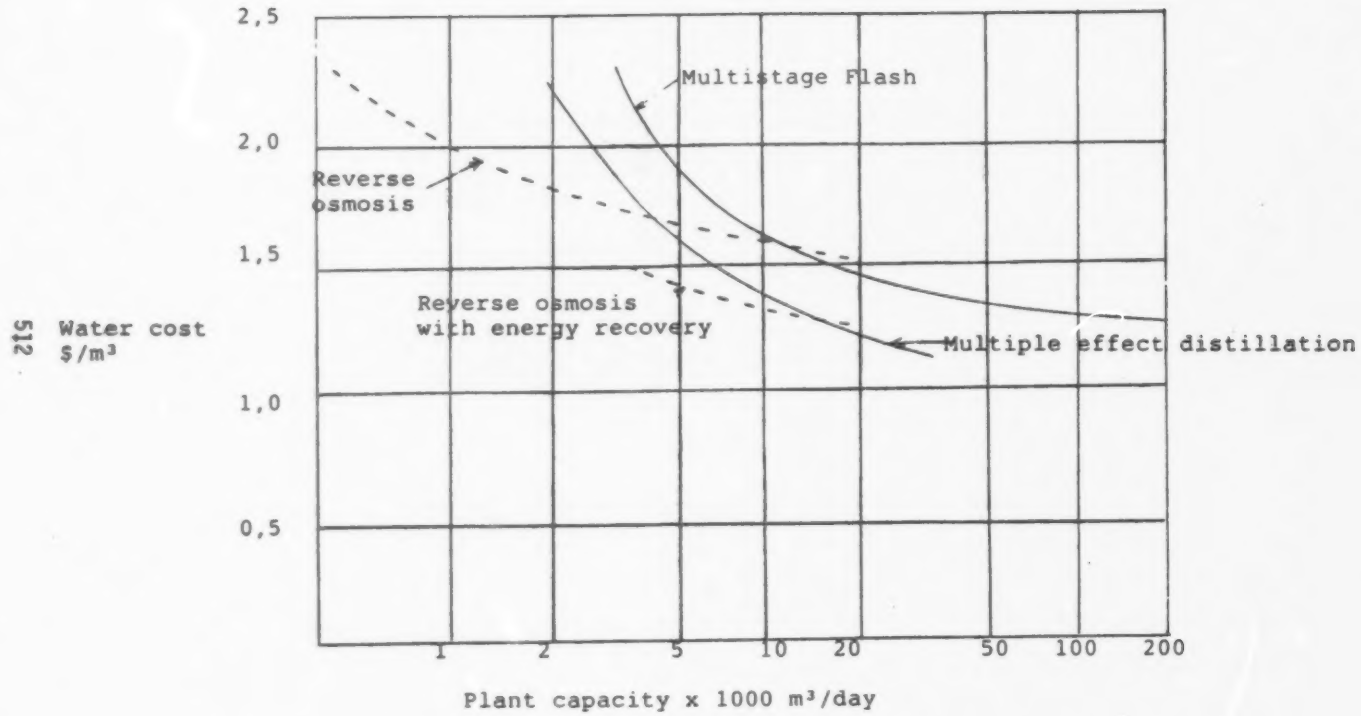

FIGURE 11.2 : WATER COST - SEAWATER DESALTING
(REED 1982)

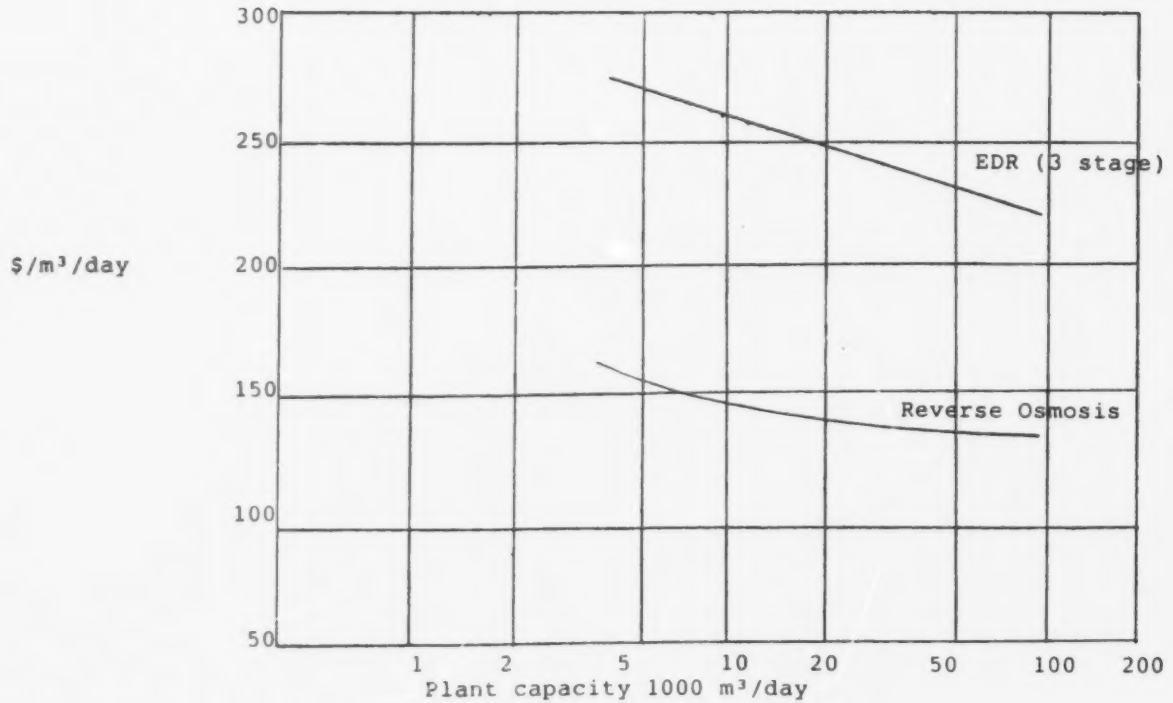

FIGURE 11.3 : CAPITAL COST- BRACKISH WATER DESALTING
(REED 1982)

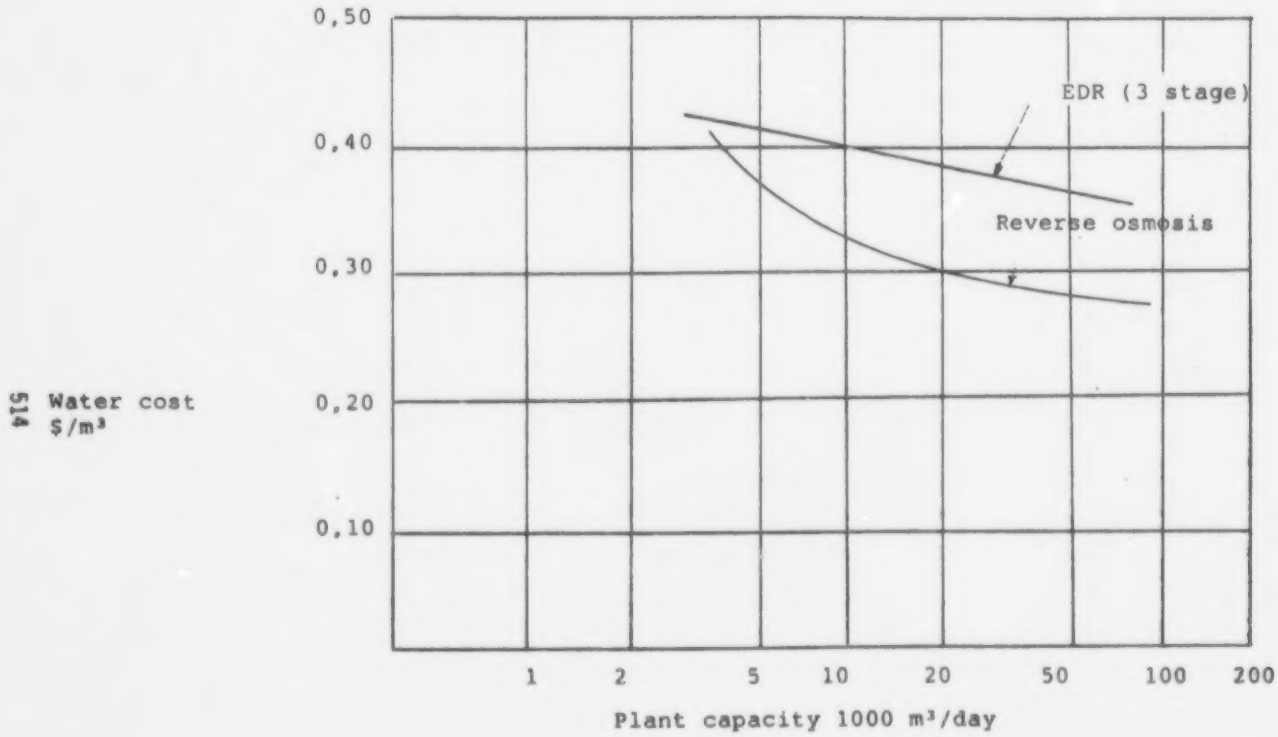

FIGURE 11.4 : WATER COST - BRACKISH WATER DESALTING
(REED 1982)

WARNING

1. Caution should be exercised when using these cost data.

2. These costs are computed for basic desalination facilities in the USA. These costs include no storage capacity and allow for only fundamental feedwater development and brine disposal. If storage capacity is added and/or more complex feedwater or brine facilities are required, overall project costs can significantly increase. This is especially true with brackish water facilities. Construction in locations outside the USA can also add to the overall cost. Actual costs of up to 300% (or more) of those shown on this figure (especially at lower capacities) would not be unusual for projects in many developing areas.

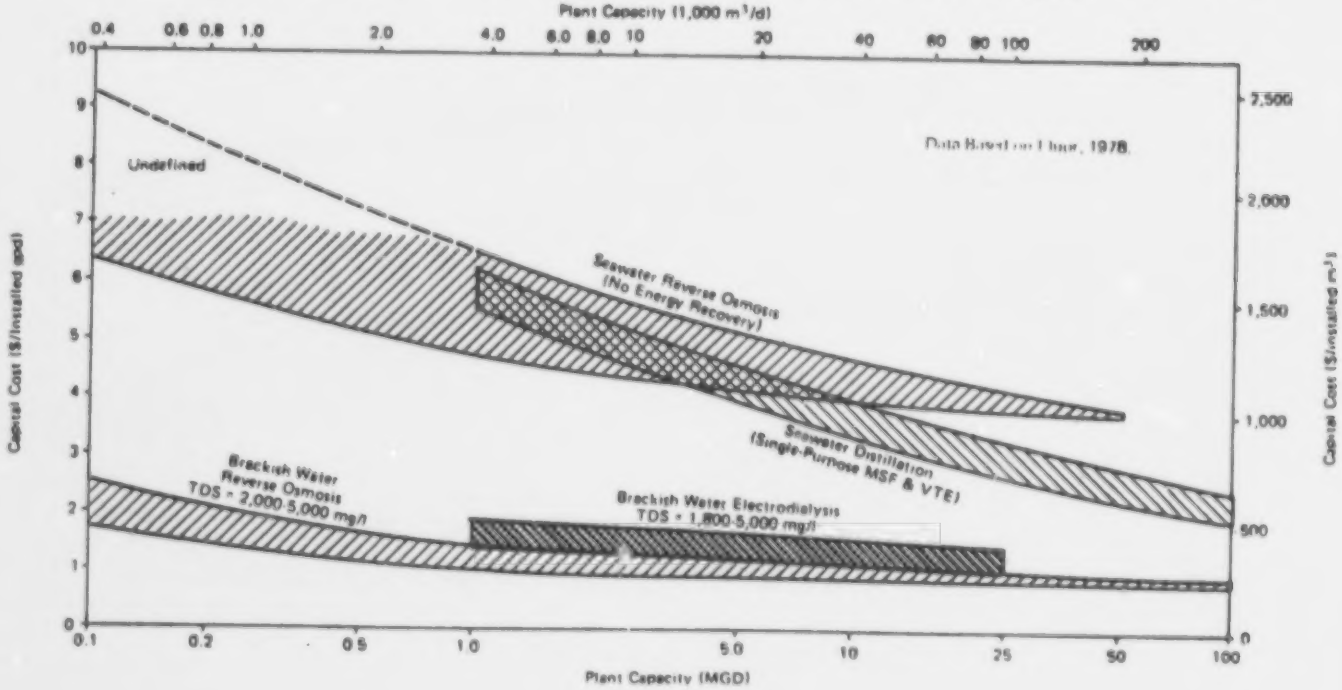

FIGURE 11.1 Generalized capital cost estimates for desalination processes. (USAID 1980)

WARNING

1. Caution should be exercised when using these cost data.
2. These costs are computed for basic desalination facilities in the USA. These costs include no storage capacity and allow for only fundamental feedwater development and brine disposal. If storage capacity is added and/or more complex feedwater or brine facilities are required, overall project costs can significantly increase. This is especially true with brackish water facilities. Construction in locations outside the USA can also add to the overall cost. Actual costs of up to 300% (or more) of those shown on this figure (especially at lower capacities) would not be unusual for projects in many developing areas.

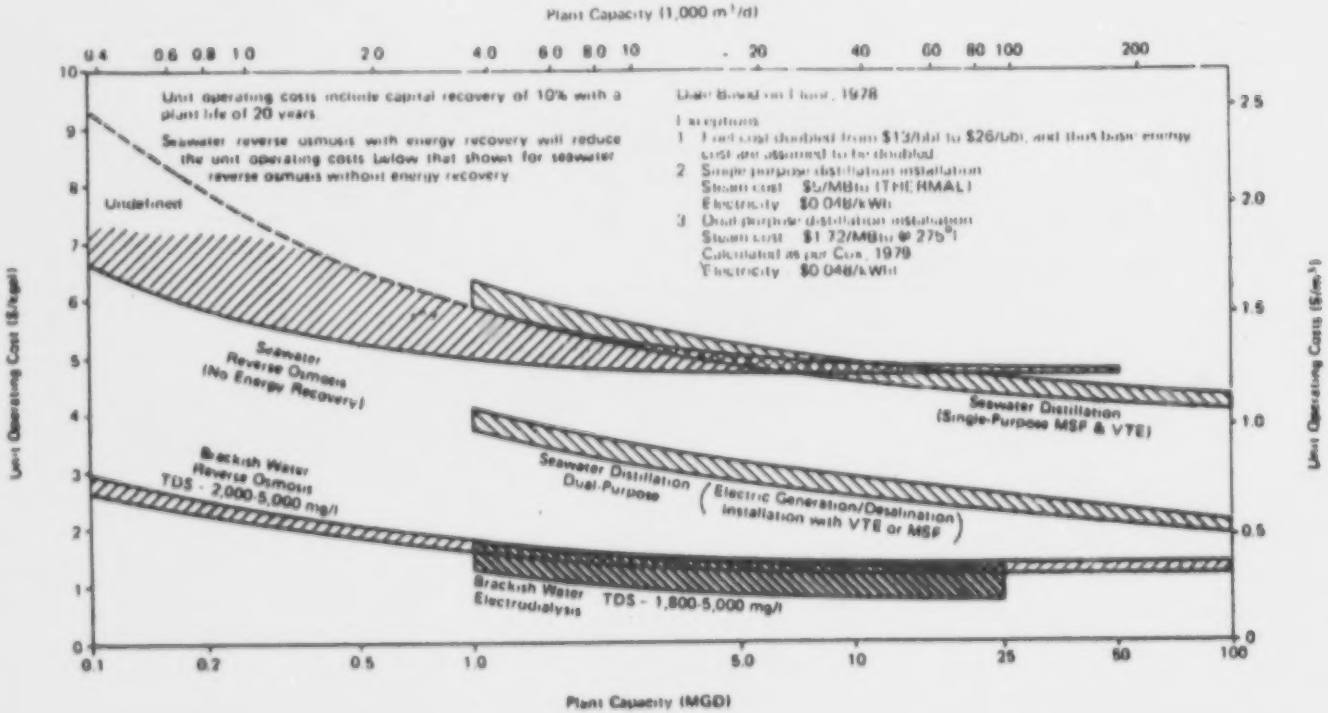

FIGURE 11.2 Generalized unit production cost estimates for desalination processes. (USAID 1980)

- Several EDR plants operate in South Africa. The impressive plant at the Kriel power station, Transvaal, is described briefly in Appendix I. It pretreats Vaal River water ahead of an IX demineralization plant to take the load off the IX system. TDS is reduced from 240 mg/l in feedwater to around 50 mg/l to the IX system. Concentrate is returned to the general water supply, so this is not a valid test of yield or performance required for acid mine drainage treatment, although it demonstrates that a large EDR plant can be installed to work well and gives an impression of what such an installation looks like.

- Various experimental projects have attempted to use ED and EDR for reagent recovery in metallurgical operations, e.g., H_2SO_4 and NaOH from $(NH_4)_2SO_4$ effluents.

- Cost data for EDR application at power plants for boiler feed treatment would not be applicable to projects where ED/EDR is to be used for desalination of AMD. Although treatment of AMD containing gypsum between the EDR stages should be less expensive because EDR is not a high-pressure system, there remains the need for a complex water treatment system that is larger than the EDR plant itself.

- EDR membranes are prone to fouling, but the membrane stack can be dismantled and each membrane physically cleaned. This is, however, a laborious labor-intensive operation.

- IONICS is designing an EDR process system to yield a concentrate at 120,000 ppm TDS for use in a solar pond experiment. This is an indication that high salt concentrations can be handled by EDR under certain circumstances. These are likely to be NaCl, not $CaSO_4$ solutions however, and minewater desalination presents a different set of parameters.

- In Japan, ASAHI is said to use EDR to concentrate seawater to generate brine slurries up to 110,000-150,000 ppm salt which exits as a slurry. Very thin, efficient membranes are reputedly used.

- DE VILLIERS, et al. (1983) tested and evaluated EDR using a pilot Ionics aquamite unit to treat brackish groundwater containing 6,000 mg/l TDS at 70-80% recovery to yield a water product at 620 mg/l with overall salt rejection of 90.6%. The indicated 1982 cost was R0.69/m³ including plant amortization. Energy consumed by the EDR stack amounted to 4.6 kWh/m³.

- MELZER and VAN DEVENTER (1983) estimated a cost of EDR water recovery on a discounted cash flow basis for a plant recovering about 2 million m³/year water to be R0.35/m³ ($0.18/m³) but since this study was done by the S.A. Electricity Supply Commission (ESCOM) which used an internal power cost of R0.0167/kWh

($0.0084/kWh), this cost assessment would not be generally applicable. At U.S. $0.08/kWh, the cost of water using their calculations would be roughly double at R0.75/m³ ($0.36/m³) at this South African location treating water at 1,184 ppm TDS to produce a product of 219 mg/l TDS, yielding a reject at only 3,760 mg/l TDS of which 2,234 mg/l was sulfate.

- Capital cost in 1983 for the above EDR plant recovering 2 million m³/year was R5,200,000 ($2,600,000) which would have now to be adjusted upwards for the increased price of imported components at the devalued rand value compared to when this unit was purchased.

- The above cost estimates do not take into account the cost of disposing of concentrates.

EVAPORATION

- Evaporation/water recovery systems are commercially available and in routine use for water recovery from a variety of chemical and metallurgical industry wastewaters, some containing high salt concentrations.

- There are several different evaporation/water recovery process and equipment concepts in commercial use:

  Mechanical Vapor Recompression - Rustenburg Refiners, South Africa
  Multi-Effect Evaporators, Mechanical Vapor Recompression
  Vapor Compression Distillation - Sentrachem-Afprene Plant, Newcastle, Natal

- Evaporation/distillation is particularly competitive in treating was concentrated solutions where membrane processes and ion exchange cannot compete. For example, evaporation is one way of disposing of R.O. or EDR brines thereby yielding a dry, disposable salt and some additional water as products.

- Where there is available waste heat or low pressure steam from a power station, for example, evaporation is a highly attractive approach to desalination. For example, at the Virgin Islands' Water and Power Authority, 6 mm gpd (23,000 m³/d) of water is produced from seawater at an overall loss of 6 MW, i.e., 24 KWh per 1,000 gallons, 6.3 kWh/m³ product.

- The joint U.S.-Israeli Government project at Ashdod, Israel, which produces 37,500 m³/d water from seawater (10 mm gpd) using multi-effect evaporation, cost $10 million in 1980. Such units appear to be larger than required by the average

metallurgical plant, and metallurgical operations are not often located adjacent to power plants with waste heat.

- To avoid the loss of heat exchanger efficiency through scaling, crystal seeding is commonly applied in recirculating concentrates.

- Based on 2.5¢/kWh, which is available only in exceptional cases, the cost of vapor compression distillation of water ranges between $0.41/m³ and $0.55/m³ or $1.55-$2.08/1,000 U.S. gallons on small-scale applications.

	Std. AQ-500	Low Energy LE-500 Model
Energy Costs 2.5¢/kWh	$0.46/m³	$0.32/m³
Labor @ $3/Hour	$0.03	$0.03
Consumables	$0.06	$0.06
Total	$0.55/m³	$0.41/m³
	$2.08/1,000 U.S. Gallons	$1.55/1,000 U.S. Gallons

- The above cost breakdown allows adjustment to be made for realistic power and labor costs which indicates that at $9.00/hour labor and 7.5¢/kWH, evaporation desalination costs would be around $1.30/m³ or $4.65/1,000 U.S. gallons excluding the cost of concentrate disposal.

- The above costs refer to seawater desalination where recovery is of little consequence, and the concentrate is disposed of back to the sea. The IDE Aquaport MVC systems operate at temperatures between 30°C/55°C. Below 55°C' (130°F), corrosion and scale effects are minimized. Heating is provided by mechanical compression of the liquids. Brine is sprayed over a bundle of horizontal heat transfer tubes at a rate just sufficient to create thin, continuous liquid films. A centrifugal compressor provides suction on the outside of the tubes which enhances evaporation of the brine. After passing through a demister to prevent droplet carryover, the vapor is compressed and discharged to the inside of the tubes where it condenses, and the latent heat provides the heat required for the flash evaporation process. The product and brine leave the system via a heat exchanger which preheats the incoming feed.

- Evaporators using horizontal and vertical tubes are in commercial operation. Israeli Desalination Engineering Co. prefers horizontal tubes. Swenson, Lurgi, and the Resource Conservation Co. prefer vertical tybe evaporators.

- Special corrosion-resistant materials are used in brine evaporators. Israeli Desalination Engineering uses a unique aluminum alloy which is corrusion-resistant and has an efficient heat transfer coefficient.

- The evaporator at Sentrachem's Afprene plant, Newcastle, Natal, treats 750 m^3/d of feed with 17,000 mg/l salt content to yield 736 m^3/d product water with less than 50 ppm TDS yielding 13.4 m^3/d concentrate, i.e., 98% recovery. Power consumption is 21.4 kWh/m^3 overall of which 17-18 kWh/m^3 is for the evaporator. Feed is delivered to the plant at 20-30°C'. Overall costs are R0.85/m^3, \$.43/m^3. The system is suitable for use with gypsum seeding at which gypsum solids up to 8% are recirculated at temperatures up to 85°C'. Without seeding, the operating temperature is limited to 70°C', and a $CaSO_4$ wt percent between 0.5-1.5%.

- Innovative new welded thin-wall plate heat exchangers are available from Germany which are claimed to save energy in evaporation desalination but, to date, no commercial-scale units have been observed in mine-mill environments.

ION EXCHANGE

- Ion exchange is routinely used for demineralization of boiler feedwater for powerplants and steam plants in mines and mills. Usually, these are fixed-bed cation/anion exchanger systems.

- Ion exchange is also used for the recovery of metal ions, particularly uranium from pregnant solutions. Continuous ion exchange systems using fluid beds are employed for the most part. Popular systems in use are:

  - The NIMCIX System Developed by MINTEK, South Africa
  - Porter System and Modification Thereof
  - Old Fixed-Bed Merry-Go-Round System
  - Resin-in-Pulp Systems

- Resin-in-pulp systems are used where solid/liquid separation is impractical for recovery of values from leached ore pulps rather than from water. Continuous fluid bed systems can tolerate a considerable amount of suspended solids in feed solution. CIX systems are also routinely used at in situ leach operations.

- A continuous downflow CIX system was installed by Himsley Engineering at the Cotter Corporation's Schwarzwalder Mine for uranium recovery from minewater before it can be discharged. This system also removes several other metals from solution and achieves very low levels of uranium down to less than 10 ppb. It is described in Appendix I.

- A CHEMSEPS Higgins Loop ion exchange system is installed for molybdenum removal from Climax Molybdenum's tailings effluent, Climax, Colorado, and at WYOMING MINERALS' facility at the Bingham Canyon pit in Utah for recovery of uranium from mine drainage.

- CHEMSEPS IX systems are used for a variety of water softening applications and for nitrate removal from a fertilizer plant's wastes.

- One objection to ion exchange for desalination of mine-mill effluents is that in the elution step, more chemicals must be added. This means that in the disposal of eluant solutions, greater amounts of salt must be disposed of than were removed from solution because of the amount added in the elution process.

- In Australia, the CSIRO 'Sirotherm' process is now being tested by AMDEL for desalination of a municipal water supply that is high in NaCl content. The 'Sirotherm' process uses a resin which desorbs at high temperature and adsorbs at low temperatures. Hot water rather than chemicals is used to elute the resin which would overcome the objection of salt addition. However, it appears that this process is limited to the removal of NaCl rather than species that usually occur in mine drainage, e.g., H_2SO_4, Fe^{2+}, Ca^{2+}, Mg^{2+}, etc.

- The University of Cape Town has derived an innovative ion exchange system for desalination of minewater and effluents. Despite several interesting and innovative aspects, their system, requiring three or four CIX columns in series does not appear to be very practical for mine environments. impractical.

- In general, IX is more economical than other desalination processes at low ion concentrations. For example, in extractive metallurgy, IX is used for U_3O_8 recovery from solutions below about 200 ppm; above that level, SX becomes more cost effective. Similarly, in desalination, IX is generally competitive where very low-level ion concentrations are required, e.g., demineralized boiler feed at 10 ppm total dissolved salts produced from water with less than 500-1,000 ppm TDS, for example. Where feedwater contains higher salt levels to 10,000 ppm, it may pay to apply one of the membrane processes, e.g., R.O. or EDR. At above 1%-2% TDS levels, evaporation is likely to be the more economical approach.

FREEZING

- Freeze desalination processes, while theoretically possible, were not encountered in test programs for the treatment of AMD or other mine-mill related water treatment needs.

- DELKOR TECHNIK (PTY) LTD., Johannesburg, were investigating a method of generating ice on a large scale aiming at a reduced cost. Their idea was to combine freezing with AMD desalination and mine cooling on the Witwatersrand, but no mention has since been encountered of plant-scale tests of this idea referred to by Theo Stielan before he retired.

DELKOR TECHNIK (PTY) LTD.
Post Office Box 39744
Bramley 2018
South Africa
(011) 643-6751
Errol Amm

COMPARISON OF DESALINATION PROCESSES

Selection of an appropriate desalination process depends on the following:

- Compositon of Feedwater:

High TDS, +10,000 mg/l	: Evaporation
Mid TDS, 1,000-10,000 mg/l	: R.O., EDR
Low TDS, -1,000 mg/l	: IX and CIX

- Nature of Contaminants:

High $CaSO_4$	: R.O. Slurry Seeded
Non-Scaling	: EDR/R.O.
Fe, Mn	: EDR/R.O. with Pretreatment
NaCl, LT 2,000 mg/l	: Sirotherm IX
U_3O_8 Specific Recovery	: CIX

- Disposal of Concentrates:

Deep Well Disposal
Ocean Discharge ($CaSO_4$, H_2SO_4, NaCl)
Evaporation Plants
Evaporation Ponds

DISPOSAL OF CONCENTRATES

In most cases, there is a point of diminishing return in the use of IX, R.O., and EDR as concentration of feedwater increases. These processes yield concentrates containing salts removed from the desalinated water and, as the volume of concentrate diminishes, its salt

concentration increases correspondingly. Eventually, it must be bled, and the cost of disposal of this concentrate must be included in an economic evaluation of the process.

Where the plant is located at the ocean, for example for seawater desalination, the concentrate can be discharged back to where it came from. If used for mine-mill related effluent treatment, ocean discharge would depend on the nature of the concentrate composition and the marine environment protection laws in effect but is seldom possible due to location.

Where low-cost land is available and the operation is located in net evaporation climates, evaporation ponds are most likely to be the more economical solution, especially where naturally impermeable formations exist on the surface which can be used in impoundment construction.

Where water is valuable and land is not available, evaporation to dryness in a plant is probably going to be attractive, especially if waste heat from a power plant is available or if a market can be found for the salt product.

At the Rustenburg Refinery, an acid metallurgical processing solution is treated with NaOH, and the Na_2SO_4 is recovered from wastewater after a lime-soda softening step using a Swenson evaporator. The Na_2SO_4 is sold to the fertilizer industry.

On the other hand, at mines such as the Beisa Mine, which is part of the GENCOR LTD. GROUP, minewater in large quantities containing 2,000 ppm NaCl is generated by mine dewatering. It is more economical to simply evaporate it from large shallow ponds. Where ponds have to be lined, where water is expensive or where there is net precipitation, the desalination/injection or desalination/concentrate evaporation alternative may prove most economical.

Selection of waste water treatment/disposal must be based on site-specific requirements and conditions.

R.O., evaporation, and ion exchange are discussed in greater detail in the chapters that follow to provide some insight into suppliers, existing installations, and sources of expertise. This is a highly competitive market, and some vendors may be led into making promises beyond their capabilities due to their general inexperience with mine-mill effluents.

A final word of caution is in order. Desalination processes are expensive in terms of capital and operating costs and somewhat more complex, more sensitive, and less familiar than most metallurgical processes. Solving one problem may introduce another, e.g., disposal of concentrates. Unless it really cannot be avoided, mining and mineral processing operations are best advised not to consider desalination processes.

As a starting point in the investigation of deep-well disposal of concentrates, the following person may be able to provide useful leads as to cost, sources of technology, and regulations in the U.S.A.:

ERLE C. DONALDSON
Research Chemist
Basic Production Research
U. S. Dept. of the Interior
Bureau of Mines
Post Office Box 1398
Bartlesville, OK 74003

Mr. Donaldson has undertaken surveys of disposal wells used by chemical industries in the U.S.A. and has described two disposal systems that may be of particular interest to the mining industry which were studied over a ten-year period by the Bureau of Mines.

Various cementing processes have been developed for the permanent safe disposal of precipitated solids. Amongst these systems are:

STABLEX CORPORATION
#110, Two Radnor Corporate Center
Radnor, PA 19087
(215) 688-3131
Telex: 834477
William T. Howard
J. T. Schofield

CHEMFIX TECHNOLOGIES, INC.
1675 Airline Highway
Post Office Box 1572
Kenner, LA 70063
(505) 467-2800
Scott A. Othkiese

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CHAPTER 14

PRECIPITATION PROCESSES

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INTRODUCTION

Precipitation processes were discussed in the preceding chapter which pointed out that precipitation is the most commonly used process for the removal of contaminants from water.

Precipitation processes are discussed time and again in the following chapters on the removal of contaminants in which it is referred to specifically, contaminant by contaminant. Chapter 25 on Removal of Contaminants in particular contains much detailed discussion on various precipitation processes.

Here, it remains to draw attention to some of the innovative process ideas and equipment sources available. Since so much is said on this subject in later chapters, this chapter is designed to be no more than a summary overview of important features.

PRINCIPLES

The principles of chemical precipitation are discussed in all classical chemistry texts. Solubility of chemical species in water is governed by the solubility product Ksp which,

in turn is a function of temperature. Classical chemistry is not very good at quantifying phenomena such as supersaturation or co-precipitation effects. Consequently classical chemistry, while useful in providing a guide as to what one might expect to happen in a solution, does not compare with empirical results of what actually happens in practice, especially when dealing with complex solutions.

Porbauix diagrams represent a major step forward in explaining the stability in solution or solid form (precipitate) of a whole variety of species. These do not take into account the effects of the presence of complexing agents or other sequestering agents. In addition, so much also seems to depend on the nature of the surfaces to which a solution of salts is exposed as to whether they will be precipitated or not. In terms of adopting a systems approach to selection of precipitation reagents and conditions, it is important to think not only in terms of the solubilities that can be reached, but also to determine the degree to which suspended precipitates can be removed from the solution, the type of equipment required for this, and the cost thereof, as well as disposal of the precipitate.

An excellent example of this is the mammoth study undertaken by the Calgon Corp. to assemble empirical data on scaling and corrosion in power plants as a function of solution chemistry. This has resulted in a computerized databank on empirical and fundamental reaction data that is believed to have cost $7-8 million to assemble overy many years to accurately predict the solution chemistries and stabilities under various conditions as well as to predict the correct dose of scale inhibiting or anti-corrosion chemicals. This is known as their Calgard program.

RANDOL believes that for prediction of solution stabilities in metallurgical processes, the same type of empirical approach would be required--build a quantitative base for reliable salt balance modelling in integrated processes. However, such an empirical databank does not exist, nor is it likely because the cost would be even higher than it was for the Calgard system due to the more complex nature and variety of metallurgical processing plants. Information on the Calgard program is available from:

CALGON CORPORATION
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Dr. Frank Daniher

APPLICABILITY

Precipitation is applicable as a means of removing contaminants from solution when:

1. The contaminant can be removed to satisfactory levels for the solution to be recycled or discharged.

2. The precipitate can be economically separated from the solution.

3. The reagent used in the precipitation process does not make the solution more toxic than the species that was precipitated.

4. The precipitate can be disposed of safely.

5. If more than one species needs to be removed from solution, a process that simultaneously removes all of them will be most applicable.

OXIDATION OF IRON

Ferric hydroxide precipitates at around pH 3.5 whereas, ferrous hydroxide is more soluble and precipitates at a higher pH. For more effective removal of iron from solution, it is best ot oxidize it to ferric iron. The normal procedure for this is by air oxidation. The rate at which ferrous ions oxidize in air to ferric is very pH dependent and varies from many hours at low pH, say 2, to minutes at high pH values. Consequently, it is normal practice to add lime before aeration of acid solutions containing ferrous ions.

EQUILIBRATION

When water is in contact with the atmosphere, it adsorbs CO_2 from the atmosphere. At low pH values, this CO_2 is present in solution as H_2CO_3, carbonic acid. Below pH 7.2, it is present as HCO_3^- bicarbonate, and above pH 7.2, it is present in solution as carbonate ions $CO_3^=$.

A solution is in equilibrium when it has adsorbed CO_2 from the atmosphere to an equilibrium level. Since some carbonates, e.g., $CaCO_3$, are a lot less soluble than the hydroxides, e.g., $Ca(OH)_2$ of the same metal or the bicarbonates, e.g., $Ca(HCO_3)_2$, solutions in an acid medium will adsorb CO_2 until the solution is saturated. If the pH were to be increased to over pH 7.2, the bicarbonate ions convert to carbonate ions, and insoluble carbonate precipitates may settle out, thereby consuming CO_2 from the solution. Sometimes these processes take a long time, and non-equilibrium conditions may exist.

LIME ADDITION PROCESSES

Lime may be added in several ways for pH adjustment or to precipitate contaminants:

- Direct addition of unslaked lime to a tank or effluent stream as described at INCO, Copper Cliff, in Appendix I can and does achieve satisfactory contaminant removal to fulfill the needs of some operations.

- Slaked lime makeup and addition as a solution.

- Addition of dry slaked lime as a powder as described at Waite-Amulet in Appendix I.

- Lime slakers, lime solution dosing equipment is standard and available through most mine supply houses. The system installed at Noranda Waite-Amulet is very practical and is designed to be completely automated with no operator on site.

Lime addition makes it possible to reach pH values in excess of pH 12.

The lime feeder and slaking system installed at the Mount Emmons water treatment plant uses a slaker that feeds lime from a silo at 1,000 lb./hour to make a 6-8% slaked lime slurry. This system operates reliably and was supplied by:

WALLACE AND TIERNAN DIV.
Pennwalt Corporation
25 Main Street
Belleville, NJ 07109
(201) 759-8000

Slaked lime addition is automatically controlled by a pH meter and a solution level probe. There is always a backup probe on standby. The pH probe used was supplied by:

GREAT LAKES INSTRUMENTS, INC.
8855 North 55th Street
Milwaukee, WI 53223
(414) 355-3601

At the Copper Cliff water treatment plant of INCO Ltd., Sudbury, Ontario, 272,000 m^3/d of water is treated. A slaked lime slurry is pumped into the creek feeding the water treatment plant about 50 yards upstream of the plant inlet. The slaked lime slurry is generated on site from quicklime. A total of 4,000-5,000 tpa is consumed annually to adjust the solution to pH 10-10.5.

INCO has found that by moving the lime addition point upstream of the plant inlet, a significant improvement in reactor-clarifier performance and final effluent clarity resulted.

At Key Lake, a high acidic uranium raffinate mixed with large volumes of excess minewater is neutralized in their "bulk neutralization" plant which employs four flash mixer tanks in series which are inserted before each of four reactor tanks. The addition of lime in this way is effective at precipitating a sludge that can be densified to 20% solids

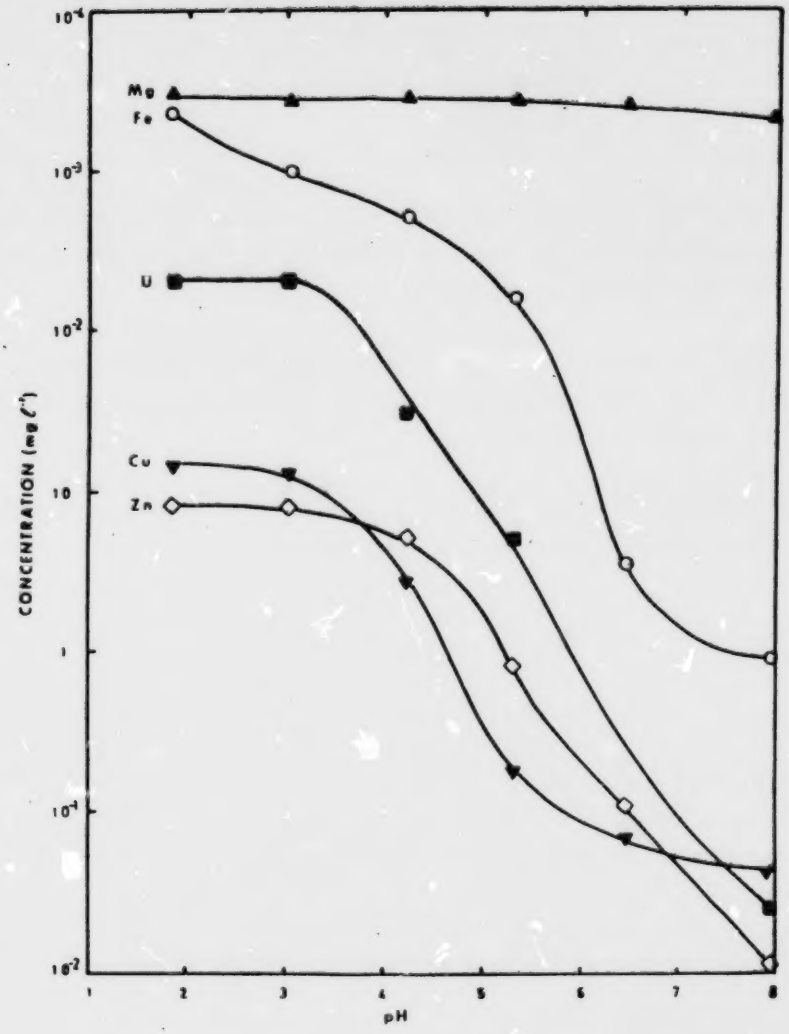
in a lamella settler and has also proven effective at precipitating arsenic. This system was designed and pilot tested for Key Lake Uranium by:

SHERRITT-GORDON MINES LTD.
Fort Saskatchewan, Alberta
Canada T8L 2P2
(403) 988-6911
Herb Veltman
D. Robert Weir
Roman Berzowsky

The manner in which lime is added in precipitation processes has a lot to do with the nature of the precipitate density and can also influence lime consumption as can be noted from the next paragraphs on HDS precipitation.

Where a lime slurry or solution is to be spray irrigated through nozzles in water treatment processes, then the type of lime used is significant as it should be free of silica particles that can clog the sprinklers.

LEVINS (1978) showed how dissolved salts in Alligator Rivers area acid leached uranium tailings solution are reduced as pH is increased by addition of lime.



CONCENTRATION OF MAGNESIUM, IRON, URANIUM, COPPER AND ZINC
IN LIME TREATED, JABILUKA TAILINGS-RAFFINATE SLURRIES

Source: LEVINS (1978)

THE HIGH DENSITY SLUDGE PROCESS (HDS)

The high density sludge process was first described by the Bethlehem Steel Corp. and has since been used and, in some cases, improved on by at least the following mining companies:

Rand Mines (Mining and Services) Ltd., Johannesburg
Cominco Ltd., Kimberly, B.C., and Trail, B.C.
Noranda Mines Ltd., Waite-Amulet and Several Locations
Bethlehem Steel Corp., Several Locations
Anglo American Corp., Kromdraai

Several of these installations are described in Appendix I trip reports, and the process is described in detail in Chapter 24 on acid mine drainage treatment. The paper by WATSON and TURNBULL (1983) overleaf describes the application of HDS at Cominco's Trail, B.C., metallurgical operation.

The main advantages of the HDS process are:

- Generation of high sludge densities that settle easily and are easily disposed of.
- More efficient lime utilization.
- Non-amphoteric precipitates.
- Clearer clarifier overflow.

The main feature of HDS is the recycling of underflow sludge which is premixed with lime before it is added back to the circuit.

There are several sources of up-to-date information on the latest applications and performance of HDS. These include:

WALTER J. KUIT
Cominco Ltd.
200 Granville Street
Vancouver, B.C. V6C 2R2
(604) 682-0611

BERNARD W. BROOKS
Noranda Mines Ltd.
Horne Division
BP 4000
Noranda, Quebec
Canada J9X 5B6
(814) 762-7764

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18016
(215) 694-2424
Stewart T. Herman

The Bethlehem International Engineering Corp. (BIEC) offers a commercial service to design HDS systems for specific applications as well as for sludge disposal. BIEC has recently patented improvements in HDS applications for base metals removal from water--for example, zinc precipitation, and another for manganese precipitation when iron is present at low levels. The Bethlehem Steel HDS plant at their Panther Valley Mines operation, Mauch Chunk, Pennsylvania, uses an innovative preaeration technique which reduces lime consumption cost effectively in an area where lime is inexpensive.

1982 ENVIRONMENTAL ENGINEERING DESIGN AWARD

Cominco Ltd is the winner of the second Environmental Engineering Design Award of the Association of Professional Engineers of BC. Cominco's Effluent Treatment Plant at the Trail Metallurgical Operation was judged the best design for 1982 and their submission is published here in full.

The Award was presented by APEBC President Ken Williams PEng to authors Roger Watson PEng and John Turnbull PEng at the West Kootenay Branch Meeting in Castlegar on March 24, 1983.

Seven other submissions were received from coal mines, pulp mills, engineering consultants, municipalities and government departments. Extracts from these submissions were prepared by Kelly Kline PEng of the Environment Committee and, with the authors' permission, are published in this issue.

1982 Environmental Engineering Design Award Winner

Cominco Ltd's Effluent Treatment Plant at its Trail, BC, Metallurgical Operation

R H Watson PEng, Manager
J D Turnbull PEng, Assistant Manager
Trail Modernization Project

INTRODUCTION. Cominco Ltd's huge metallurgical complex is located in Trail, British Columbia, a city with a population of 10,600 located in the Columbia River Valley in the West Kootenays, 18 km north of the Canada-US border. The lead-zinc production complex is the largest in the world with an annual capacity of over 400,000 tonnes combined lead and zinc. As a consequence of this installation, 30 tonnes of silver and over 325,000 tonnes of chemicals and fertilizers are produced annually. Gold, cadmium, bismuth, antimony, arsenic, and indium are also recovered as by-products.

John D Turnbull PEng, Assistant Manager, Roger H Watson PEng, Manager, Trail Modernization (centre), receive the APEBC 1982 Environmental Engineering Award from Ken Williams PEng

Trail Operations' Effluent Treatment Plant is part of the modernization and expansion program announced by Cominco in 1977. To the end of December 1982, Cominco has expended about $335-million. It is expected that the modernization program will cost in excess of $700 million when completed and that the internal and external aspects of environmental control will amount to approximately $200-million.

From its earliest days, Cominco has demonstrated a responsible corporate attitude towards the environment and has made concerted efforts to minimize the impact of its metallurgical operations on the environment. Its efforts with respect to environmental control date back to 1927 when it undertook steps to control sulphur dioxide and heavy metal particulate emissions from its smelting operation with the installation of a chamber plant to produce sulphuric acid from zinc roaster gas.

Cominco's efforts, which anticipated environmental legislation by several decades, have paid handsome environmental dividends over the years. The Columbia River at Trail has continued to be a favourite among local sportsmen whose fishing activities range from shoreline angling to trolling from boats. Fish caught above and below the Trail plants are of excellent quality and comply with Canadian and foreign standards for food as shown by studies carried out between June 1977 and October 1981. Studies concerning blood-lead levels, lung function and

general health of local residents have shown that Trail is a good place in which to live and bring up children.

NEW WASTE MANAGEMENT BRANCH REGULATIONS

Notwithstanding the fact that Columbia River water downstream from the Trail plants was well within drinking water standards for metal content, it was anticipated that new, discharge-related Waste Management Branch regulations would ultimately necessitate an effluent treatment plant. Consequently, Cominco Engineering prepared a feasibility proposal which outlined the process and plant design, project schedule and capital cost. Funds for the project were appropriated and the project team was mobilized in October, 1978.

On November 29, 1978, Cominco Ltd was issued Pollution Control Permit No PE-2753. The permit requires that the contaminant loadings in effluents discharged into the Columbia River from Trail metallurgical operations be reduced to meet specific maximum levels of contamination by January 1, 1983. The effluent treatment plant was to operate in conjunction with various metallurgical process improvements and other environmental projects to achieve the stringent quality objectives specified in this permit.

PROCESS TECHNOLOGY

The Trail Operations Effluent Treatment Plant uses the high density sludge (HDS) version of the basic lime precipitation process which was researched intensively by Cominco Ltd. Cominco's first application of this process was the $10 million Effluent Treatment Plant at its Kimberley Operations, officially opened in October 1979.

The HDS process recycles a substantial proportion of the clarifier underflow sludge. This material is blended with the lime slurry necessary for neutralization prior to mixing in the main reaction vessels. The pre-mix is an important feature of the process that modifies the physical characteristics of the sludge solids from a fluffy slime to an almost particulate texture.

In the course of pilot plant testing of Trail Operations effluent, Cominco Technical Research personnel simulated various upset conditions in order to be able to design a plant that would handle the combination of varying flow rates and effluent characteristics from various sewer systems of the complex metallurgical operation.

$9-MILLION TREATMENT PLANT

The $9-million Effluent Treatment Plant for Cominco's Trail lead-zinc operation is one of several environmental projects that ultimately will allow Cominco to meet the new Provincial environmental standards.

Because the plant is located next to a residential area, it was built with aesthetic considerations in mind. Extensive landscaping and an attractive exterior were features of the design.

The plant has a treatment capacity of 4500 litres of effluent process water per minute, but because of the incorporation of a large holding tank for incoming feed, the plant can handle emergency surges of up to 9000 litres per minute. Flows from various sewer systems from 20 separate areas at the Trail metallurgical complex are treated in the plant.

The collection system connecting the various industrial sewers to the treatment plant involved the construction of an underground gravity flow piping system. Thirteen effluent streams from the zinc operations are collected and drained to the treatment plant. The major flow from the zinc plants, roaster off-gas cooling water, is stripped to SO_2 prior to being sent to the treatment plant, thereby minimizing sludge production. Effluent streams from the lead smelter are first collected in a thickener where they are neutralized to pH 6.5. Thickener overflow is then pumped to the plant for treatment.

Effluent streams from the lead smelter and zinc operations are received in a 23-metre diameter mild steel storage tank lined with neoprene rubber for corrosion resistance. The tank is aerated to keep the solids in suspension. Tank exhaust air is water scrubbed and the scrubber effluent water is sent to the reaction tank for neutralization. The storage tank provides a 15-hour surge capacity for blending of the varied feed streams, dilution of acid spills and allows for short-term plant maintenance shutdowns.

From the storage tank, a controlled flow of the combined effluent is pumped to the first of two 106,000-litre fibreglass reinforced plastic (FRP) reaction tanks in series, for neutralization with lime to pH 10. Both reaction tanks are baffled and agitated to ensure proper mixing.

Pulverized quicklime is received pneumatically in a 150-tonne bin from a bulk delivery truck. The bin is provided with a vibrating bin discharger bottom that ensures a continuous flow of material and prevents bridging and rat-holing in the bin. Air is exhausted via a pulse jet bag filter mounted on top of the silo.

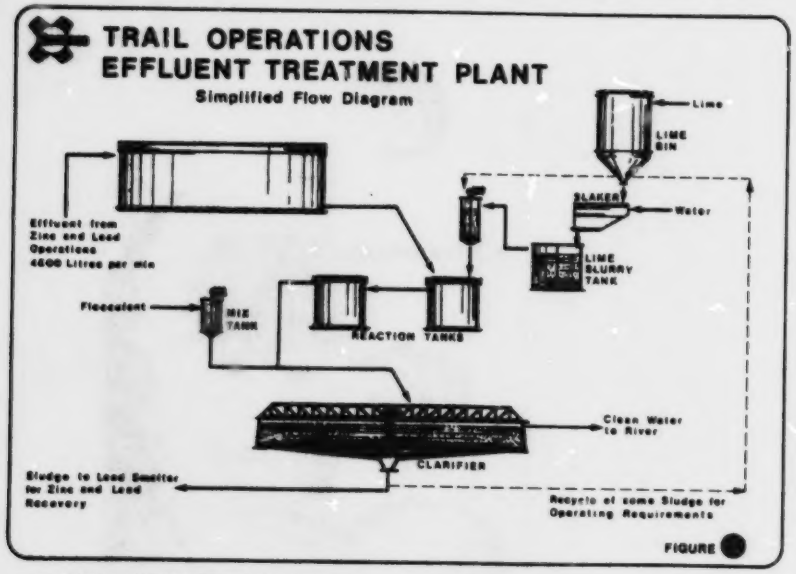
A variable speed screw feeder meters the quicklime into a paste-type lime slaker where it is hydrated. The lime slaker is essentially a mild-steel conveyor trough in which lime and water are mixed with rotating paddles. Hydrated lime is stored as a 10% lime slurry in a 106,000-litre FRP tank. The tank has four internal baffles and is agitated to maintain a homogeneous mixture. Quicklime is drawn off the tank by centrifugal pumps and pumped to a 4000-litre capacity opened top FRP tank where it is pre-mixed with recycled clarifier underflow sludge.

The combined slurry overflows the premix tank and is mixed with the effluent in the reaction vessels where neutralization and precipitation is accomplished. The pH in the reaction tanks controls the lime slurry flow rate to the premix tank.

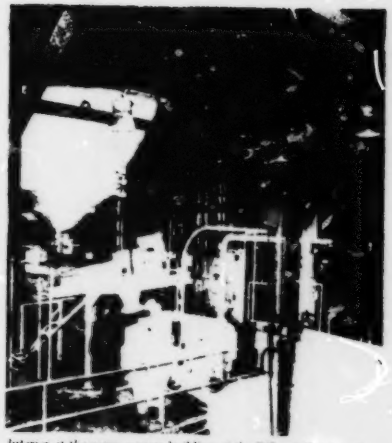
Neutralized effluent slurry from the reaction tanks is mixed with a flocculant in a 3500-litre mix tank which overflows to a clarifier for liquid-solid separation. The flocculant, an organic polymer, is added to improve the settling characteristics of the fine precipitate. This promotes rapid settling of the sludge particles in the clarifier producing a clear effluent overflow for discharge to the Columbia River. This overflow is continuously monitored for turbidity and pH.

The clarifier is a 25-metre diameter by 3-metre deep concrete tank with a slow moving rake mechanism that draws the settled solids to the bottom center cone while allowing incoming solids to settle undisturbed. Settled sludge is removed from the clarifier at about 25% solids. A major portion of this sludge is recycled and mixed with the lime slurry used for neutralization. The balance is pumped intermittently, depending on the sludge production rate, to the Lead Sinter Plant. In the Sinter Plant, the sludge is combined with a reclaimed lead slurry stream, dewatered on a drum filter and mixed with zinc leaching plant residue slurry for treatment and recovery of the metal values. The filtrate joins other Sinter Plant effluent streams for return to the Effluent Treatment Plant.

A simplified flow diagram of the plant is shown in Figure 1.

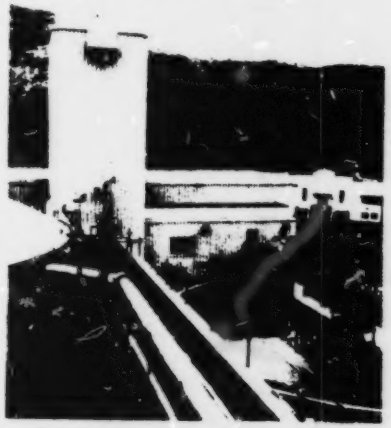


FIGURE



Interior of the main process building of the Effluent Treatment Plant showing the bottom of the lime bin and the lime slaker (beside the operator).

Detail of Cominco's Effluent Treatment Plant at its Trail Operations. At the left is the surge tank, in the background is the main process building and to the right the clarifier.



PLANT PERFORMANCE

Plant commissioning proceeded in an orderly manner with no major problems and the plant was started on June 8, 1981. The startup went smoothly and the maximum design rate was achieved after only three days of operation. Design limits on the discharge turbidity and pH were met from the very first day.

Since startup the new plant has performed as expected.

Recovery of zinc, lead and cadmium from the processed streams has been good:

	% Recovered
Zinc	98.9
Lead	99.5
Cadmium	97.5
Suspended Solids	92.9

The Effluent Treatment Plant has contributed to an overall reduction in heavy metals in the effluent leaving the Trail plants. Columbia River water quality data are shown in Table I.

Operating costs have averaged $50,000 per month with lime cost contributing 40% of the total. The metals recovered in the plant, after subsequent reprocessing costs and other associated savings, serve to offset the operating costs to a large extent. Typical of most environmental control projects, there is no return on the capital invested.

An unexpected benefit of the treatment plant is that it has acted as a "policeman" to the metallurgical operation. Any short term process upsets that previously resulted in unrecognized discharges to the river are now readily detected, their origin traced and corrective action taken. During such upsets, the Effluent Treatment Plant, with its conservative design and surge capacity, acts as an effective buffer to prevent the discharge of metallic effluents to the Columbia Rover.

ENGINEERING AND CONSTRUCTION

The Effluent Treatment Plant was designed to meet the strict requirements of the BC Ministry of the Environment. The process and design specifications which served as the basis for detailed design (see Table II) were established by Cominco Technical Research and the Trail Modernization Group. Because of the environmental focus of the plant, extreme attention was paid to minimizing periods of plant downtime. As a consequence of this philosophy, features such as 100% surge capacity, double piping in certain areas, and installed standby pumps were included in the design criteria.

Project management, project services, overall design responsibility and construction were provided by Cominco Engineering. Hatch Associates Ltd of Toronto were responsible for the detailed design work while process technical services were provided by Cominco Technical Research.

The technology, design, construction and operating expertise developed as a result of this project is now being made available to third parties through Cominco Engineering Services Ltd (CESL), a wholly-owned subsidiary of Cominco Ltd.

ACKNOWLEDGEMENTS. Successful implementation of a project of this nature required the broad spectrum of technology, know-how and experience of a large number of professional engineers, technicians, technologists and specialists from within the Cominco organization. Particular acknowledgement is accorded the following key members of the project team:
P Huszti, Operations Representative
W J Kuit, Assistant Manager, Environmental Control
A R Babcock, Research Chemist
D A Burnett PEng, Project Superintendent
H M Ichiyen PEng (Ontario), Design Superintendent (Hatch Associates Ltd.)
D K MacDonald PEng (Alberta), Construction Superintendent

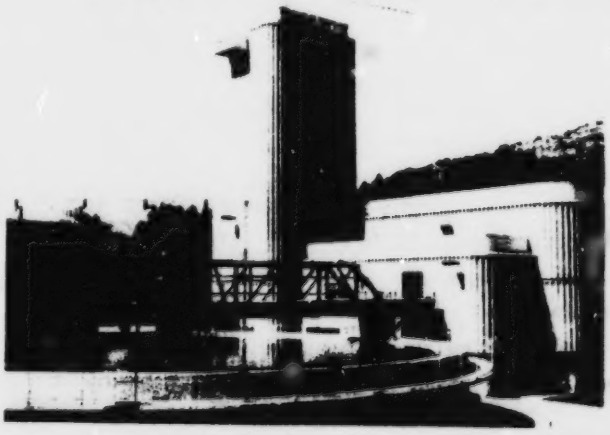
Table I. Typical Columbia River water analysis above (Stoney Creek) and below (Waneta) Trail discharges for 1982

	Stoney Creek	Waneta	Drinking water standard
pH	7.6	7.5	6.5-8.3
Conductivity	153.0	153.0	
Turbidity	2.0	2.0	
	mg/l	mg/l	mg/l
Hardness	67.0	68.0	<180.0
Sulphate	7.9	11.0	<500.0
Fluoride	0.09	0.14	<1.0
PO_4, total	0.03	0.09	<0.2
Mercury, total	<0.00005	0.00005	<0.001
Iron, dissolved	0.04	0.04	<0.3
Lead, dissolved	0.02	0.02	<0.05
Zinc, dissolved	0.02	0.03	<5.0
Copper, dissolved	<0.005	<0.005	<1.0
Arsenic, dissolved	<0.005	<0.005	<0.05
Cadmium, dissolved	<0.005	<0.005	<0.01

Average flow = 2,380 m^3/sec

Table II. Effluent Treatment Plant Data
- Capital cost: $9.0-million
- Completion: June, 1981
- Effluents treated: Contaminated streams from 20 areas in Lead and Zinc Operations
- Effluent collection capacity: 4500 LPM normal; 9000 LPM surge capacity
- Surge tank: 23 metre diameter; 3.6-million litres capacity
- Lime silo: 150 tonnes quicklime
- Lime slaking capacity: 1.8 tonnes per hour
- Process
  - Feed: 4500 LPM normal; 6000 LPM maximum
  - Reactors: two in series, 20 minutes retention time each
  - Lime neutralizes acid and precipitates metal present (usage 11 tpd).
  - Flocculant: use 6 kg/d; added to assist solids settling in clarifier
- Clarifier: 25 metre diameter; 1.7-million litres capacity
- Products: clean water to river; 20 tonnes of sludge per day to Lead Smelter
- Labour: 1 operator per shift
- Operating cost: $50,000 per month

The Effluent Treatment Plant at Cominco's Trail Operations. At the left is the surge tank, to its right the main process building with a tower housing the lime bin and in the foreground the clarifier from which the overflow reports to the Columbia River and the underflow back to the metallurgical plants for the recovery of metal values.



MAGNESIUM CARBONATE TREATMENT PROCESS

BLACK and THOMPSON (1974) describe plant-scale studies of the magnesium carbonate water treatment process in which three primary water treatment chemicals, magnesium, carbon dioxide, and lime are recycled within the process. This process has been installed for municipal water treatment at Montgomery, Alabama, and at Melbourne, Ohio, and it offers significant savings in land disposal requirements and reagents.

The increased floc density of the magnesium process allows higher clarifier loading rates. At the Melbourne, Ohio, plant loading rates were doubled without deterioration in water quality of clarifier effluent.

The levels of several base and heavy metals in water product was significantly lower when the magnesium carbonate process was used compared with conventional lime precipitation tests on the same solutions. The report by BLACK and THOMPSON (1974) on magnesium carbonate water treatment is available from the National Technical Information Service, Springfield, VA, 22151.

The consultants that evaluated this process were:

BLACK, CROW and EIDSNESS, INC.
777 South Lawrence Street
Mongomery, AL
A. P. Black

The address of the Montgomery magnesium carbonate water treatment plant is:

MONTGOMERY WATER AND SANITARY
SEWER BOARD
Post Office Box 1631
Montgomery, Alabama 36102

No references have been found to magnesium carbonate use in minewater treatment. This would be more applicable perhaps for very large installations, large enough to justify recycling plants to recover lime, $MgCO_3$, and CO_2, or where low-cost sources of $MgCO_3$ and CO_2 are available.

MAGNESIUM OXIDE PROCESS

SHILLER and KHALAFALLA (1981) patented a process whereby a substantial excess of essentially dry, powdered magnesium oxide is added directly to feedwater. The resulting precipitate is found to settle very readily to a small volume. The precipitate is not readily redispersed or redissolved. The product water is claimed to be recoverable by simple decantation avoiding the need for filtration, and metals such as Cd, Cr, Cu, Zn, Fe, Mn, Ni, and Pb are effectively removed. An essential difference in the way the

reagent is added is that MgO powder is added dry to the water being treated rather than as a slurry or solution.

The patent application US 325269 is available from the National Technical Information Service, Springfield, VA, 22151, but contains very little information. Their document number is PAT-APPL-6-325-269. The authors are employed by the U.S. Dept. of the Interior; they are Joseph E. Schiller and Sanaa E. Khalafalla, but Randol was unable to find out where.

LIMESTONE ADDITION PROCESSES

Limestone addition can bring pH of solutions up to around pH 6.7 or so, but not high enough to precipitate most base metals quantitatively.

The biggest problem with limestone addition is that iron and other hydroxides precipitate on the surface of the limestone rendering it passive. Several ways around this have been devised:

1. Fine grinding of limestone before addition as a slurry as described at the Onaping operations of Falconbridge in Appendix I and by a Bureau of Mines ROI inserted in Chapter 24 on Acid Mine Drainage Treatment.

2. The use of granular limestone in tumblers driven by a waterwheel powered by the effluent stream itself as demonstrated in Pennsylvania by the state and descirbed in the chapter on acid mine drainage treatment.

3. At Greenside Colliery, South Africa, Gold Fields Mining in conjunction with a supplier, Water Care (Pty) Ltd., attempted to use granular limestone in a "hog trough" shaped contactor fitted with air hoses for periodic attritioning to remove coatings. This proved unsuccessful as a means of neutralizing acid mine drainage. Details and contacts are also provided in Chapter 24 on Acid Mine Drainage Treatment.

NaOH ADDITION

NaOH addition for metal precipitation in effluents works both cleanly and rapidly. The main disadvantage is the extra cost of NaOH which is usually much more expensive than lime.

NaOH addition is, however, convenient and cost effective for small installations where it does not pay to install and operate a lime slaking facility. One such example at the

Onaping minewater neutralization plant is described in the trip report on Onaping in Appendix I. An important consideration is the high freezing point of NaOH solutions, which in all other respects are very convenient to use.

In Chapter 24 on acid mine drainage treatment, a system employing a jet pump and static mixer for instantaineous flash precipitation of metals is described. This system, developed by the Bureau of Mines, Pittsburgh, is portable and requires a minimum capital investment. More information on this innovative system can be obtained from:

BUREAU OF MINES
U.S. Dept. of the Interior
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Terry Ackman

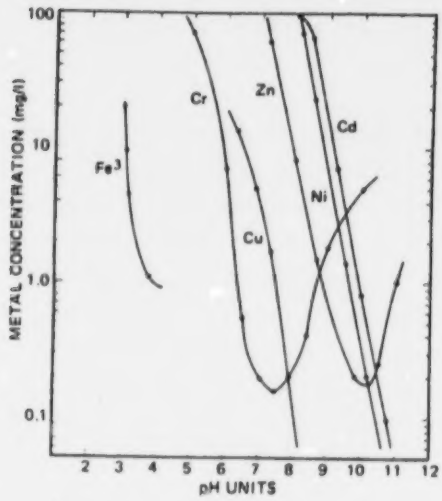
A most innovative new device for flash precipitation of metals using this type of equipment is the flash mixing jet pump for mixing air, NaOH solution, and the feed solution to be treated, as described in Chapter on acid mine drainage treatment. More information on this versatile item of equipment with several different process uses could be obtained from:

BARRETT HAENTJINS CO.
225 North Cedar Street
Hazelton, PA 18201
(717) 455-7711
John R. Ackerman

MINIMUM CONCENTRATIONS ACHIEVABLE BY LIME PRECIPITATION

Metal	Minimum Conc. (mg/l)
Iron	5×10^{1}
Zinc	3×10^{2}
Cadmium	3×10^{0}
Nickel	7×10^{-1}
Copper	2×10^{-2}
Lead	2×10^{0}
Mercury	6×10^{-4}
Silver	2×10^{-1}
Chromium	1×10^{-3}

The above data was taken from the Permutit Co. Technical Bulletin No. 6, Vol. XIII, Code 4413 2002, which references the source as Lange's Handbooke, 11th Edition. More reliable data appears to be that presented in the following graph of metal concentrations at various pH values published by the EPA.



Precipitation of metal salts versus pH

CHEMICAL INTERFERENCE WITH PRECIPITATION

The above indications of minimum concentrations refer to levels in deionized water for pure chemicals. In real life, complexing agents tend to keep higher levels of most metals in solution than the idealized levels. Other factors could reduce the solubility below the levels indicated above; for example, lead would likely be precipitated well below the 2.0 mg/l indicated in the table at alkaline pH due to carbonate levels that occur naturally in water.

HDS and cross-flow microfiltration processes introduce co-precipitation and surface phenomena that reduce metal levels below their theoretical solubilities.

Common complexing agents which would interfere with hydroxide precipitation of metals are:

Humic Acids (Decaying Plant Matter)
Fulvic Acids (Decaying Animal Matter)
Cyanide Ions
Ammonia Ions
EDTA
Solvent Extraction Reagents - Colloidal Suspension
Ion Exchange Resin Fragments
Activated Carbon Particles in Suspension

Frequently, even if metals have been precipitated to their solubility limits, samples of solution, even after settling or filtration, may show higher levels when analyzed. This is

often due to suspension of colloidal particles of precipitate which report in the sample analyzed.

It is wellknown that sequestering agents can be added to $CaSO_4$ and $CaCO_3$ solutions which increase the solubility of these compounds in water by a factor of 300%. Is it not possible that the same type of effects could influence solubilities of other metals, even those that are more sparingly soluble. It is also known that commonly occurring anions such as carbonate, sulfides, and thiosalts can act as complexing agents. For example, carbonate ions complex uranium and also calcium ions. In situ leach leaching solutions are injected underground under pressure, and CO_2 is injected as a lixiviant. When pressure is released and CO_2 allowed to escape, $CaCO_3$ precipitates. H_2S under pressure may dissolve base metals and keep them in solution. At Steamboat Springs, just outside Reno, Nevada, base metals can be observed to precipitate from a hotsprings as sulfur gases exsolve. Of course, temperature effects probably also pay a roll.

H_2S POLISHING OF SOLUTIONS

Sulfides of many metals are much less soluble than the hydroxides. However, a common objection raised against sulfide precipitation is that the sulfide precipitates themselves may potentially become "hazardous wastes" as defined in U.S. regulations. The concern is that if sulfide precipitates are oxidized at some time in the future, the metals will resolubilize. What is unclear is what is so much different about redissolution of metals from a sulfide or from a hydroxide precipitate as to make one preferable to the other?

However, another alternative is to use sulfide addition as a polishing means after as much as possible of the metals have been precipitated using lime or other precipitants. The sulfide may be added in one of several forms including Na_2S, NaHS, or freshly prepared FeS.

Sulfide precipitation and its performance in several cases is discussed in the chapter on acid mine drainage treatment and on the removal of individual cations. A highly innovative use of sulfide precipitation in which sulfide is introduced in the form of FeS was invented by the Permutit Company for application in the treatment of plating wastes.

Information on the patented Permutit process and equipment for their SULFEX Process is provided in Chapter 25 or can be requested from:

THE PERMUTIT CO., INC.
Post Office Box 355
Paramus, NJ 07652
(201) 967-6000
Telex: 134-488
Robert V. Nagiel
Product Manager

It is believed that the General Electric Laboratories have developed a process employing CaS or a mixture of lime and Na_2S for solution polishing, but they failed to respond to enquiries.

In the mining and mineral processing industry, no examples were found where sulfide precipitation is being used in North America for effluent treatment or polishing. During the course of this investigation, the American Mining Congress was suing the EPA on behalf of the mining industry to have them retract the requirement for the use of sulfide precipitation under the BAT regulations for effluents from base metal refineries.

An EPA summary report described the use of sulfide precipitation of heavy metals from a solution containing arsenic, copper, zinc, and fluoride at one of Boliden's smelters in Sweden is included in the section on arsenic removal and on copper removal in a later chapter.

Possibly because of the litigation in progress through 1984 between the EPA and the mining industry, this subject was considered sub-judice.

One metallurgical plant in the midwest was precipitating base metals by sulfide addition before using lime to neutralize a waste acid stream. Before sulfide precipitation was applied, the lime precipitated-gypsum did not pass the EP leach test. However, after inserting the sulfide precipitation step, the gypsum precipitated was disposable in a sanitary landfill. The mining company involved asked not to be identified.

LIME-SULFIDE PRECIPITATION

MIKHNEV, et al. (1978) describe the use of a sulfide solution in $Ca(OH)_2$ to precipitate heavy metals from metallurgical plant effluent. The Cu, Ni, and Fe were precipitated at pH 5.2, 7, and 7-9 respectively. The degree of removal depended on pH and the composition and dosage of the added $Ca(OH)_2$- $S^=$ solution, and to a very limited extent, on temperature (20-80°C). The treatment at final pH 7.5-8 decreased the metal concentrations as follows:

	Inflow	Outflow
Cu (mg/l)	70	0.1
Ni (mg/l)	80	0.01
Fe (mg/l)	10	0.01

The precipitate contained about 12% Cu, 12% Ni, and 20% CaO as CuS, NiS, and $CaSO_4$.

Importantly, the use of $Ca(OH)_2$- $S^=$ solution increased the clarification rate by 50-100%.

USE OF PLANTS TO POLISH EFFLUENTS

In most mining districts where there is adequate precipitation for there to be yearround or even seasonal water flow, marshes are commonly observed in shallow drainage areas.

These naturally occurring marsh-type environments have been observed to "polish" discharged mine and millwater effluents. This phenomenon is discussed in some detail in Chapter 25.

Examples of systems where these polishing phenomena have been observed include AMAX Inc.'s Buick Mine and Mill where a meander system containing macro algae growth polishes metals and flotation reagent organics from the effluent. St. Joe Minerals' Edwards mill tailings final effluent at Balmat, New York, is polished as it traverses a natural marsh. A hugh swamp at Falconbridge Nickel Mines operations outside Sudbury, Ontario, is another example of a marsh containing plants and algae that play a role in water cleanup.

The mechanism for water cleanup may be through metabolic metal uptake by plants and/or algae. Also, however, as the biomass dies back and forms a carbon-rich anaerobic zone at the bottom of the marsh, bacterial action is likely to release enough H_2S (marsh gas) to precipitate metals from solution. Sulfates in the water provide the source of sulfur which is reduced to H_2S or to soluble sulfides or even FeS which would provide a reservoir of sulfide for base metal precipitation. The metal sulfides sink to the sediments on the marsh bed.

Marsh environments serve to host aquatic plants, algae such as Chara, and, of course, bacteria. In developing and engineering such systems to gain optimum results, it is the whole marsh ecosystem that must be examined, not just parts of it. This means that a multi-disciplined R&D effort is needed, not isolated laboratory studies on plants, algae, and bacteria separately.

The huge surface area presented by plants and algae in natural marshes has been observed to polish suspended solids from effluents. It is worth investigating further to what extent such marshes could be engineered to be even more effective. In Ontario, marsh plants and algae are prolific around mine-mill areas in summer but die back during winter. In South Africa on the Witwatersrand, similar marshes are observed wherever water is released, i.e., downstream from minewater discharges, tailings pond runoff release areas, natural springs, etc. The water in the marsh environments closest to tailings dumps is usually red-brown in color, either due to colloidal $Fe(OH)_3$ suspensions or organic marsh-derived compounds. Further downstream after the water has passed through a larger area of marsh, prolific aquatic birdlife is supported in these marshes indicating that the aquatic environment is suitable for numerous aquatic invertebrates as well. Much more work is needed to try and make use of these systems.

The use of plants is largely still in the early stage of investigation. In Canada, the Ontario Ministry of the Environment undertook an interesting experiment to engineer a marsh for the treatment of raw sewage. Also, Dr. Margaret Kalem of Boogum Research is involved in the study of volunteer species in tailings ponds of uranium mills in the hope of finding species that thrive in that environment.

DENSIFICATION AND DISPOSAL OF PRECIPATED SLUDGES

Disposal of precipitate sludges is almost as important as the technology used to form the sludges in the first place. The sludges contain the unwanted contaminants that were removed from water, only in a very much more concentrated form.

Several disposal techniques are employed:

- At Noranda Mattabi Division, a copper-lead-zinc mine, zinc precipitate sludges were formerly added to their zinc concentrate for shipment to the refinery where incremental zinc metal values would be recovered from them.

- At most copper-lead-zinc mine/mill complexes, precipitate sludges are returned to the tailings pond. These sludges are amphoteric for the most part, i.e., they go back into solution if the pH is allowed to become acid, and it is conceivable that this could well happen in tailings ponds containing sulfide minerals. At INCO's Copper Cliff mine and smelter complex, precipitate from the lime-settle-filter water treatment plant is pumped back to the tailings pond. It is true that the amount of metals in the tailings material is usually greater than the amount that is pumped back as a sludge, but is it all as amphoteric as the sludge?

- The (HDS) high density sludge process yields precipitates with up to 50% solids. These sludges, when mixed with cement or certain types of fly ash and lime set up in a pozzolonic reaction which meets the EP toxicity tests and are, therefore, suitable for disposal in sanitary landfills. The Bethlehem Steel Corp. has demonstrated the equipment and process for the formation of pozzolans for safe sludge disposal:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18016
(215) 694-2424
S. T. Herman

- AMAX, Inc., at the Mount Emmons water treatment plant, takes a 2-3% solids precipitate sludge and dewaters it on a Parkson belt press before mixing the dewatered sludge at 12% H_2O with cement in a special mixing device which is cured

and then disposed of elsewhere. After dewatering and mixing with cement, the precipitate passes the EP leach test.

- Where amenable, one of the most innovative ways of disposing of precipitated metal sludges is to dispose of them with tailings that are disposed of using the "semi-dry" or "subaerial" tailings disposal technique. These can have such low permeabilities that the mixing of precipitated metal values into the tailings should effectively encapsulate them preventing metals from leaching out again. It also prevents CO_2 from the air from reaching the precipitates which could become unstable were they to spend years in contact with water and atmospheric CO_2, as described in the case of barium arsenate precipitates, for example. However, "semi-dry" tailings disposal works best in a drier climate and does not make very low impermeability tailings from all types of material. More research is needed to investigate and optimize this aspect.

The stability of sulfide precipitates after these are disposed of is raised as a questionmark. Sulfide precipitates seem to be a lot more stable than hydroxides, and it is curious that industry should be able to live with hydroxide/lime precipitate disposal more easily than with sulfide precipitate disposal. One possible reason is that lime precipitates can be disposed of with an excess of lime which would prevent their acidification and redissolution. Excess sulfide addition to precipitate sludges is not recommended--it seems that acidification of sulfide precipitates may result in the generation of H_2S, a gas more toxic than HCN. However, possibly sulfide sludges could be mixed with lime before disposal to inhibit acidification thereof. Ideally, sulfide sludges should be encapsulated in impermeable "sub-aerial" tailings or mixed with an encapsulating pozzolon. Sponsors are reminded that the Black Sea is named for the color of the sediments found on its shores and on the lake bottom which are black in color because of FeS precipitates that have settled there over millions of years by bacterial action on sulfates. Nature's sulfide precipitate disposal seems to be stable enough.

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Volume

2

VOLUME 2

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FOR

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.)	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon (U.S.)	0.05841
Milligrams per liter	Tons per acre-foot	.001360
Tons per acre	Metric tons per hectare	2.217
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Gallons (Imperial)	Gallons (U.S.)	1.2009
Acre-feet	Gallons	325,851
Acre-feet	Cubic feet	43,560
Cubic feet	Cubic meters	.028317
Cubic feet	Gallons	7.481
Cubic meters	U.S. Gallons	264.2
Cubic meters	Imp. Gallons	220.0
1,000 m^3/d	I gpm	152.8
1,000 m^3/d	U.S. gpm	183.6
U.S. gallon	Cubic meter	0.3785

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Reverse osmosis is an emerging technology for water recovery from saline and brackish water. Numerous, very large reverse osmosis plants are in operation, particularly for potable water recovery from seawater, and a huge number of small units are installed for production of germ-free water, boiler feedwater, and potable water, the latter on board trawlers and naval vessels. A huge effort has gone into membrane development and into the development of improved R.O. modules as well as the ancillary equipment required for R.O. systems (e.g., pumps, valves, controlers, etc.). This effort promises to reduce the cost of installation and to expand the applicability of reverse osmosis. Already, several R.O. systems have been installed in mine-mill environments for boiler feedwater treatment, effluent treatment (one unit at Matthey Rustenburg), and tiny units to supply battery water.

Even though R.O. modules, pumps, valves, etc. may appear simple to hook up and operate, these systems are frought with operating problems. LEGER (1983) described some of the pitfalls and problems experienced by some South African operators who treat Johannesburg tapwater. Most problems could be ascribed to inadequate recordkeeping and lack of knowledge about the sensitivities of R.O. In order for conventional R.O. processes to work reliably, pretreatment of the water is often needed. This would be particularly likely in the treatment of typical mine and mill effluents which contain iron, manganese, Ca^{++}, $SO_4^{=}$, $CO_3^{=}$, and colloidal organic species. WILMOTH (1973) and SASTRI & ASHBROOK (1976) reviewed applications of R.O. to acid mine drainage treatment, but their testwork would have not been able to take into account more recent R.O. improvements.

In order to be used as drinking water, the permeate from R.O. units, as with most desalting processes, may well require post treatment, but this is no major problem.

SOURCES OF INFORMATION ON R.O.

There are several excellent reviews on reverse osmosis including: SRI (1983), SCHUTTE (1983), and BURNS and ROE (1979).

Equipment vendors can supply a wealth of information, but their guidance generally includes a recommendation of their own products.

There are very few companies with experience in mining and metallugical operations and their water needs that also have experience with desalination operations. The closest that one can come would appear to be the service and engineering companies:

RESOURCES CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 828-3400
Telex: 350166
Thomas Wolfe

CH2M HILL
Post Office Box 91500
Bellevue, WA 98009-2050
(206) 453-5000
James D. Mavis

An important aspect about R.O. installations in mine-mill operations is where in the overall system to insert the desalination process. More important even, is the ability and motivation to review the overall water and salt balances of the complex to determine whether installation of a desalination plant can somehow be avoided by creative water management.

PRINCIPLES OF R.O.

There are several good basic texts on reverse osmosis technology. Unfortunately, these are written by academicians who appear more interested in the science of membranes than in their practical application, and their treatises rapidly become complicated and deeply involved with mathematical modelling of membrane transport phenomena which would be of little real interest to a mine or mill operator faced with the need to select an appropriate process for a water treatment problem. One reference book is by KING (1971).

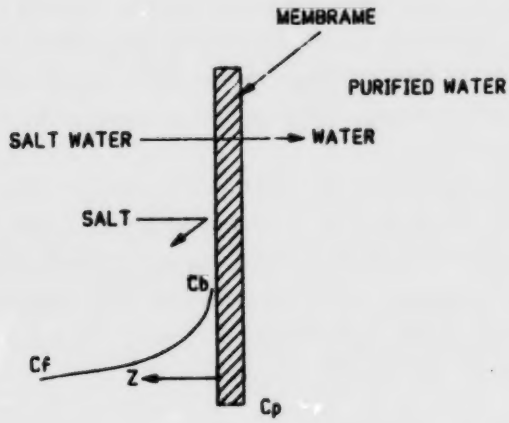
Burns and Roe Industrial Services Corporation, Paramus, New Jersey, prepared a comprehensive document for the U.S. Dept. of the Interior, Office of Water Research and Technology, titled, "Reverse Osmosis Technical Manual," Work Order 4803-01, Contract No. 14-34-0001-8530, July 31, 1979, which provides a very comprehensive description of the reverse osmosis process. Possibly, this document is available from the National Technical Information Service, Springfield, VA, 22151.

In the reverse osmosis process, water flows selectively out of a concentrated salt solution and diffuses through a polymeric membrane and into a solution of low salt concentration. The natural process of osmosis would cause the water to flow in the opposite direction until a pressure imbalance equal to the differential osmotic pressure is built up. The osmotic pressure is proportional to the solute activity and, hence, is approximately proportional to the salt concentration. For natural seawater, the osmotic pressure is about 25 atm. This means that in the absence of other forces, water would tend to flow from pure water into seawater across a membrane permeable only to water--until a static head of 25 atm or 848 ft. of water was built up on the seawater side. At this point, this system would be at equilibrium. If the pressure difference across the membrane were less than the osmotic pressure, water would enter the seawater solution by osmosis but, when the pressure difference across the membrane is greater than the osmotic pressure, water will flow from the seawater solution into pure water side by reverse osmosis. In order for the water passing through the membrane to be salt free in a reverse osmosis process, it is necessary that the membrane be permeable to water but relatively impermeable to salt, since the salt would pass through the membrane with the water if the membrane were salt permeable, i.e., the membrane needs to exhibit good salt-rejection properties.

Reverse osmosis is distinguished from ultrafiltration and dialysis which are also rate-governed separation processes employing thin polymeric membranes. In rate-governed separation processes, mass transfer limitations in the fluid phase on either side of the separation barrier can reduce both the rate of product water transport across the membrane and the separation factor provided by the device.

The diagram below gives a schematic of the mass transfer processes occurring during reverse osmosis. Water passes through the membrane under impetus of the pressure drop

across the membrane (in excess of the osmotic pressure difference corresponding to the drop in salt concentration across the membrane).



Mass transfer processes occurring during reverse osmosis of salt water.

$$F_w = K\ (\Delta P - \Delta\pi) \qquad \text{---1.}$$

Similarly, the salt flux through a membrane is given by the equation:

$$F_s = k\ (C_b - C_p) \qquad \text{---2.}$$

where:

F_w, Fs	=	The water and salt fluxes across the membrane.
ΔP	=	The drop in total pressure across the membrane.
$\Delta\pi$	=	The drop in osmotic pressure across the membrane.
C_b, C_p	=	Salt concentration on the two sides of the membrane.
K, k	=	Empirical constants which depend on the membrane structure and the nature of the salt.

Water coming toward the membrane on the salt water side conveys dissolved salt with it; however, the salt cannot diffuse through the membrane at the rate the water does. As a result, there is an accumulation of salt at the membrane surface. The salt can be removed from the membrane surface only by diffusion back into the bulk salt water. The

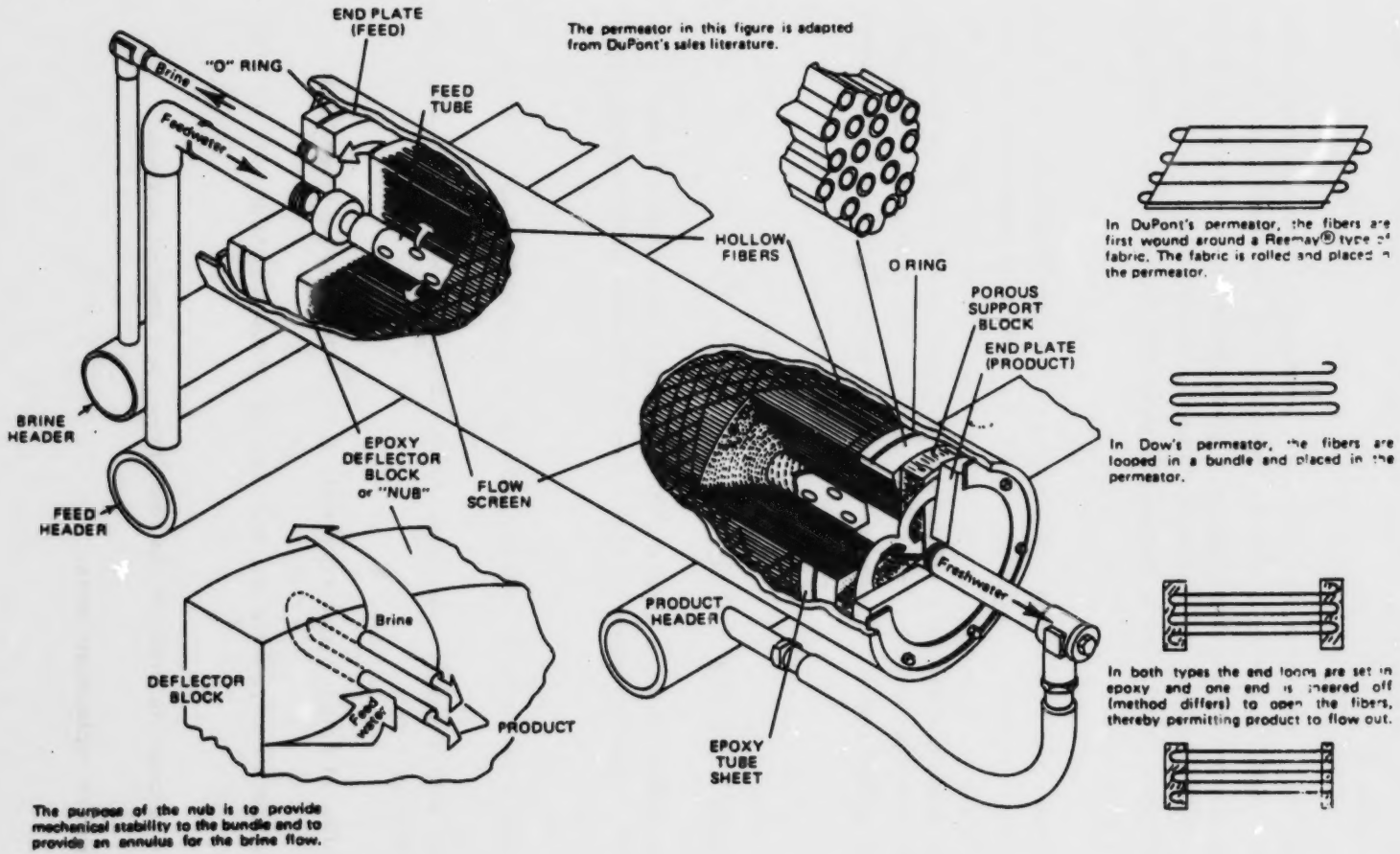


FIGURE 6.3 Permeator assembly for hollow fine fiber membranes. (USAID 1980)

salt builds up a concentration gradient near the membrane surface as shown in the figure below. The flux of salt across the membrane F_s is equal to the difference between: (1) the rate of salt arrival through concentration by the water flux arriving at the membrane surface; and (2) the rate of salt removal from the membrane surface through diffusion back into the bulk liquid.

The increase in salt concentration at the membrane surface--concentration polarization--has two deleterious effects: (1) an increase in C_b increases in equation 1; hence, the water flux across the membrane for a given applied P is reduced; and (2) an increase in C_b gives a higher concentration difference driving force for passage of salt through the membrane in equation 2; hence, the separation factor between water and salt for the process is reduced.

All these effects increase the capital cost and the power requirements per unit of potable water produced. Concentration polarization cannot be eliminated completely in any reverse osmosis process; its magnitude, however, can be reduced in two ways: (1) the bulk solution can be made turbulent to keep the stagnant boundary layer at the membrane surface as thin as possible; and (2) entrance effects can be utilized by using thin channels in the lamina flow region. Commercially available units operate in the turbulent region.

ENGINEERING PROBLEMS AND DESIGN TASKS

The Burns and Roe report identified several difficult engineering problems in the design of a reliable, low cost reverse osmosis system. Some of the more difficult design tasks are:

a. Supporting a fragile membrane to withstand differential pressures of 250-1,000 psi.

b. Preventing the high-pressure feed and brine streams from contact with the low-pressure product water.

c. Obtaining a sufficiently high packaging density to minimize pressure vessel costs.

d. Minimizing concentration polarization and fouling through design of the feed channels.

e. Avoiding parasitic pressure drops in the feed, brine, and product streams.

f. Minimizing membrane replacement costs.

Attempts to solve these problems while meeting economic and reliability criteria have led to four different module designs:

1. Plate and Frame
2. Large Tubes - Tubular R.O.
3. Spiral Wound Membranes
4. Hollow-Fine Fiber Membranes

Each configuration is currently in use for water recovery from various types of wastewater or solutions.

Cellulose acetate and nylon are used as membrane materials. Reverse osmosis units can be arranged either in parallel to provide adequate hydraulic capacity or in series to effect the degree of demineralization. A scale-free quality feed is required for efficient operation of a reverse osmosis unit and, hence, feedwater pre-treatment is usually necessary--or was until seeded slurry tubular R.O. was demonstrated.

R.O. MEMBRANES

The ideal membrane for desalination by reverse osmosis would consist of a thin, inperfection-free film of polymeric material. The transport properties of the material would be such that water can pass through with little hindrance, while presenting a virtually impermeable barrier to salts.

Most polymers approximate this ideal behavior by exhibiting different flow rates or different permeabilities to water and salts. In order for water and simple salts to be transported across the barrier, they must first dissolve into the polymer material. Once dissolved, passage through the polymeric barrier is controlled by diffusion with different ions having different rates of diffusion. This model of transport is commonly referred to as the solution-diffusion model.

To provide a large flowrate of water, and R.O. membrane must be:

- Extremely thin (typically a few hundred angstroms).
- Extremely strong, which requires special support methods.
- Have as large a surface area as possible.
- Be resistant to scaling.
- Be chemically stable to the solution chemistry.
- Be chemically stable to Cl_2 used as a biocide in feedwater.

Support systems have included woven and unwoven fabric, resin starred fiberglass, porous ceramic and metals, hemp paper, and porous plastic.

Commercial R.O. polymer candidates to date have been made from cellulose diacetate (CA), cellulose triacetate (CTA), blends of diacetate and triacetate, polyamide (PA), a nylon-type material, and more recently, composite membranes of polyamide and polyurea. Cellulose acetate, the standard industry "workhorse" is a high flux, low salt rejection membrane which works satisfactorily for brackish water desalination between pH 5-7. Hydrolysis of cellulose acetate reaches a minimum at pH 5 and increases with temperature.

Numerous membrane research and development companies have developed improved membrane materials. These include Albany International who has developed a new sulfonated polysulfonated membrane which is stable from pH 2-12 up to 90°C' and resists Cl_2 attack.

A. D. LITTLE, INC., R.O. MODULE COMPARISON CHARTS

J. D. Birkett of Arthur D. Little compared 125 membrane modules from twelve manufacturers. He computed the flux per unit volume of module and pressure. Membrane manufacturers usually compare flux on the basis of unit area of membrane, but the user is more interested in flux per unit volume of the equipment. BIRKETT (1983) presented the curves showing "pragmatic flux" = $g\ d^{-1}\ ft^{-3}\ PSI^{-1}$. His comparison bring manufacturer data into a comparable format which would be useful in making a preliminary selection of membranes for testing in a pilot plant program.

BIRKETT (1983) can be reached as follows to request copies of his pragmatic flux comparison charts:

J. D. BIRKETT
Arthur D. Little, Inc.
Acorn Park
Cambridge, MA 02140
(617) 864-5770
Telex: 921436

R.O. MEMBRANE LIFE EXPECTANCY

LEGER (1983) and others have pointed out that the life of R.O. membranes should range from 2-6 years. Their life, their flux, and salt rejection performance is mainly dependent on two factors:

1. Fouling which results in decreased permeate flux and, depending on the nature and type of fouling, either an increase or decrease in salt rejection according to BELFORT and ALTENA (1983).

2. Chemical and biological degradation of the active membrane surface which is characterized by an increase in permeate flux and a decrease in salt rejection.

About 150 small R.O. systems have been installed on the Witwatersrand and of those, few kept adequate records. However, the longest production life recorded was 7,400 hours which is equivalent to 10.5 months continuous operation--much shorter than they should last. Permeate quality (conductivity) was the criterion used to determine the need for membrane replacement. Bacteria attack cellulose acetate membranes if feedwater is not sterilized and unless the pH is adjusted, CA membranes also hydrolyze.

R.O. MEMBRANE MANUFACTURERS

FILMTEC CORPORATION
7200 Ohms Lane
Minneapolis, MN 55435
(612) 835-5475
Telex: 290899
Roy E. Larson
R. J. Peterson
P. K. Erikson

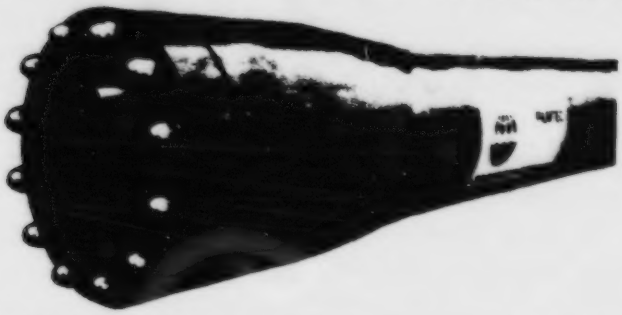
FilmTec manufactures a wide range of membranes, some of which are advanced and sophisticated. Their FT-30 membrane is non-cellulosic and is of a thin-film composite configuration. It satisfies the main requirement of having high flux and excellent salt rejection but, in addition, it is chemically stable, can operate over a broad pH range, and is partially resistant to chlorine exposure and shows good stability at high feedwater termperatures. The latter characteristics facilitate both acid and caustic cleaning, an important consideration under fouling conditions. The membrane was described by LARSON, et al. (1983) at the Florence conference on desalination. The FilmTec FT-30 spiralwound membrane is made of an 0.2 m polyamide barrier layer over a 50 m microporous polysulfone support supported by a 125 m polyester web. LARSON, et al. (1983) showed that the flux and salt rejection of their FT-30 membrane is pH dependent, with a maximum at pH 8.

Literature on commercially available membranes and membrane fabrication and testing for R.O. is very extensive. The Japanese have made major advances in this area as have a handful of U.S. companies. The following test list suppliers of commercial R.O. membrane modules and also companies known to be involved in R&D of improved membranes.

The Filmtec pressure vessel illustrated here costs about $3,000 and can accommodate three R.O. modules, each costing $2-3,000 each. That is, the Tube capable of yielding 17,600 gpd (67 m^3/d) of permeate would cost about $10,500. A 20' pressure vessel with 6 modules costing $21,000 could produce 30,000 gpd (110 m^3/d), with pump, frame, etc. extra.

FILMTEC ANNOUNCES

3-ELEMENT SEAWATER RO MODULE



For single-pass seawater desalting applications where space is limited, such as shipboard use. Made exclusively for FilmTec Corporation by Advanced Structures.

Seawater Performance

Product Water Flow	**17,000 GPD (64m³/d)**
Salt Rejection	**98.8%**

Test Conditions

Average Brine Pressure	850 PSI (5.9 MPa)
Feedwater Temperature	25°C
Recovery	30%

Physical Dimensions

Maximum Diameter	12 in. (.305 m)
Length	11 ft. 2 in. (3.4 m)

OCEANS OF FRESH WATER

FILM TEC CORPORATION

7200 OHMS LANE • MINNEAPOLIS, MINNESOTA 55435 U.S.A.
TELEPHONE (612) 835-6475 • TELEX 29-0899 FILMTEC EDNA

NITTO ELECTRIC INDUSTRIAL

NITTO ELECTRIC INDUSTRIAL CO. LTD.
Ibaraki
Osaka

KAMIYAMA, et al. (1983) reported a new thin-film composite reverse osmosis membrane. Their NTR-7100 R.O. membrane desalts seawater in one pass; it has a high Cl^- rejection. Their NTR-7250 membrane has a low NaCl rejection (50%), but it has an excellent (90%) rejection of divalent ions and organic solutes.

DOW CHEMICALS

DOW CHEMICALS, RHEINWERK GmbH
Water Treatment and Process Prod. Div.
Industriestr 1, Post Office Box 20
D 7587 Rheinmunster 2
West Germany
Dr. Dennis Liebman
Section Head, R&D

The Dow spun holofiber R.O. module produces 20,000 gpd water (75 m^3/d) from seawater.

DOW CHEMICAL U.S.A.
Functional Products and Systems Dept.
2300 Mitchell Drive
Walnut Creek CA 94598

UOP FLUID SYSTEMS DIV.

FLUID SYSTEMS DIVISION
UOP, Inc.
10124 Old Grove Road
San Diego, CA 92131
(714) 695-3840
Randy Truby

This 12" Ø x 60" module recovers 20,000 U.S. gallons per day (75 m^3/d) and accepts feedwater filtered to minus 25 m. These modules will be installed at the Colorado River water treatment plant, Yuma, Arizona.

Randy Truby can be reached as follows:

RANDY TRUBY
515 Navarra Drive
Scots Valley, CA 95066
(408) 438-5079
(408) 459-1166

UOP, FLUID SYSTEMS DIVISION
Johnson House
Browells Lane
Feltham, Middlesex
England TW13 7EQ
(01) 890-7130
Telex: 296718
Dennis Sherman

Developing a polyamide thin-film composite membrane to achieve higher salt rejections and to extend the pH range; now working on developing a Cl_2-resistant TFC membrane.

UOP, FLUID SYSTEMS DIVISION
Membrane Development Group
Des Plaines, IL

ROPUR A.G.
CH 4001 Basel
Switzerland
(061) 232309
Telex: 62069
Klaus Kallenberg

TORAY INDUSTRIES, INC.
Otsu, Shiga, 520, Japan
R. Bairinji

TORAY INDUSTRIES, INC.
New Projects Development Dept.
2-2, Nihonbashi-Muromachi
Chuo-ku, Tokyo 103, Japan
(03) 245-5708
Telex: J22623

BAIRINJI, et al. (1983) described the characteristics and operating history of cellulose acetate membranes in which performance and durability were improved by using new additives. The membrane is an asymetric structure reinforced by fabric and is wound in a spiral-type configuration which differs from other spiral-wound elements.

Toray Industries also manufactures composite membranes with 0.2 u protective layers, 300 Å salt barrier layer and porous supporting membranes of polysulphone. The Toray synthetic composite membrane PEC 1000 offers the following advantages:

1) High Salt Rejection
2) High Flux Rate
3) High Temperature and Pressure Durability; however, dechlorination and O_2 removal is necessary.

The Water Research Promotion Council at Chigasaka, Japan, has tested Toray membrane modules.

HYDRONAUTICS

HYDRONAUTICS WATER SYSTEMS
Post Office Box 3690
Santa Barbara, CA 93105

HYDRONAUTICS WATER SYSTEMS
Post Office Box 1068
Goleta, CA 93017

This company is also a supplier of modules for the U.S. government Colorado River R.O. plant, Yuma, Arizona.

RESEARCH PRODUCTS COMPANY

RESEARCH PRODUCTS COMPANY
Membrane Products Div.
Kiryat Weizman Ltd.
Post Office Box 138
Rehovot,
Israel

R&D R.O. membrane products for hostile environments.

DU PONT (PERMASEP MEMBRANES)

E. I. DU PONT NEMOURS & CO. (INC.)
Permasep Products
Glasgow Site
Wilmington, DE 19898
(302) 453-2400
Telex: 835420
Tom Sackinger

DU PONT (U.K.) LIMITED
Polymer Products Dept.
Maylands Avenue
Hemel Hempstead
Herts, England
(0442) 61251
Telex: 825713

Du Pont Permasep holofine fiber membranes are installed in dozens of desalination plants throughout the Middle East and the Carribbean. Permasep holofine fiber R.O. modules are installed at the 20,000 m^3/d seawater desalination plant at Ghar Lapsi, Malta, which consumes 6 kWh/m^3 water recovered. This plant employs 10 trains of 136 Permasep modules, i.e., 1,360 in all. Five cartridge filters screen suspended solids at 1 m but when the plant settles down, these will be changed to 5 m filters.

ALBANY INTERNATIONAL
Membrane Technology Group
Norwood, MA
(617) 769-6310
Myron Coplan
General Manager
Alla Kan
Michael Nahl

R&D R.O. membrane products also for gas separations.

TOYOBO HOLOSEP MEMBRANES
Environmental Plant Engineering Dept.
8-2 Marunouchi 1-chome
Chiyoda-Ku, Tokyo, Japan
(03) 218-6467
Telex: 222-3601

ENRO®

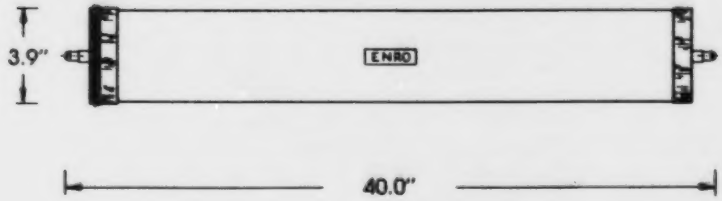
ENVIROGENICS SYSTEMS COMPANY

EL MONTE, CALIFORNIA

ENRO® SPIRAL WOUND REVERSE OSMOSIS ELEMENT

BRACKISH WATER ELEMENT 495-18

Shipping Weight
11 lbs.



INITIAL PERFORMANCE UNDER STANDARD REFERENCE TEST CONDITIONS

Chloride Ion Rejection	Design:	95%			Min:	93.5%
Permeate Flux (GPD)	Design:	1750	Max:	1950	Min:	1550

STANDARD REFERENCE TEST CONDITIONS

Net Driving Pressure	400 PSI
Solution Temperature	77°F (25°C)
Recovery Rate	10%
Feed Water Solution	2000 mg/l NaCl

OPERATING CONDITIONS*

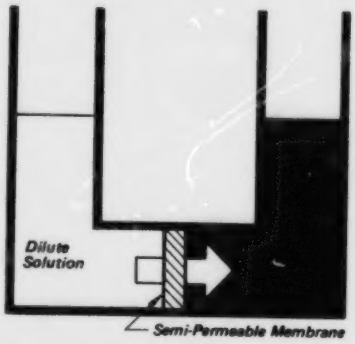
Operating Pressure-	
Normal applied pressure	420 PSI
Maximum applied pressure**	600 PSI
Operating Temperature-	
Normal temperature	77°F (25°C)
Maximum temperature**	104°F(40°C)
Suggested Maximum feed flow	12 GPM
Suggested Minimum concentrate to permeate flow ratio for any element	6:1
Maximum Element Pressure drop	12 PSI
Maximum Vessel Pressure drop	60 PSI
Feed Water pH (preferred range)	5.0 - 6.0
Feed Water pH (maximum range)	4.0 - 6.5
Maximum Feed water turbidity	1.0 NTU
Maximum Feed water S.D.I.	4.0
Feed water chlorine-	
Maximum continuous exposure	1.0 mg/l
Preferred continuous exposure	0.5 mg/l

*Information appearing on this data sheet is supplied for comparison purposes only. Further information is required to properly design a reverse osmosis system utilizing ENRO® elements. For additional details on system design contact EBCO OEM Sales Department.
**Operating pressures should normally be reduced as temperature increases.

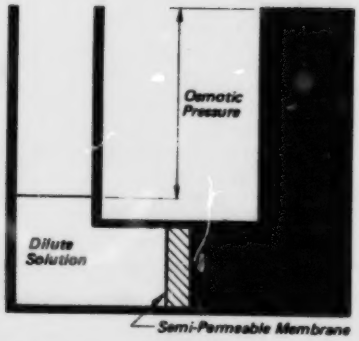
ENVIROGENICS SYSTEMS COMPANY

9255 TELSTAR AVENUE • EL MONTE, CALIFORNIA 91731 • (213) 573-9220 • TELEX 698706

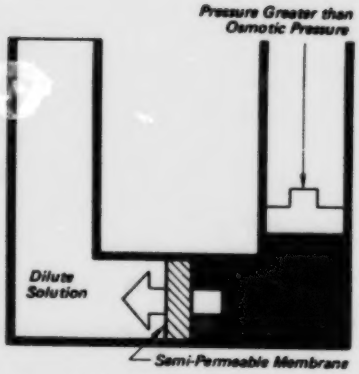
Reverse Osmosis at a Glance



When fluids of different degrees of concentration are separated by a semi-permeable membrane, the water permeates through the membrane from the dilute solution into the concentrated solution. This is known as *Osmosis.*



The osmotic flow continues until a state of equilibrium is reached. Once equilibrium is attained, the difference in fluid level becomes equal to what is known as *Osmotic Pressure* of the solutions.



Should pressure in excess of osmotic pressure be applied to the concentrated solution, the water in this solution will permeate into the dilute solution. This is called *Reverse Osmosis,* a process involving neither phase transition nor chemical reactions. Reverse osmosis process can thus be applied to any water purification process requiring the separation of fluids into permeate and concentrate forms.

Toray Reverse Osmosis Modules: Description

Reverse osmosis process requires the use of modules, of which there are three types on the market. Toray Modules are the spiral type and, as you can see on the following comparative table, are distinguished by economy, high performance and other features compared to the tubular and hollow fiber types.

Item / Module Type	Toray Spiral	Tubular	Hollow Fiber
Water Recovery Ratio and Efficiency	High	Low	Moderate
Product Flow Rate (Flux) per Module	Moderate	Small	Large
Pre-Treatment and Membrane Cleaning	Simple	Simple	Complicated and Laborious
Quality and Level of Operation Required	Stable and Easy Operation	Stable and Easy Operation	Much Attention Required
Water Cost	Low	High	Low

Holofine fiber system used in the Koberox system marketed by Kobe Steel Ltd.

BINTECH (PTY) LTD.
Post Office Box 344
Paarl 7620
South Africa
(02211) 2-3031
Telex: 57-27181
Peter S. Wart
Commercial Manager
D. B. Smit
Managing Director
Johan Barnard
Project Manager

BINTECH (PTY) LTD. manufactures a highly innovative low-cost plastic supported tubular R.O. cellulose acetate membrane module and system. Each module is capable of producing 1 m^3/d permeate. These modules were installed on the RCC seeded slurry test plant at East Rand Proprietory Mines Ltd. acid mine drainage desalination demo facility in South Africa. Bintech R.O. modules are installed for seawater desalination at Robben Island off Cape Town and for sewage water reclamation at Port Elizabeth, South Africa, as well as in an experimental unit for preparation of boiler feedwater at Vaal Reefs Exploration and Mining Co., Orkney, Transvaal.

ABCOR, INC.
850 Main Street
Wilmington, MA 01887

ENVIROGENICS SYSTEMS CO.
9255 Telstar Avenue
El Monte, CA 91731
(213) 573-9220
Telex: 698706

OSMONICS, INC.
15404 Industrial Park
Hopkins, MN 55343
(612) 933-2277
Dean Spats

DDS-RO-DIVISION
Post Office Box 149
DK-4900-NAKSOV
Denmark
Mr. W. Kofod Nielsen
Division Manager,
Membrane Science

This division of Danish Sukerfabriken manufactures plate and frame R.O. membranes and systems primarily to treat cheesewhey.

R.O. SYSTEMS AND COMMERCIAL EXAMPLES

There are many companies that build reverse osmosis systems around commercially available R.O. modules discussed above. These applications vary from hand pumped miniature systems to provide emergency drinking water for lifeboats to 20,000 m^3/d and larger seawater desalination systems such as the one at Malta. The U.S.A. is constructing a mammoth R.O. system at Yuma, Arizona, to reduce the salt content of the Colorado River before it flows into Mexico. The Yuma desalting test program at the Yuma Desalting Test Facility tested eight reverse osmosis units and four ED units accumulating 120,000 hours of operating time between November, 1974, and April, 1977, operating on pretreated brackish water from the Wellton-Mohawk Irrigation and Drainage District. This feedwater has a salinity in excess of 3,500 mg/l. Their test results not reported here are useful.

There are several system configurations that can be considered, depending on the nature of the feed and the quality objectives of the product.

Most conventional systems for desalination of brackish water require a pretreatment plant for disinfection to inhibit bacterial action, pH adjust, removal of iron and manganese by lime treatment, softening, Cl_2 dechlorination, and final pH adjustment to around 5.5, etc. as needed.

The actual R.O. system may be a combination of modules in series and in parallel. The seeded slurry R.O. system arrangement incorporates a special slurry recirculation system.

Advanced system designed for maximum recovery and minimum concentrate volume may combine a pretreatment system, R.O. system (several series systems in parallel) followed by an evaporator for brine concentrate treatment and further recovery of water.

The only two R.O. systems observed in operation to treat mine and mill effluents were:

1) Seed slurry R.O. pilot plant at 5.0 m^3/d at East Rand Proprietory Mines Ltd. on mine drainage (Rand Mines). See the Appendix I trip report.

2) Cass Africa (Pty) Ltd. conventional R.O. System to treat utilities water effluent at the Rustenburg Refinery (Platinum) in South Africa, also described in an Appendix I trip report.

Companies that design and install reverse osmosis water treatment systems include:

RESOURCES CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Tom Wolfe

CH2M HILL
Post Office Box 91500
Bellevue, WA 98009-2050
(206) 453-5000
James D. Mavis

FOSTER WHEELER ENERGY LTD.
Foster Wheeler House
Rosebank, Sandton
South Africa

CASS AFRICA (PTY) LTD.
Post Office Box 51051
Randburg 2125
(011) 789-2908
Telex: 4-22152

CASSCORP
6777 Nancy Ridge Drive
San Diego, CA 92121
(619) 450-2114
Telex: 697134

BINTECH (PTY) LTD.
Post Office Box 344
Paarl 7620
South Africa
(02211) 23031
Telex: 57-27181
D.B. Smit
DESALINATION SYSTEMS, INC.
1107 West Mission Drive
Escondido, CA 92025

ENVIROGENICS SYSTEMS CO.
9255 Telstar Avenue
El Monte, CA 91731

FLUID SYSTEMS DIVISION
Universal Oil Products
2980 North Harbor Drive
San Diego, CA 92101
(714) 299-9920

HYDRONAUTICS WATER SYSTEMS
Post Office Box 1068
6338 Lindmar Drive
Goleta, CA 93017

OSMONICS, INC.
15404 Industrial Road
Hopkins, MN 55343
(612) 933-2277
Dean Spatz

AJAX INTERNATIONAL DIV.
Babcock & Wilcox Ltd.
Scripps Ranch Industrial Park
San Diego, CA

BASIC TECHNOLOGY, INC.
1744 Donna Road
West Palm Beach, FL 33409

Culligan U.S.A.
One Culligan Parkway
Oak Brook, IL 60062

ECODYNE GRAVER WATER DIVISION
2720 U.S. Highway 22
Union, NJ 07083

ILLINOIS WATER TREATMENT
1669 Shepard Trail
Rockford, IL 61105

INFILLO DEGREMONT, INC.
Kroger Executive Center
Box K-7
Richmond, VA 23288

LOS ANGELES WATER TREATMENT DIVISION
Chromalloy American Corporation
17400 East Chestnut Street
City of Industry, CA 91749

PERMUTIT CORPORATION
#49 Midland Avenue
Paramus, NJ 07652

NEPTUNE Microfloc
Membrane Systems
1965 Airport Road
Post Office Box 612
Corvallis, OR 97330

BATEMAN ENGINEERING LTD.
Post Office Box 565
Boksburg 1460
South Africa
(011) 899-9111

TRITON WATER SYSTEMS, INC.
4867 Mercury Street
San Diego, CA 92111

WATER SERVICES OF AMERICA, INC.
Post Office Box 23421
Milwaukee, WI 53223

SEABRACK PTY LTD.
Post Office Box 14377
Waderville 1422
South Africa
(011) 340415
Dennis Mitchell
(Small Shipboard Potable Water
and Battery Water Units)

AQUAMEDIA, INC.
20 Park Street
Princess Resborough
Buckinghampshire HP179AL
(08444) 7177
Telex: 837268
Michael Stefanic

OSMONICS, INC.
15404 Industrial Road
Hopkins, MN
(612) 933-2277
Dean Spats

DOW CHEMICALS U.S.A.
Functional Products and Systems Dept.
2300 Mitchell Drive
Walnut Creek, CA 19898

E.I. DU PONT DE NEMOURS & CO. (INC.)
Permasep Products
Glasgow Site
Wilmington, DE 19898
(302) 453-2400
Telex: 835420
Tom Sackinger

FILMTEC CORPORATION
7200 Ohms Lane
Minneapolis, MN 55435
(612) 835-5475
Telex: 290899

UOP, INC.
Fluid Systems Div.
10124 Old Grove Road
San Diego, CA 92131
(714) 695-3840
Randy Truby

KOBE STEEL LTD.
Environmental Plant Engineering Dept.
8-2 Marunouchi 1-Chome
Chiyoda-Ku, Tokyo, Japan
(03) 218-6467
Telex: 222-3601

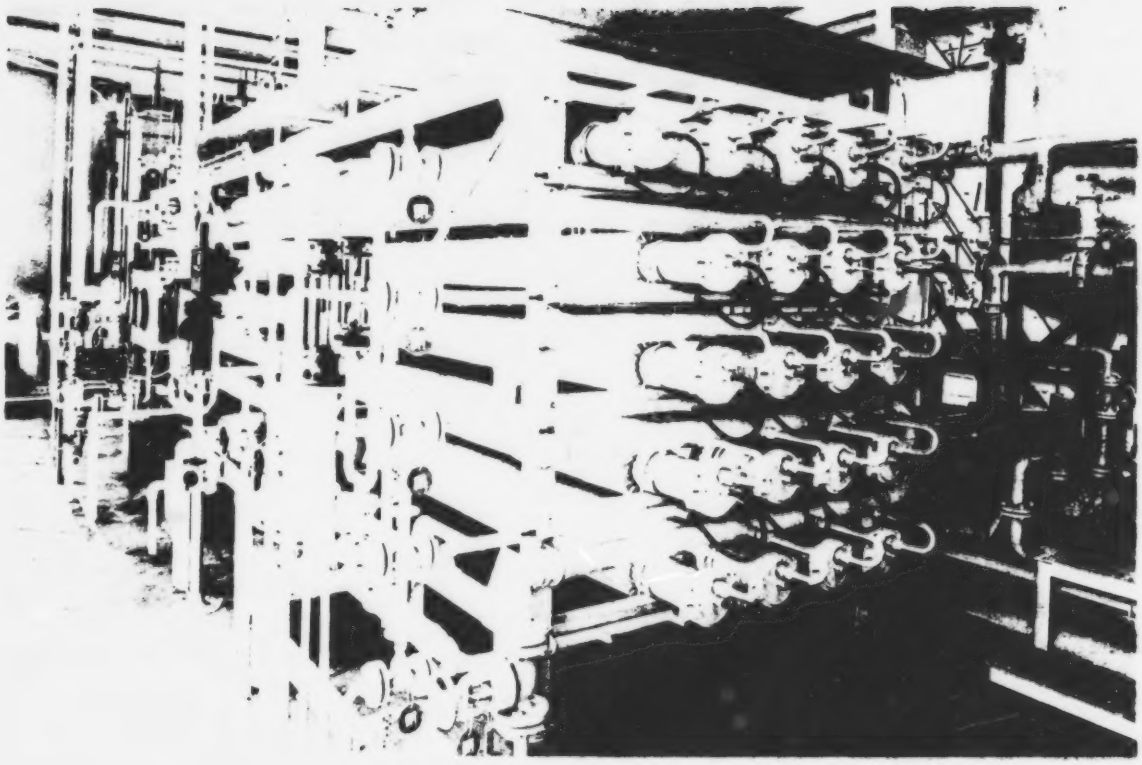
POLYMETRICS, INC.
1005 Timothy Drive
San Jose, CA 95133
William T. Andrews

TYPICAL R.O. PERFORMANCE

Conventional R.O. performance in seawater desalination is typically 30-35%. Since there is an unlimited supply of feed and a cost-free disposal opportunity, there is little or no incentive to tackle the problems of recovering more than this.

Conventional R.O. processes recover 60-70% from brackish water before the concentrate becomes so concentrated as to present problems. These could be overcome by retreating the concentrate, depending on its gypsum concentration to squeeze additional recovery, perhaps to 80%. In general, R.O. can treat $CaSO_4$-containing water until the $CaSO_4$ concentration in the concentrate reaches 300% of saturation which is the maximum that can be kept in solution by anti-scaling agents. The recovery at which this level in the concentrate is reached is generally as far as one can safely go before the membrane would become fouled.

Seeded slurry R.O. has been demonstrated on a scaling $CaSO_4$-containing minewater to achieve over 95% recovery.



Now, you know why Toray Modules are ideal for reverse osmosis plants

You save on energy.

Compared to other desalting processes, reverse osmosis process gives you savings on energy because the process needs only compression energy and no phase transition. Furthermore, Toray Reverse Osmosis Process provides the highest recovery ratio and requires less energy than other reverse osmosis processes.

You save on space.

Toray Spiral Wound Reverse Osmosis Modules are compact, high-membrane-density modules, thus requiring less space for installation.

Operation is simple.

Toray Process does not require any complicated plant installation. "Start up" or "Shut down" requires only to switch ON/OFF – no special training is required.

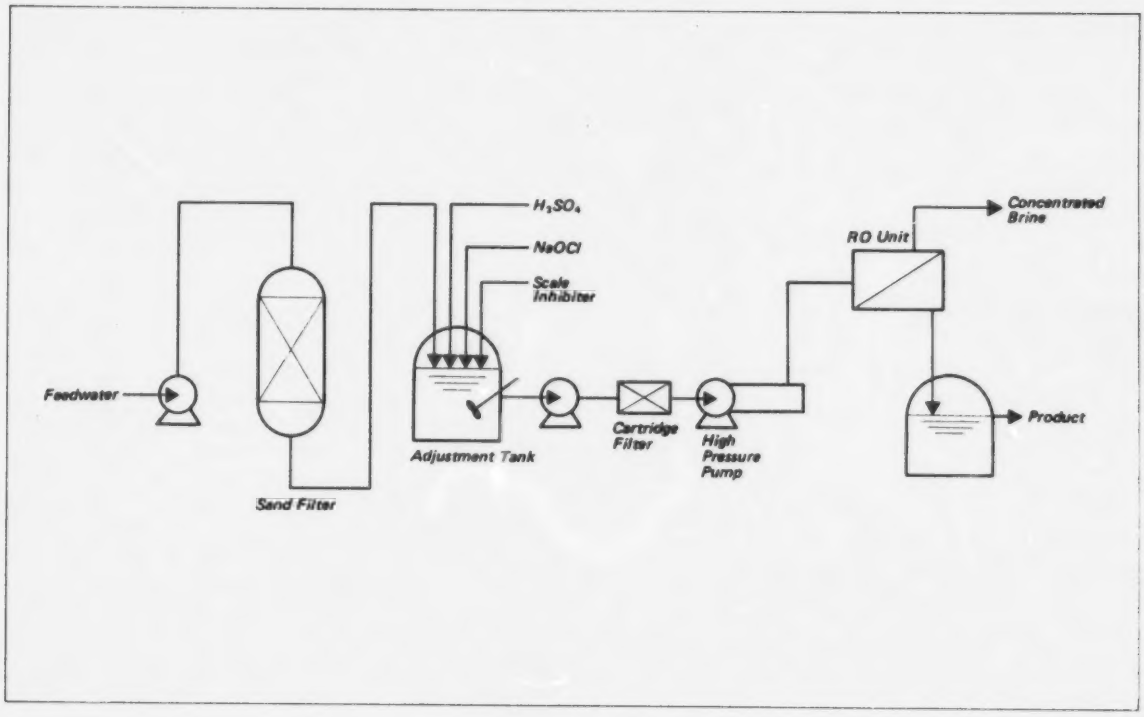
Maintenace is easy.

There is little trouble in the operation and the maintenance is very simple and easy with periodical module exchange; you do not need specially skilled operators.

You can get the modules promptly.

Toray Modules are promptly supplied at short notice. We can supply you with a complete reverse osmosis plant in no time at all.

Brackish Water Desalination and Wastewater Treatment



This technique, which also utilizes Toray Spiral Wound Module, offers such standout features as high recovery operation due to uniform flow and less polarization. The module itself is tough, assuring low maintenance cost.
The large membrane surface area is complemented by large permeate flow. The product water itself is characterized by a high level of purity, allowing its use in potable water or industrial water.

Item		Raw Water	Desalted/ Treated Water
TDS	ppm	1525	149
M-Alkalinity	ppm ($CaCO_3$)	118	11
Total hardness	ppm ($CaCO_3$)	681	48
Calcium hardness	ppm ($CaCO_3$)	532	35
Chloride	ppm (Cl^-)	860	78
Sulphate	ppm (SO_4^{2-})	110	1.5
Silica	ppm (SiO_2)	23	3
pH		7.1	6.5
Turbidity	ppm	5	0

Specifications

4-Inch Modules

Type	Salt Rejection (%) Min.	Salt Rejection (%) Ave.	Flux (m^3/d) (GPD) Min.	Flux (m^3/d) (GPD) Ave.
SC-1100 (High Flux)	94	95	5.2 1370	5.8 1530
SC-3100 (High Rejection)	96	97	4.0 1060	4.4 1160
SC-5100 (Seawater Desalination)	95	96	2.0 530	2.2 580

8-Inch Modules

Type	Salt Rejection (%) Min.	Salt Rejection (%) Ave.	Flux (m^3/d) (GPD) Min.	Flux (m^3/d) (GPD) Ave.
SC-1200 (High Flux)	94	95	20.8 5480	23.2 6120
SC-3200 (High Rejection)	96	97	16.0 4240	17.6 4640
SC-5200 (Seawater Desalination)	95	96	8.0 2120	8.8 2320

Test Conditions

Item	*Module*	*SC-1100, 1200 3100, 3200*	*SC-5100, 5200*
NaCl Solution (ppm)		*1,500*	*35,000*
Pressure *(kg/cm²)* *(psi)*		*30* *430*	*56* *800*
Temperature *(°C)* *(°F)*		*25* *77*	*25* *77*
Recovery Ratio (%)		*30*	*15*
Operation Time prior to Data Collection (hr)		*1*	*1*

Dimensions and Weight

Type	Dimensions	Weight	Membrane
4-Inch Module	ϕ102mm x 1016mm ϕ4in x 40in	6.3 kg 13.9 lb	Modified Cellulose Acetate
8-Inch Module	ϕ201mm x 1016mm ϕ7.9in x 40in	22 kg 48.5 lb	Modified Cellulose Acetate

Operating Conditions

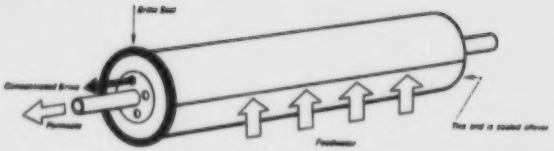
Item	Recommended Conditions	Allowable Conditions
Maximum Pressure SC-1100, 1200, 3100, 3200 SC-5100, 5200	 30 kg/cm² 430 psi 56 kg/cm² 800 psi	 42 kg/cm² 600 psi 70 kg/cm² 1000 psi
Maximum Temperature	30°C 86°F	40°C 104°F
pH Range	4 – 7.5	3 – 8.5
Maximum Feedwater Chlorine Concentration	1 ppm	3 ppm

P-Type Modules

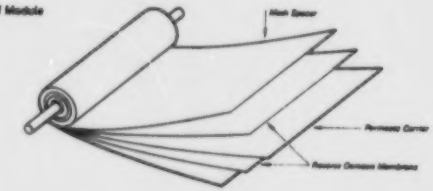
Designed for special applications, this type of module produces ultra-pure and germ-free water for use in the electronics and medical industries. It is available in 4-inch and 8-inch configurations. Reverse osmosis performance is equivalent to that of standard types.

Basic Configuration

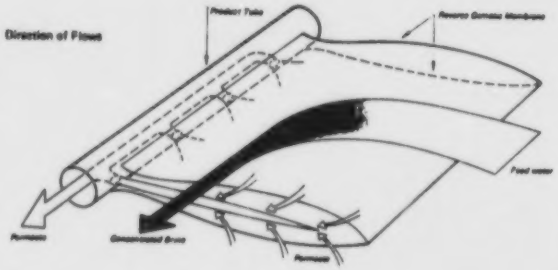
Exterior View of Module and Direction of Flows

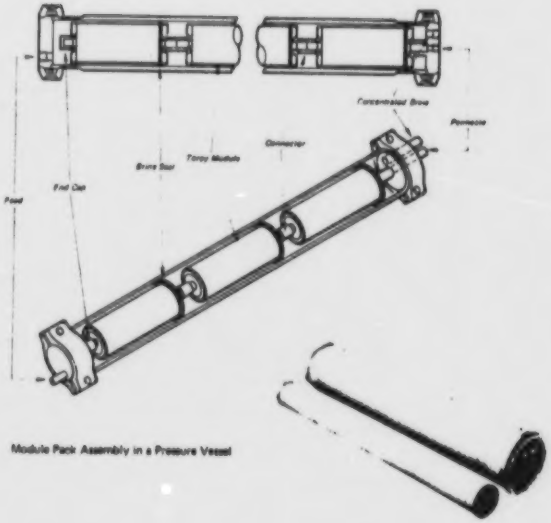


Materials of Module



Direction of Flows





Module Pack Assembly in a Pressure Vessel

Main Advantages of Toray Spiral Wound Modules

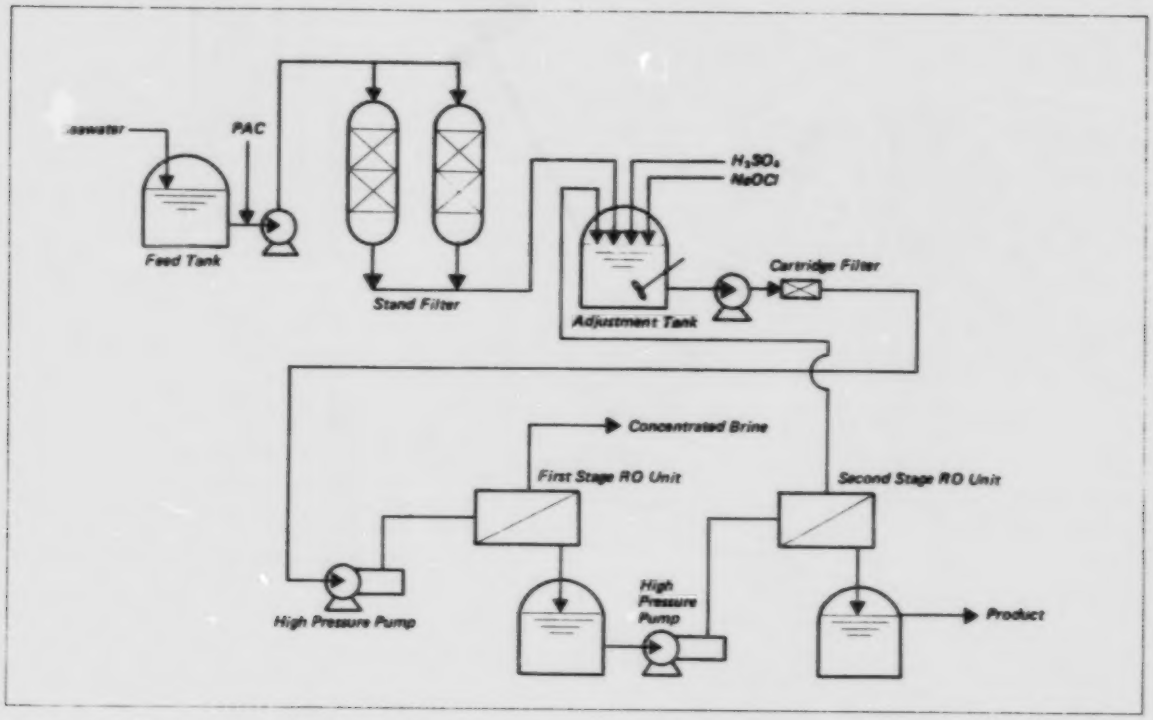
1. The high water speed of the brine on the membrane's surface minimizes possible polarization trouble.
2. Reverse osmosis performance does not deteriorate, even when the recovery ratio is increased or the brine flow rate is reduced.
3. There is no dead space trouble as the position of the brine seal is different from that of other spiral wound modules.
4. There is no telescope deformation trouble.

Major Applications

1. Desalination of seawater provides potable water in isolated islands or coastal areas.
2. Desalination of brackish water provides potable water or industrial water.
3. Wastewater reclamation provides industrial water.
4. Production of ultrapure water for electronics industry or germ free water for medical and pharmaceutical industries.
5. Recovery of valuable and useful substances from wastewater in food and painting industries.
6. Various solutions containing saccarides, proteins and enzymes can be concentrated.

Toray Reverse Osmosis Process in Action

Seawater Desalination



Toray's two-stage seawater desalination technique is distinguished by superbly constant and stable performance to produce high quality sweet water. Thanks to its unique module structure, Toray Modules assure a high recovery ratio, minimized polarization effect and no telescopic deformation whatsoever. The overall performance is the world's most outstanding and requires the use of very little energy, further enhancing the system's economy.

Item		Seawater	Desalted Water
TDS	ppm	34080	133
M-Alkalinity	ppm ($CaCO_3$)	29	1.5
Sodium	ppm (Na^+)	11100	48.5
Potassium	ppm (K^+)	403	2.8
Calcium	ppm (Ca^{2+})	324	0.1
Magnesium	ppm (Mg^{2+})	1260	0.3
Chloride	ppm (Cl^-)	18300	76.7
Sulphate	ppm (SO_4^{2-})	2690	tr
pH		8.2	5.4
Turbidity	ppm	5	0

Fluid systems by uop

CURRENT INSTALLATIONS

NAME	SIZE/GPD	APPLICATION
Acuamem (Argentina)	20,000	Potable Water (Arsenic Removal)
Aquabaja (Mexico)	50,000	Potable Water
Arco Polymers (Pennsylvania)	30,000	Boiler Feedwater
Beverage Canners (Florida)	100,000	Potable Water
Bryn Mawr (Florida)	110,000	Potable Feedwater
Burroughs (California)	50,000	Electronic Rinse Water
Burroughs (California)	30,000	Ultrapure Water
CODELCO (Chile)	132,000	Potable Water (Arsenic Removal)
CODELCO (Chile) (expansion)	132,000	Potable Water (Arsenic Removal)
Coca-Cola (Campeche, Mexico)	61,000	Soft Drink Manufacture
Coca-Cola (Can-Cun, Mexico)	60,000	Soft Drink Manufacture
Colorado River Desalting Project (Arizona)*	73,100,000	Irrigation Waste Treatment
Comision Federal de Electricidad, Nachi Cocom (Mexico)	64,000	Boiler Feedwater
Comision Federal de Electricidad, Rio Bravo (Mexico)	444,000	Boiler Feedwater
Compania Peñoles (Torreón, Mexico)	264,000	Potable Water
Continental Can Company (Wisconsin)	60,000	Process Water
Culligan (Ecke Ranch, California)	50,000	Irrigation of Seedlings
Denver Water Board (Colorado)	125,000	Process Tertiary Effluent
D.I.G.A.A.S.E.S. (Mexico)	50,000	Potable Water
El Dorado (Kirkwood Meadows, California)	50,000	Sewage Reclamation
Electra-Tronics (Florida)	6,000	Potable Water
Electricidad de Caracas (Venezuela)	100,000	Potable/Process Water
Fairchild Semiconductor (California)	30,000	Electronic Rinse Water
Fairchild Semiconductor (Maine)	120,000	Ultrapure Water
FAMOSA (Ensenada, Mexico)	165,000	Boiler Feedwater
Gasparilla Shores (Florida)	10,000	Potable Water
G & M Finishing (Pennsylvania)	272,000	Textile Waste for Reuse
Hill AFB (Utah)	30,000	Potable Water

*Letter of Intent received.

Fluid systems Division
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uop Inc

Rev 5/82

CURRENT INSTALLATIONS

NAME	SIZE/GPD	APPLICATION
HRH - The Crown Prince (Saudi Arabia)	26,400	Potable Water
HRH - Prince Abdullah Bin Abdul Aziz (Saudi Arabia)	26,400	Potable Water
HRH - Prince Sultan Abdul Aziz (Saudi Arabia)	26,400	Potable Water
Hughes Aircraft (Arizona)	500,000	Potable Water
IBM, Austin (Texas)	756,000	Electronic Rinse Water
Jeddah (Saudi Arabia)	3,200,000	Seawater to Potable Water
Kuwait	4,000	Irrigation
Monolithic Memories (California)	30,000	Electronic Rinse Water
Pinellas County (Florida)	164,000	Boiler Feedwater
Riegocan (Canary Islands, Spain)	50,000	Process Water
R. D. Nixon Power Plant (Colorado)	432,000	Cooling Tower Blowdown
Ocean Reef (Florida)	930,000	Potable Water
Orange County Water District (California)	5,000,000	Process Tertiary Effluent
Resorts International (Bahamas)	30,000	Seawater to Potable
Royal Family (Saudi Arabia)	75,000	Potable Water
San Diego Country Estates (California)	225,000	Sewage Reclamation
San Diego Gas & Electric (California)	6,000	Gas Turbine Injection Water
San Diego Gas & Electric (California)	30,000	Gas Turbine Injection Water
San Diego Gas & Electric (California)	25,000	Gas Turbine Injection Water
San Juan Power Plant (New Mexico)	2,300,000	Power Plant Waste Water
Servico Agricola (Canary Islands)	50,000	Irrigation Water
Sogener (Ecuador)	10,000	Potable Water
South Florida U.M.Y. Camp (Florida)	10,000	Potable Water
Spanish Lakes (Florida)	72,000	Potable Water
Sunflower Electric (Kansas)	55,000	Boiler Feedwater
Swedlow (California)	15,000	Process Rinse Water
Spanish Wells (Bahamas)	7,000	Potable Water
Texas Instruments-Attleboro (Massachusetts)	72,000	Precious Metal Plating Rinse
Texas Instruments-Dallas (Texas)	1,100,000	Electronic Rinse Water
Texas Instruments-Austin (Texas)	58,000	Electronic Rinse Water
Texas Instruments-Lubbock (Texas)	320,000	Electronic Rinse Water
Texas Instruments-Lubbock North (Texas)	115,000	Electronic Rinse Water
Texas Instruments-San Salvador	50,000	Electronic Rinse Water
Texas Tech University (Texas)	144,000	Boiler Feedwater
Umm Lujj (Saudi Arabia)	1,200,000	Seawater to Potable Water
Upjohn Company (Michigan)	120,000	Medical Makeup
U.S. Government (Virgin Islands)	80,000	Seawater to Potable
Warren Petroleum (Texas)	110,000	Boiler Feedwater
Warren Petroleum (Texas)	20,000	Boiler Feedwater
Warren Petroleum (North Dakota)	17,000	Boiler Feedwater

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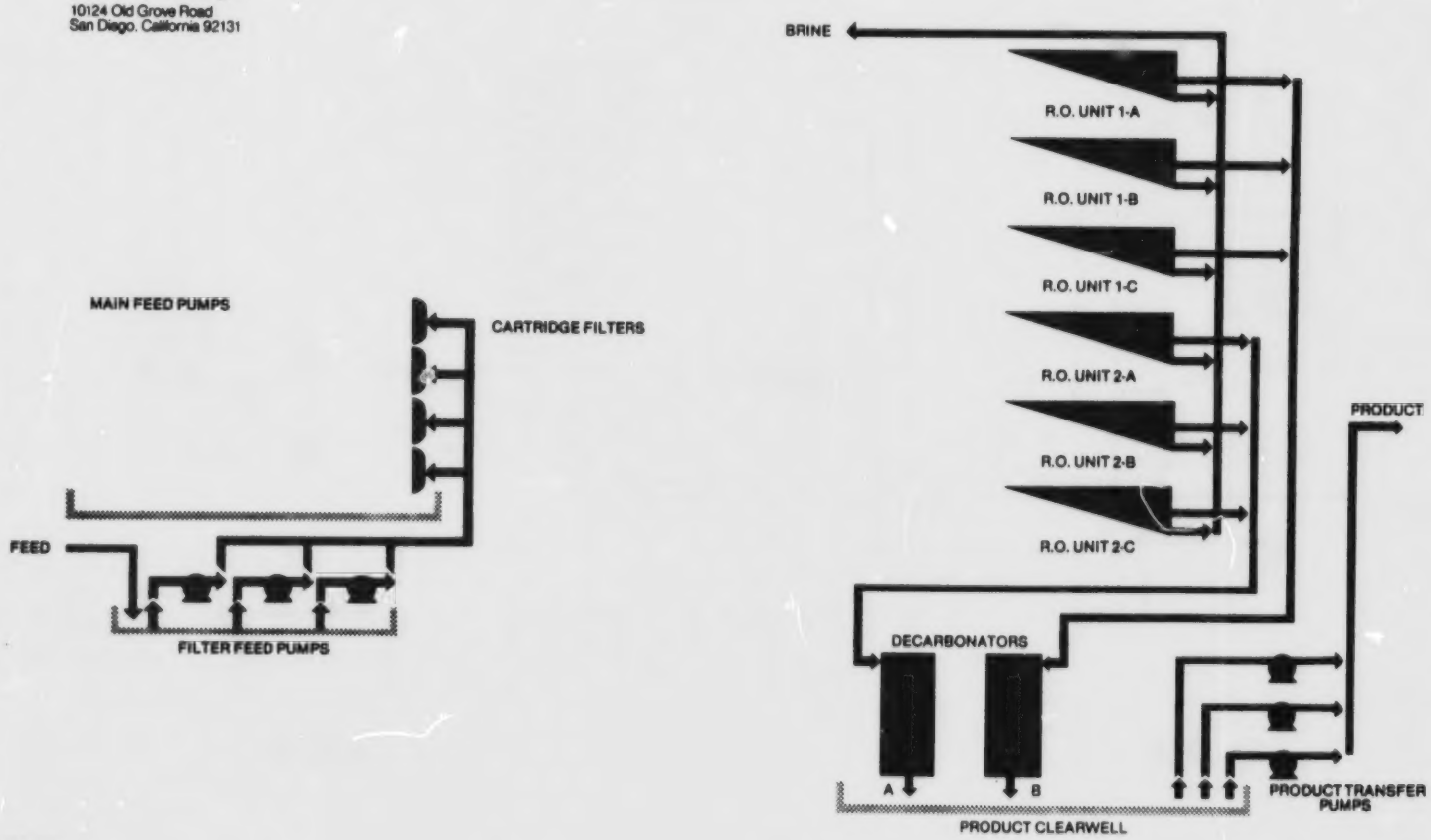
LARGE REVERSE OSMOSIS PLANT FLOW DIAGRAM (BRACKISH WATER)



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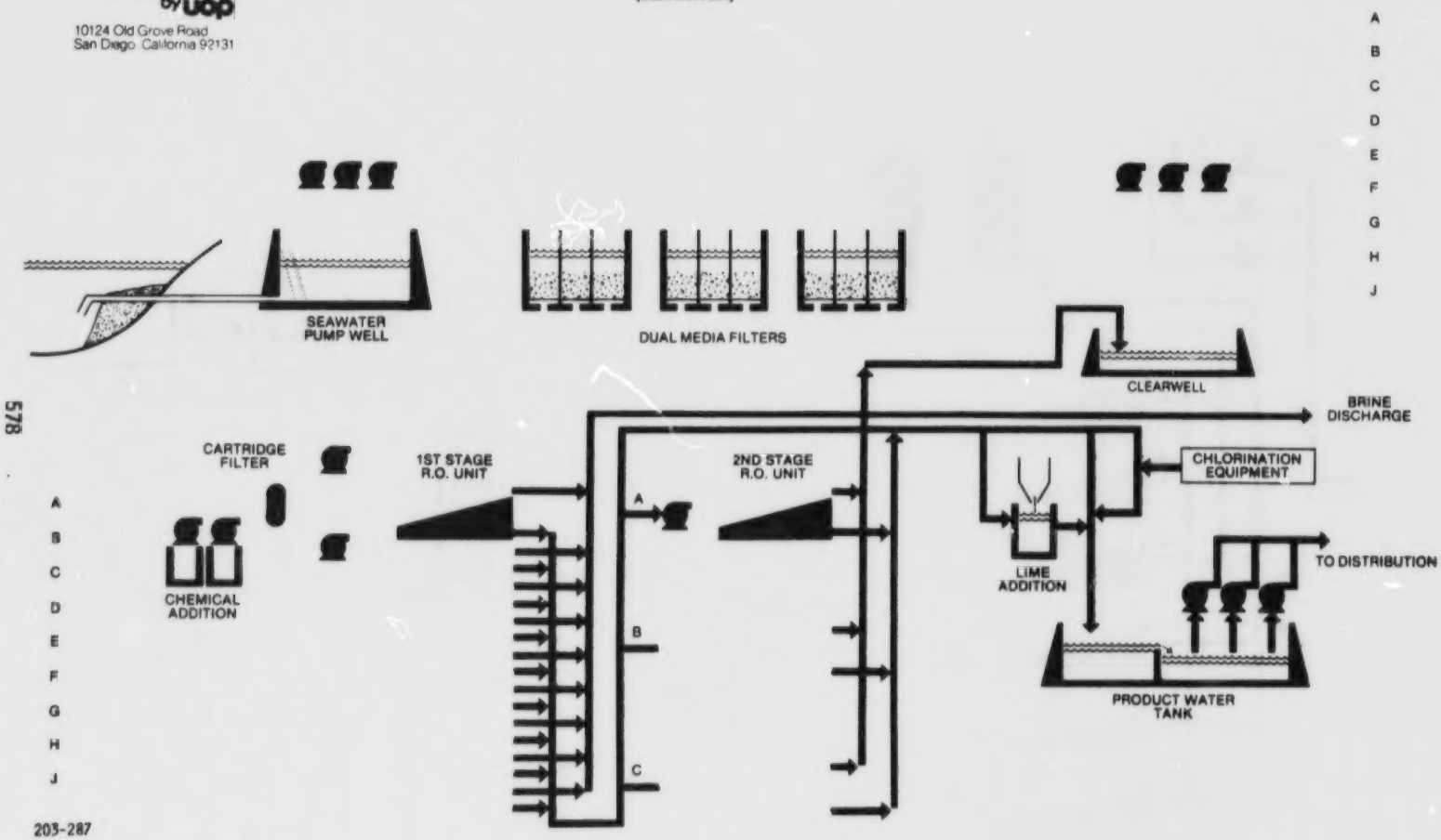
LARGE REVERSE OSMOSIS PLANT FLOW DIAGRAM (SEAWATER)



203-287

CAPE CORAL, FLORIDA
REVERSE OSMOSIS PLANT

Operating Performance Summary Permeators

May, 1983

by

DOW CHEMICAL COMPANY

I. INTRODUCTION

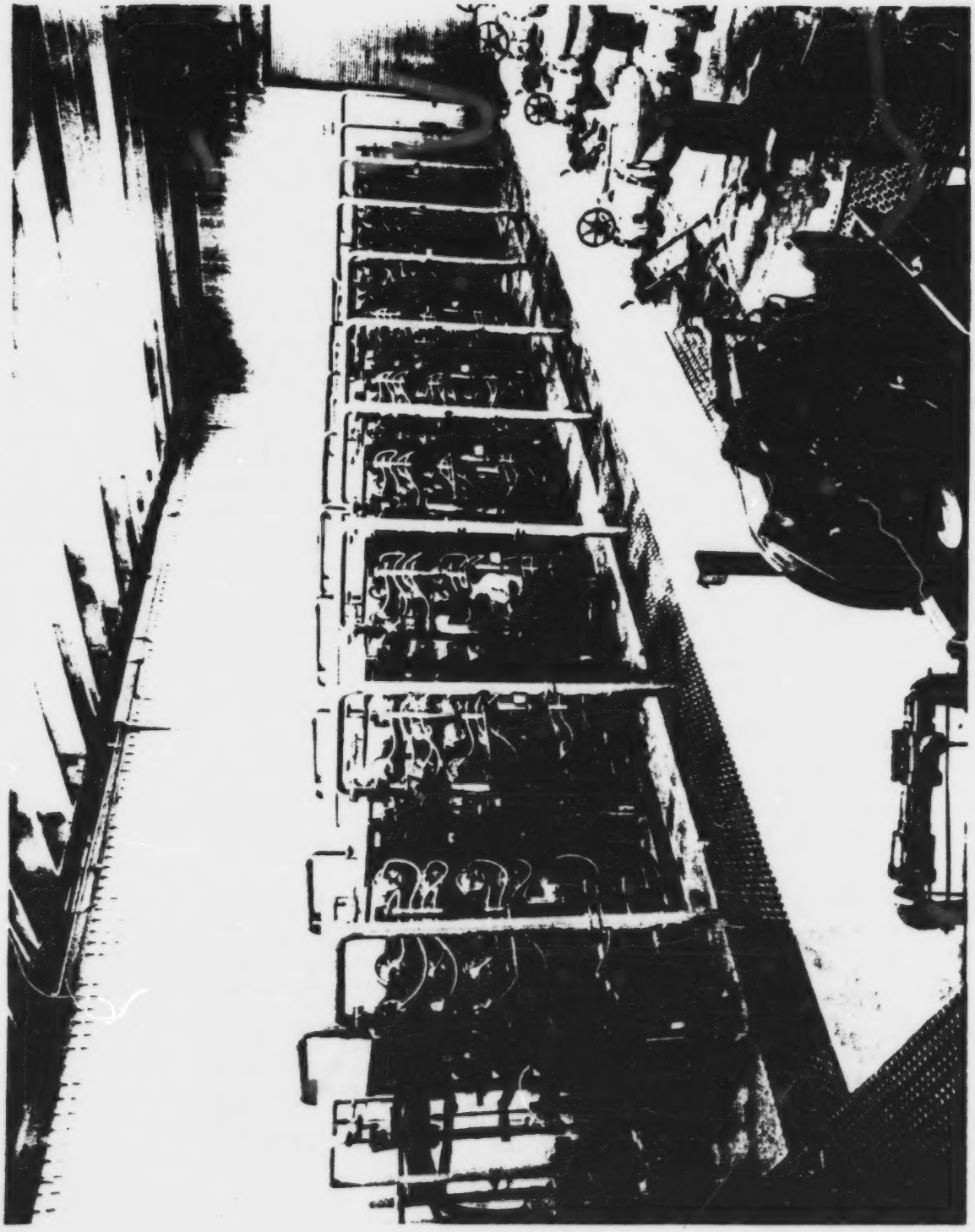
Since start-up of the 3 MGD DOWEX RO-20K reverse osmosis system at Cape Coral, Florida, in March 1977, the performance of this water treatment plant has far exceeded original expectations. During this time, the DOWEX reverse osmosis system has operated virtually flawlessly with a minimum of pretreatment and without cleaning for the first six years of operation. (Two skids of 0.5 MGD each were cleaned by Basic Technologies in March 1983.) In addition, none of the original 132 permeators supplied by The Dow Chemical Company has had to be replaced.

In June of 1980, Cape Coral expanded their RO capacity from 3 MGD to 5 MGD. Another hollow fiber membrane consisting of polyamide was chosen for the expansion rather than DOWEX RO-20K which is based on cellulose triacetate. (Note that 1980, the year of the expansion, was one year before Dow commercialized DOWEX Low Pressure permeators which would have allowed a 40% savings in energy costs.)

The City of Cape Coral has received a number of awards from various organizations relating to both the operation of the facility itself as well as the efforts of the city to effectively manage their water resources.

II. SYSTEM DESIGN

Figure 1 is a simplified flow diagram of the RO system. The original 3 MGD system consisted of six wells supplying approximately 1300 ppm TDS feedwater to the water treatment plant and has since been expanded to more than 10 wells. The pretreatment of the combined well water consists of acidification with sulfuric acid to avoid calcium carbonate precipitation, addition of sodium hexametaphosphate for sulfate salt scale control, and filtration through 5 micron cartridge filters. The water pressure is increased at each of six skids and sent to the RO modules. Each skid consists of 22 DOWEX RO 20-K permeators in a 16x6 array equipped with a Goulds vertical turbine pump, model 10ALC, and 250 horsepower motor. The product water from each stage of the RO system is combined, blended with raw water and sent to a forced draft degasifier to remove H_2S and CO_2. The pH is adjusted with caustic, then the water is chlorinated and sent to the ground storage tanks for subsequent distribution. Auxiliary features include an automatic flush system when the modules are shut down and a cleaning system.



III. OPERATING COSTS AND SYSTEM PERFORMANCE

The operating costs for the reverse osmosis system at Cape Coral have been summarized in Table 1. Note that most of the increase in operating cost over time was due to the increased cost of electricity.

Comparative operating data for the DOWEX RO-20K permeators versus the other hollow fiber permeators have been documented in Table 2. Note that six-year old DOWEX RO-20K permeators compare quite favorable with the three-year old other hollow fiber permeators in terms of salt rejection (83% versus 84%) and have significantly higher productivity (458M gpd versus 405M gpd) at a lower feed pressure (320 psi versus 390 psi).

As part of a continuing program between Dow and the City of Cape Coral to help maximize operating efficiency of the entire RO plant and therefore reduce operating costs, two studies have been undertaken. First, starting in December 1982, one skid has been operated at 75% recovery on a continuous basis instead of the design recovery of 65%. Increased recovery appeared technically feasible because the original system design was dictated by a projected degradation in feedwater quality which has not materialized. After three months of operation at higher recovery with no loss in performance, recovery is now being increased on additional skids.

Secondly, in April 1983, Basic Technologies, Inc., cleaned two of the Dow skids including the skid which had operated at 75% recovery and the skid which had been used as the control and had operated at 65% recovery. After cleaning and treatment, salt rejection of the two skids were 89.5% and 90.0% respectively, which is very close to the performance of these skids after only three years of operation. The remaining skids can now be cleaned by the city at their convenience.

The performance data from the City of Cape Coral clearly show that RO is a cost effective means for treating brackish water and can indeed provide a reliable source of quality product water. In addition, the history of Cape Coral also shows that with proper operator attention to detail, the life expectancy for a RO system can not only be met but can be exceeded.

TABLE 1

REVERSE OSMOSIS SYSTEM[1] OPERATING COST SUMMARY FOR

CITY OF CAPE CORAL, 1977-1982

	Cents/1,000 Gallons				
	1977-78	1978-79	1979-80	1980-81	1981-82
H_2SO_4	3.0	3.4	4.0	5.5	6.0
Caustic	1.1	1.7	2.1	2.0	1.0
Sodium Hexametaphosphate	1.2	0.9	1.8	1.0	3.0
Chlorine	1.5	0.4	0.4	0.3	0.3
Electrical	26.3	34.5	42.0	47.0	56.0
Labor	11.2	10.4	9.6	10.5	13.0
Total	44.3	51.3	59.9	66.3	79.3

[1]Reverse Osmosis system capacity was 3 MGD from 1977-1980 and 5 MGD from 1980 to the present. Capacity utilization averaged about 55% over this time period.

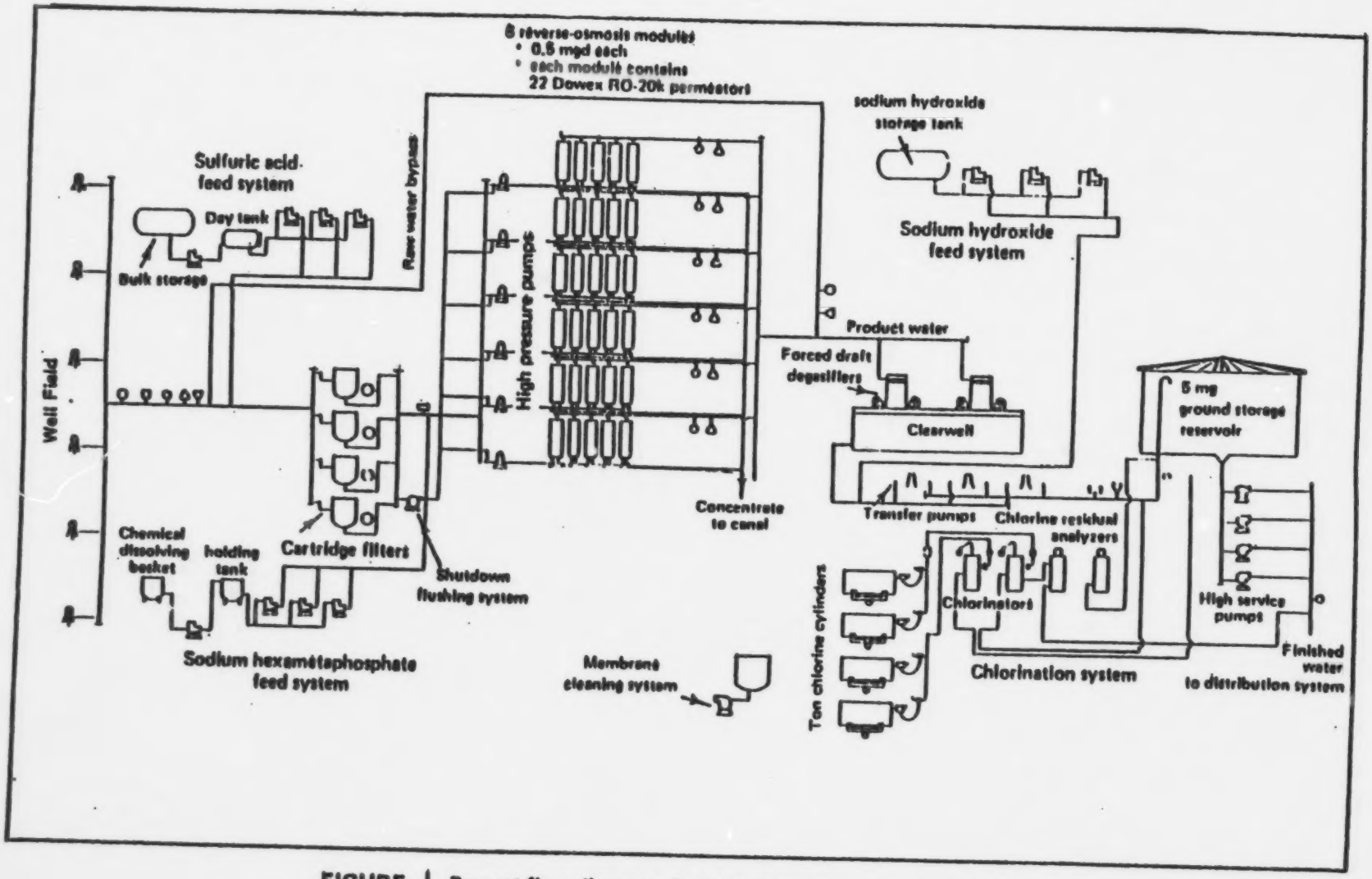


FIGURE 1 Process flow diagram of the Cape Coral reverse osmosis plant.

CITY OF VENICE, FLORIDA
R.O. PLANT-OPERATING PERFORMANCE SUMMARY

Using Dowex Low Pressure Permeators

May, 1983

by

DOW CHEMICAL COMPANY

I. INTRODUCTION

The City of Venice, Florida, started up their first reverse osmosis water treatment plant using a standard pressure polyamide hollow fiber type permeator in 1975. In 1981 when their need for potable water increased, DOWEX Low Pressure permeators were chosen for the 1 MGD expansion primarily because of the low pressure advantage and resultant 40% energy savings. This expansion started up in September 1982 and was installed on schedule by Basic Technologies, Inc., of Riviera Beach, Florida.

II. SYSTEM DESIGN

The Venice system utilizes two water treatment technologies, lime softening and reverse osmosis. Traditionally, the lime softening process has consisted of the addition of alum, lime, and caustic for the precipitation of carbonate and non-carbonate hardness. Pretreatment for the RO plant consists of sulfuric acid addition to prevent carbonate scale, sodium hexametaphosphate for sulfate scale control (Ca, Mg, Ba, and Sr) and 5μ cartridge filtration. Product water from the two plants is combined, degasified, and clorinated prior to storage.

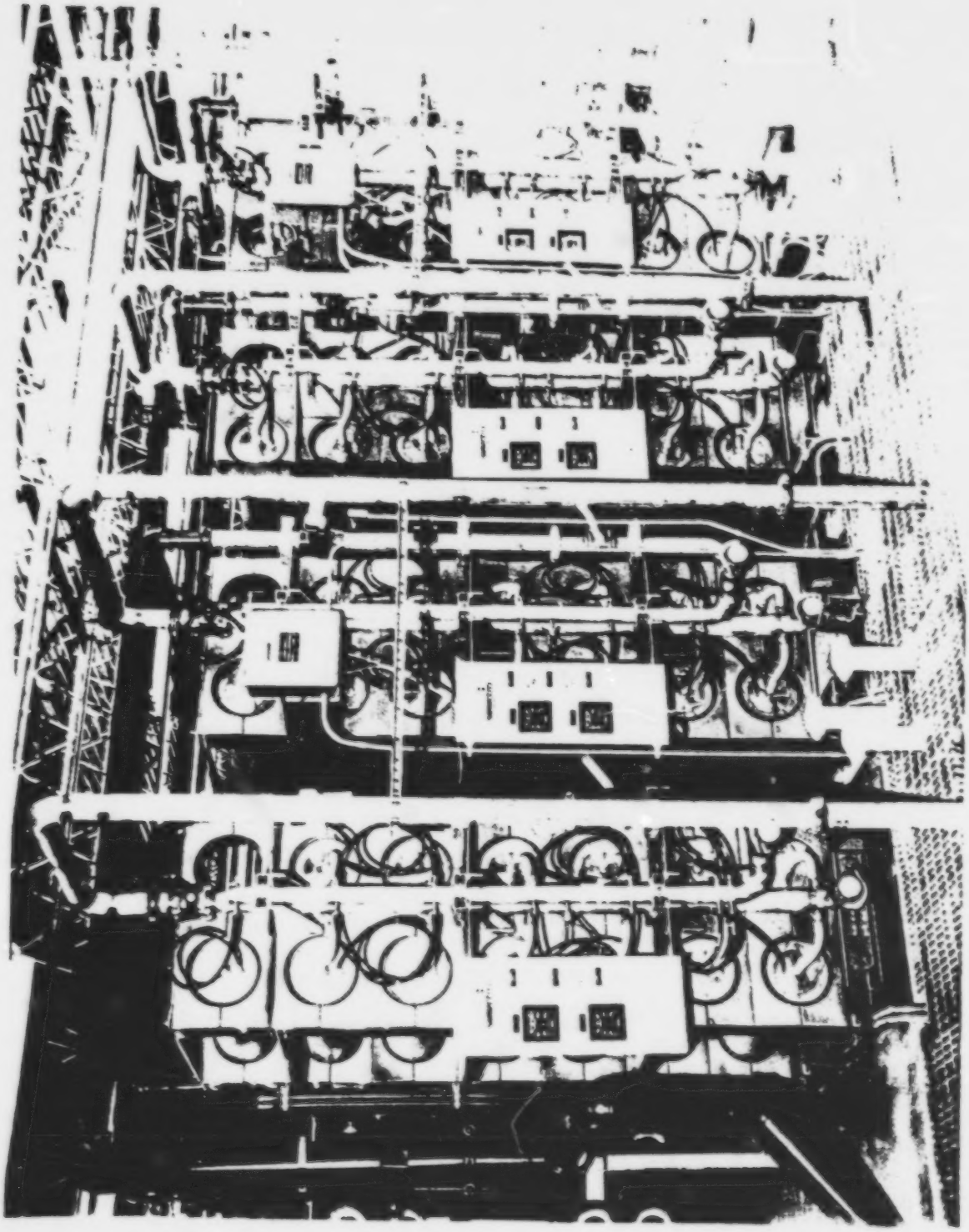
The Dowex Low Pressure RO system consists of 52 permeators in a 1 stage array operating at 55% recovery.

III. OPERATING COSTS AND SYSTEM PERFORMANCE

The combined operating costs for the reverse osmosis plant have been outlined for you in Table 1 for three representative months of operation. The data from August 1982 (before start-up of the low pressure system) is included as a reference point for before and after comparisons. Difference between electrical cost in October and January are due to variation in use of the old high pressure system. This variation reflects the fact that the DOWEX Low Pressure system is used 100% of the time while the high pressure system is used for peak demand periods only.

System performance has been documented in Table 2 for the DOWEX Low Pressure skid only. As you can see, 97% salt rejection is being achieved at only about 230 psi operating pressure after eight months of operation.

The energy savings from low pressure operation have been estimated by the engineering firm, Post, Buckley, Schuh, and Jernigan, at about $80M/yr. In addition, permeate quality from the DOWEX Low Pressure system is so



much better than the old standard pressure system (85 ppm versus 250 ppm) that the city has been able to reduce the amount of caustic used in the lime softening plant for removal of non-carbonate hardness, and still meet their blended water quality standards. The city has estimated the savings in lower caustic usage at about $100M/yr. Therefore, the total savings in operating costs to the City of Venice by installing the 1 MGD DOWEX Low Pressue RO system is estimated at a very significant $180M/yr.

TABLE 1

REVERSE OSMOSIS SYSTEM[1] OPERATING COST FOR

CITY OF VENICE, FLORIDA

Item	Cost (Cents)/Thousand Daily Gallons		
	Aug 82	Oct 82	Jan 83
Acid	10	8	6
Sodium Hexametaphosphate	14	11	7
Chlorine	0.4	0.2	0.1
Electricity	61	35	31
Total[2]	86 cents	54 cents	44 cents

[1]System consists of 1 MGD DOWEX Low Pressure Permeators and 1 MGD of another standard pressure hollow fiber permeator. Costs listed are an average and vary with run time of each skid.

[2]Total operating cost excludes labor which is split between RO and lime softening plant for a total average of 20¢/1000 gallons.

TABLE 2

DOWEX LOW PRESSURE

REVERSE OSMOSIS SYSTEM PERFORMANCE[1]

CITY OF VENICE, FLORIDA

Feed Pressure (PSI)	225-235
Recovery (%)	55
Average Skid Productivity (GPD)	500,000
Average Skid Salt Rejection (%)	97
Feed Water Quality (ppm)	~2450
Permeate Quality (ppm)	85

[1]Performance after eight months operation.
Start-up was September 1, 1982

TORAY PEC-1000 COMPOSITE MEMBRANE MODULE

for desalination and seperation process

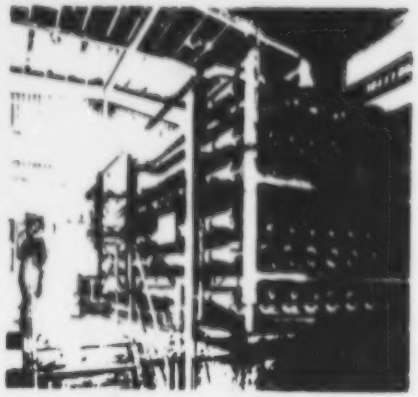
TORAY PEC-1000 COMPOSITE MEMBRANE MODULE

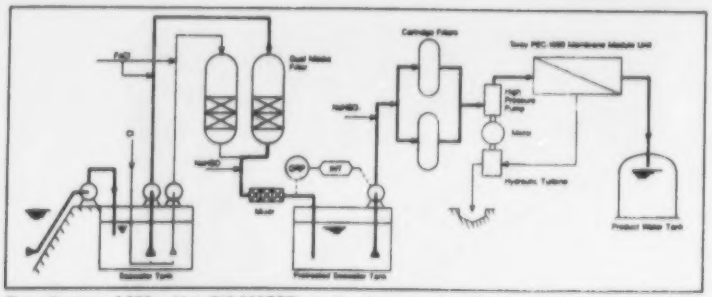
for desalination and seperation process

800m³/day (212,000GPD), Single-Stage Seawater R.O. Desalination Plant at Chigasaki (Water Reuse Promotion Center), Japan.

In July 1981, 800m³/day (212,000GPD) single-stage seawater desalination plant using PEC-1000 membrane elements (SP-120) started operation at Chigasaki Plants of W.R.P.C.

The unit has operated in excess of 1200 hours (since July 1981), and the performance maintained without any significant decline in salt rejection and water flux. Permeate purity is constantly kept less than 130ppm TDS and water flux maintained constantly at 800m³/day (212,000GPD), 53~55kg/m², 20~29℃, 40% recovery and 3.5% seawater concentration. The system operates with 29 Today modules containing 174elements of SP-120.





Flow diagram of 800m³/day (212,000GPD) single-stage seawater R.O. desalination plant at W.R.P.C. - Using Toray PEC-1000 Membrane Module (SP-120)

Toray PEC-1000 Composite Membrane

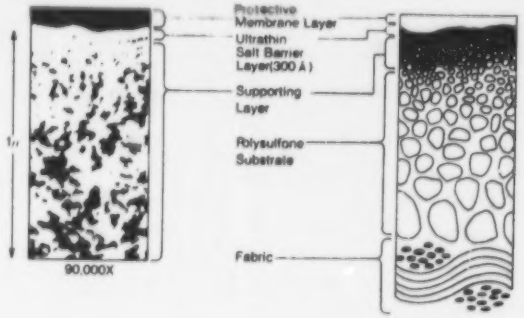
Toray's new composite membrane, designated PEC-1000, has been developed from many years of reserch, development, testing and represents the latest in membrane technology.

PEC-1000 has been specially designed for complete single-stage seawater desalination and takes into consideration both membrane performance and mechanical structure.

Complete single-stage seawater desalination permits low TDS permeate from high temperature - high salinity seawater feed and at high recovery rate of feedwater.

To meet the challenge of dependability and durability in basic seawater membrane performance, Toray has built into its design, the highest salt rejection,permeate flow rate, and durability for high temperature and high pressure operation. This combined quality can not be found in other conventional single-stage, partial single-stage or double-stage membranes.

The PEC-1000 membrane is made of a composite type structure consisting of, (1) a thin 300 Å salt barrier layer(being thicker than the other composite membranes), (2) a porous supporting membrane made of polysulfone and, (3) the composite structure being reinforced by a polymeric material and fabric.



Electron-micrograph of the cross-section and sectional drawing of PEC-1000 composite membrane.

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Tel: Tokyo(03)245-5235 Telex J22621

TORAY PEC-1000 COMPOSITE MEMBRANE MODULE

Specifications

4inch Element

Type	Salt Rejection (%) Min.	Salt Rejection (%) Ave.	Flux (m³/d) (GPD) Min.	Flux (m³/d) (GPD) Ave.
SP–110	99.5	99.7	1.9 500	2.25 595

8inch Element

Type	Salt Rejection (%) Min.	Salt Rejection (%) Ave.	Flux (m³/d) (GPD) Min.	Flux (m³/d) (GPD) Ave.
SP–120	99.5	99.7	7.6 2000	9.0 2380

Test Conditions

Item	
NaCl Solution (ppm)	35,000
Pressure (kg/cm²) (psi)	56 800
Temperature (°C) (°F)	25 77
Recovery Ratio (%)	13.5
Operation Time prior to Data Collection (hr)	24

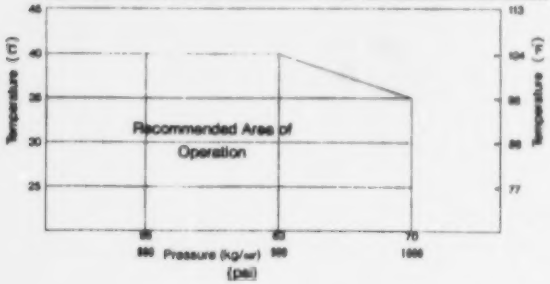
Dimensions and Weight

Type	Dimensions	Weight
4-inch Element	φ108mm × 1016mm φ4in × 40in	6.3kg 13.8lb
8-inch Element	φ201mm × 1016mm φ7.9in × 40in	23kg 46.5lb

Operating Conditions

Item	Recommended Conditions	Allowable Conditions
Applied Pressure	56 kg/cm² 800 psi	70kg/cm² 1000 psi
Operating Temperature	<35°C <95°F	40°C 104°F
pH Range	5–8.5	1–12
Maximum Feedwater Chlorine Concentration	0 ppm	0 ppm

Normal operating range for Pressure and Temperature



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Main Advantages of Toray PEC-1000 Composite Membrane Modules

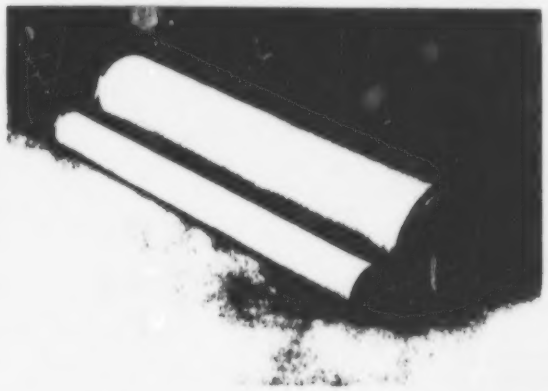
Toray PEC-1000 Composite Membrance Module was developed especially for uses in **single stage seawater desalination** and in **recovery of valuable organic materials.** It has the following outstanding features:

1. High salt rejection, reaching average **99.7%** in seawater desalination.
2. High organic materials rejection, reaching more than **92%** in ethanol recovery.
3. Wide range of operating temperatures, with a maximum operating temperature of **40°C (104°F)**.
4. Wide range of operating pressures, with a maximum operating pressures of **70kg/cm² (1000 psi)**.
5. Wide pH range of **pH 1 through 12**.

Major Applications

Toray PEC-1000 Composite Membrane Module was designed to be used in the following major applications:

1. **Complete single stage seawater desalination** to produce fresh water for drinking, industrial and agricultural use.
2. Concentration and recovery of valuable organic materials from dilute aqueous solution.



Basic Reverse Osmosis Performance of Toray PEC-1000 Membrane for Various Solutes in Aqueous Solutions

A. Organic Solutes (Evaluated at 56kg/㎠ (800psi), 25˚C (77˚F))

Functional Group	Solute	Molecular (weight)	Performance: Rejection (%)	Performance: Flux (㎥/㎡·day)	Performance: Flux (gallon/ft²·day)	Operating Conditions: Concentration (%)	Operating Conditions: pH
Alcohol	Methanol	(32)	41	0.36	*9.33*	5	6.9
	Ethanol	(46)	92	0.30	*7.36*	5	5.0
	iso-propanol	(60)	99.5	0.32	*7.85*	5	6.5
	n-Butanol	(74)	98	0.30	*7.36*	5	5.6
	Benzylalcohol	(108)	82	0.10	*2.46*	4	7.0
	Ethylene glycol	(62)	94	0.36	*8.83*	5	6.6
	Propylene glycol	(76)	98.7	0.40	*9.82*	5	5.8
	Glycerin	(92)	99.9	0.43	*10.55*	5	5.8
	Phenol	(94)	99.0	0.24	*5.89*	1	5.2
Carboxylic acid	Formic acid	(46)	34	0.52	*12.76*	5	1.9
	Acetic acid	(60)	91	0.37	*9.08*	5	2.6
	Propionic acid	(74)	97	0.39	*9.57*	5	2.7
	Oxalic acid	(90)	98.1	0.69	*16.93*	0.5	1.8
Aldehyde	Formaldehyde	(30)	69	0.30	*7.36*	5	3.6
	Acetaldehyde	(44)	80	0.46	*11.29*	3	3.6
	Acetone	(58)	97	0.29	*7.12*	4	6.7
Ketone	Methyl ethyl ketone	(72)	98	0.21	*5.15*	4	6.6
Ester	Ethyl acetate	(88)	99.2	0.18	*4.42*	4	6.6
	n-Butyl acetate	(116)	99.6	0.38	*9.33*	1	6.9
Ether	Tetrahydrofuran	(72)	99.8	0.28	*6.87*	5	6.7
	1, 4-Dioxane	(88)	99.9	0.40	*9.82*	5	6.6
Amine	Ethylene diamine	(60)	99.5	0.08	*1.96*	5	12.1
	Aniline	(93)	95	0.11	*2.70*	1	8.3
Amide	Urea	(60)	85	0.56	*13.74*	1	6.9
	N, N-dimethylformamide	(73)	98	0.32	*7.85*	5	6.5
	N, N-dimethylacetamide	(87)	99.6	0.30	*7.36*	5	6.5
	ε-Caprolactam	(113)	99.9	0.30	*7.36*	5	5.8
Sulfoxide	Dimethylsulfoxide	(78)	99.6	0.34	*8.34*	5	6.4

B. Inorganic solutes (Evaluated at 56kg/㎠ (800psi), 25˚C(77˚F))

Solute(s)	Performance: Solute Rejection (%)	Performance: Flux (㎥/㎡·day)	Performance: Flux (gallon/ft²·day)	Operating Conditions: Concentration (%)	Operating Conditions: pH
Sodium chloride	99.92	0.36	*8.59*	3.5	7.0
Lithium chloride	99.98	0.48	*11.78*	1	5.9
Sodium nitrite + Potassium nitrate	99.0	0.54	*13.25*	3 + 2	7.0
Sodium cyanide	99.5	0.83	*20.37*	0.02	12.0
Potassium ferrocyanide	99.94	0.97	*23.80*	1	7.8
Calcium chloride	99.90	0.49	*12.02*	1	7.0
Magnesium chloride	99.89	0.44	*10.80*	1	4.9
Aluminum sulfate	99.96	0.71	*17.42*	0.6	3.1
Zinc chloride	99.87	0.48	*11.78*	1	5.8
Cupric sulfate	99.95	0.49	*12.02*	1	5.0
Cobaltic nitrate	99.91	0.41	*10.06*	1	5.8
Nickel chloride	99.94	0.49	*12.02*	1	5.4
Ammonium chloride	99.84	0.81	*19.88*	1	5.2

Product Bulletin

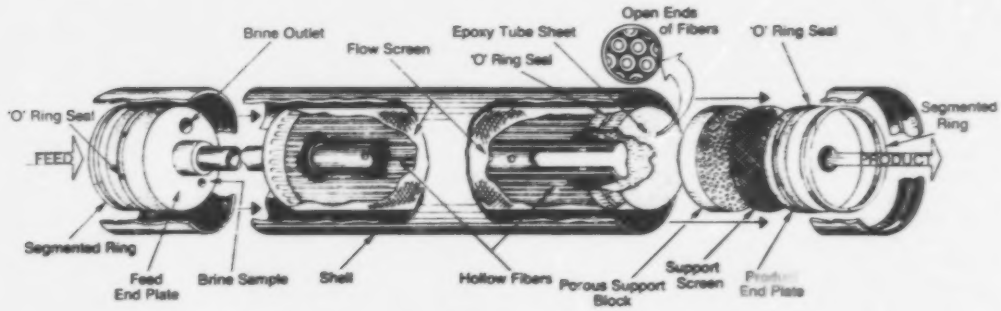
No. 276

Du Pont Company, Polymer Products Dept., Permasep* Products, Wilmington, DE 19898

8" DIAMETER B-10 PERMASEP® PERMEATOR
MODEL NO. 6840
PRODUCT SPECIFICATIONS

Membrane type	B-10 aramid
Membrane configuration	Hollow fiber
Initial product water capacity[1]	6,300 GPD (23.85 m^3/day) nominal ± 10%
Salt rejection[1]	>98.5%
Rated operating pressure[2,3]	800–1,000 psig (5,515–6,895 kPa)
Temperature range[3]	32°–95°F (0°–35°C)
pH range[3], continuous exposure	4–9
Minimum brine rate[4]	6,000 GPD (22.71 m^3/day) /10,100 GPD (38.2 m^3/day)
Maximum brine rate	40,000 GPD (151.4 m^3/day)
Shell dimensions	10⅜" OD x 8½" ID x 59" long (26.4 cm OD x 21.6 cm ID x 149.9 cm long)
Shell material	Filament-wound fiberglass epoxy
End plates and segmented rings	Fiberglass epoxy
Connections	Feed, product and brine ¾" female, NPT Brine sample, ⅜" female, NPT
Permeator weight, filled with water	225 pounds (102 kg)
Operating position	Horizontal or vertical

Notes:
[1]Based on operation with a feed of 30,000 mg/l NaCl, 800 psig (5,515 kPa), 77°F (25°C), and 30% conversion, standard test conditions.
[2]Rated operating pressure varies with feed water temperature.
[3]For operation outside this range, consult Permasep® Products.
[4]Brine rate for typical seawater; brine rate for highly brackish waters and concentrated waste streams.

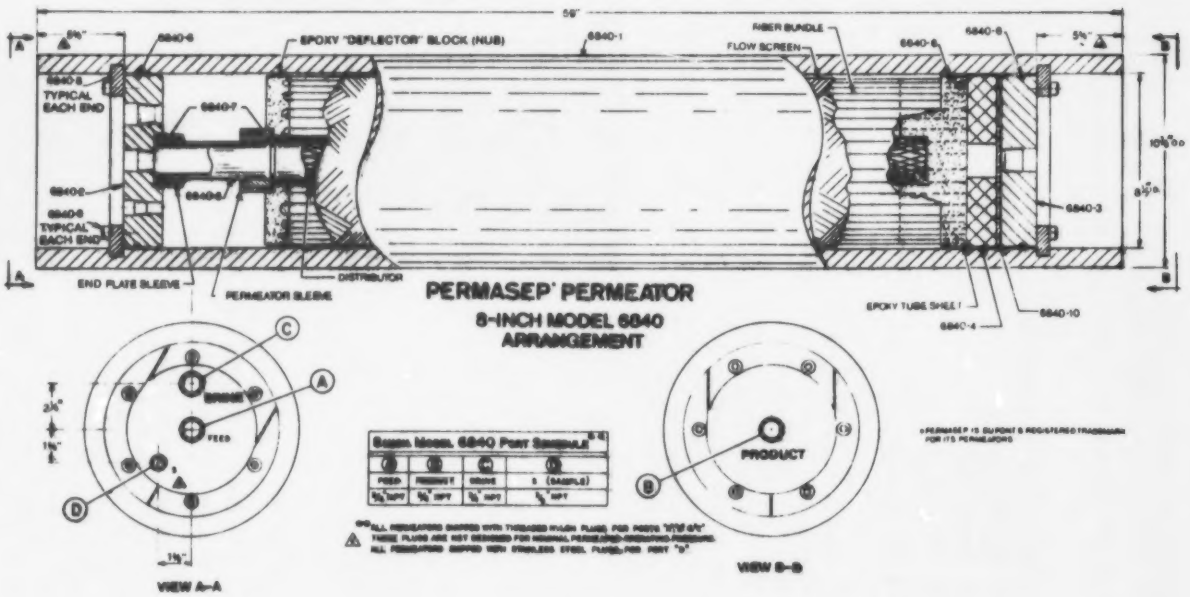


*Reg. U.S. Pat. & Tm. Off.

Printed in U.S.A.

8-INCH MODEL 6840 REPLACEMENT PARTS LIST

PART NO.	DESCRIPTION	MATERIAL	REFERENCE	NO. REQ'D.
6840-1	SHELL	FIBERGLASS	PP-100192	1
6840-2	END PLATE-FEED	FIBERGLASS	PP-200292	1
6840-3	END PLATE-PRODUCT	FIBERGLASS	PP-200290	1
6840-4	SUPPORT BLOCK (POROUS)	ALUMINA		1
6840-5	FEED TUBE	PVC	PP-200145	1
6840-6	O-RING,END PLATES & TUBE SHEET	BUNA-N RUBBER	NO. 2-266.,8.26" O.D. x 7.98" I.D. x 0.139" THK.	3
6840-7	O-RING, FEED TUBE	BUNA-N RUBBER	NO.2-131.,1.88" O.D. x 1.67" I.D. x 0.103" THK.	2
6840-8	SEGMENTED RING	FIBERGLASS	PP-300084	2
6840-9	CAP SCREW	STAINLESS STEEL	3/8"16UNCx1"LG. SOCKET HEAD CAP SCREW	12
6840-10	SUPPORT SCREEN	PLASTIC NETTING		1



PERMASEP® PERMEATOR

8-INCH MODEL 6840 ARRANGEMENT

Sizes Model 6840 Port Sizes[1]			
A	B	C	D
FEED	PRODUCT	BRINE	S (SAMPLE)
¾" NPT	¾" NPT	¾" NPT	¼" NPT

[1] ALL PERMEATORS SHIPPED WITH THREADED NYLON PLUGS FOR PORTS "C"/"D" & "S". THESE PLUGS ARE NOT DESIGNED FOR NORMAL PERMEATOR-OPERATING PRESSURE. ALL PERMEATORS SHIPPED WITH STAINLESS STEEL PLUGS FOR PORT "D".

®PERMASEP IS DU PONT'S REGISTERED TRADEMARK FOR ITS PERMEATORS

CAUTION: Follow manufacturers' recommendations on containers or in product bulletins for the safe handling of all chemicals and cleaning agents used with PERMASEP products.

The information contained herein is based upon technical data and tests which we believe to be reliable and is intended for use by persons having technical skill, at their discretion and risk. Since conditions of use are outside Du Pont's control, we can assume no liability for results obtained or damages incurred through the application of the data presented. This information is not intended as a license to operate under or a recommendation to infringe any patent of Du Pont or others covering any material or use.

ALBANY INTERNATIONAL

Information Memo

December 6, 1982

Company Launches New Business Based On Membrane Technology

After nearly ten years in development, Albany International's reverse osmosis/membrane separation technology is starting to come to fruition. We recently licensed a portion of this technology to Millipore Corporation, the world leader in separations technology based in Bedford, Massachusetts, and shortly thereafter established our Membrane Development Venture in Norwood to further develop and commercialize these purification processes.

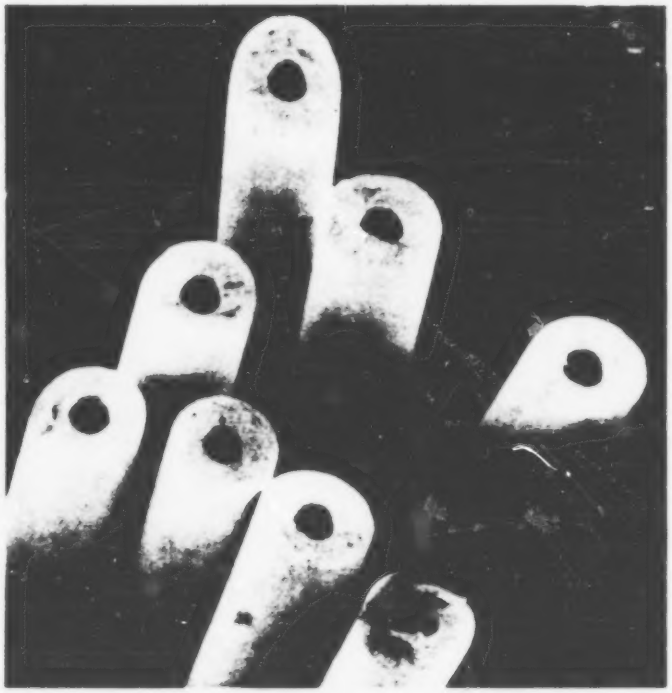
On November 2, Albany International announced its agreement with Millipore to grant that company an exclusive, worldwide license to use our patents and know-how for certain applications in liquid purification. In turn, we have received an initial payment of $2 million and will receive royalties of five percent on all product sales through 1998. Under the terms of the agreement, we retain the right to exploit this technology in other liquid applications and in gas separations.

A week later, the company announced the formation of the Membrane Development Venture to continue to explore applications for the technology and to pursue avenues to its commercialization. Heading up the new business is Mike Coplan, formerly Senior Corporate Scientist, who will serve as General Manager. Mike has been instrumental in this research effort since its inception. Reporting to Mike will be three Assistant Managers, Ben Bikson, Doug Burchesky and Fred Bilewski, with responsibility for Laboratory, Production, and Administration and Engineering, respectively. Ben, Doug and Fred were previously Senior Research Associates.

The venture's specific objectives are to attempt to generate membrane separation packages for license, sale, joint venture or internal development; to perform collaborative research with potential partners or principal users; to seek and exploit opportunities for joint development of advanced methods and products in the membrane separations technology area; and to advance Albany International's technological expertise in the entire area.

Albany International Research Company has been actively exploring new materials and processes in reverse osmosis for a number of years now. The basic technology employs bundles of tiny hollow fibers coated with a semipermeable membrane which, under pressure, allows certain solutes to pass through while rejecting other dissolved materials.

(continued)



These hollow fibers, magnified about 75 times, form the basis of Albany International's reverse osmosis/membrane separation technology for liquid purification and gas separation. Our unique method of preparing the porous fiber substrate enables us to use very thin membrane coatings which enhance the separation process.

*Reprinted from Albany International's management newsletter.

Information Memo

Company Launches New Business from page 1

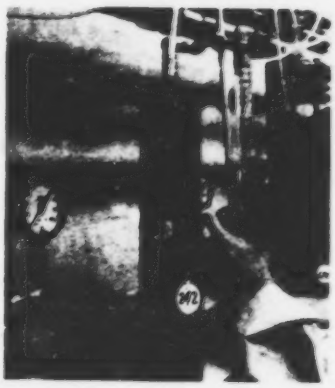
Much of our work in this area has evolved from the Research Company's hollow fiber technology development, which dates back to 1964-65. In more recent years, efforts have been concentrated on developing a superior membrane that would be durable in chlorine, operable over wide pH ranges and at high temperatures.

Membrane separation processes can be used to separate water from other liquids, remove substances such as salt and metals from liquids, concentrate substances such as dissolved sugar, and separate gases.

Albany International will be seeking opportunities to exploit this technology in several liquid applications, such as desalination of seawater, treatment of process and waste streams generated in the fields of mining and mineral extraction, and petroleum and synfuel production and refining.

In addition, the corporation will explore applications in gas separations, with emphasis on several energy-related areas. These include production of oxygen-enriched air for increased efficiency of fossil fuel combustion in smelting and other industries, the use of carbon dioxide for rejuvenation of dormant oil wells, and removal of sour gas components from natural gas.

Reverse osmosis/membrane separation technology is still relatively new — the first reverse osmosis membranes were developed only about 20 years ago and the process has been commercially viable only since about 1969 — but the opportunities for growth in this area are great. We believe our superior, proprietary technology gives us a good edge over the competition.



A reverse osmosis module for water purification is tested at our Norwood laboratory. Liquid to be purified is pumped into the module, consisting of a bundle of hollow fibers inside a fiberglass reinforced plastic pressure shell, at pressures up to 1000 psi. The pure water, or permeate, and the concentrate emerge in two separate streams from the lower end of the module.

ALBANY INTERNATIONAL RO MEMBRANE FEATURES

COMPOSITE MEMBRANE MAKES POSSIBLE CHEMICAL TAILORING FOR SPECIFIC USES.

HOLLOW FIBER CAPABLE OF OPERATING OVER RANGE FROM HOUSEHOLD PRESSURE TO 1000 PSI OR MORE.

SYSTEM DURABLE TO STERILIZATION BY 100 PPM CL_2, AND LONG-TERM EXPOSURE TO 5 PPM CL_2, pH 5-8.

CHEMICAL RESISTANCE PERMITS OPERATING AGAINST FEEDS HAVING pH LEVELS AS LOW AS 1 AND AS HIGH AS 12+.

TEMPERATURE STABILITY UP TO 80°C.

SEAWATER DURABILITY TESTED TO 25,000 HOURS (AS OF 1/1/83).

UNIQUE MODULE DESIGN AND FLUID DYNAMIC FEATURES REDUCE FOULING SUSCEPTIBILITY.

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member of the bakke group of companies
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Bintech (Pty) Ltd
Bintech (Edms) Bpk
✉ 344 Paarl 7620
Rep. of South Africa
☎ (02211) 2-3031
✆ 57-27181 SA

18th December 1984

Randol International Ltd
21578 Mountsfield Drive
Golden, Colorado 80401
United States of America

Attention : Hans von Michaelis

Dear Sir

TUBULAR REVERSE OSMOSIS/WATER TREATMENT

I am responding to your letter 16 November 1984 to Mr D.B. (Skottie) Smit. Your comments about the mining industry although brief and to the point confirm my feelings on the mining industry insofar as desalination is concerned. However I am hoping that the next five years will be the transition period from traditional water treatment methods to the inclusion of large scale desalination at the mines.

Our most recent successes have been outside of the mining industry. During 1984 we ran a pilot plant at the Grootvlei power station with very good results on cooling tower recycle waters. This in turn led to the award of a 6,5mℓ/d Effluent Concentrator Plant contract at Lethabo (Escom).

The main contractor in the venture is Foster Wheeler Energy Ltd with Bakke being the sub-contractor insofar as technology is concerned. During 1984 we also installed and commissioned two plants operating on brakish waters in remote areas. The one plant has to contend with in excess of 5 000 TDS and has a permeate capacity of 360 m^3/day. The other plant is operating on a water with a very high iron content in the arid north-west Cape region. At Port Elizabeth Municipality the City Engineers Dept. have run one of our pilot plants for sixteen months, at time of writing, on secondary sewage effluent from activated sludge plant filtration, with a view to producing potable water for the future. Comprehensive analysis indicates a water quality from this plant well within SABS potable standards - in fact better than anything we are drinking at the moment. The Anglo American Research Laboratories intend to run a similar pilot study during 1985 - possibly on a mix of secondary sewage effluents and other waters.

The Water Research Commission has taken a keen interest at what is happening at P.E., and might soon be involved in part sponsoring a commercial project to produce process water for industry in P.E.

Enclosed is a brochure recently printed plus two photographs of our third generation pilot plant. The fourth generation pilot plants are fairly similar, however for some reason I do not have any photographs available. We have since improved our coupling and module array design.

Directors/Direkteure: J. A. LOUW, D. B. SMIT, A. R. D. KOCH, P. A. HATTINGH.

As far as Seeded Slurry Reverse Osmosis is concerned things are going well. I suggest you contact Herb Rothschild in Seattle at RCC to get the status of present projects.

Your asked for information on prices - what I can tell you is that our operating costs including the capital component vary between 50 cents (SA) and one Rand (SA) for medium to large applications. Both operating and capital costs are highly variable depending on feed waters, design parameters, size, recovery required, rejection required etc. At a later stage I will draw up some standard comparisons for categorised applications.

Thank you for your interest.

Yours Sincerely

PETER SWART
COMMERCIAL MANAGER : MEMBRATEK

P.S. Skottie and Johan send their regards.

PRETREATMENT

The purpose of pretreating feedwater to cellulose acetate R.O. modules is to obtain optimum plant performance and membrane life:

1) Removal of colloidal substances that may foul the membranes and reduce plant output.

2) To remove, modify, or inhibit sparingly soluble substances that may precipitate and foul the membrane surface, bearing in mind that ions in the concentrate are concentrated in proportion to the degree of recovery of permeate achieved, e.g., if recovery is 80%, then the salt concentration in the concentrate (20%) will be increased by about 500%, assuming salt rejection is 100%).

3) To remove or modify chemical such as chlorine and other oxidants which may chemically destroy some membrane types.

4) To prevent bacterial growth and consequent membrane fouling or degradation.

Typical pretreatment measures required:

1. Chlorination to destroy bacteria and algae growth.

2. Lime treatment and settling to remove manganese and iron.

3. pH adjustment to the pH 5-6 range. Higher pH than pH 7 results in degradation of CA membranes. Rand Water Board water, for example, is typically in excess of pH 8. Calcium carbonate and magnesium scale is also controlled by keeping the pH below 6.7. pH adjustment to prevent hydrolysis of the membrane is not required for polyamide or polysulfonate membranes.

4. Removal of residual chlorine by sodium bisulfite addition or activated carbon column.

WATER SOFTENING

Water softening reduces the calcium and magnesium concentration in feedwater and minimizes the risk of scaling.

SCALE INHIBITORS

Sodium hexametaphosphate is used as a scale inhibitor. Inhibitors are required when conventional plants operate at high recoveries to prevent calcium carbonate and calcium sulfate from precipitating on the membrane surface. However, most R.O. units are operated at low recoveries. Only when the purpose would be recover dischargable water from industrial or minewater, for example, would the goal to be optimize recovery and reduce the volume of concentrate to a minimum.

DECHLORINATION

Polyamide and some composite membranes require dechlorination of feedwater (e.g., reduction by sodium metabisulfite addition or by activated carbon) to prevent oxidation of the membrane.

MEMBRANE CLEANING

Membranes at one South African plant were replaced seven times in seventeen months following startup. When a weekly membrane cleaning schedule, using EDTA and citric acid, was started, the eighth membrane set lasted 14 calendar months (7,600 hours of operation).

Some membrane manufacturers recommend that R.O. membranes should be cleaned when the flux has decreased by 10%, or the salt passage has increased by 25%.

PLANT OVERDESIGN

Often plants may be overdesigned in the mistaken belief that this will compensate for flux decline due to fouling.

When fouling occurs, permeate quality also generally deteriorates as flux drops. This is because the salt rejection by the membrane is related to permeate flux (JOHNSON, et al, 1966), and foulant deposits on the membrane surface cause increased concentration polarization which in turn results in an increase in solute passage (SHEPPARD and THOMAS, 1971).

Chemical degradation of membranes continues whether the plant is in operation or not. This process is a function of time, not permeate production. When the plant is off-line, membranes tend to deteriorate more quickly due to microbiological growth, particularly when they are not preserved (e.g., by formaldehyde).

Foulant deposits become more difficult to remove with time. Over capacity means that plants initially do not require regular cleaning since production requirements are met despite fouling. However, when cleaning is implemented, it will probably not be as effective in restoring productivity due to the "aging" of foulant deposits.

LEGER (1983) points out that the installation of suitable storage tanks, instrumentation, and controls to allow semi-continuous unattended operation would result in a cost savings due to fewer membrane replacements and would probably provide better quality water at a lower cost.

Membranes should always be flushed before shutdown to avoid precipitation of salts concentrated at the membrane surface.

MEMBRANE FOULING

LEGER (1983) analyzed foulant deposits on membrane modules from several desalination units treating Johannesburg tapwater. At some plants, the main foulant turned out to be calcium carbonate, probably because the pH of the feed had not been adjusted. At other plants, the fouling contained high levels of aluminum and silica which indicated that fouling may have been caused by clay colloids or particulates, by precipitation of aluminum hydroxide, aluminum silicate, and colloidal silica, or combinations thereof.

Iron and zinc were significant components of deposits on other membranes, and LEGER (1983) concluded that the source of these ions must have been galvanized iron pipes used for water reticulation. Iron fouling may be removed by cleaning with chelates such as EDTA or citric acid. If operated at a slightly acid pH, say pH 5, ions such as zinc, copper, lead, cadmium, and nickel will be kept in solution.

At some of the plants tested, organic fouling was identified, the nature of which was still under investigation when he presented his paper.

The conclusion drawn from LEGER (1983) is that if such significant problems were encountered in treating tapwater by R.O., then imagine the potential problems to be catered for in treating mine drainage or mill effluents. In this respect, the seeded slurry R.O. system proposed by Resources Conservation Company is that much more attractive.

SEEDED SLURRY REVERSE OSMOSIS

Recycling of slurries to present nucleation points in the treatment of scaling solutions is not a new concept. Seeding is used in filtration of nearly saturated or supersaturated

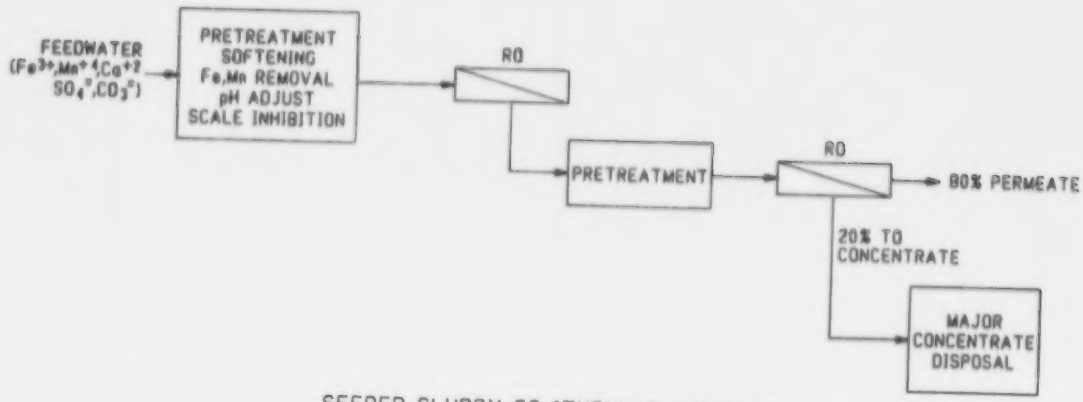
solutions, it is used in clarifiers and settlers, e.g., the HDS process, and in cross-flow microfiltration as well as untrafiltration membrane processes. It has also been used to precipitate $CaCO_3$ from recycled in situ uranium leach solutions and in seeded slurry evaporation processes.

Seeded slurry reverse osmosis using tubular R.O. modules was first demonstrated by Resources Conservation Company as described by: HERRIGAL (1984), RCC (1981), KIRCHNER and O'NEIL (1980?), and GOODLOE (1984), all inserted below. See also the trip report on ERPM in Appendix I.

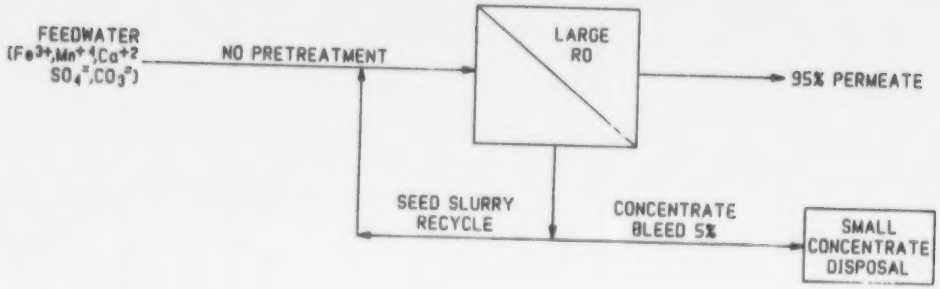
One of the conclusions of this investigation is that seeded slurry reverse Osmosis is the most useful and practical application of membrane processes for the treatment of acid mine drainage and metallurgical process recycle solutions.

Although tubular R.O. modules yield only, say 1 m^3/d permeate compared with 80 m^3/d from holofine-fiber modules of comparable size, seeded slurry R.O. avoids the need for feedwater pretreatment and makes it possible to achieve much higher water recoveries while leaving a much smaller volume of more easily disposed of concentrate. Overall capital costs are likely to be comparable. Overall operating costs are likely to be lower using seeded slurry R.O., and the operation of seeded slurry R.O. systems for the treatment of mine-mill effluents will be very much simpler and easier to operate, i.e., more compatible with the mine-mill environment than the more sophisticated, high-capacity R.O. modules requiring extensive multi-step water treatment steps.

SPIRAL WOUND/HOLOFINE RO MODULES



SEEDED SLURRY RO (TUBULAR MODULES)



Conventional R.O. requires multi-step pretreatment to achieve 80% recovery without fouling the membranes. Seeded slurry R.O. requires no pretreatment to achieve 95%-plus recovery with correspondingly smaller concentrate disposal needs.

REVERSE OSMOSIS COST DATA

There is a relatively wide range in R.O. costs, depending on the scale of operation and how it is to be applied. For example, treatment of tapwater to yield a low TDS permeate for use after ion exchange demineralizing where low R.O. recoveries and cost-free concentrate disposal of cencentrate is possible would be at the low end of the range. These variations are very well illustrated by SCHUTTE (1983) whose chapter entitled "Economic Considerations" was inserted at the end of Chapter 13 to show a comparison of various desalination processes. Desalination of seawater, which has a high TDS level (3.5-4.0%) but where recoveries can be low, and concentrate disposal is cost-free (back to the ocean), usually costs between $4.00-$11.00 per 1,000 U.S. gallons ($1.00-2.80/m^3), depending on the scale of operation and pretreatment required. (Note that desalination of seawater with high natural organic polymer loads along the South West Africa/Namibian coast proved not to b feasible.)

Desalination of brackish water by R.O. for recovery of potable water, excluding concentrate, based on case studies by the Dow Chemical Co. inserted above for a 2 mGD operation, ranged between $0.44-$0.86 per 1,000 g at City of Venice, Florida. Interestingly, the lower cost was for the more recent year (1983).

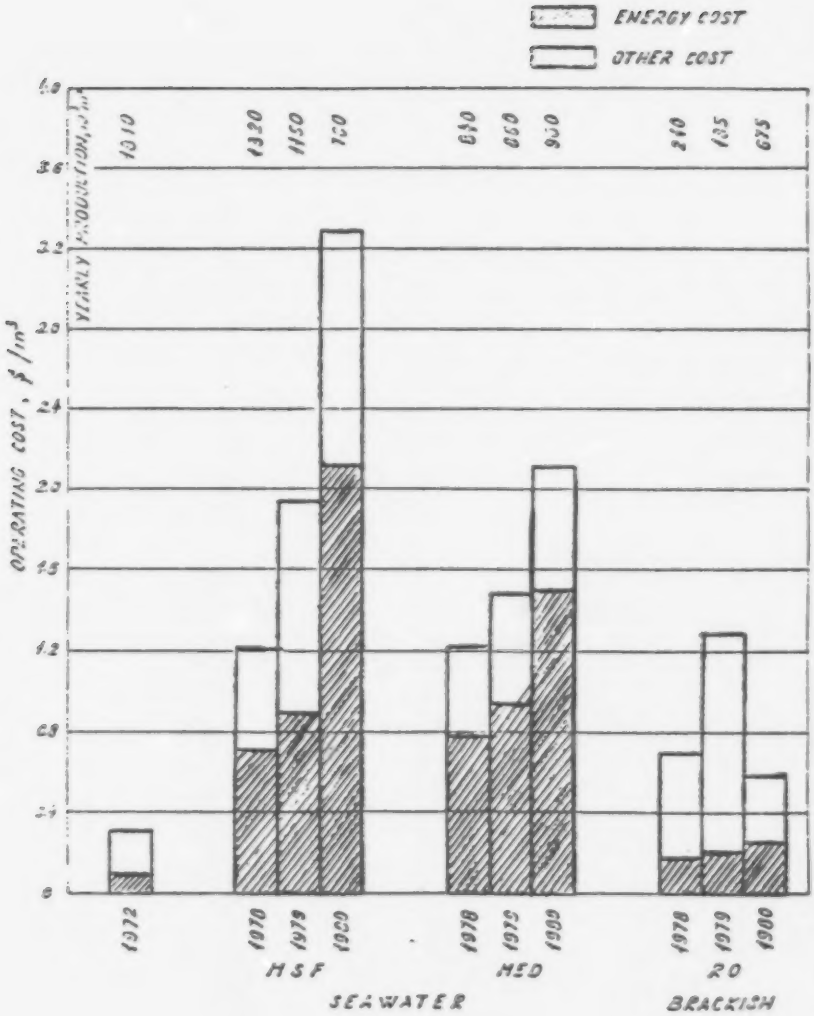
Bintech (Pty) Ltd. has demonstrated operating costs between R0.50-R1.00/m^3 ($1.90-$3.80/1,000 U.S. g), including capital amortization, for various small-scale operations.

U.S. AID (1980) published a cost estimate for various desalination processes at various plant sizes indicating costs for R.O. desalination of brackish waters at around $1.90/1,000 g ($0.50/m^3).

GLUECKSTERN (1982) compared costs of R.O. and evaporation processes for seawater and brackish waters in Israel and summarized his 1978-1980 data in the graph shown overleaf. His almost two decades of experience in this field make him a valuable reference source:

DR. PINHAS GLUECKSTERN
Mekorot Water Company Ltd.
Post Office Box 20128
Tel Aviv, Israel

It is important to note that where desalination of minewater or mill effluents is the objective of the desalination plant, i.e., to remove salts from effluents, then the disposal of the concentrate is an important consideration and represents an additional cost factor which must be taken into account when comparing alternative system options.



Operating Cost of Eilat Desalting Plants

(1978-1980)

Source: GLUECKSTERN (1982)

WARNING

1 Caution should be exercised when using these cost data

2 These costs are computed for basic desalination facilities in the USA. These costs include no st[illegible]e capacity and allow for o[illegible] fun[illegible] [illegible] (water develop-ment and brine disposal. If storage capacity is added and/or more complex feedwater or brine facilities are required, o[illegible] all pr[illegible] can significantly increase. This is especially true with brackish water facilities. Construction in locations outside the USA can also add to t[illegible] overall [illegible] A. tual costs of up to 300% (or more) of those shown on this figure (especially at lower capacities) would not be unusual for projects in many deve[illegible]ping a[illegible]

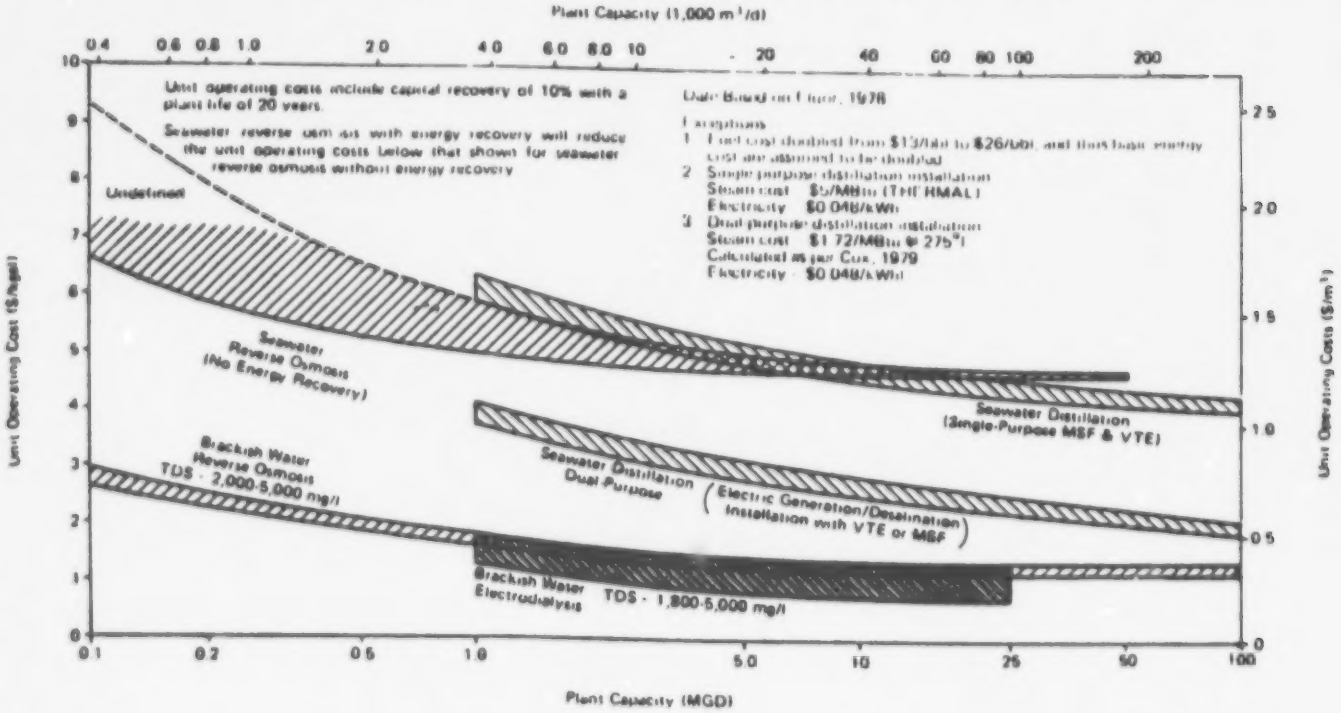
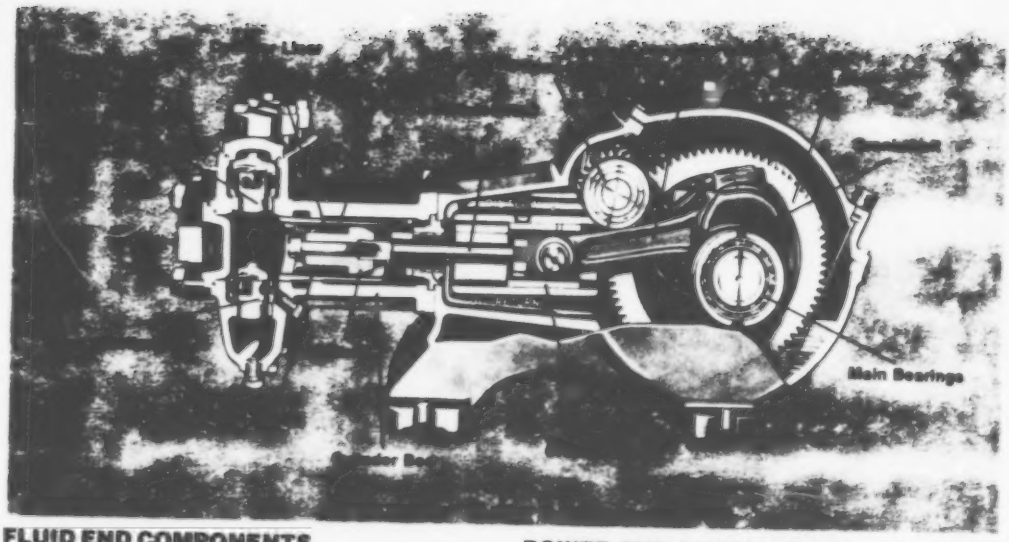


FIGURE 11.2 Generalized unit production cost estimates for desalination processes. (USAID 1980)

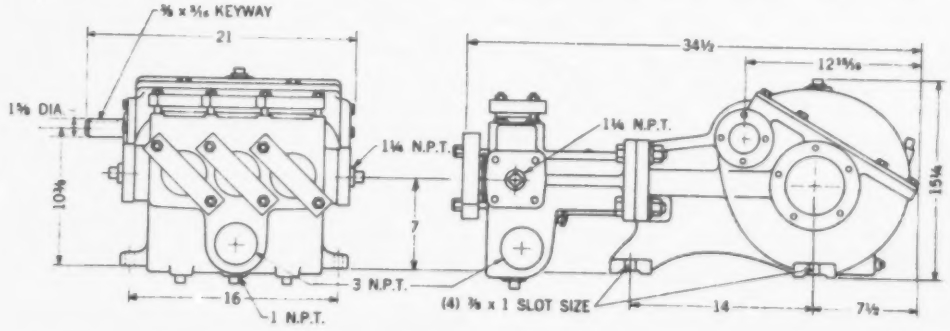


FLUID END COMPONENTS

CYLINDER BODY. High strength ductile iron.
CYLINDERS. Tapered fit steel shells with smooth, hard K-Ramic® lining to resist wear and corrosion.
SUCTION AND DISCHARGE. Three large tapped suction ports, two on sides and one front. Two discharge ports are tapped and flanged.
PISTON PACKING MATERIAL. Molded composition Buna-N V-rings.
PISTON ASSEMBLY. V-ring packing is supported by a fabric reinforced phenolic follower. 416ss stud, 303ss pressure ring, 303ss retainer. Entire assembly is attached to piston rod with 304ss cap screw.
SPRING LOADED FLAT VALVES. Positive, fast acting 301ss valves, 302ss valve springs and hardened 420F seats. Seats tapered into body casting for easy removal.
VALVE AND CYLINDER CAPS. Feature recessed neoprene O-rings held in place by heavy bolted clamps. Ductile iron caps have no threads to corrode or hinder easy access to valves and pistons.

POWER END COMPONENTS

GEAR CASE. Made from durable cast iron. Serves as oil reservoir for constant, splash type lubrication of all working parts. Lid removes for easy inspection without draining oil.
PINION AND GEAR. Induction hardened alloy steel. Helical cut and shaved for smooth, quiet and efficient operation.
PINION SHAFT. Gear integral with shaft is made from alloy steel for strength and resistance to fatigue.
BEARINGS. Crankshaft and pinion shaft have tapered roller bearings for minimum friction and power loss.
CONNECTING LINKS. Cast iron with replaceable bronze wrist pin bearings.
CRANKSHAFT JOURNAL BEARINGS. Steel backed babbit inserts.
CROSSHEADS AND PISTON RODS. Crossheads are made from ductile iron. Bronze bushings serve as crosshead pin bearings. Stainless steel piston rods are ground and polished to a smooth finish. Rods are pinned and threaded in perfect alignment with crosshead and cylinder.



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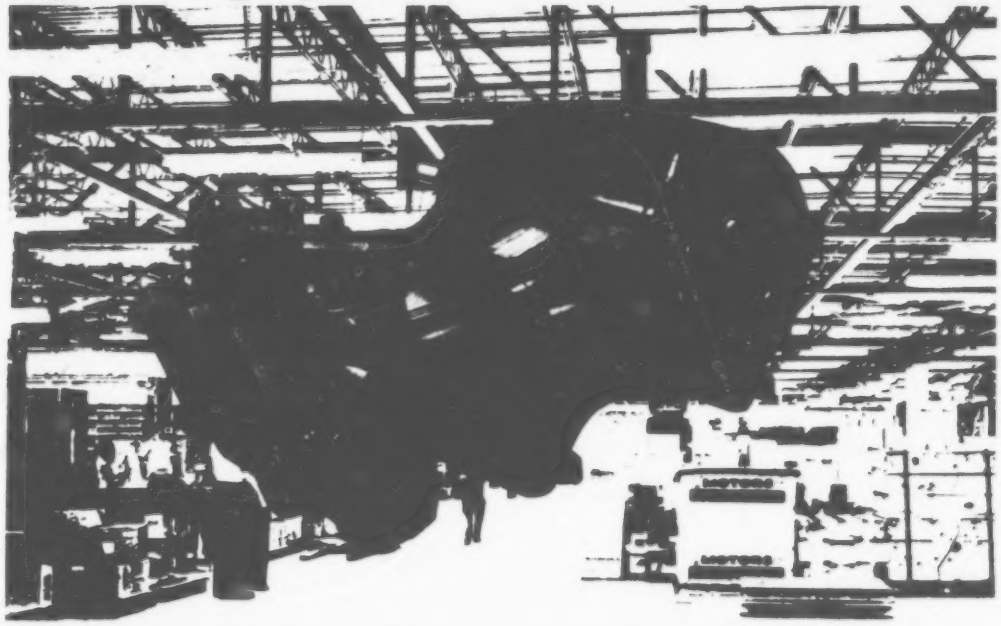
Myers

F.E. MYERS CO. DIVISION OF McNEIL CORPORATION

Myers high pressure industrial pumps



D65-16CVD/65 GPM/1600 PSI

Designed for high capacity/high pressure applications, the Myers D65-16CVD has established a proven record of reliable service. A triplex, single-acting, reciprocating pump, it has been built to withstand the strain of rugged industrial use. In addition to normal industrial installations, the D65 fulfills the requirements of modern high pressure fire fighting equipment and is recommended for fire pump service.

The pump features a single helical gear reduction drive which provides smooth, quiet and efficient operation. The slow crankshaft speed minimizes parts wear and extends pump life. A splash type oil bath system assures continuous lubrication of all internal parts. The crankshaft may be rotated in either direction for ease of installation.

The high strength ductile iron fluid end permits continuous operation at 65 GPM and 1600 PSI with maximum performance and dependability. All valve and piston assemblies are easily serviced through front and top cylinder body openings. Servicing of both the power and fluid ends can be accomplished without removal of the pump or disturbing the system piping. The heavy duty construction and durability of the D65 will give years of trouble free operation.

SPECIFICATIONS

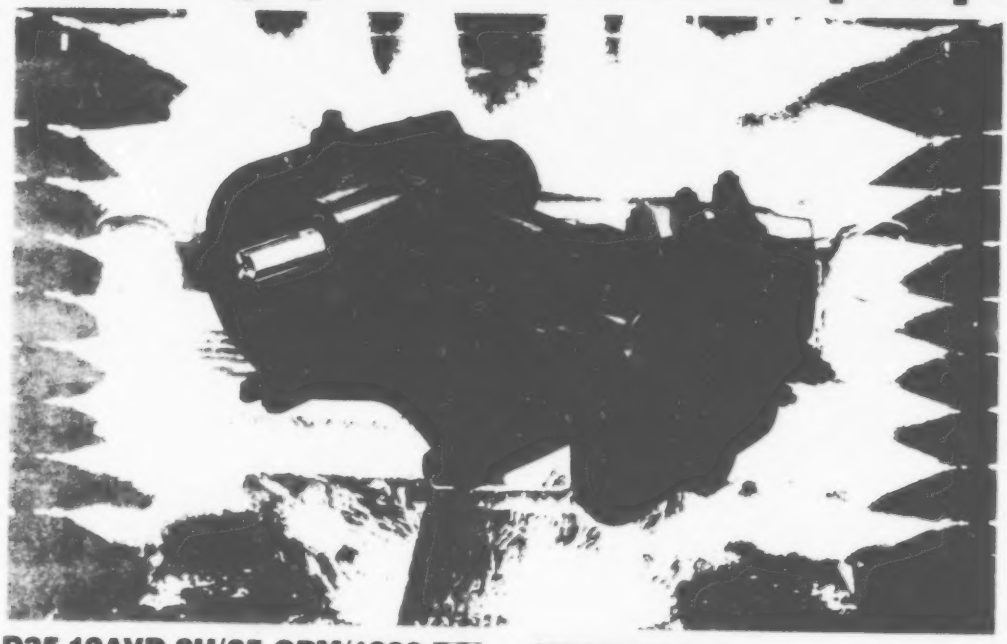
Rated Capacity	65 GPM @ 376 SPM
Pinion Shaft Speed at Rated Capacity	1487 RPM
Gear Reduction Ratio	3.95:1
Rated Pressure	1600 PSI
Temperature Rating	120°F.*
Cylinder Bore	2.125"
Piston Stroke	3.750"
Suction Size	3" NPT
Discharge Size	1¼" NPT
Pinion Shaft	1⅝" Dia.
Keyway	⅜" x 3/16" Straight
Approximate Weight	525 Lbs.

*If liquid temperatures are to exceed 120°F., consult factory

REQUIRED HORSEPOWER CHART

GPM	RPM	PSI			
		1000	1200	1400	1600
36.1	825	32.5	39.0	45.5	52.0
40.4	925	36.5	43.8	51.1	58.4
47.0	1075	42.3	50.8	59.3	67.7
65.0	1487	43.6	52.3	61.1	69.8
68.5	1570	46.0	55.2	64.3	73.5

Myers high pressure industrial pumps



D35-12AVD-2H/35 GPM/1200 PSI

The Myers D35-12AVD-2H is a triplex, single-acting, positive displacement pump for high pressure service. It is designed primarily for pumping water, detergent solutions and similar liquids in an unlimited variety of industrial applications. The heavy duty construction and reliable performance allow this pump to be installed in areas where durability is a must.

The power end utilizes internal single helical gear reduction drive for smooth, quiet and efficient operation. Constant lubrication is assured with a splash type oil bath system. Either direction rotation of the crankshaft permits easier installation. The high strength ductile iron fluid end affords a range of continuous operating pressures up to 1200 PSI. The pump features V-ring packed pistons which permits not only handling of higher temperatures, but offers extended packing life as well.

Slow speed operation of the pump provides minimum wear of parts and extends service life considerably. Maintenance is made easier with fluid and power end components being readily accessible. Excellent performance and serviceability are two outstanding features of all Myers reciprocating pumps.

SPECIFICATIONS

Rated Capacity	35 GPM @ 317 SPM
Rated Pressure	1200 PSI
Pinion Shaft Speed at Rated Capacity	1075 RPM
Gear Reduction Ratio	3.39 to 1
Temperature Rating	180°F.*
Cylinder Bore	2.000"
Piston Stroke	2.875"
Suction Size	2" NPT
Discharge Size	1¼" NPT
Shaft Extension	1⅝" Dia.
Keyway	⅜" x 3/32" straight
Approximate Weight	410 Lbs.

*If liquid temperatures are to exceed 180°F., consult the factory.

REQUIRED HORSEPOWER CHART

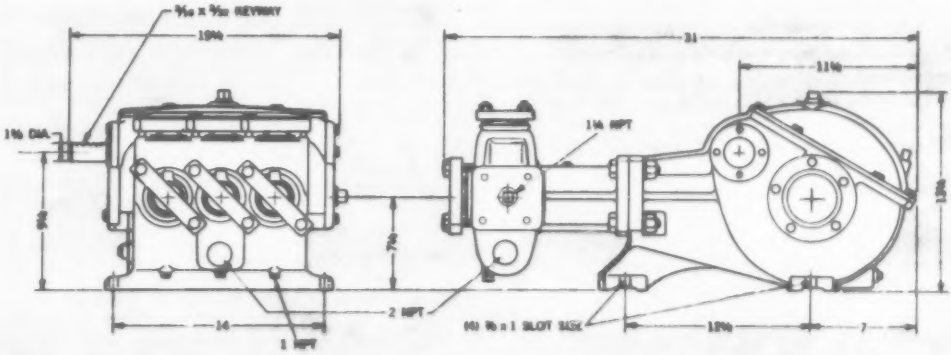
GPM	RPM	PSI			
		600	800	1000	1200
28.0	825	11.9	15.5	18.4	21.0
31.4	925	13.3	17.0	20.3	23.5
34.7	1025	14.9	18.9	23.0	27.0
38.3	1075	15.7	20.5	25.2	30.0

FLUID END COMPONENTS

CYLINDER BODY. Made from high strength ductile iron to withstand high pressure operation.
CERAMIC CYLINDERS. Tapered fit steel shells with smooth, hard coating for longer wear. Corrosion and abrasion resistant.
V-RING PACKING. Durable fabric reinforced Buna N piston material forms multiple lip seal in liner for maximum efficiency.
PISTON ASSEMBLY. V-Ring packing is supported by a fabric reinforced phenolic follower. Stud, pressure ring, spring and retainer are all stainless steel. Entire assembly is attached to piston rod with stainless steel cap screw.
SPRING-LOADED FLAT VALVES. Positive, fast-acting valves, valve springs and valve seats are all made from corrosion-resistant stainless steel. Hardened seats are tapered into body casting for easy removal.
VALVES AND CYLINDER CAPS. Cast iron with O-ring inserts. Held in place by bolted steel clamps. Caps have no threads to corrode, makes valves and pistons easily accessible.
SUCTION AND DISCHARGE. Large suction openings, two side and one front. Two flanged and tapped discharge ports.

POWER END COMPONENTS

CAST IRON GEARCASE. Serves as oil reservoir for continued lubrication of all working parts. Lid can be removed for inspection without draining oil.
PINION AND MAIN GEAR. Helical cut and shaved for smooth, friction-free operation. Alloy steel, induction hardened.
PINION SHAFT. Gear integral with the shaft. Made from alloy steel for strength and fatigue resistance.
CRANKSHAFT. Forged carbon steel.
MAIN BEARINGS. Crankshaft and pinion shaft have tapered roller bearings for minimum friction and power loss.
CRANKSHAFT JOURNAL BEARINGS. Steel backed babbit inserts.
CONNECTING LINKS. Cast iron with replaceable bronze wrist pin bearings.
CROSSHEADS AND PISTON RODS. Crossheads are made from ductile iron. Stainless steel piston rods are ground and polished to a smooth finish. Rods are pinned and threaded in perfect alignment with the crosshead and cylinder.



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Myers

F.E. MYERS CO. DIVISION OF MARMON CORPORATION

LES PRODUITS POMPES GUINARD DANS LES APPLICATIONS ENERGIE
PG PRODUCTS FOR ENERGY APPLICATIONS

Type Silhouette / Size Silhouette											
ND	●	●									
	●	●									EVN
BMKD	●	●									
			●	●		●	●			●	HMBS
KBMK	●	●		●	●		●			●	
BMK								●	●		TPMDX
DVMX	●		●			●	●		●	●	
	●	●		●							MDBO
EVE										●	
	●			●							HYDRO PRESS
OLMX DVBS DVDS			●						●		V VM VB VMB
	●	●	●	●	●		●			●	
LH	●		●								
				●	●						VMBFO VBFO VMBF
EVS	●										
		●					●				F

Services / Services / Industrie / Industry	NE	NX	NC NT	NF	NG	Pompes à vis / Screw pumps	Multicellulaires / Multistage pumps	Immergées / Submerged pumps

PRINCIPALE UNITÉ DE PRODUCTION
DU DÉPARTEMENT ÉNERGIE
POMPES ALTA-GUINARD
Z A E 45, avenue du Pont-de-Tassel
MEYTHET
74015 CRANGEVRIER - BP 726 - France
Tél. (50) 57.52.84 Télex 385065

POMPES GUINARD Une seule activité : - la pompe -
Quatre grands départements –
Only one activity : - pumps -
Four main departments –
H : Habitat - A : Agriculture - I : Industrie - E : Energie

POMPES GUINARD

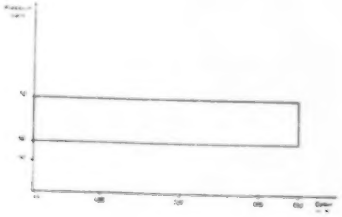
TPMDX

pompes guinard patent

the integrated turbo pump unit
for sea water reverse osmosis desalination

MAIN FEATURES :

— Working pressure : up to 70 bars (1020 PSI)
— Flow rate : between 15 m³/h (65 USGPM) and 350 m³/h (1500 USGPM)
— Running speed : 5000 to 10 000 RPM
— Power : up to 600 KW (800 HP)
— Energy recovery : up to 40 PCT



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INTRODUCTION

POMPES GUINARD is the only pump manufacturer proposing a turbo-pump specifically adapted to the desalination by reverse osmosis : the TPMDX.

This integrated turbo-pump unit, composed of a pump and a turbine back to back, mounted on the same shaft and in the same casing, separated by a hydrostatic bearing is specially designed to meet the requirements of the Reverse Osmosis Desalination.

This is why the TPMDX is the product which offers the most advantages for this application.

This particular design, patented in most countries, insures the best compromise between investment cost and running cost.

MATERIALS

All casing parts	316 L
Hydraulics	316 L with surface treatment
Wear rings	21 % Cr 8 % Ni + Mo + Cu
Shaft Labyrinth	21 % Cr 8 % Ni + Mo + Cu
Hydrostatic bearing	316 L with stellite grade 6
Hydrostatic bearing sleeve	316 L with stellite grade 12

RELIABILITY : ADVANTAGES

— Compactness — Hydrostatic bearing	— Critical speed at 120 PCT of running speed — Very low vibration level (< 4 μ)
— No mechanical seal	— Low maintenance cost
— Actual hydraulics of turbine	— Very high efficiencies — Low back pressure at turbine outlet
— Low liquid speed	— No risk of cavitation — No risk of erosion-corrosion

TOULON DEMONSTRATION BENCH

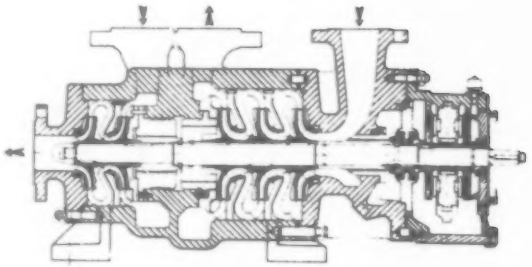
In order to prove the high qualities of this exclusive energy recovery turbo-pump unit, POMPES GUINARD has constructed a demonstration-test stand in TOULON (FRANCE), in cooperation with "Commissariat à l'Energie Atomique".

This stand consists in :

— A complete TPMDX unit size VI designed for a standard R/O plant of 2.5 million GPD fresh water (5 lines each of 1 500 GPM sea water).
— A pre-treatment system identical to the one standard of the industrial sea water desalination plants.

Characteristics :

Sea water : PH : 6 - 39 000 ppm - Temperature : 30-35° C
Process : R/0 1 000 PSI - Conversion rate : 25 %
TPMDX : Pumped capacity : 1 500 USGPM (340 m³/H)
Turbined capacity : 1 120 USGPM (255 m³/H)
Break horse power : 676 HP (504 Kw)
Energy consumption : 1,8 HP/USGPM (5,9 Kwh/m³) fresh water



For further informations and visit of the TOULON bench, please contact our ANNECY PLANT.

Phone : (50) 57.82.84

Telex : 385 385

Address : Pompes Guinard — 45, avenue du Pont de Tasset - BP 725
74015 CRAN GEVRIER - FRANCE

THE SEEDED REVERSE OSMOSIS PROCESS FIELD TESTING

H. R. Herrigel
Vice President - Research
Resources Conservatio Co.
3103 N.E. Northup Way
Bellevue, Washington 98004

The success over the past decade (1970-1980) of the reverse osmosis process for water desalination is impressive. The rapid growth in capacity of R.O. installations since 1973 is seen in Figure 1 [taken from Katz (1)], amounting to about 20 percent of total capacity for all processes by mid-1980. A consideration of the number of installations reveals that by mid-1980, R.O. accounted for about one-half of the total number of installations of all processes.

As would be expected, such success has not been achieved without effort. The earlier literature contains numerous reports of problems, but nowadays, the requirements for a successful application are fairly well established, at least for the typical desalination application. Applications of R.O. to wastewater recovery appear to have more problems. Requirements based on osmotic characteristics of the membranes used and on the colligative properties of the solutions handled have been codified and are subject to rational analysis, prediction and design. Requirements based on chemical and mechanical characteristics of the membrane and the configuration in which it is used, have been established semi-empirically on the basis of tests and experience.

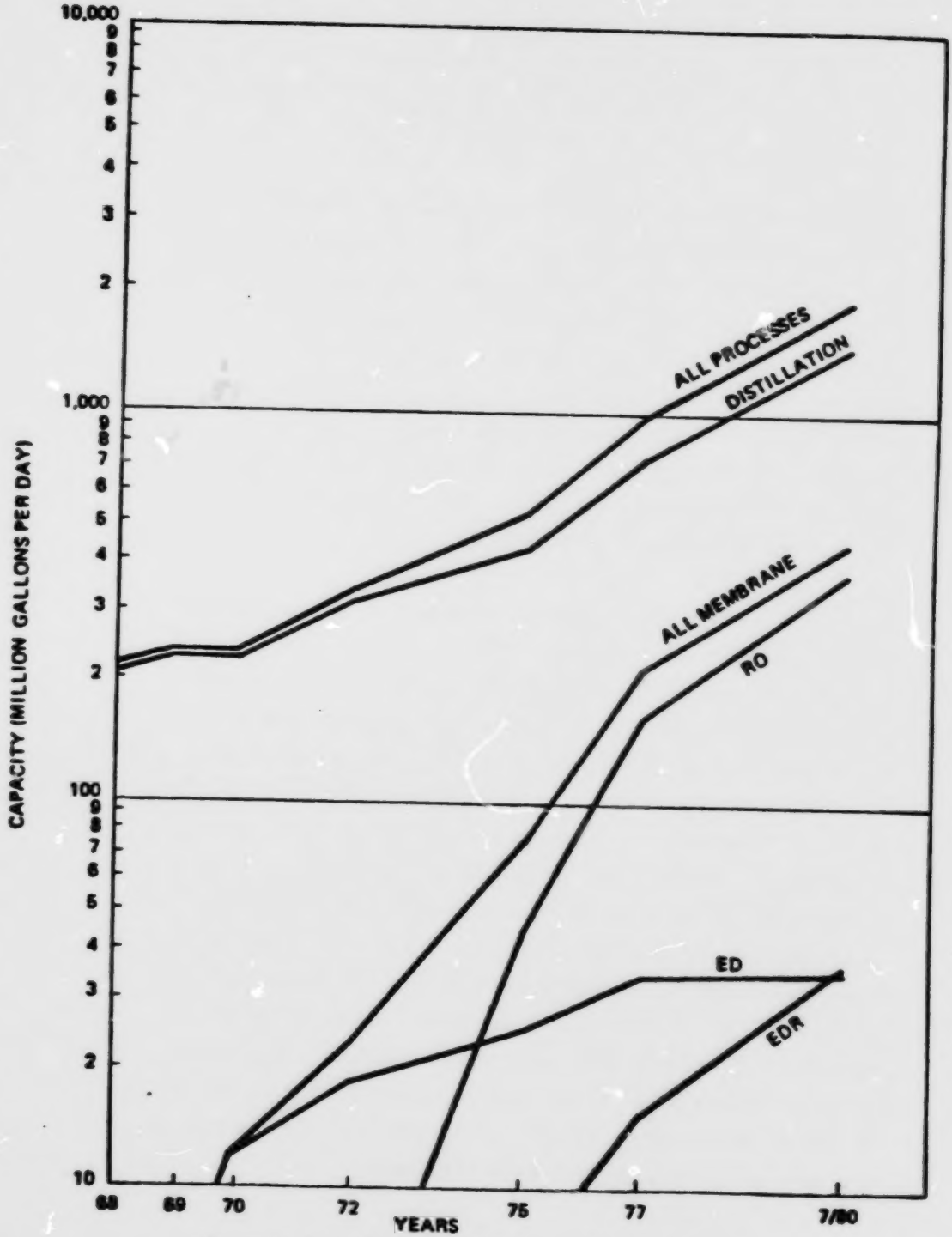


Figure 1. Capacity (Millon Gallons per Day) of Water Desalting Installations over 25,000 GPD

Among others, the standards adopted to prevent plugging, fouling, and scale precipitation fall in this category.

To avoid plugging and fouling by particulate matter, rather stringent requirements are placed on the presence of these materials in the R.O. feed, e.g., a silting density index less than 5.0 for spiral (or 3.0 for hollow fine fiber), or a turbidity less than 0.2 NTU. Standards have tended toward greater stringency in recent years. To achieve such cleanliness, a filtration pre-treatment system is almost always required. Typically, a multi-media filter would be used, often with a preceeding coagulator-clarifier. Even with particulates and colloids controlled, fouling of R.O. membranes can occur if heavy metals (Fe, Al, Cu, etc.) or oil and certain other organics are present in the feedwater. Such materials may be removed in the particulate/colloid pretreatment section by manipulation of pH, and sometimes addition of activated carbon treatment for organics. Often foulants cannot be removed completely, and resort is made to periodic cleaning of the R.O. with detergent/chelant solutions. Scaling, the precipitation of low solubility solutes on membrane surfaces, can be a serious problem in R.O. equipment. The most common scale formers are calcium carbonate, calcium sulfate, and silica. One obvious method of avoiding scale is to restrict operation such that the solubility limit of the scale former is not exceeded, and just that is done in many cases. In recent years, some increased tendency in that direction has been noted.

Solubility limits may be exceeded to a limited extent if a scale inhibitor is added, and this is a common practice. The limit of effectiveness of a scale inhibitor is often difficult to predict, but seldom exceeds twice the uninhibited concentration and is often lower. If operation beyond scale former solubility limits and the effective range of inhibitors is desired, resort is made to pretreatment system removal of one constituent of the scale former. Prevention of calcium carbonate scale is achieved by acid addition (necessary for other reasons as well) which converts carbonate ions to the soluble bicarbonate form. Reduction of calcium by softening will allow higher concentrations before reaching the calcium sulfate solubility limit. Similarly, silica may be removed along with calcium during softening.

It is apparent that, even for a relatively simple desalination R.O. application with common feedwaters, pretreatment system requirements are significant. If operation is desired beyond the solubility limits of scale formers such as calcium sulfate and silica, pretreatment requirements become much more extensive. The cost, both capital and operating, of such pretreatment systems can double system costs as shown in Figure 2 [taken from O'Neail, Kirchner and Day (3)]. The principles described above apply to wastewater applications of R.O. as well as the straight forward desalination applications. However, the magnitude of the problems is greatly increased with wastewaters.

Wastewaters tend to be high (very high in R.O. terms) in particulates and colloidal material. Wastewaters, particularly industrial wastewaters, usually contain some oil, organics of varying nature, and small-to-medium amounts of heavy metals. A majority of wastewaters are near saturation in calcium sulfate and silica - Figures 3 and 4.

In any case, saturation is usually reached in operation since high recovery (in excess of 90 percent) is desired to reduce reject disposal problems. Extensive pretreatment facilities are needed for R.O. to operate successfully on such feeds. Further, wastewaters almost always vary widely and rapidly in composition and characteristics. Figure 5 [Gianelli (4)] shows the variation with time of the silting index of a natural pond water as an example. All of these factors lead to greater-than-anticipated expense, operational difficulty and upsets not only in the pretreatment section but in the R.O. system itself. While some successful installations can be adduced, the general history of R.O. in high recovery wastewater applications is, at best, of mixed success.

Field testing of a new, patented (2) process approach to the prevention of scale precipitation and fouling in R.O. equipment is the subject of this paper.

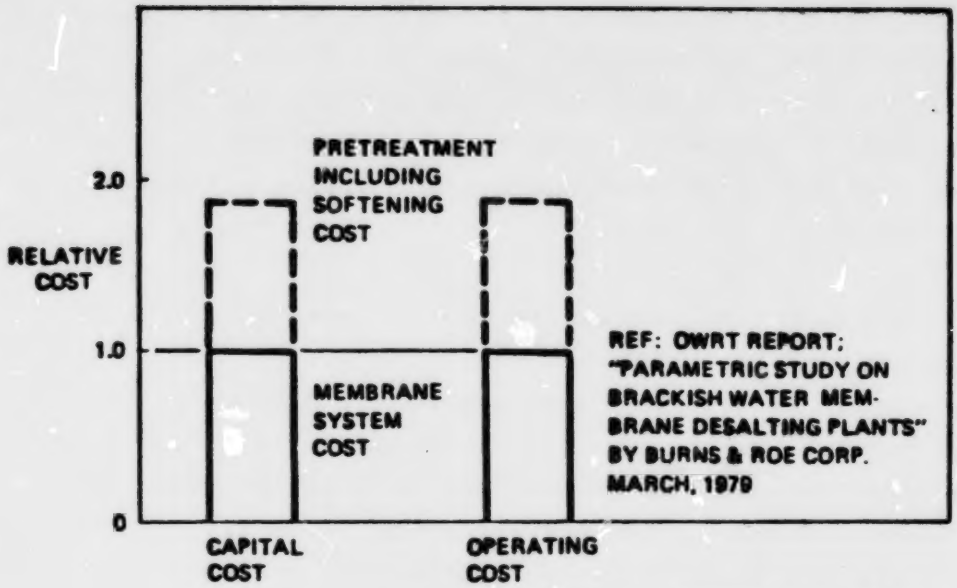


Figure 2. Impact of Pretreatment on Total Reverse Osmosis Costs

	mg/l (AS ION)
SODIUM	106
CALCIUM	540
MAGNESIUM	280
CHLORIDE	58
BICARBONATE	20
CARBONATE	0
SULFATE	2,450
SILICA	60
TOTAL DISSOLVED SOLIDS	3,491
pH	5.5

NOTE: This water is saturated with $CaSO_4$

Figure 3. Utah Water Chemistry (Acidified)

ALL CONSTITUENTS AS mg/l, AS IONS			
CATIONS		**ANIONS**	
Ca	800	HCO_3	70
Mg	86	SO_4	1900
Na	110	Cl	80
K	11	F	0.5
Mn	110	NO_3	4
		SiO_2	50
	pH	6	

Figure 4. Mine Water

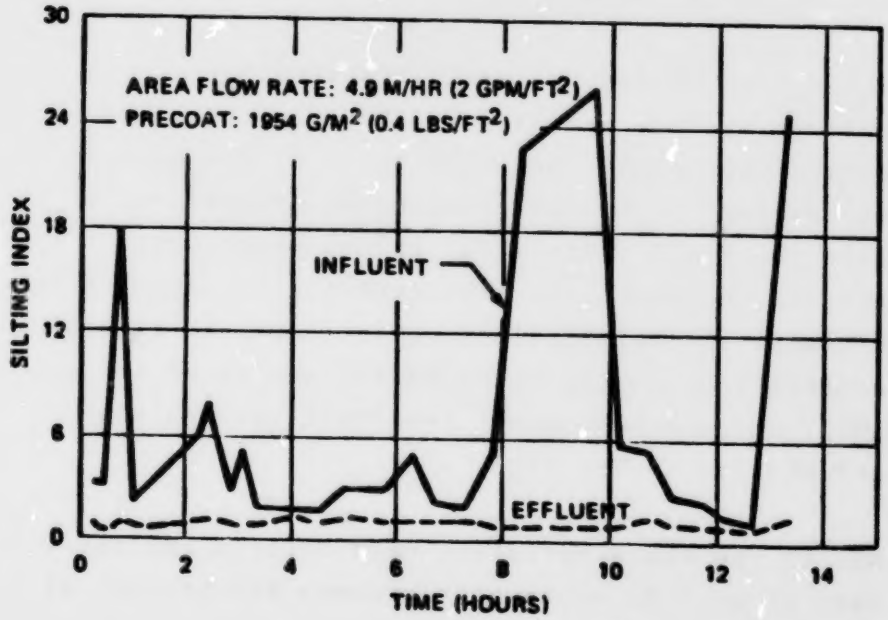


Figure 5.

This process has been called "seeded R.O.," from the fact that seed crystals are deliberately introduced in the brine stream to induce preferential precipitation of scaling components on the seed. Since the slurry circulating in the R.O. apparatus carries in excess of 20,000 mg/l of fine seed crystals, the tubular R.O. configuration is used, although other configurations are under investigation.

Results of earlier laboratory testing were reported by O'Neail, Kirchner, and Day in 1982 (3). The feedwaters for these tests were:

- laboratory synthesized cooling tower blowdown

- A well-water blend, (OWRT Roswell Test Facility Plant Blend Number 3).

These test feedwaters were at saturation in calcium sulfate and silica. However, they did not exhibit the other characteristics of industrial wastewaters mentioned previously. Therefore, a site for field testing was sought which would possess the wastewater characteristics expected in a practical installation. An appropriate site and cooperating, owning organization was found in late 1982, and a five-element test unit was installed and started in May 1983.

All of the characteristics needed for a realistic test of an R.O. wastewater process are present at this site.

- The R.O. feed is a mine wastewater.
  - saturated in calcium sulfate
  - moderately high in silica
  - contains significant quantities of aluminum and iron, other heavy metals present
  - contains oil on occasion
  - other organics present in small amounts
  - particulates present in quantities to cause a murky appearance
  - temperature is 85°F to 90°F
  - variable in composition
- The location is overseas.
- Operation is by local personnel, inexperienced with R.O.
- Operation was day only, six days a week for the first three months.
- The R.O. elements are a new design not previously used for the "seeded" process.
- Recovery is 95 percent.

Two analyses of the raw mine water are shown; one taken in August 1983 (Figure 6), the other in February 1984 (Figure 7). A photograph of the raw mine water feed to the seeded R.O. unit is shown in Figure 8.

Before discussing the test results, a brief description of the process, the test unit, and the test protocols is in order. The process itself is quite simple in concept, although not quite so simple in practical application. As is well known, the activation energy for cystallization from solution varies with the surface presented to the saturated (or supersaturated) solution.

RAW MINE WATER – AUGUST 1983	
CALCIUM (Ca)	333 mg/l AS ION
MAGNESIUM (Mg)	120
SODIUM (Na)	132
POTASSIUM (K)	13
STRONTIUM (Sr)	2.8
BARIUM (Ba)	0.04
ALUMINUM (Al)	25
IRON (Fe)	6.4
MAGANESE (Mn)	8.4
ZINC (Zn)	2.1
NICKEL (Ni)	8.1
TOTAL ALKALINITY (TO pH 4.5)	NIL
(TO pH 3.7)	17.4
FREE AMMONIA (N)	8
NITRITE NITROGEN (N)	0.11
NITRITE NITROGEN (N)	8.2
CHLORIDE (Cl)	88
FLUORIDE (F)	1.2
SULFATE (SO4)	1825
TOTAL PHOSPHATE (P)	0.18
SILICA (SiO_2)	44
pH	4.24
CONDUCTIVITY AT 25°C, µS/cm	2850
SUSPENDED SOLIDS	86

Figure 6.

RAW MINE WATER – FEBRUARY 1984	
CALCIUM (Ca)	404 mg/l AS ION
MAGNESIUM (Mg)	113
SODIUM (Na)	126
POTASSIUM (K)	11
STRONTIUM (Sr)	1.2
BARIUM (Ba)	0.08
ALUMINUM (Al)	46
IRON (Fe)	27
MANGANESE (Mn)	8
ZINC (Zn)	2
NICKEL (Ni)	6
SULFATE (SO_4)	1785
SILICA (SiO_2)	67

Figure 7.

Taking advantage of this fact, it has been found that, if a sufficiently large amount of "seed crystals" are present in a supersaturated or supersaturating solution, precipitation down to saturation will occur only on the "seed crystal" surfaces and not at all on other surfaces presenting to the supersaturated solution. Questions that must be decided for a particular application are:

- What material for "seed"?
- What quantity of "seed"?
- How to keep "seed" uniformly distributed?

In general, the "seed" material should be crystals of the material which will precipitate. However, it has been found that limited amounts of foreign precipitants can be "seeded" on certain "seed" crystals and scale formation by the foreign precipitant thereby prevented. Silica, for instance, can be "seeded" on calcium sulfate crystals (within limits) and silica scaling prevented.

The amount of seed depends, among other things, upon the nature of the precipitating material and its solubility, the rate of precipitation, and the size of the "seed" crystals. Slurry concentrations can range from 1 to 30 percent suspended solids. More detailed discussion is contained in the patent for the process, to which reference is made (2).

The matter of keeping the "seed" uniformly distributed, while a matter of careful mechanical design, is of great importance to the success of the process. All the usual precautions exercised in handling slurries must be observed: avoid stagnant areas, maintain velocities, avoid obstructions, flow passages must be large relative to the largest crystals. For these reasons, the tubular R.O. configuration has been used to date for the "seeded R.O." process. Some variations of spiral configurations have been tried, unsuccessfully so far. Other configurations are under consideration.

The test unit was a skid-mounted assembly of up to six tubular R.O. elements in series with associated pumps, tanks, valves, chemical addition equipment, etc. The unit had been used for previous tests equipped with different R.O. elements. A photograph is shown in Figure 9, and a flow schematic in Figure 10. (The feed tank, pump and filter were bypassed early in the test.) Note that the flow schematic shows a recycle of the reject brine to the feed tank. This is done so that a 95 percent recovery can be attained with a small number of modules, while maintaining the minimum brine flow required in tubular elements - especially when handling a slurry. A hydroclone is used on the reject flow to reduce the suspended solids in the reject to equal the amount of solids precipitated. The remainder is recirculated to the system. Not long after system start-up, the feed tank, feed pump, and feed filter shown on the schematic were eliminated. Feed supply and chlorine addition were thereafter made to the recirculation sump.

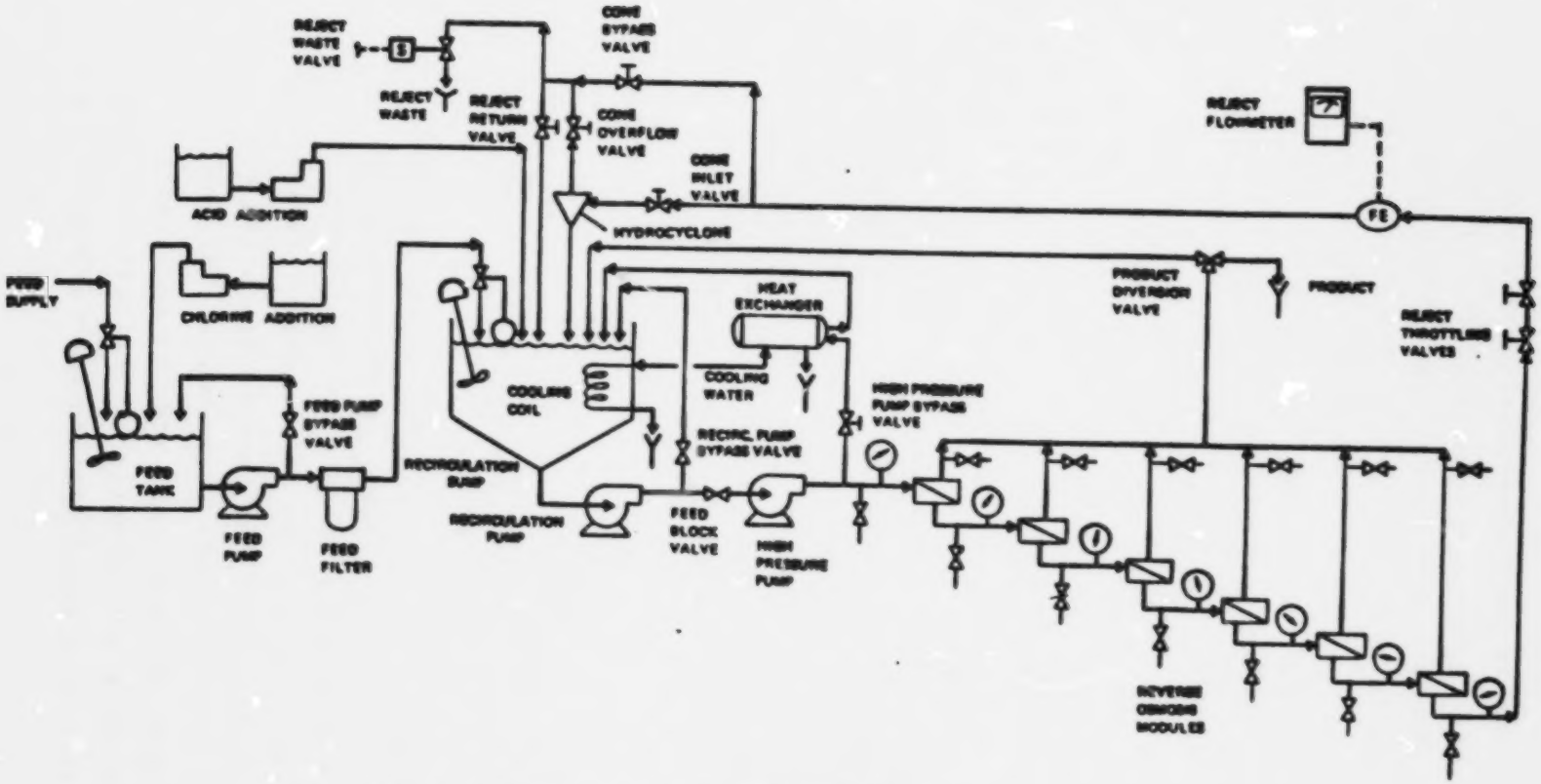


Figure 10. Schematic Showing Seeded RO Test Unit

The R.O. elements used were obtained from local manufacturers in the overseas location. In many respects, they are a standard, approximately eight foot, tubular element containing 19 one-half inch tubes in series. These elements do use a unique proprietary tube support system. The membrane is a nominal 90 percent rejection cellulose acetate with conventional flux characteristics. These particular tubular R.O. elements had not previously been used for the "seeded R.O." process, although limited laboratory tests had been completed before overseas start-up.

The test protocol aimed in general to test the feasibility of the "seeded R.O." process to treat the calcium sulfate saturated mine water previously mentioned to a high recovery, preferably in excess of 90 percent. To that end, evaluation factors were concentration factor (recovery), permeate flux, pressure drop, and permeate quality and rejection. The variation of the factors with time is, of course, important. To these objective factors were added the more subjective factors of reliability, adaptability to changing conditions, and operability by local operators.

The test procedure finally adapted was rather simple. A baseline element performance on two percent sodium chloride solution was first established. A rerun of this baseline is intended at the conclusion of the test to establish comparative data on module performance. At the beginning of the test, all modules met their specified flux and rejection. The test unit was then placed in a concentrating mode (recycling all

reject) with one R.O. element installed, and mine water feed started.

At this time seeding of the recirculation sump with gypsum "seed crystals" was necessary since no level of "seed" had built up in the system by natural precipitation. When the desired reject concentration representing 95 percent recovery (20 concentration factors) was reached, the unit was switched to a normal operating mode wherein both permeate and reject are discharged. Due to the size of the recirculation sump, and the one-shift-a-day operation imposed by operator availability, the concentrating mode took about two weeks.

After reaching concentration, the normal operating mode was continued for about two weeks (96 hours) with the single R.O. element. This established that satisfactory non-scaling operation had been achieved, and served to further familiarize the operators with the equipment and procedures. Then R.O. elements were added one at a time until the applied pressure differential to the R.O. membrane was too low to be useful. For the equipment used and this feedwater, five elements in series was the limit.

About this time, the operator availability was improved and 24-hour-a-day, six-day-a-week operation was possible. Operation on that basis has continued and is continuing. About 2,600 hours have been accumulated on the high-time element.

At 95 percent recovery (20 concentration factors), the original feed of 3,000 mg/l total dissolved solids has been concentrated to a reject containing approximately 60,000 mg/l total solids. Of this, about 20,000 mg/l remains dissolved while about 40,000 mg/l is present as suspended solids having precipitated from solution. Figure 11 is a picture of the liquids in the recirculation sump, which is about 50,000 mg/l total solids since the recirculated reject is somewhat diluted by the incoming feed. This, of course, is the slurry circulating through the R.O. elements.

An analysis of the sump recirculation brine is shown in Figure 12. Note the presence of significant amounts of heavy metals, especially iron, aluminum, manganese and nickel. Incidentally, this analysis would indicate that, at the time of sampling, recovery was running closer to 90 percent than 95 percent. This analysis also illustrates the difficulty of precisely measuring concentrations in these concentrated solutions. The mass balances for sodium, magnesium, and chloride (all presumably non-precipitating) each yield different results for concentration factor. Figure 12 also gives an analysis of the permeate. The permeate is of good quality and quite suitable for mine reuse. An analysis of the precipitated solids is shown in Figure 13. As expected, the major constituent is calcium sulfate, apparently in the gypsum form.

	SUMP RECIRCULATION BRINE	PERMEATE
CALCIUM (Ca)	440 mg/l AS ION	10.9 mg/l AS ION
MAGNESIUM (Mg)	1025	8.3
SODIUM (Na)	1560	81
POTASSIUM (K)	66	3.6
STRONTIUM (Sr)	40	0.1
BARIUM (Ba)	0.45	< 0.02
ALUMINUM (Al)	280	0.5
IRON (Fe)	100	0.06
MANGANESE (Mn)	69	0.48
ZINC (Zn)	18.3	0.13
NICKEL (Ni)	72	0.30
TOTAL ALKALINITY (TO pH 4.5)	NIL	2.1
(TO pH 3.7)	36	12.8
FREE AMMONIA (N)	41	2.6
NITRITE NITROGEN (N)	0.08	0.11
NITRATE NITROGEN (N)	15.5	6.3
CHLORIDE (Cl)	380	50
FLUORIDE (F)	7.5	< 0.1
SULFATE (SO_4)	8250	112
TOTAL PHOSPHATE (P)	0.75	0.12
SILICA (SiO_2)	92	12.9
pH	4.44	5.22
CONDUCTIVITY AT 25°C µS/cm	12200	545
SUSPENDED SOLIDS	44050	< 1

Figure 12.

PRECIPITATED SOLIDS		
SAMPLE DRIED AT 105°C PRIOR TO ANALYSIS		
LOSS ON IGNITION		
% LOSS TO 180°C	4.85	
180 – 450°C	1.73	
450 – 600°C	2.71	
600 – 1000°C	1.82	
ANALYSIS OF DRIED SOLIDS		
ACID INSOLUBLE (SILICACEOUS)	5.38%	
CALCIUM (Ca)	247,000	mg/kg
MAGNESIUM (Mg)	496	
STRONTIUM (Sr)	766	
BARIUM (Ba)	150	
ALUMINUM (Al)	8,238	
IRON (Fe)	2,343	
MANGANESE (Mn)	22	
ZINC (Zn)	32	
NICKEL (Ni)	200	
COPPER, COBALT, CHROMIUM, LEAD	25–34	
SULFATE (SO_4)	563,600	

Figure 13.

Note the presence of about five percent precipitated silicaceous material, as well as the presence of significant amounts of precipitated iron and aluminum. The 4.6 percent loss on ignition for the solids after initial drying at 105°C is probably due to loss of hydration water, although such loss is frequently due to the presence of organics.

By January 1984, calendar time for the field test was eight months. Accumulated running time was 2,600 hours. Downtime was due almost entirly to operator availability -- during the first months of the test, operation was only eight hours a day for this reason. Judged on both the subjective and objective criteria, the process and test unit performance has been satisfactory. Despite the difficult conditions and severe service described, the unit has operated, and continues to operate, with no evidence of scaling. No cleaning of the R.O. elements was performed from start-up in May 1983, until January 1984.

Mechanical problems have been relatively minor. The high pressure pump seals required replacement in January but have been otherwise free of troubles. This pump had seen considerable service in our laboratories before the start of the current test. The feed pump motor proved unreliable, and this whole section was bypassed early in the test. At first, some incidents of hose blow-off from the R.O. elements occurred. This was solved by a change of hose and hose fittings.

Some early incidents of membrane rupture in the R.O. elements caused concern that erosion of the membrane might be occurring. Inpection, however, showed no evidence of erosion. Instead, cracking of the membrane support structure was found. Change in the support element has solved this problem.

The more objective measures of performance (flux, pressure drop, rejection) are presented in Figures 14 to 24. As can be seen, rejection and pressure drop have remained essentially constant throughout the test. An unexplained period of higher pressure drop is seen for module 4 (Figure 23) from time 300 hours to 1,000 hours. From 1,000 hours to 2,600 hours, however, pressure drop for module 4 has remained constant at about the original value. The flux versus time plots (Figures 14 to 21) are of some interest. First, the short-time modules, 1A and 2A, are R.O. modules which were replaced due to the membrane rupture mentioned previously. The flux values shown are normalized to 25°C and 2,758 kPa (400 psi). Flux has remained stable since about test time 500 hours. Prior to that time, a pronounced drop in flux was experienced especially for the first elements in the string. The reason for this behavior is not clear at this time. Scaling is not the cause, since pressure drop remains constant, and elements removed and examined show no sign of scaling. Fouling by organics or heavy metal oxides might be a cause. If so, the reason for the stabilization after 500 hours is unclear. Further, in January 1984, one R.O. element was cleaned with detergent and citric acid with no significant change in performance. Investigation is continuing.

The described field test of the "seeded R.O." process is regarded as successful and encouraging. The test will continue until mid-1984. Design of units for commercial offerings is in progress.

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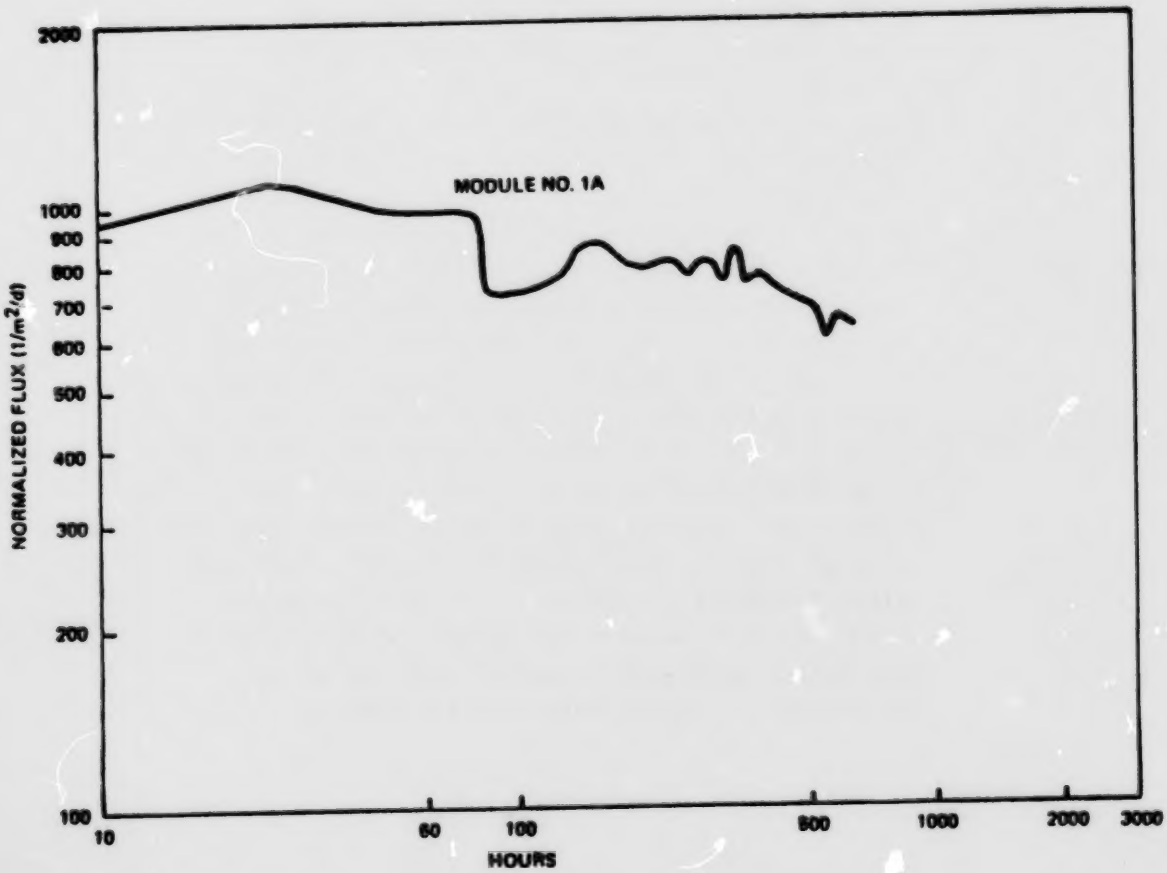


Figure 14.

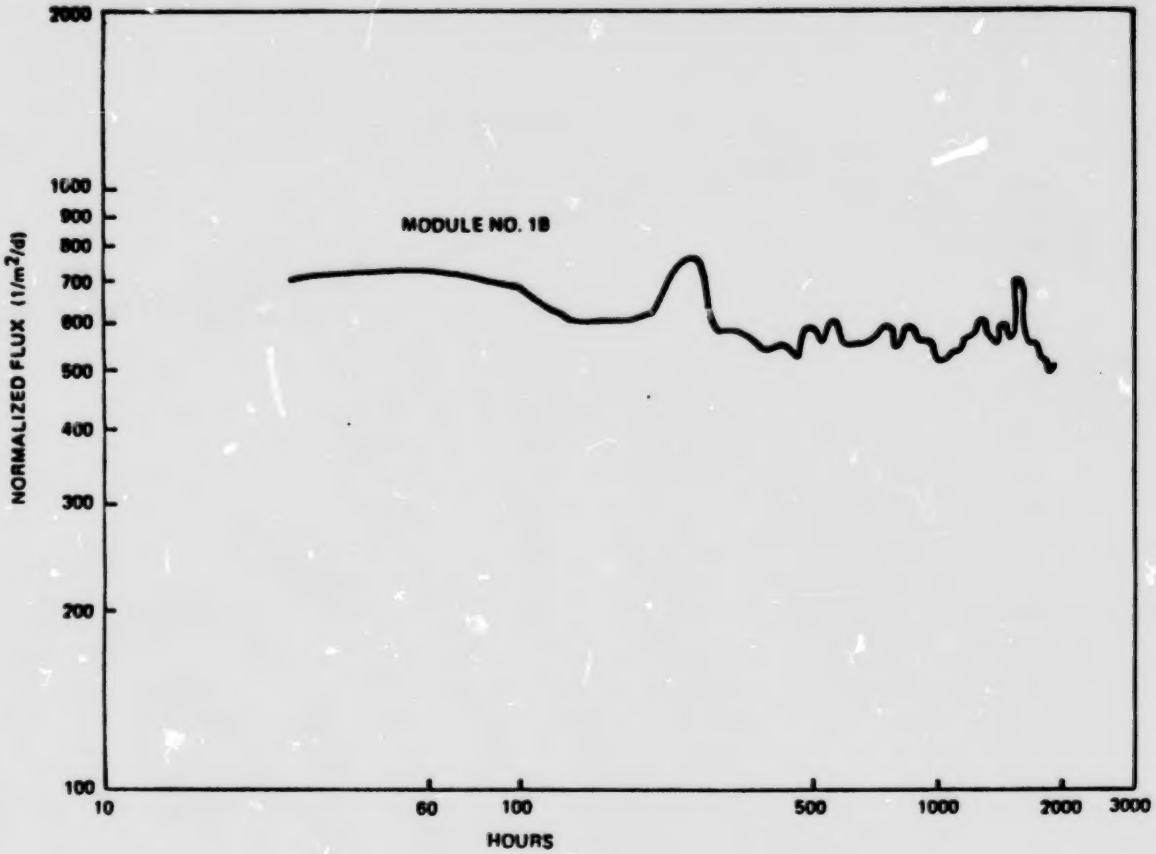


Figure 15.

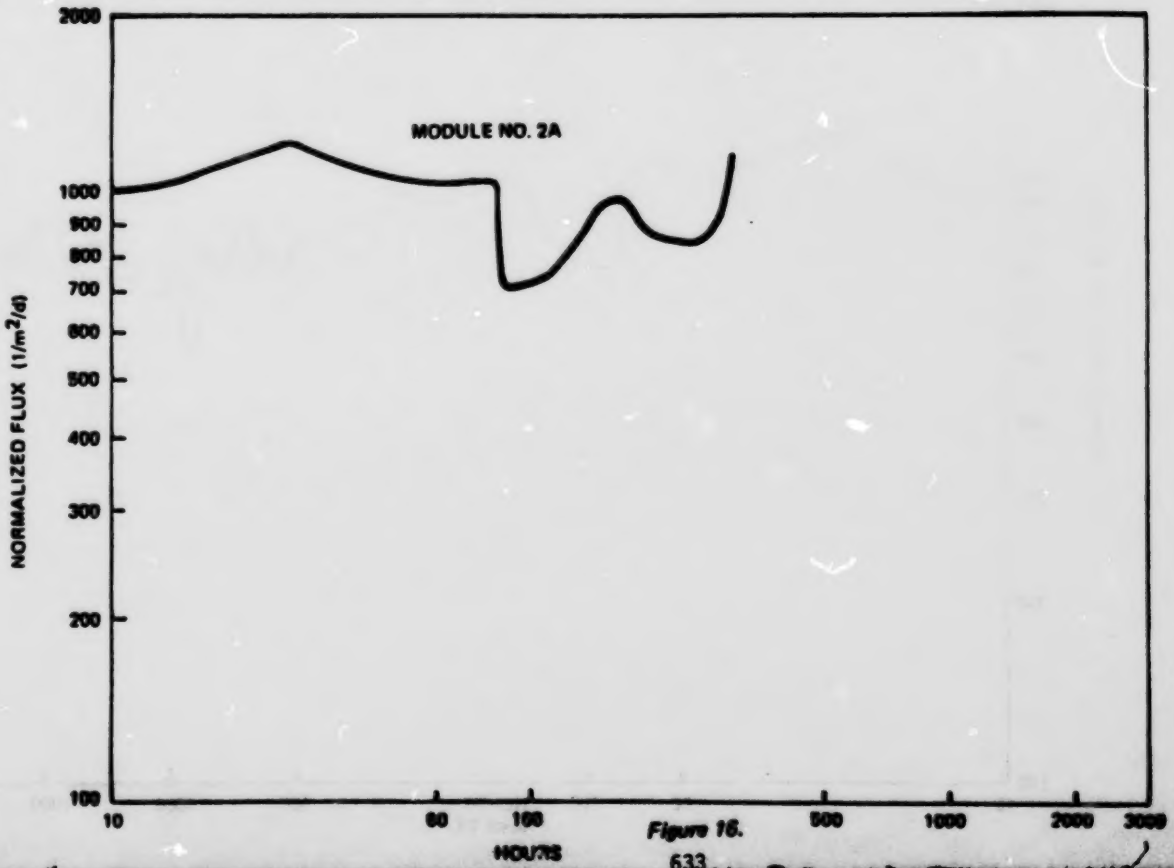


Figure 16.

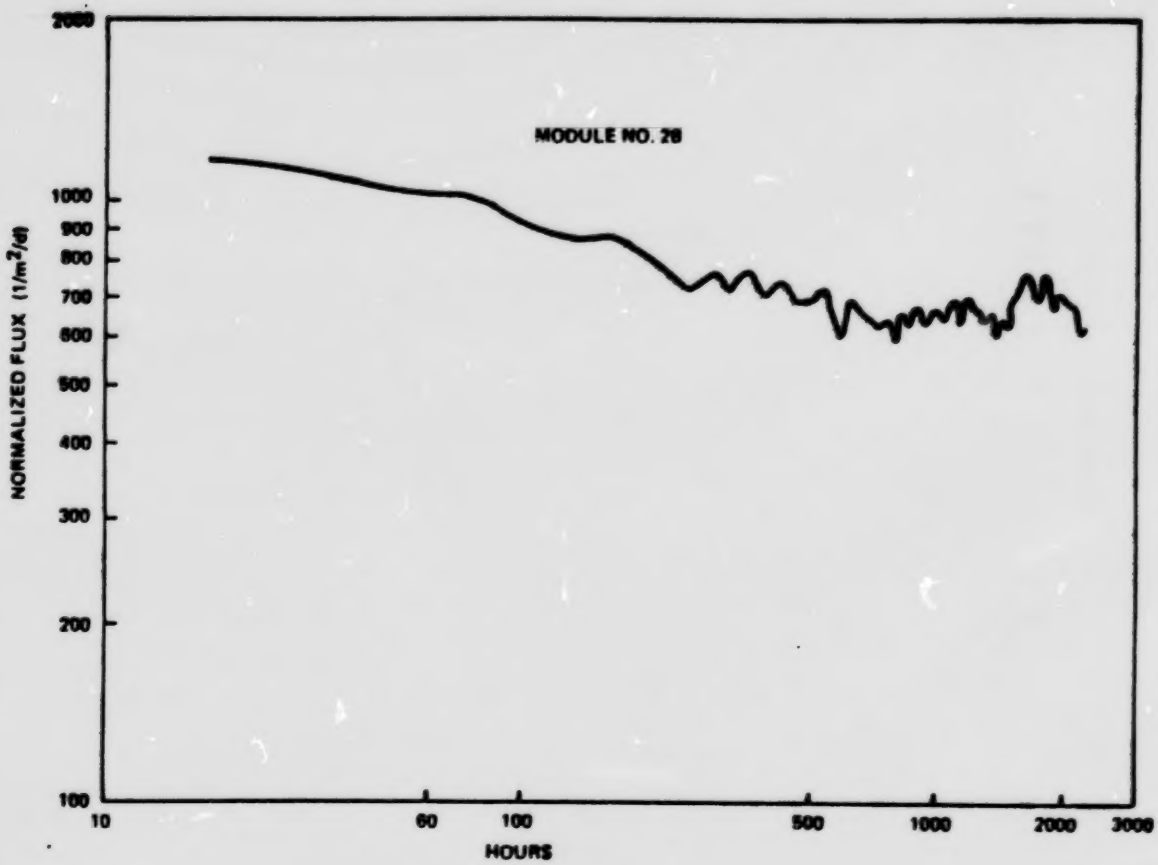


Figure 17.

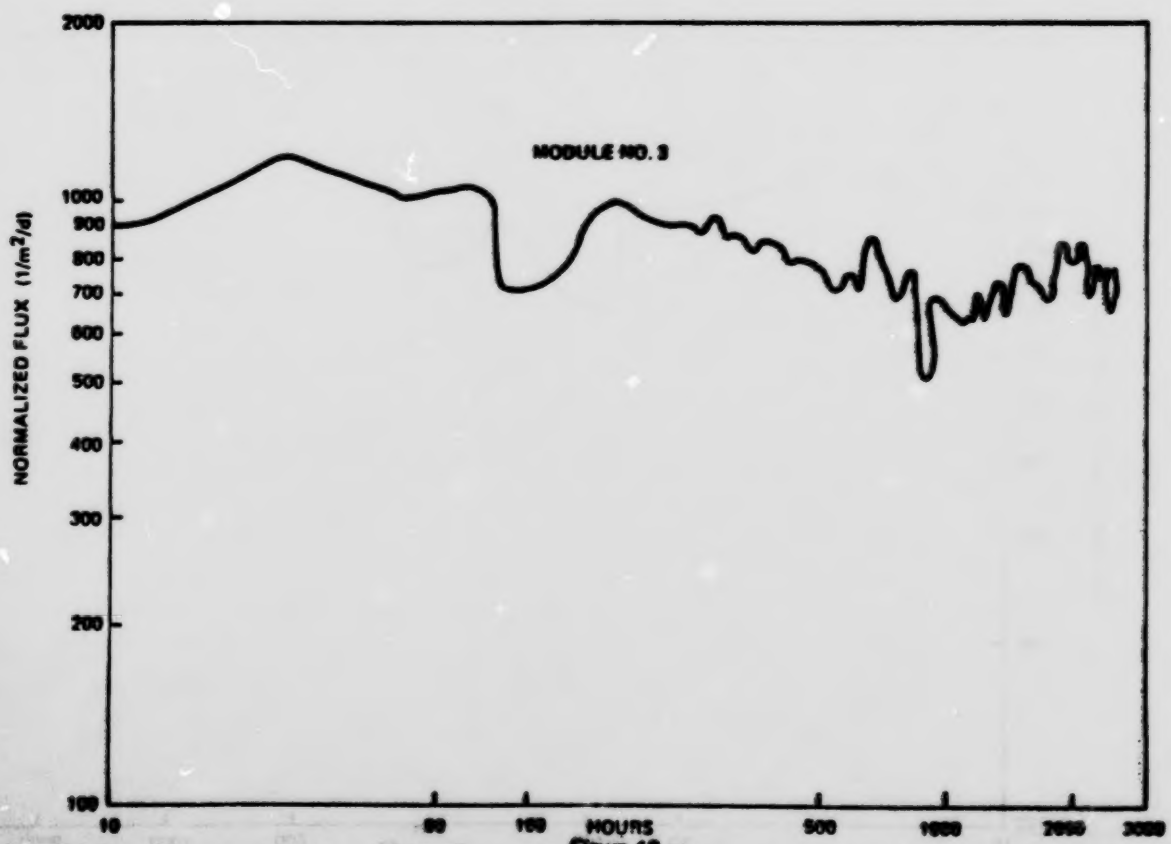


Figure 19.

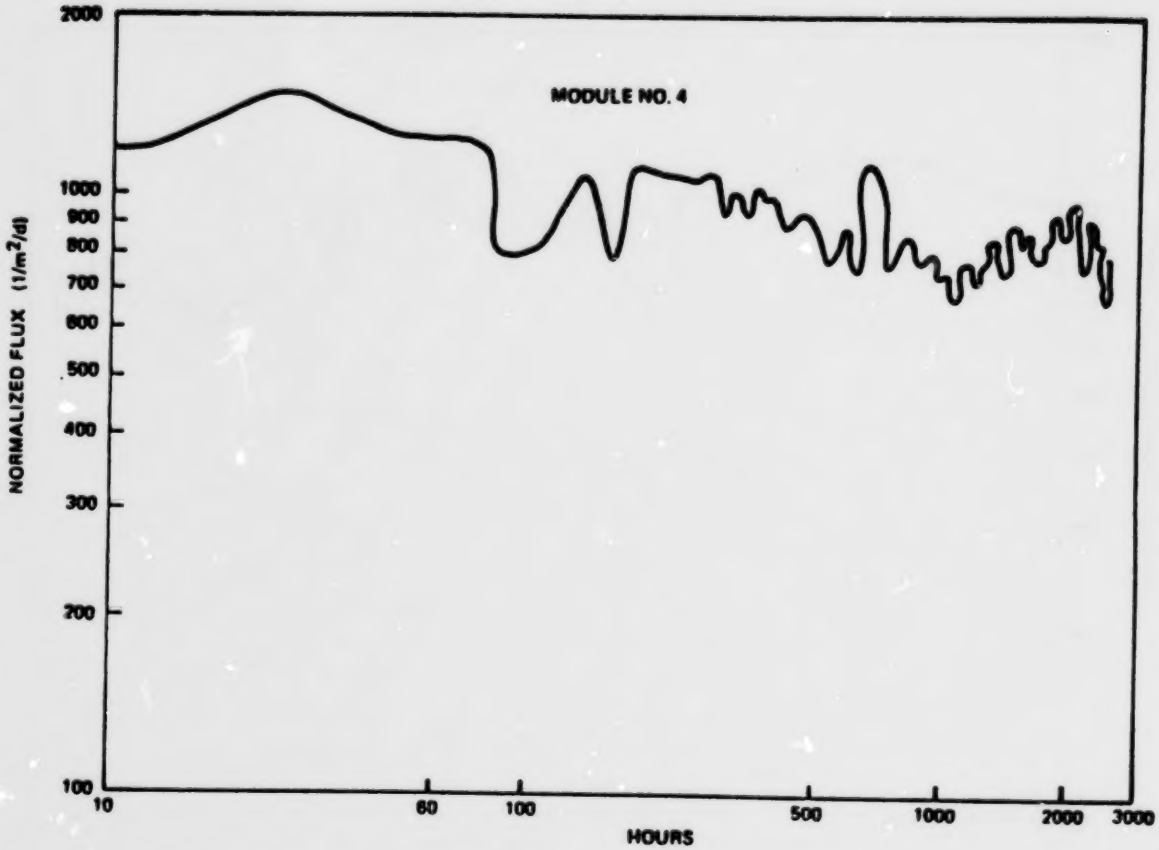


Figure 19.

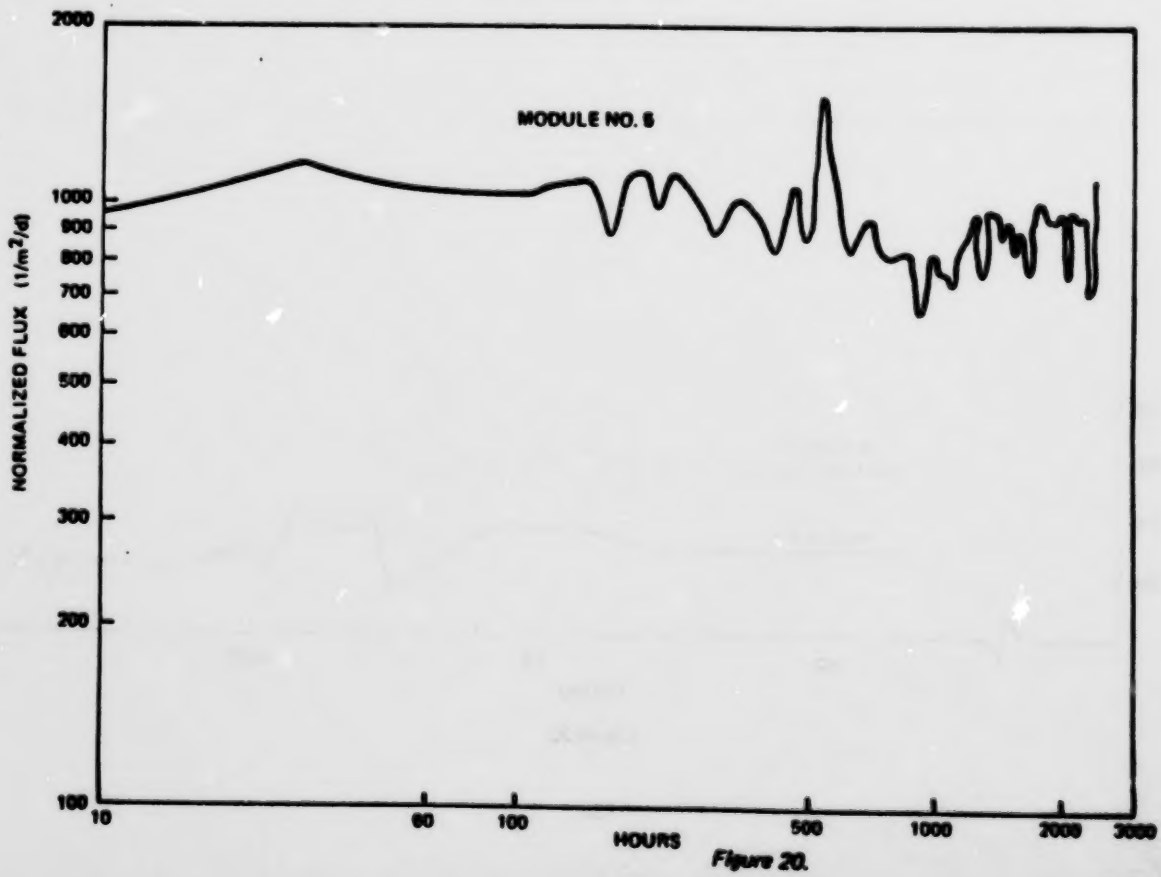
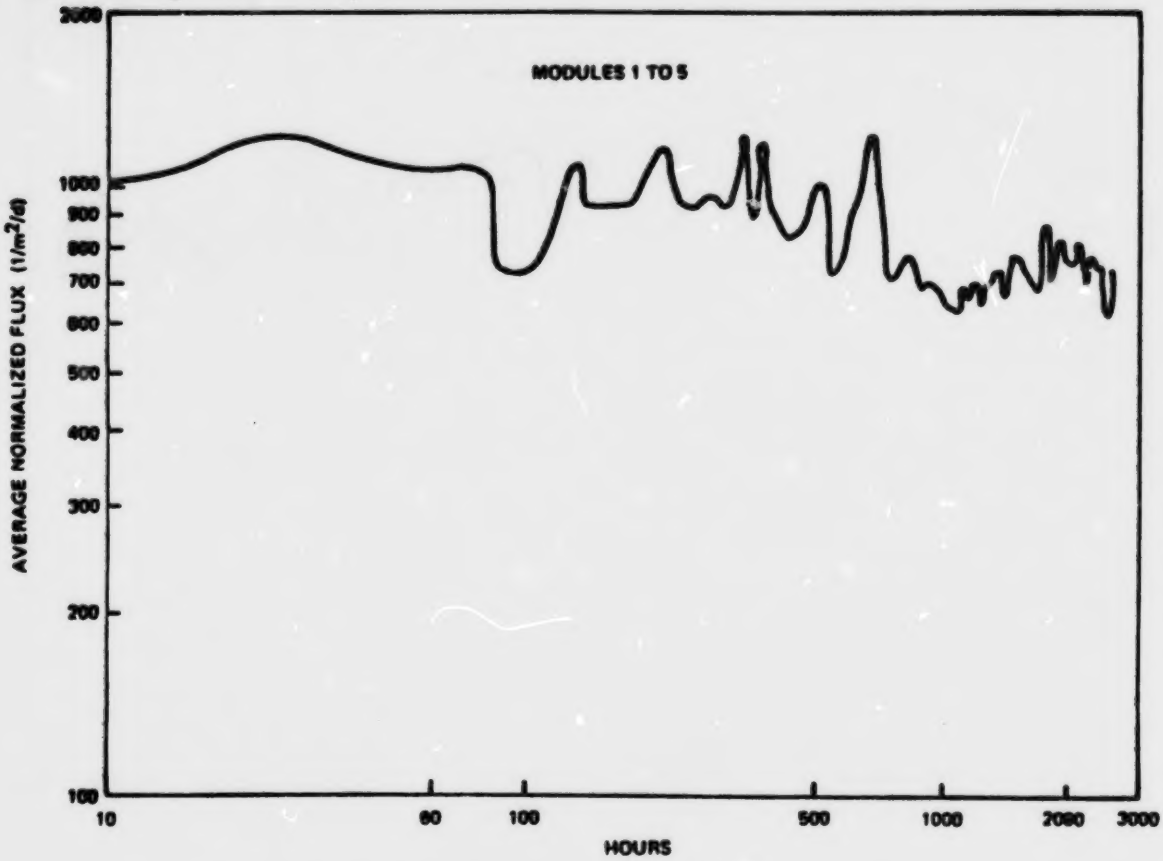


Figure 20.



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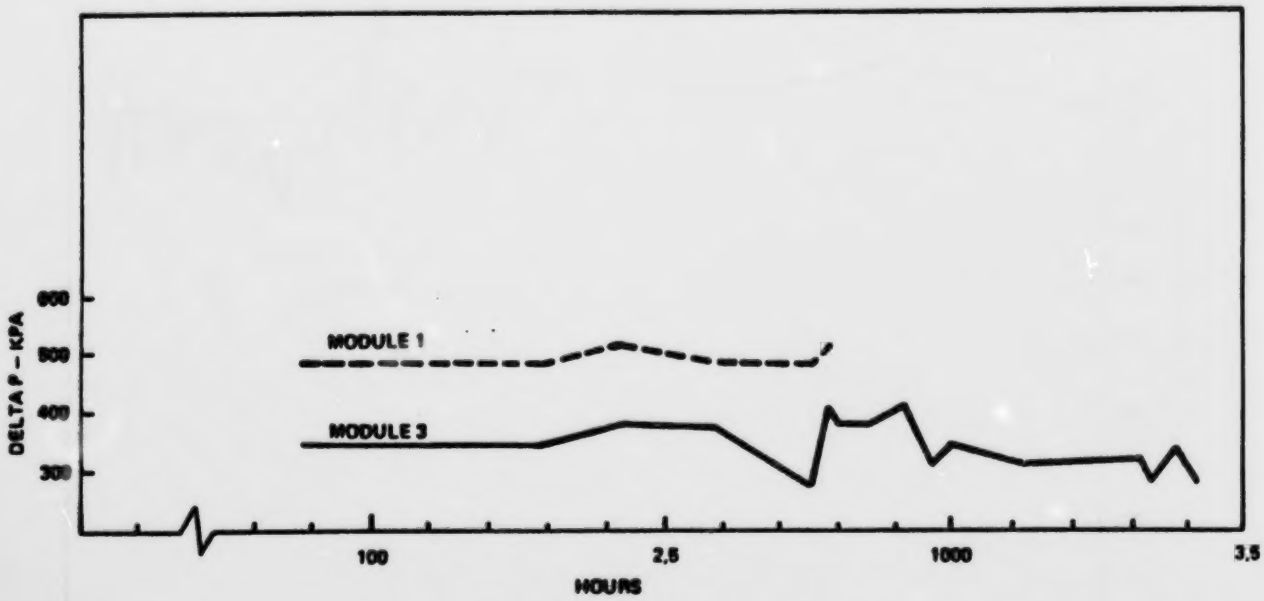

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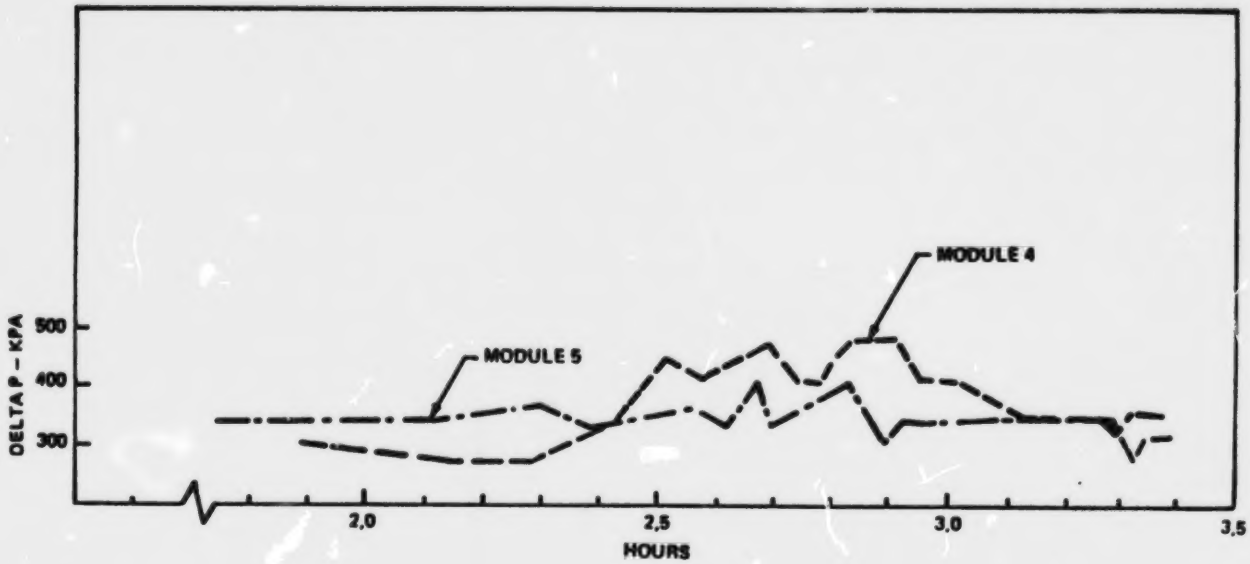


Figure 23.

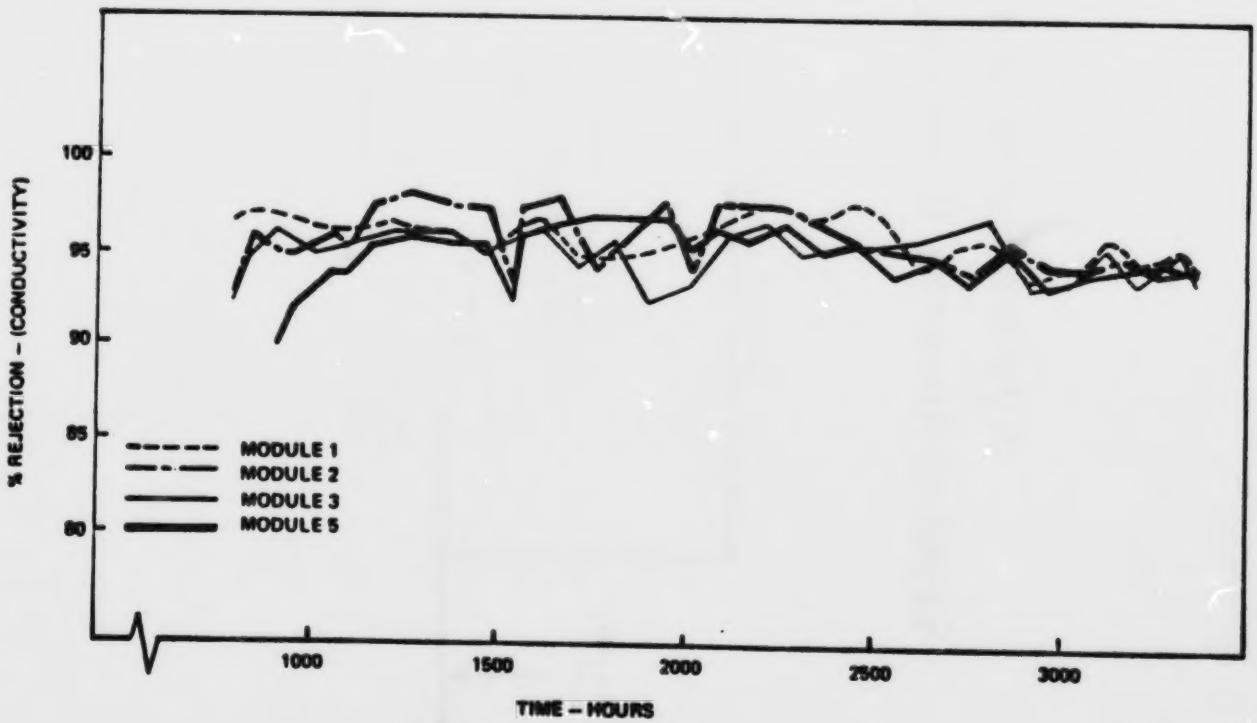
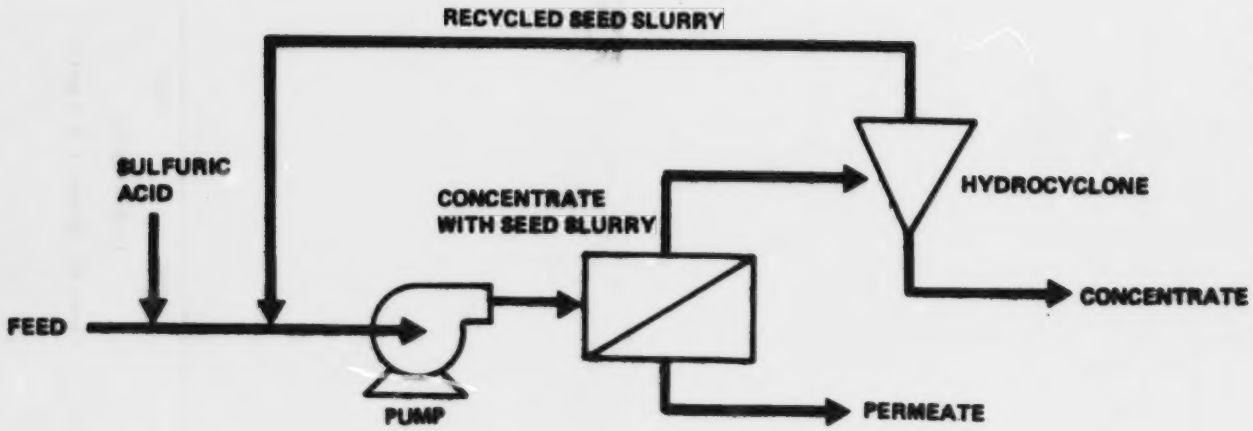


Figure 24. Module 1, 2, 3 and 5

System Schematic
Seeded Reverse Osmosis Process



HIGH RECOVERY SEED SLURRY REVERSE OSMOSIS DEMONSTRATION FOR DESALTING WATERS SATURATED IN CALCIUM SULFATE

Final Report

by

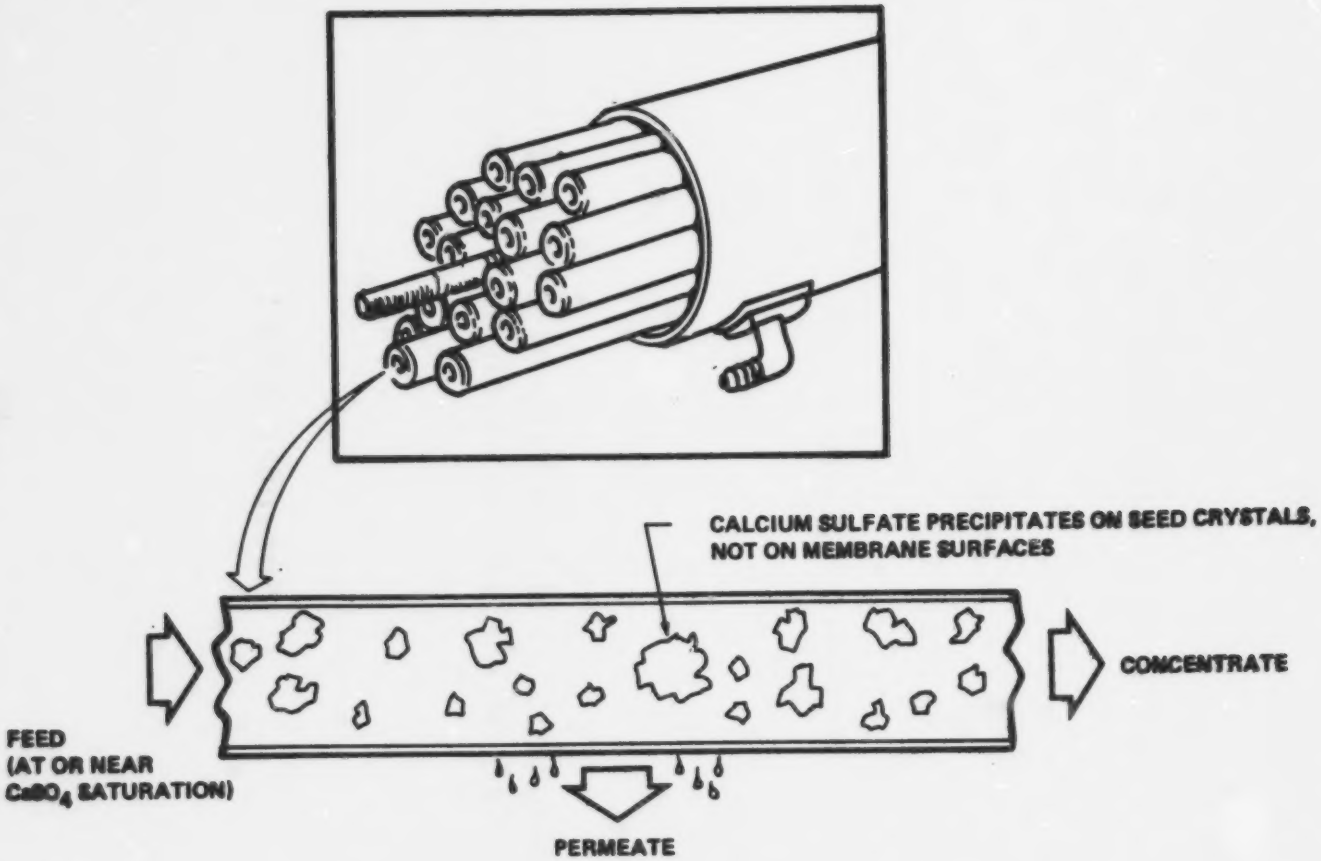
Resources Conservation Co.

for

United States Department of the Interior
Office of Water Research and Technology

February 1981

Seeded Reverse Osmosis Concept



SUMMARY

A demonstration of Resources Conservation Co's patented seeded reverse osmosis (RO) process was conducted at the Office of Water Research and Technology test facility in Roswell, New Mexico. This work was carried out under OWRT Contract No. 14-34-0001-0451.

Seeded RO is a process that enables an RO system to be operated at high recoveries on a feed water that is saturated or nearly saturated with calcium sulfate. This is accomplished by adding crystals to the feed. These crystals provide sites to which material may precipitate.

Three separate tests were conducted. These tests demonstrated the unique RO process. The seeded slurry test was preceeded and followed by sodium chloride (NaCl) baseline tests. These tests provided a performance standard and a means to detect any adverse effects of seeded operation.

The seeded test was operated for 760 hours. During most of this time the system operated on a feed that was close to saturation with calcium sulfate and concentrated it by a factor of 10. The only pretreatment used was 25 micron filtration, acidification and chlorination. The level of suspended solids circulating through the RO modules was 15,000 mg/l or more.

During the seeded test the product flowrate fluctuated between 0.60 and 0.65 gpm. This is slightly higher than the product flowrate that is predicted for the water and operating conditions used.

The rejection began at 81% and decreased to 74% where it appeared to level off toward the end of the test. This rejection is lower than expected. It is felt that both the low rejection and high product flowrate is a result of normal performance decline since the modules have experienced a variety of previous service. The decrease in rejection over the course of the test is postulated as an indication that the system was in a dynamic state and finally reached steady state near the end of the test.

The module pressure drop was constant or decreased slightly during the test. There was no indication of any scaling or fouling.

The initial and final NaCl tests were run for approximately 44 hours preceeding and following the seeded test. There was an increase in product flowrate and a decrease in rejection from the initial to the final NaCl test. It is believed this was also a result of membrane performance decline, although further work may be warranted to explore the change in performance.

1.0 INTRODUCTION AND BACKGROUND

This report describes the test work performed by Resources Conservation Co. (RCC) under contract to the Office of Water Research and Technology. The overall objective was to demonstrate RCC's seeded reverse osmosis (RO) process.

Seeded RO describes a process conceived by RCC to allow RO systems to operate at a high recovery without the normally required pretreatment. A major operating limitation for conventional RO systems is the requirement that the solubility limit of any dissolved species must not be exceeded at any point in the system. When this happens the membrane is likely to become scaled as material precipitates on it. This results in decreased membrane permeability and increased pressure loss. Species commonly encountered which present this problem are calcium sulfate, silica and sometimes calcium carbonate.

In order to operate at recoveries where scaling by slightly soluble material may be a problem, conventional RO systems include equipment to pretreat the feed water. Pretreatment is aimed at either reducing the concentration of the dissolved species or inhibiting its precipitation. Common techniques to accomplish this are: lime, lime-soda and sodium zeolite softening, pH adjustment and sodium hexametaphosphate (SHMP) addition. These increase both the cost and complexity of the system.

A seeded RO system may be operated at recoveries exceeding 90% with minimal pretreatment. This is accomplished by adding seed crystals to the feed to the RO system. These crystals provide sites where the material may precipitate, rather than on the membrane. It should be mentioned that once the seed level is established, it is not necessary to add additional seed. As the

dissolved solids precipitate, additional seed crystals solids are formed. A portion of this material may be recovered from the reject and recycled to the feed to maintain the seed level. Tubular RO modules have been selected for use in this process because they provide an unobstructed flow path for the seed suspension.

RCC has been developing the seeded RO process since mid-1977. The project began with preliminary economic and technicial evaluations and has progressed through laboratory experiments and more detailed studies. Much of the early work has been described in a paper presented at the 1978 IDEA conference [1]. In June of 1980 RCC was assigned a patent covering the seeded RO process.[2]

One of the limitations of laboratory testing has been the use of synthetic feed water. Because of the volume required, it was not feasible to transport water from various locations to the laboratory. In order to have the ability to demonstrate the seeded RO process on real water at various locations, RCC fabricated a portable seeded RO test unit. At the end of 1979 RCC submitted a proposal to the OWRT entitled, "High Recovery Seed Slurry Demonstration for Desalting Water Saturated in Calcium Sulfate" and proposed operating the portable test unit at the OWRT test facility in Roswell, New Mexico. This proposal was accepted and on-site activities began on September 9, 1980.

2.0 OBJECTIVES

The primary objective of this program has been to demonstrate the feasibility of the seeded RO process for operation at high recovery on a water saturated with calcium sulfate. Minimal pretreatment would be used during the test. In addition, the operation of the test unit at the Roswell facility marks the

first time the seeded RO process has been run using a real feedwater rather than a laboratory synthesized simulation of actual existing waters.

3.0 APPARATUS

The demonstration program was conducted using RCC's portable seeded RO test unit. This is a skid mounted unit containing the RO modules, pumps, tanks and other equipment. It is shown schematically in Figure 1. Feedwater is supplied to the unit from a pressurized source through a float-actuated valve located at the feed tank. This valve maintains a constant level in the feed tank. Chlorine in the form of sodium hypochlorite is injected in the feed tank to prevent the growth of biological material. A propeller-type mixer is mounted on the tank to provide mixing.

Water is pumped from the feed tank by the feed pump. Some of the water is recirculated back to the feed tank while the rest is pumped through a cartridge filter. This is a string-wound filter rated at 25 microns. From the filter the water is fed into the recirculation sump. It enters through a float-actuated valve that keeps a constant level in the recirculation sump. Acid is added to the sump to prevent membrane hydrolysis and carbonate scaling. A propeller-type mixer is provided to mix the acid and also keep the seed particles in suspension. Since much of the liquid is recirculated an appreciable amount of heat is added to the system from the pumps. To prevent overheating, a cooling coil is located in the recirculation sump. Cooling water is circulated through this coil to remove heat from the system.

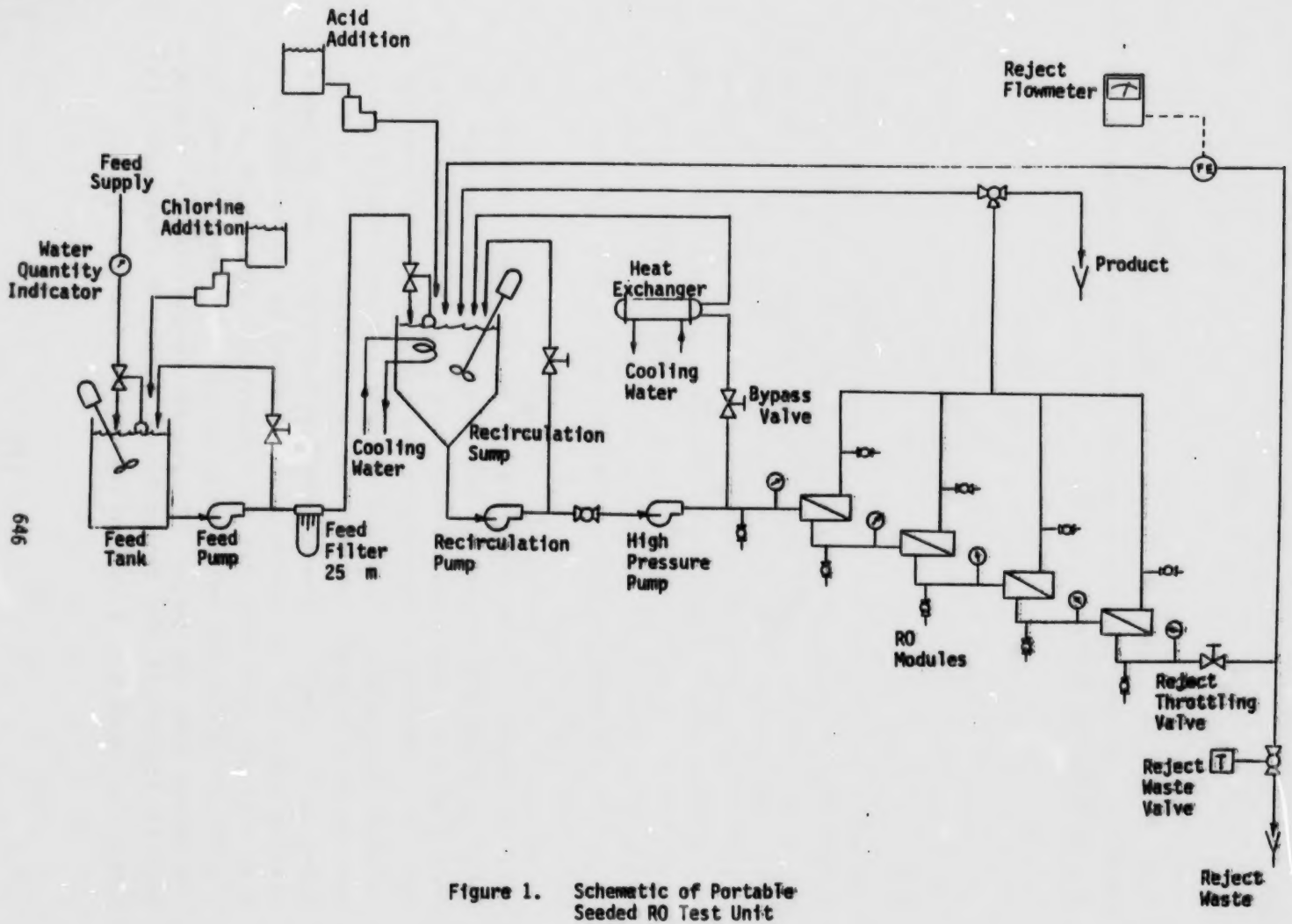


Figure 1. Schematic of Portable Seeded RO Test Unit

The recirculation pump draws water from the recirculation sump. A portion of the discharge is recirculated back to the sump. This aids in keeping the seed particles suspended. The remainder of the discharge is fed to the high-pressure pump. This is a multi-stage centrifugal pump and it provides the required pressure feed to the modules. A portion of the discharge from the high-pressure pump is directed back to the recirculation sump through a bypass valve and a shell-and-tube heat exchanger. This provides additional heat removal capacity. The rest of the discharge from the high-pressure pump feeds the tubular RO modules.

The modules used in this test are Osmotik Type 520 RO modules manufactured by Fluid Systems Division of UOP Inc. Appendix A contains product data relating to these modules. A series arrangement of four modules was used. Sample valves are provided to collect samples from the feed, reject and product from each module. Also, pressure gauges are located upstream and downstream from each module to measure feed and reject pressures. The product from each module is collected in a manifold. The total product then flows to a 3-way valve. With this valve the product may be directed to either the drain or back to the recirculation sump.

The reject stream from the final module flows through the reject throttling valve. By adjusting this valve in coordination with the bypass valve the system feed pressure and overall reject flowrate may be set at the desired values. The overall reject flowrate is measured using a magnetic flowmeter located in the reject line, just downstream of the reject throttling valve. The reject waste leaves the system through the reject waste valve. This is a timer-actuated valve and the reject flowrate is adjusted by changing the frequency and duration that the valve is actuated. The rest of the reject from the final module is recirculated back to the recirculation sump.

Figure 2 shows a photograph of the test unit.

The unit was packaged and shipped to the OWRT test facility in Roswell, New Mexico. It was moved into a test bay and the following connections were made:

1. Feed. The feed used was a blend of brackish well water and city water. It is a standard blend used at the plant and is designated Blend No. 3. The water had passed through an activated carbon filter and a manganese green sand filter before reaching the feed tank. A typical analysis of this water is presented in Figure 3.

2. Reject waste. Connected to plant drain.

3. Product. Connected to plant drain.

4. Cooling water. Reject brine from another test system was used for cooling water. City water was used as a back-up.

5. Electrical power. A 100 amp service was provided.

Another seeded RO test unit used by RCC in extensive long term tests is shown in Figure 4. The unit is located in RCC's test facility in Seattle, Washington. The modules shown have completed nine months of continuous operation with no change in flux or rejection.

Sodium (Na^+)	710 mg/l
Potassium (K^+)	4 mg/l
Calcium (Ca^{++})	240 mg/l
Magnesium (Mg^{++})	66 mg/l
Chloride (Cl^-)	1,141 mg/l
Sulfate ($SO_4^=$)	620 mg/l
Bicarbonate (HCO_3^-)	226 mg/l
Carbonate ($CO_3^=$)	0 mg/l
Silica (SiO_2)	13.4 mg/l
TDS	3,007 mg/l
Conductivity,	4,780 μmho/cm
pH	7.5

Figure 3. Typical analysis of feedwater used in seeded test.

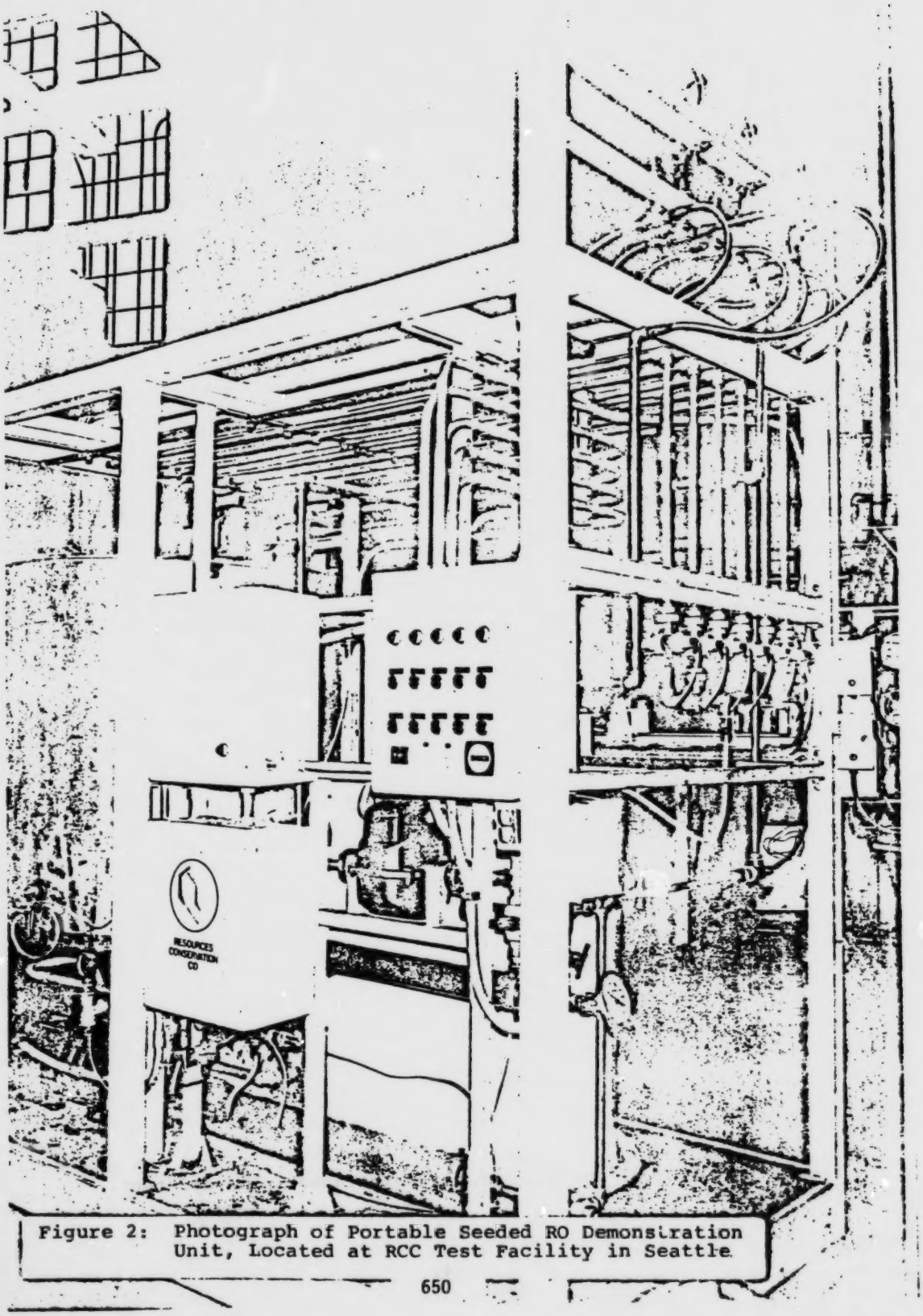


Figure 2: Photograph of Portable Seeded RO Demonstration Unit, Located at RCC Test Facility in Seattle

4.0 PROCEDURE

This demonstration program was performed in three phases.

1. Initial sodium chloride (NaCl) test.
2. Seed slurry test.
3. Final NaCl Test.

4.1 Initial NaCl Test

The purpose of the initial NaCl test was to establish a performance baseline for the test unit under specific operating conditions. At the completion of the seeded slurry test there operating conditions would be repeated in the final NaCl test. By comparing the performance obtained in the two tests under the same operating conditions, any effects of the seed slurry operation could be detected.

The initial NaCl test was run with the unit in the complete recycle mode. In this mode the unit was operated in a closed loop by returning all of the product and reject to recirculation sump. This was accomplished by positioning the 3-way valve in the product line so that all of the product was directed back to the sump. Also, the reject waste valve was not put into operation.

The sump was loaded with a 2,000 mg/l NaCl solution. This was created by filling the sump with RO product water, procured from another test system, and adding 4.19 lb of NaCl. The unit was initially operated at low pressure, using only the recirculation pump, for 5 minutes. The product and reject streams were discharged to drain in order to purge the storage solution from the modules.

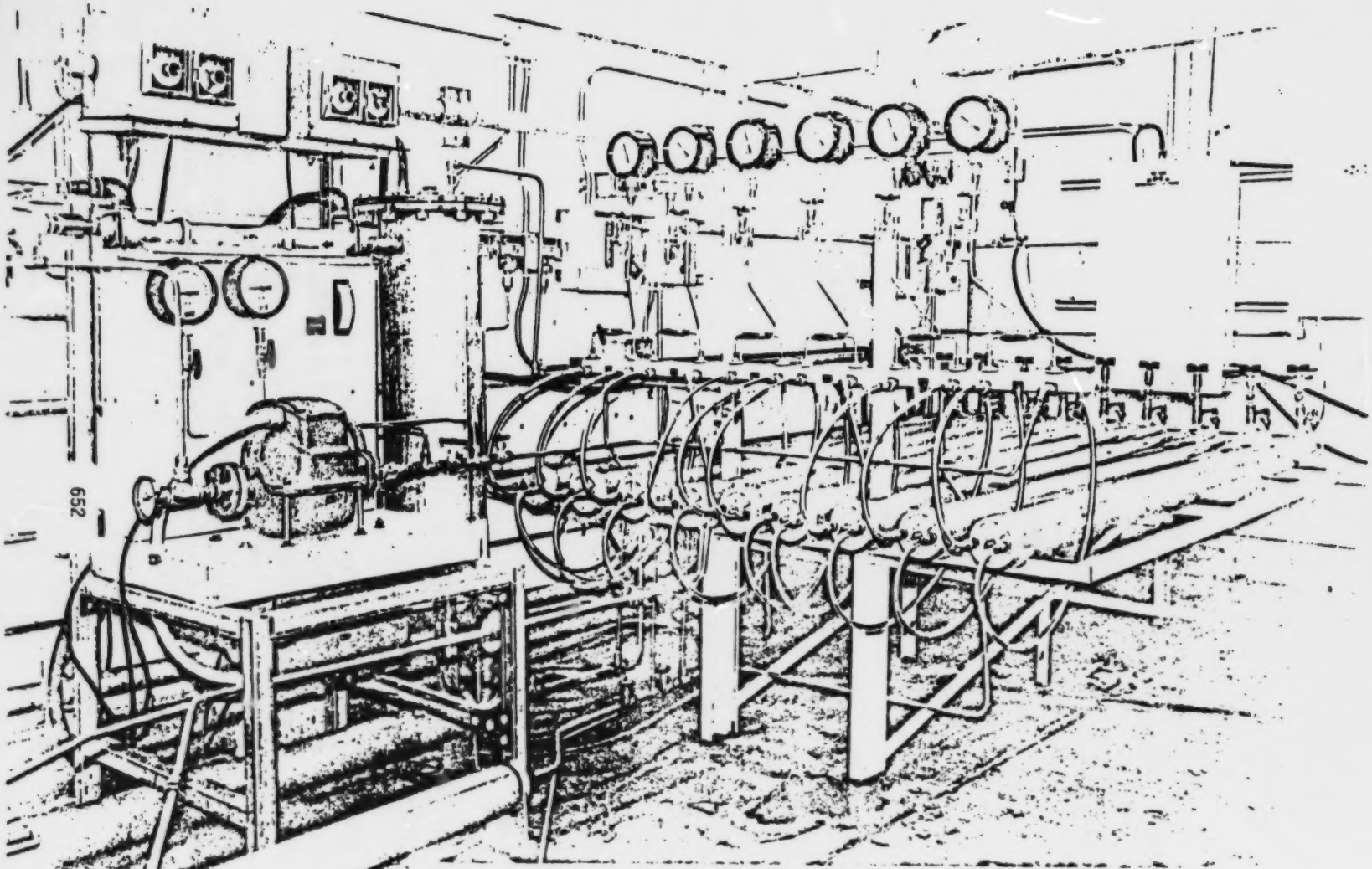


Figure 4: Photograph of Seeded RO Bench Model Test Unit, located at RCC Test Facility in Seattle

The unit was then put in the complete recycle mode and the high pressure pump was started. The feed pressure was adjusted to 500 psi and the reject flow was adjusted to 3.0 gpm. This was done by simultaneously adjusting the reject throttling valve and the by-pass valve. Figure 5 summarizes the operating conditions during both the initial and final NaCl tests.

The test was run for approximately 2 days. During this period 5 sets of data were collected at similar intervals. Figure 6 shows the data that was collected.

4.2 Seeded Test

For the seeded test the unit was switched from the complete recycle mode first to the concentrating mode and later to the normal mode. In the concentrating mode the valves were positioned so that the product was discharged to the drain and all of the reject was returned to the recirculation sump. This was achieved by positioning the 3-way valve in the product line so that the product was discharged from the system. Also, in this mode the reject waste was closed at all times. With the unit operating in this configuration the liquid in the recirculation sump became more concentrated as the system was operated.

Before starting the unit, an initial seed level was established in the recirculation sump. This was done by adding 75 lbs. of pharmaceutical grade terra alba (calcium sulfate) to the sump. This produced a suspended solids concentration of 20,000 mg/l. During the addition of the terra alba the mixer and recirculation pump were operated to mix the terra alba and keep it in suspension. The block valve in the high-pressure pump suction line was closed to prevent the slurry from being fed to the modules during the mixing process.

Figure 5. Summary of Operating Conditions for Initial and Final NaCl Tests

Feed Solution	2,000 mg/l NaCl
Feed Pressure	500 psi
Reject Flowrate	3.0 gpm
Feed pH	4.5 - 5.5
Feed Chlorine	0.2 - 0.5 mg/l

Figure 6. Data Collected During Initial and Final NaCl Tests

Operating Data:

- Elapsed time from start of test
- Feed pH
- Feed Chlorine
- Feed Temperature
- Feed Pressure
- Feed Conductivity
- Reject Flowrate

Performance Data:

- Product Flowrate
- Product Conductivity
- Module Pressure Drop

With the terra alba well mixed in the recirculation sump the unit was put into operation. The block valve in the high-pressure pump suction line was opened and the pump was started. The feed pressure was adjusted to 500 psi and the reject flow was adjusted to 500 psi and the reject flow is adjusted to 3.0 gpm. This was done by simultaneously adjusting the reject throttling valve and the by-pass valve. Figure 7 summarizes the operating conditions during the seeded test.

The unit was operated in the concentrating mode until the liquid had been concentrated 10 times, on a volume basis. The degree of concentration was determined by monitoring the quantity of water fed into the unit using the water meter in the feed line. When a volume of water equal to 10 times the system volume had been fed into the unit, the water had been concentrated 10 times. When this point was reached the unit was put in the normal mode.

In the normal mode the reject waste valve was put into operation and a portion of the reject was discharged. The amount to be discharged depends on the desired concentration factor. The concentration factor, CF, is the degree of concentration of the reject stream and is calculated using the expression,

$$CF = \frac{\text{Feed flowrate}}{\text{Reject waste flowrate}}$$

The unit was operated at a CF of 10. Since the feed flowrate could be measured and the CF was known, this reject waste flowrate could be calculated. The timer actuating the reject waste valve was adjusted to give the required reject waste flowrate.

During the seeded test a simulated seed recycle system was used to maintain a seed level. It was not practical to install a system to recover seed from the waste stream on a test system

Figure 7. Summary of Operating Conditions For Seeded Test

Feed Solution	Plant Blend No. 3
Feed Pressure	500 psi
Feed pH	4.5 - 5.5
Feed Chlorine	0.2 - 0.5 mg/l

such as this. Instead, 12 lbs. of terra alba were added to the recirculation sump approximately every 12 hours. This simulated the operation of a seed recycle system operating under similar conditions.

The unit continued operating in the normal mode for a month. During this time operating and performance data were collected twice daily. Figure 8 summarizes the data collected during the seeded test.

At the completion of the seeded test the unit was shut down and the sump drained. After this the final NaCl test was run.

4.3 Final NaCl Test

This test was conducted in the same manner as the initial NaCl test. The identical data were also collected.

5.0 RESULTS

The initial NaCl test was carried out over a 46 hour period. This was followed by the seeded test which was terminated after 760 hours. During this test the unit was in continuous operation except for a 5-hour period after an interruption in the electrical supply to the plant. The final NaCl test followed the seeded test and lasted for approximately 43 hours.

5.1 Seeded Slurry Test

The performance of the test unit was evaluated on the basis of the following calculated parameters:

Operating Data:

- Elapsed time from start of test
- Feed pH
- Feed chlorine
- Feed temperature
- Feed pressure
- Feed conductivity
- Feed TDS
- Feed SS
- Reject flowrate
- Reject TDS
- Reject SS

Performance Data:

- Product flowrate
- Product conductivity
- Module pressure drop

Figure 8. Data Collected During Seed Test

a) Recovery
b) Product flowrate, corrected to 77°F
c) Rejection
d) Pressure drop (Delta P)

These were determined from the data collected during the test, using the equations given below.

$$\text{Recovery} = \frac{\text{Product Flowrate}}{(\text{Product Flowrate} + \text{Reject Flowrate})}$$

$$\text{Rejection} = \frac{\text{Feed Conductivity @ Module 1}}{(1 - \text{Reject Conductivity @ Module 4})}$$

$$\text{Pressure Drop} = (\text{Feed Pressure @ Module 1}) - (\text{Reject Pressure @ Module 4})$$

The product flowrate was measured directly and was corrected to a reference temperature of 77°F. This was done using the expression,

$$Q_{77} = Q_T \, 1.013^{(77-T)}$$

Where: Q_{77} = product flowrate corrected to 77°F, gpm
Q_T = measured product flowrate, gpm
T = Actual temperature, °F

This expression represents an average of the temperature correction factors used by different membrane manufacturers and is considered reasonable at 77 ± 18°F [3].

Figure 10 shows the recovery of the test unit as a function of time. Since the product flowrate was equal to the feed flowrate during the concentrating stage, the recovery was 100% during this stage. Once the water in the recirculation sump had become

	Average	Minimum	Maximum
Feed Temperature, ^{o}F	85	81	88
Feed pH	5.0	4.0	7.0
Feed Chlorine, mg/l	.35	0.0	1.0
Feed TDS, mg/l	4,670	4,500	4,900

Figure 9. Feedwater Conditions During Seed Test

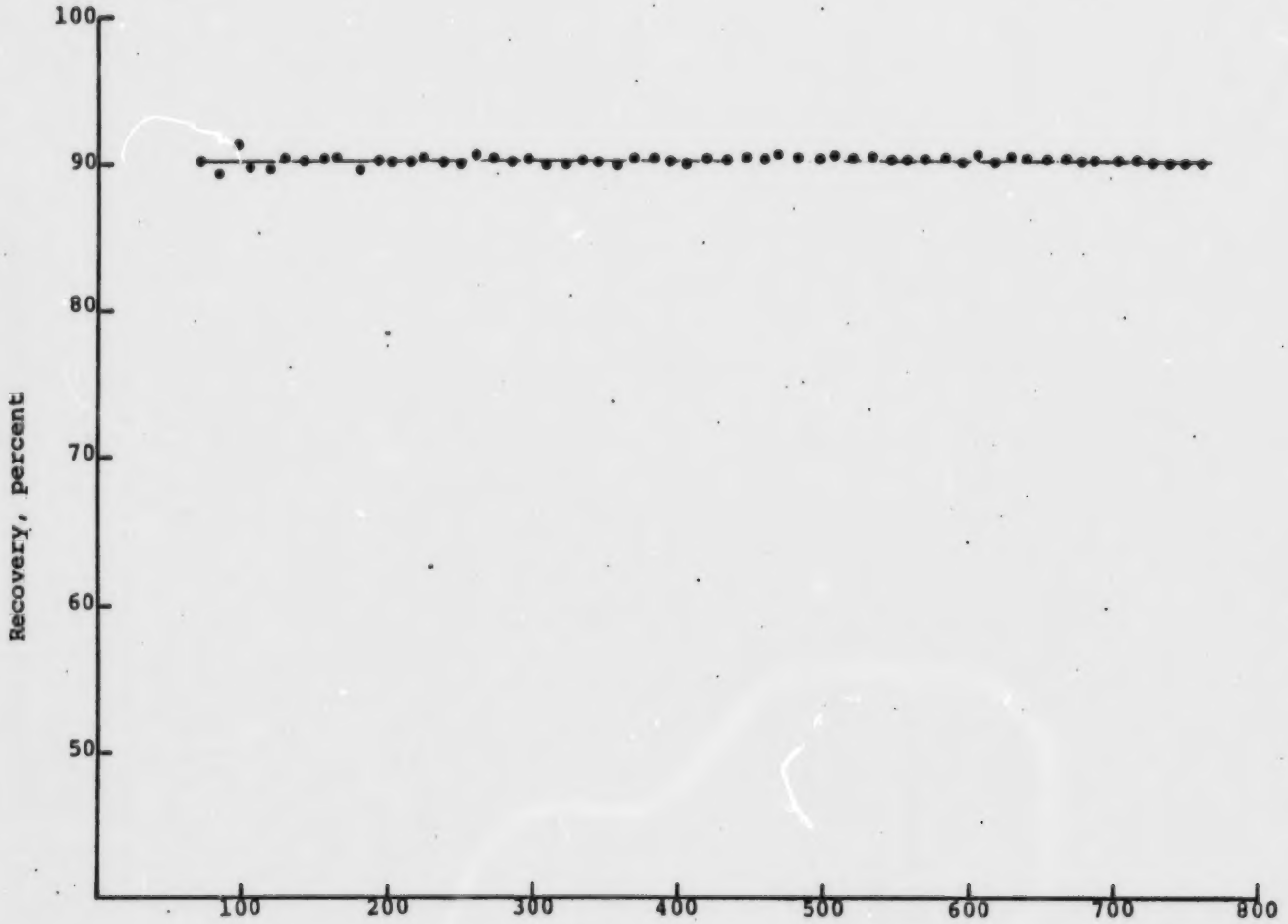


Figure 10. Plot of Recovery vs. Time for Seeded Slurry Test

concentrated by a factor of 10 the waste valve was put into operation and the reject waste flowrate was adjusted to maintain a recovery of 90% or greater. Figure 10 shows that this was accomplished during the seed slurry test.

Figure 11 shows a plot of product flowrate, corrected to 77°F, as a function of time. This shows that the product flowrate was about 0.65 gpm at the beginning of the test and dropped to slightly less than 0.55 gpm during the concentrating stage. This decrease is expected since the TDS of the recirculation sump is constantly increasing during this stage. This decreases the effective feed pressure as a result of the higher osmotic pressure.

After the unit was switched from the concentrating to the normal mode, the product flowrate increased and throughout the rest of the test fluctuated between 0.60 and 0.65 gpm. Calculations based on manufacturer's data indicate the expected product flowrate for four modules in series operating under these same conditions is approximately 0.55 gpm. The higher measured product flowrate is a symptom of brine-to-product leaks. This is not completely unexpected. These modules were purchased in 1978 and have been the subject of several tests in RCC's laboratory. It is felt that the high product flowrate is a result of normal membrane deterioration.

A plot of rejection vs. time is shown in Figure 12. This shows the rejection at the start of the test was about 81%. During the test this declined steadily to 74% where it appeared to level off. This rejection is lower than expected for these modules. However, it is felt that this may also be attributed to membrane deterioration since both high product flow and low rejection are a symptom of brine-to-product leaks.

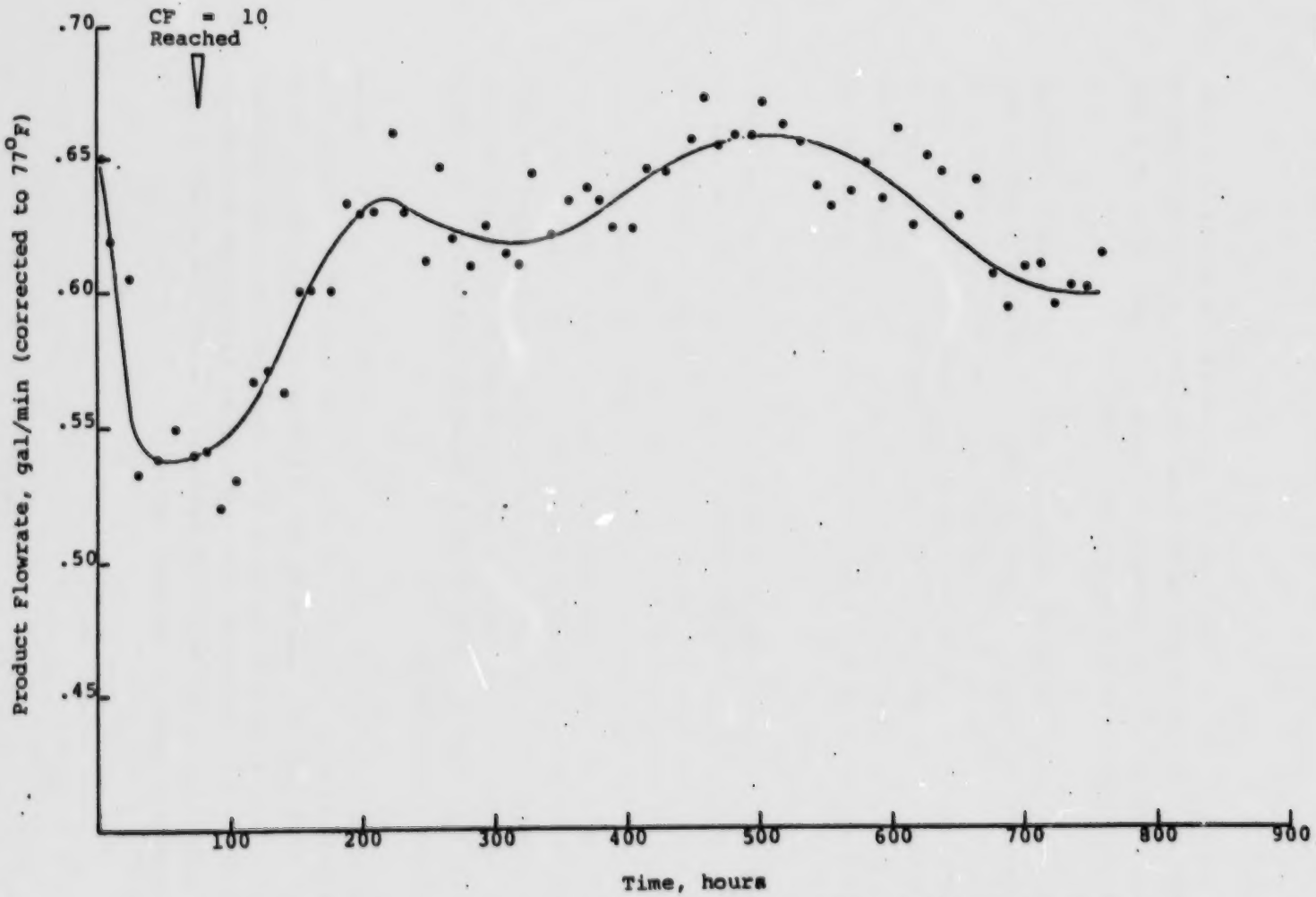


Figure 11. Plot of Product Flowrate vs. Time for Seeded Slurry Test

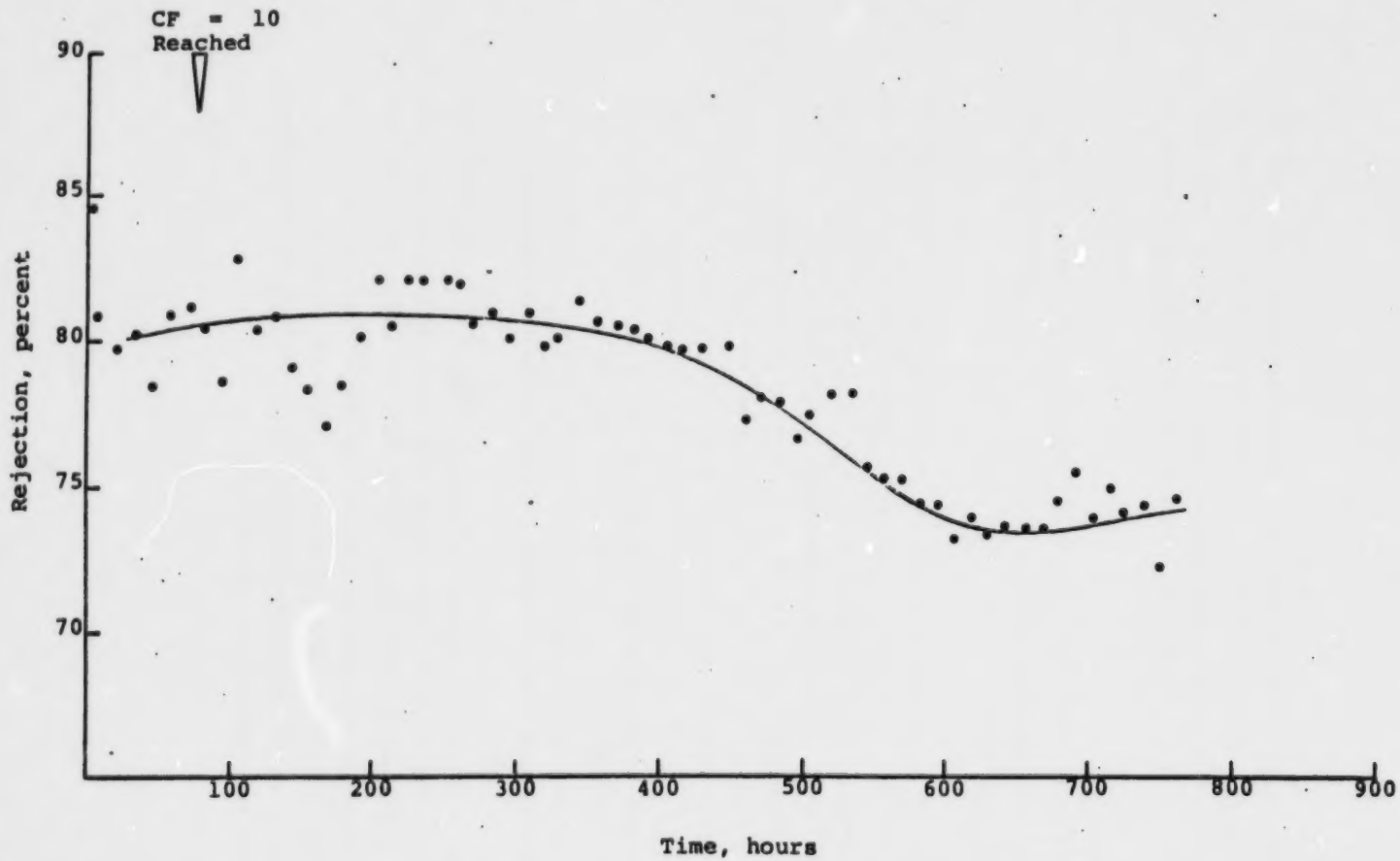


Figure 12. Plot of Rejection vs. Time for Seeded Slurry Test

Initially the decline in rejection, which amounted to 8.6% in less than 30 days, was viewed as a possible indication of module scaling/fouling. However, the other usual indicators were not present. The product flowrate fluctuated, but did not show a steady decrease.

The module pressure drop was steady or declined slightly. Also, the rejection did seem to reach a constant level toward the end of the seed slurry test.

It is postulated that the decline in rejection is an indication that the system was in a dynamic state. It is recognized that RO membranes reject trivalent and divalent ions better than monovalent ions. During the concentrating stage all of the product is discharged and all of the reject is returned to the recirculation sump. Thus the relative proportion of multivalent ions in the sump becomes greater than that of the feed. When the unit is switched from the concentrating to the normal mode the multivalent ions begin leaving the system at a greater rate. As a result, the concentration of the multivalent ions in the sump drops which causes a decrease in the rejection. It appears that the system had reached equilibrium toward the end of the test.

Figure 13 is a plot of module pressure drop as a function of time. This shows that the pressure drop fluctuated and experienced a slight decline toward the end of the test. If the system had experienced fouling as a result of operating on a slurry of seed crystals, an increasing pressure drop would have been expected. Since this was not the case it can be concluded that this type of fouling did not occur.

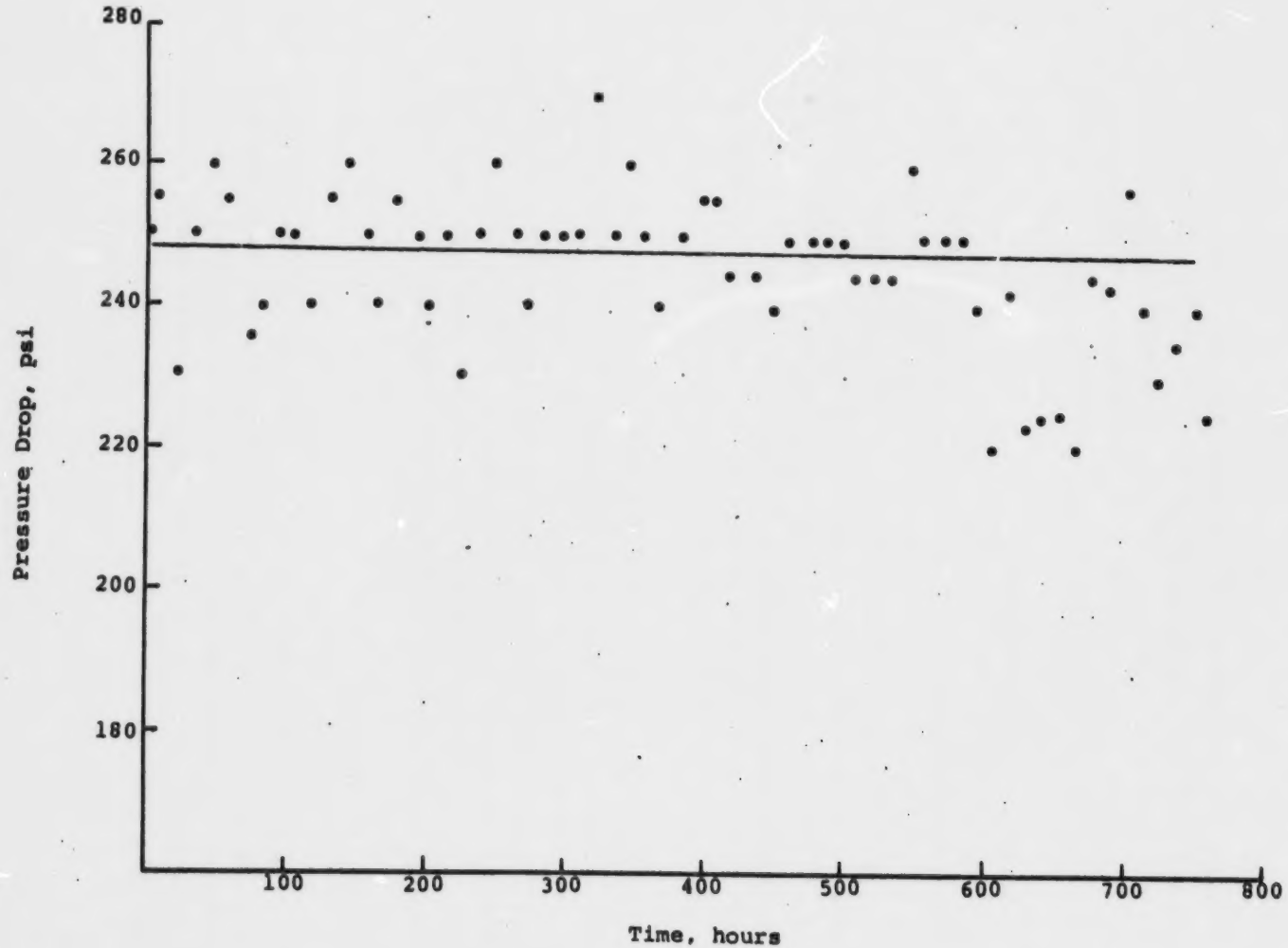


Figure 13. Plot of Pressure Drop vs. Time for Seeded Slurry Test

The results of the seeded test demonstrate that the seeded RO process may enable an RO system to be operated at a recovery that would not normally be possible. Scaling by precipitating species is not a problem. Also, the modules are not subject to fouling by the suspended seed crystals.

5.2 Initial and Final NaCl Tests

A comparison of the results from the initial and final NaCl test is shown in Figure 14. The operating data indicate that the tests were carried out under similar operating conditions. The performance data shows an increase in product flowrate and a decrease in rejection from the initial to the final NaCl test. The average product flowrate was 11% higher during the final NaCl test than during the initial NaCl test. The average rejection decreased 9.2% from the initial to the final NaCl test.

It is possible the different performance in the 2 tests may be caused by normal membrane deterioration. It is also possible this may be an effect of operation with the seed crystals. However, similar modules have been operated continuously for up to nine months in RCC's laboratory with no evidence of any such effects. It is felt that this is an area that should be explored further, possibly using fresh modules in a long term test.

5.3 Chemical Analyses

Samples of feedwater, permeate, reject, and sump concentrate were taken once a week to be analyzed on site in the OWRT, Roswell laboratory. Chemical analyses will allow direct derivation of the rejections for the different ions. This would resolve whether the decrease in rejection during the seeded slurry test

	Initial NaCl Test			Final NaCl Test		
	Average	Maximum	Minimum	Average	Maximum	Minimum
Operating Data:						
Sump Condictivity, μmho/cm	3,940	4,100	3,700	4,125	4,400	3,900
Feed Temperature, °F	86.5	90	84	85.3	86.5	83.5
Feed Pressure, psig	500	505	500	515	517	512
Performance Data:						
Rejection, percent	79.3	81.1	76.6	72.0	75.4	70.0
Product Flowrate, gal/min (corrected to 77°F)	.70	.74	.67	.785	.829	.750

Figure 14. Table Comparing Initial and Final NaCl Test Data

was indeed due to a relative increase of monovalent ions with respect to divalent ions in the sump concentrate. RCC will attempt to publish the results of these analyses when we receive them.

6.0 CONCLUSIONS

The primary objective of this test effort, that of demonstrating the feasibility of the seed RO process, has been achieved. The seeded test unit was operated for over a month at a recovery of 90% or more on a water that is nearly saturated with calcium sulfate. An analysis of the feed using the correlations of Marshall and Slusher (4) indicates that the water becomes saturated with calcium sulfate at a recovery of approximately 75%. There was no indication of fouling or scaling during the test.

REFERENCES

(1) Kirchner, O.E. and O'Neail, T.M., "Achieving High Recovery from Brackish Water with Seeded Reverse Osmosis Systems," presented at the International Desalting and Environmental Association Conference in Niece, France, October 22-26, 1979.

(2) Herrigel, H.R, "Prevention of Solute Deposition Fouling in Membrane Processes," U.S. Patent No. 4,207,183. June 10, 1980.

(3) "Reverse Osmosis Technical Manual," prepared for the Office of Water Research and Technology by Burns and Roe Industrial Services Corporation, Contract No. 14-34-001-8530, July, 1979.

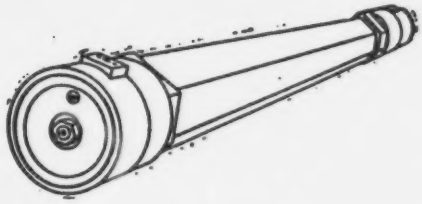
(4) Marshall, W. L. and Slusher, R., "Solubility to 200°C of Calcium Sulfate and Its Hydrates in Sea Water and Saline Water Concentrates, and Temperature-Concentration Limits," Journal of Chemical and Engineering Data, Vol. 13, No. 1, 1968.

product bulletin

No. 100

UOP OSMOTIK® MODULE

PRODUCTION MODEL

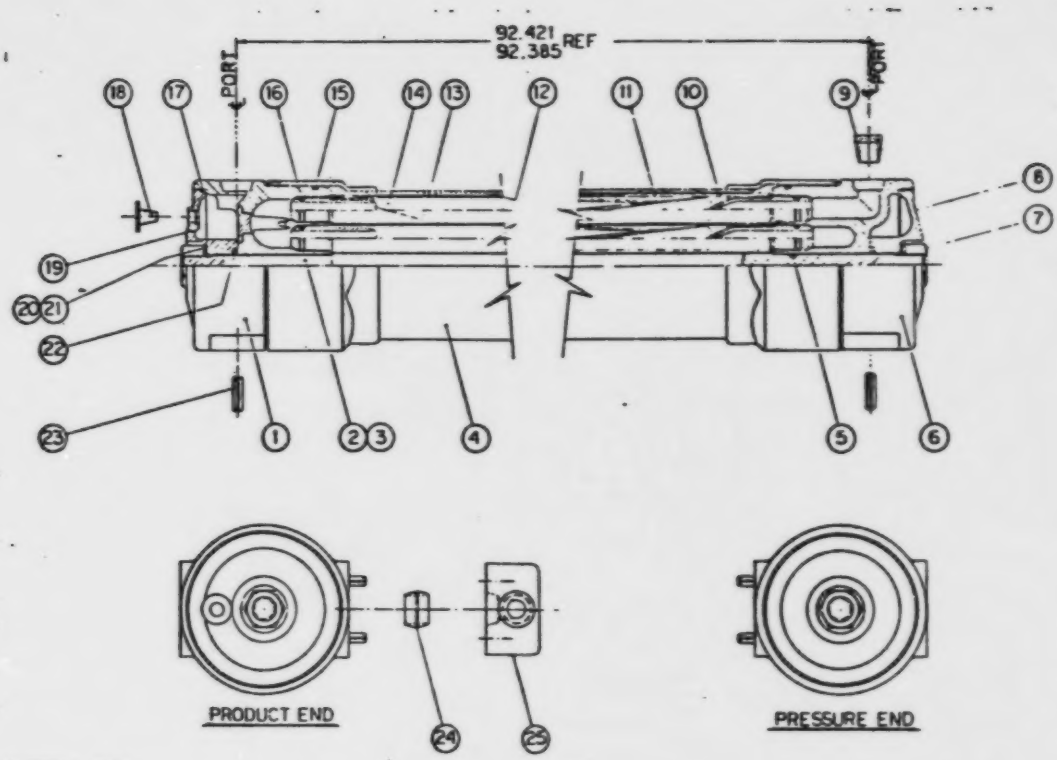


Length:	95 inches	241 cm
Diameter:	3.5 inches	8.9 cm
Number of tubes:	18	
Tube diameter:	0.500 inches	1.27 cm
Membrane surface area:	16.7 square feet	1.55 m^2
Capacity of tubes:	1.5 gallons with open tubes 0.95 gallons with VDR's	5.7 liters with open tubes 3.6 liters with VDR's
Weight filled:	25 pounds	11.34 kg
Fittings:	Standard U.S. Military 1/2" diameter, 37° flared tube. Thread is 3/4" diameter x 16 National Fine	

Fluid Systems Division 2980 North Harbor Drive • San Diego, California 92101 • (714) 299-9920
UOP Inc

MODULE ASSEMBLY

No. 100A



PART NO.	DESCRIPTION	MATERIAL	ITEM NO.
MP 101	MODULE CONNECTOR	ZYTEL 77G-33-NC-10, NATURAL	25
MP 039	GROMMET CONNECTOR	2102-80A POLYURETHANE-PELLETHANE	24
MP 010	ROLL PIN 3/16 DIA-3/4"	S S	23
MP 008	O RING	PARKER P/N 2-112, N-674	22
MP 116	WASHER, FLAT 1/2	S S 18-8 (ANS6CC 316)	21
MP 011	WASHER, FLAT 1/2	AL ALY 2024-T4 (AN960D816)	20
MP 105	COVER PROD HEAD	ZYTEL 77G-33 NC 10, NATURAL	19
MP 001	PLUG 201 A	POLYETHYLENE, GREEN	18
MP 042	O-RING	PARKER P/N 2-151, N-674	17
MP 111	O-RING	PARKER P/N S-699, E-540-80	16
MP 009	O-RING	PARKER P/N S-374, N-674	15
MP 033	COMPACT SLEEVE	2102 80A POLYURETHANE-PELLETHANE	14
MP 041	TUBE ADAPTER	ZYTEL 77G-33-NC-10, NATURAL	13
MP 000	TUBE	F.S.D. MFG SPEC NO 2.1	12
MP 030	ROD (VDR) VOLUME DISPL	NATURAL HI DENSITY POLYETHYLENE	11
MP 040	TUBE ADAPTER	ZYTEL 77G-33-NC-10, NATURAL	10
MP 002	PLUG K-8	POLYETHYLENE, RED	9
MP 103	COVER-PRESS. HEAD	109RD08 RED ZYTEL 77G-33 WITH 10% ZYTEL	8
MP 006	HEX NUT 1/2-20-28	SILICON-BRONZE	7
MP 107	PRESSURE HEAD	ZYTEL 77G-33-NC10, NATURAL	6
MP 110	O-RING	PARKER P/N 2-012, N-674	5
MP 032	SHROUD ASSY		4
MP 038	STRAIN ROD	316 S S COND B	3
MP 114	STRAIN ROD	AL ALY 7075-T6	2
MP 109	PRODUCT HEAD	ZYTEL 77G-33 NC10, NATURAL	1

LIST OF MATERIAL

product bulletin

No. 200

REVERSE OSMOSIS MEMBRANE CHARACTERISTICS

Membrane Type	620	520	420	320
Test Pressure, "P", psig	600	600	600	600
Recommended Operating Pressure, psig	600	600	600	450
Membrane Flux at "P" and 25°C (Mean) GFD	13	19	25	35
Rejection of 0.45% NaCl, %	97-98.4	95-97	88-94	62-80
Rejection of 6% Sucrose, %	>99	>99	97-98	93-95

-over-

Revised 12-16-75

Fluid Systems Division 8133 Aero Drive - San Diego, California 92123 714-278-7440
UOP Inc.

No. 200A

LIMITING OPERATING CONDITIONS

REVERSE OSMOSIS MEMBRANES

Membrane Type	Maximum Feed Temperature °C	Maximum Pressure p.s.i.g.	Feed pH Range
620	15-25	600	3-7
	25-40	600	4-6
520	15-25	600	3-7
	25-40	550	4-6
420	15-25	600	3-7
	25-40	500	4-6
320	15-25	600	3-7
	25-35	500	4-6

ACHIEVING HIGH RECOVERY FROM BRACKISH WATER WITH SEEDED REVERSE OSMOSIS SYSTEMS

OTTO E. KIRCHNER and TERRY M. O'NEAIL

Resources Conservation Co.
Seattle, Washington, U.S.A.

Since 1973 the use of reverse osmosis to reduce the salinity of feedwater has increased tenfold. The applications include the production of ultra-pure water for the manufacture of electronics, the treatment of brackish ground water for potable use and the desalination of seawater. As operational experience accumulates there is increasing confidence that reverse osmosis will perform satisfactorily so long as proper pretreatment is provided. Proper pretreatment permits the R.O. system to realize its potential performance and extends its useful lifetime. In many instances, however, pretreatment accounts for a significant portion of the capital and operating cost of the overall system and in addition, may make major demands upon the workload and skills of the plant operator. For these reasons an R.O. system operating free of pretreatment represents a highly desirable goal and major steps toward reducing the requirements for pretreatment could provide significant benefits in decreased R.O. system complexity and cost. The purpose of this paper is to describe certain development activities currently underway at Resources Conservation Co. in Seattle, Washington, U.S.A. with a patented reverse osmosis concept for reducing the pretreatment requirements of R.O. systems without compromising the permeate recovery of these systems.

The area of application considered here is the use of reverse osmosis to reduce the salinity of either surface water or ground water where softening is a prerequisite to achieving adequate recovery.

Figure 1 shows the relationship between percent recovery and the salinity of the R.O. reject for various levels of recovery, using, as an example, the feedwater at the Yuma Desalting Test Site in Yuma, Arizona, U.S.A. The feedwater has an initial salinity of approximately 3,000 parts per million (ppm) total dissolved solids (TDS). If this water is treated by an R.O. system various levels of recovery will result in reject streams having salinities as shown on the ordinate of Figure 1. For the water chemistry of this feedwater the hardness is such that if no softening were undertaken the R.O. recovery of permeate from this stream would be limited to approximately 55% or 60%. Use of cold lime softening will allow the recovery to be increased to 85%. Complete softening, using lime-soda, would permit complete recovery to the osmotic pressure limit shown on Figure 1. So it can be seen for this water that use of R.O. without softening significantly penalizes the recovery potential of the reverse osmosis.

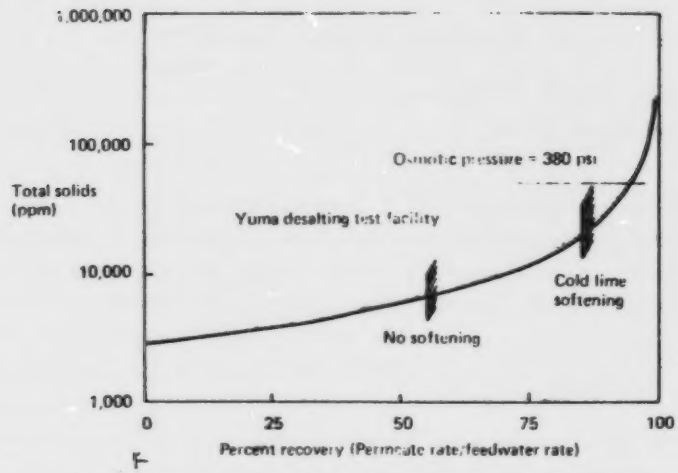


Figure 1. Effect of Softening on Reverse Osmosis Recovery

The operating and capital cost penalty for the softening pretreatment is indicated in Figure 2. These two bars represent the capital cost and operating cost respectively of an R.O. system. On each bar the value of 1.0 corresponds to the cost of the R.O. system itself, exclusive of pretreatment costs. The top of the bar indicates the total system cost including pretreatment. The magnitude of the pretreatment portion of the two bars, both with respect to capital cost and operating cost is an indication of the potential savings to be realized if softening and other pretreatment could be eliminated.

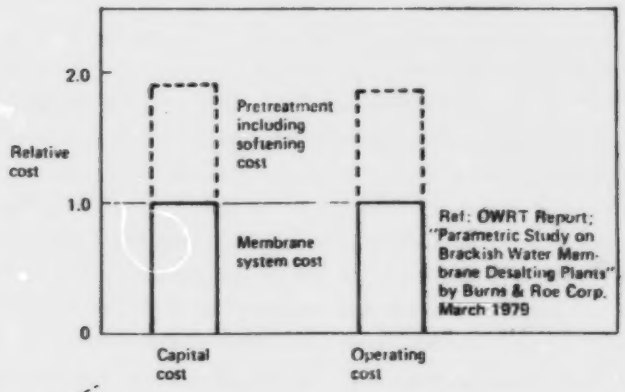


Figure 2. Impact of Pretreatment on Total Reverse Osmosis Costs

In searching for means to eliminate the requirement for pretreatment Resources Conservation Co. turned to another water treatment process with which it has become identified during the past ten years. This is the recovery of pure water from a brackish stream saturated with calcium sulfate, silica, or both through the use of the vertical tube, falling film, vapor compression evaporator. Resources Conservation Co. has been the leader in producing commercial evaporator systems for the purpose of achieving very high recoveries (90% to 99%) from brackish streams saturated with scaling components such as those mentioned above. RCC committed to a test program to determine if the same approach used to achieve high recoveries without scaling in its evaporators might also be applicable to achieving high recoveries without scaling in a reverse osmosis system with a feedwater saturated with scaling minerals such as calcium sulfate and silica.

The process used by RCC in its evaporators to avoid scaling is schematically demonstrated in Figure 3. The left-hand figure illustrates the vertical orientation of the tube-in-shell heat exchanger with its large number of vertical tubes. The incoming hot feed is mixed with the concentrate slurry in the conical sump and is continuously recirculated to the top of the evaporator. There it is distributed to the inside wall of each tube as a thin film. The central portion of Figure 3 represents a magnification of just one of the many vertical tubes with its associated brine film. In this system the vertical tube transfers heat to the falling film causing a small fraction to vaporize. The vapor thus formed enters the compressor where it is compressed about 2 psi on the shell side of the evaporator. This pressure increase causes the condensation temperature of the steam to be raised about 6 degrees above the boiling point of the recirculating brine. As this steam gives up its heat of condensation it condenses on the shell side of the tubes and is collected in the product tank. The release of the heat of condensation causes more water to be evaporated from the brine inside the tube. The right hand portion of Figure 3 depicts the key to the evaporator's thermochemical operation. As water is evaporated inside the tubes the remaining brine film becomes supersaturated, and, typically, calcium sulfate and silica precipitate. The precipitating materials promote crystal growth on the seed rather than nucleation and deposition on the heat-transfer surfaces. This scale prevention mechanism, called preferential precipitation, has proven its capability to maintain clean, scale-free, heat-transfer surfaces.

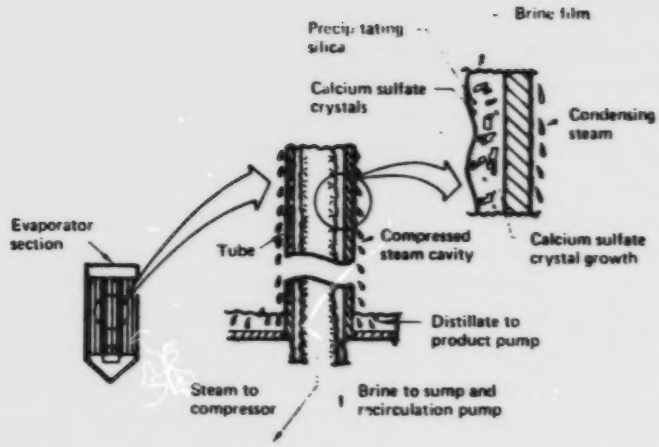


Figure 3. Scale Prevention Mechanism

Calcium sulfate crystals are introduced only at system startup since the process is a self-perpetuating one with precipitating crystals providing deposition sites in turn for future crystals. Through this process RCC has been able to achieve very high recoveries of 95% to 99%, starting with a feedwater saturated with calcium sulfate or silica. The recovery limit for these applications is therefore not limited by the presence of calcium or silica nor is softening required. In many instances the concentrate or waste stream from this system will have a salinity of from 200,000 to 350,000 ppm total solids.

This then is the mechanism which has been evaluated for its application to reverse osmosis systems to determine the possibility of achieving high recoveries without pretreatment even in feed streams saturated with calcium sulfate or silica. Figure 4 shows this concept in its simplest form. The unsoftened feedwater which is at or near saturation is circulated as a slurry within an R.O. module. Due to the nature of the slurry, the confines of the brine-side flow channel should represent a relatively smooth hydraulic zone such as that provided in a tubular R.O. module configuration. During the passage along the membrane, permeate will pass through the membrane causing the saturated calcium sulfate in solution to exceed its saturation limits and to precipitate. As in the evaporator, instead of precipitating on the flow channel wall, thereby plugging or fouling the membrane, the precipitating calcium sulfate will attach itself to existing crystals suspended in the feed stream. Consequently at the end of the membrane zone the chemistry of

the reject brine will differ from the seawater chemistry as a result of two effects. The concentration of total solids (dissolved and suspended) at the end of the tube will be greater than the concentration of like quantities in the feed due to the extraction of permeate and, the concentration of suspended solids in the reject brine will be greater than that in the feed stream as a result of precipitated calcium sulfate and silica caused by the reduced volume of the reject stream.

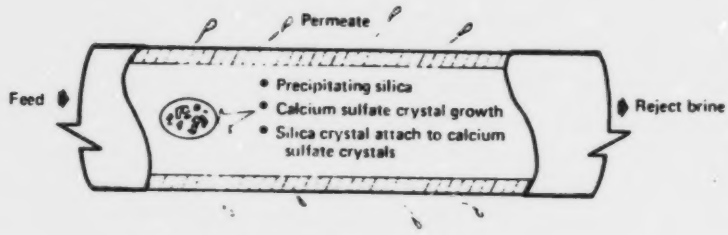


Figure 4. Seeded Reverse Osmosis Concept

As the feed stream is exposed to more membrane (or as the flow channel becomes longer) the osmotic pressure increases due to the increase in the level of dissolved solids. Correspondingly, the operating pressure along the tube reduces due to hydraulic losses within the system so that the net driving force across the membrane continues to diminish as permeate is extracted from the system. This effect is shown in Figure 5 and presents identical limitations and considerations to those observed in conventional reverse osmosis systems.

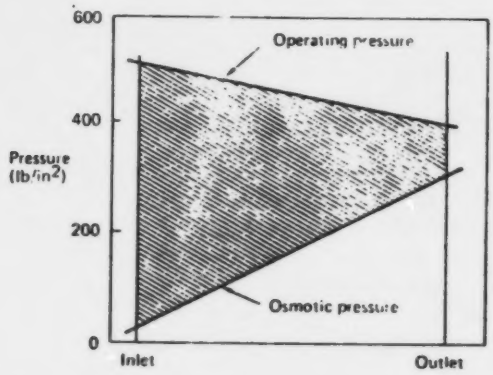


Figure 5. Effect of Extraction and Hydraulic Losses on Effective Pressure

The above discussion summarizes the idealized behavior of a "Seeded R.O." system. Following is a review of the testing that has been accomplished and a brief summary of the test results to date. The subsequent paragraphs include identification of some of the future work and the approximate timetable to which RCC is working.

Following the conception of the seeded R.O., an early activity involved a preliminary analysis of the economic potential associated with eliminating pretreatment of the feedwater to an R.O. system. That study, which was undertaken in 1977, indicated that further investigative and developmental efforts were warranted.

Actual testing commenced in March, 1978 using a one half-inch diameter cellulose acetate, tubular R.O. membrane. The modules employed were standard "off-the-shelf" tubular modules marketed by one of the major U.S. reverse osmosis equipment suppliers. A standard module contained about one hundred twenty-eight feet of this tubular membrane packaged into a module approximately four inches in diameter, seven and a half feet long. A series of tests, each about one week in duration, were undertaken to determine membrane performance using a feedwater seeded with calcium sulfate crystals. The particular water used in the tests was one familiar to RCC from some previous evaporator work in the State of Utah, U.S.A. The chemistry of this water is shown in Figure 6. The water seemed to be a good test stream because it is saturated with calcium sulfate, based on the predictions and correlations of Marshall and Slusher, and its inherent osmotic pressure is sufficiently low to permit relatively high recoveries. The purpose of these tests was to determine if the R.O. system could extract permeate from this unsoftened feed stream without scaling and, if so, what the limits of concentration might be.

	mg/l (as ion)
Sodium	106
Calcium	540
Magnesium	260
Chloride	58
Bicarbonate	0
Carbonate	0
Sulfate	2,467
Silica	60
Total dissolved solids	3,491
pH	5.5

Note: This water is saturated with $CaSO_4$.

Figure 6. Utah Water Chemistry (Acidified)

A schematic of the test system is shown in [illegible] feed is brought to a reservoir where it is mixed with reject brine [illegible] recycled from the R.O. module. The reject brine is a concentrated slurry containing calcium sulfate and silica in suspension, so it is necessary to agitate the feed tank to keep the suspended solids from settling. The feed proceeds to the high pressure pump and through the R.O. module. The permeate leaves the system and the reject brine is divided into two streams - a waste stream and recycled brine which is returned to the reservoir. The waste brine stream is throttled such that the system operation is controlled at the desired concentration factor. The reservoir was conditioned with an original charge of calcium sulfate crystals prior to start-up.

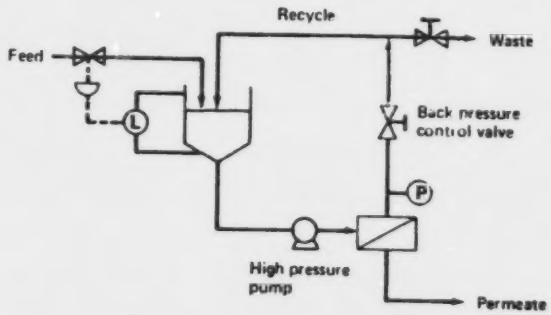


Figure 7. Test System Schematic

If a single pass through the membrane were desired, all the reject would be directed to the waste stream. However, the extraction of permeate on a once through pass employing a single module is only several percent of the feed volume. Overall recovery of the system is increased with the waste valve partially closed, causing a portion of the reject to be recirculated thereby increasing the overall system concentration capability. The feed rate to the reservoir is reduced as the recycle fraction is increased to maintain a constant feed tank level. Consequently, with the reduced feed rate the brine is recycled several times achieving a higher salinity in the reject and therefore an increased recovery of permeate. Concentration factors as high as 18 were achieved in the highest concentration tests. This is equivalent to a permeate recovery in excess of 94 percent. More importantly, this recovery was achieved in the absence of pretreatment and without scaling in the membrane module or elsewhere in the system. Logically, the raw feed was treated with a small amount of sulfuric acid to minimize the rate of hydrolysis of the cellulose acetate membrane.

Figure 8 presents the membrane performance achieved during the maximum concentration test series. The data reveals the typical and expected increase in rejection with increasing flux.

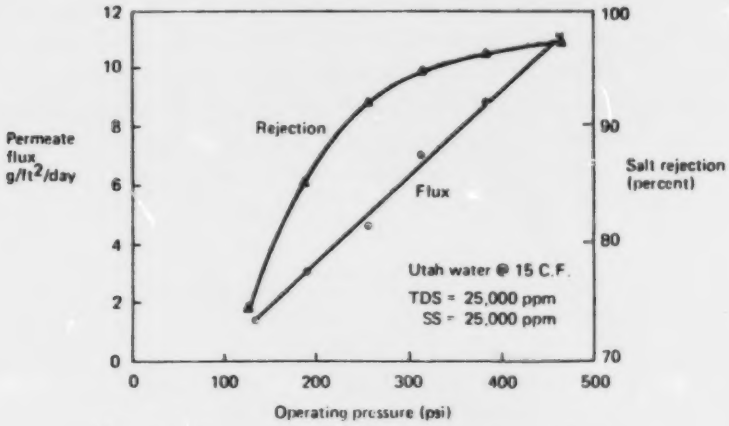


Figure 8. Membrane Performance - Seeded Reverse Osmosis

Figure 9 is a photographic view of one of the three test units employed in the Seeded Reverse Osmosis investigations. The tubular modules are visible in the left foreground and the reservoir with its mixer is seen in the right rear of the photograph.

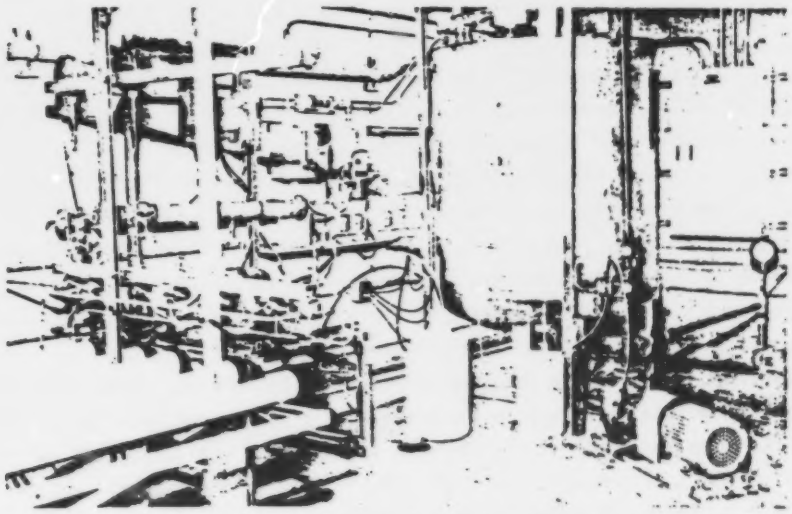


Figure 9. Seeded Reverse Osmosis Test Apparatus

Figure 10 presents a time-span display of the significant events during the Seeded Reverse Osmosis program. The preliminary analysis of the economic potential also included studies pertaining to the various reverse osmosis module configurations and suppliers. The first test unit was erected and checked out in late 1977 and testing commenced in early 1978.

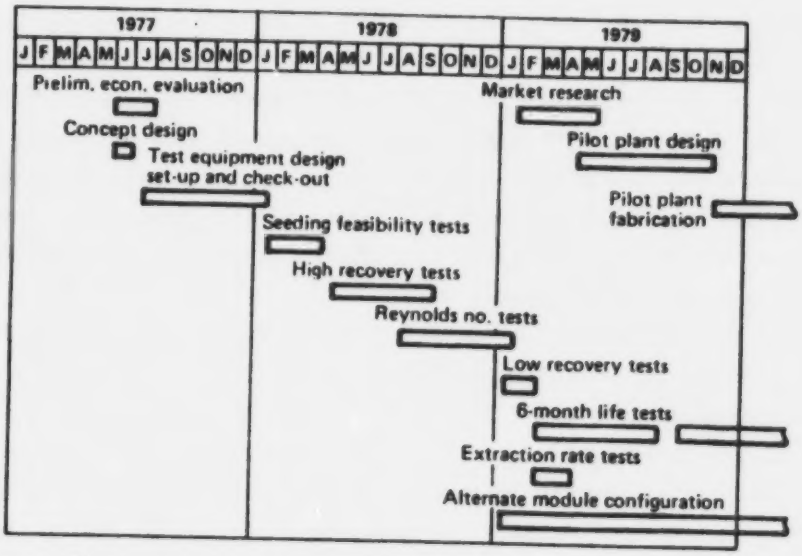


Figure 10. Seeded Reverse Osmosis Development Plan

Seeding feasibility tests in early 1978 demonstrated the preferential precipitation mechanism in a membrane separation process.

The testing activities for the following 10 month period were directed to evaluating and defining what were considered to be some of the process variables. The test conditions employed during the prior seeding feasibility tests were intentionally conservative in order to avoid confusing a process optimization malfunction with a preferential precipitation mechanism problem. One of the process variables studied was that of operating at increasing recovery or higher concentration factors. It was apparent the proposed Seeded Reverse Osmosis process would have only limited applicability if it were not functional up to the osmotic pressure limitations of conventional reverse osmosis. These tests were conducted using the Utah water (Figure 6) and were conducted up to about 18 concentration factors. At that point the total solids in the reject brine was about 60,000 Mg/l. Higher concentrations could have been attempted, but other process variables appeared more important during those early stages than extending the demonstrated 94 percent recovery.

The investigations were conducted very slowly from a time standpoint as evidenced by the appreciable time periods involved in each test. This cautious approach was necessary since it is well documented that many failures in membrane separation processes are extremely gradual in developing and not readily obvious to casual scrutiny.

Two other test units were installed and checked out before they were dedicated to evaluating other process parameters. One unit was employed to establish slurry velocity (Reynolds Number) criteria for a calcium sulfate laden brine in a one half inch tubular module. With the Reynolds Number tests a range of stream velocities through the module were studied. Minimum velocities were key to reducing pumping energy and increasing permeate extraction rates. A minimum velocity must be sufficient to maintain the feed slurry in suspension as it proceeds through the module and must minimize the concentration polarization layer.

By early 1979, the feasibility tests and parametric studies were sufficiently encouraging to warrant a two-pronged effort. The tests were continued with emphasis on membrane life characteristics, alternate membrane materials and alternate module configurations, while a parallel effort was directed toward preliminary design studies for both a pilot plant and full-size plant installations. By the end of the summer of 1979 a continuous steady state 6-month test had been completed on the Utah water at 90 percent recovery. That test is currently being extended for an additional 6 months.

Other membrane materials which have been evaluated for slurry operation include both polyamide and PBIL formulations. Currently a majority of the testing has been conducted using a cellulose acetate membrane but results would indicate other membranes are compatible with the Seeded R.O. process. Although most of the testing reported herein pertains to results from the standard tubular module configuration, several other module configurations are currently being evaluated.

The pilot plant program anticipates a test on an actual raw water in early 1980. Several alternative sites are being considered and discussions are underway with the appropriate client personnel. Based on the assumption that the pilot tests and the economic potential are encouraging RCC is planning to offer full size systems by late 1980.

Figure 11 summarizes the status of various test programs at this time. It is felt the concept of using seed slurry and preferential precipitation to avoid calcium sulfate scaling in an R.O. membrane has been verified. Tests to determine the limits of concentration factor have been completed and those results indicate that recoveries are possible up to the operating limits imposed by osmotic pressure restrictions. Flux tests and membrane per-

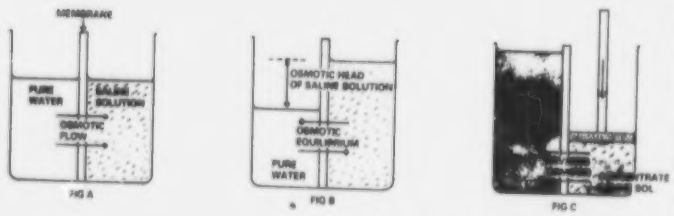
formance tests have been conducted. Tests to determine the channel size required to avoid plugging have been completed in conjunction with determinations of minimum velocity requirements for maintaining the slurry in uniform suspension. The susceptibility of pumps and membranes to erosion have been explored through periodic inspections of actual operating test equipment. Testing to evaluate alternate cleaning approaches is being planned and, as discussed earlier, the pilot plant is being designed.

Investigation	Status
Slurry process	Verified
Concentration factor - low of 1.2X to high of 18X	Complete
Brine velocities	Complete
Flux and membrane performance verification	Complete
Open flow channel requirements	Complete
Pump erosion (multi-stage)	Complete
Membrane erosion and life tests	Continuing
Hi extraction tests	Complete
Cleaning	In planning
On-site pilot demo	In planning

Figure 11. Seeded Reverse Osmosis Test Status

In summary this paper has discussed development work currently underway at Resources Conservation Co. on a unique R.O. concept. This concept, if successful, will permit high recovery without pretreatment of feedwaters saturated with calcium sulfate or silica. Testing to verify this approach has been accomplished using a tubular reverse osmosis module. Testing has also been extended to include coverage of several major design parameters such as extraction rate, stream velocity, concentration factor and operating pressure. Design effort has been initiated on a pilot plant with the objective of commencing pilot plant tests early in 1980.

REVERSE OSMOSIS PRINCIPLES



Osmosis is the phenomena by which a semi-permeable membrane allows the passage of the solvent (usually water) while it restricts the passage of solute particles which are also termed dissolved solids. (Fig A). The solvent travels through the membrane in both directions setting up a dynamic equilibrium in relation to the osmotic pressure of the solution. (Fig B.) The process of reverse osmosis involves the overcoming of the osmotic pressure of the solution which has the effect that the solvent is forced through the membrane in one direction only. (Fig C.) The solution becomes more concentrated as the solvent flows out through the membrane.

TUBULAR REVERSE OSMOSIS

Water is pumped at 30 - 50 bar inside the cellulose acetate tubular membrane with the effect that the pressure used not only overcomes the osmotic pressure of the solution, but forces enough permeate (pure water) through the membrane to derive the desired recovery (see diagram below). Between 70% and 90% of the feedwaters can be recovered, depending on what system configuration is used. Depending on the characteristics of the water, inorganic salts are rejected at the 90 - 95% level, while all bacteria, viruses, pyrogens and most organics are also rejected by the membrane.

membratek

TUBULAR REVERSE OSMOSIS DESALINATION SYSTEM

INDEX

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Inside Cover (top)	Reverse Osmosis Theory.
Inside Cover (bottom)	Mechanics of Tubular Reverse Osmosis.
1	An introduction to Membratek.
2	The Membratek Module.
2	The Membratek Module Specification.
3	Applications for Tubular Reverse Osmosis.
3	Facts and Figures — Membratek TRO.
4	Scope of supply.
Inside back cover	Schematic of TRO system.

INTRODUCTION TO MEMBRATEK

MEMBRATEK

Membratek is a division of Bintech (Pty) Ltd which in turn is a subsidiary of Bakke Industries Ltd, being part of the JSE listed Malbak Investment Group.

TYPE OF SYSTEM

Membratek offers a tubular Reverse Osmosis system with its primary function being the desalination of various types of water and industrial effluents, in fact all waters containing dissolved salts, organics, bacteria, viruses, etc.

SYSTEM CHARACTERISTICS

The robust characteristics of the tubular system include minimal pretreatment, reverse flow sponge ball cleaning which helps prevent fouling of the membrane, the solid cast module ends are leak-free due to the absence of traditional sealing methods, higher pressures can be accommodated by the system.

RESEARCH AND DEVELOPMENT

The ongoing R & D programme involves close ties with the Polymer Institute (University of Stellenbosch), the Water Research Commission and the National Institute for Water Research (CSIR).

MANUFACTURE

Low cost tubular modules and membranes are manufactured in their entirety at our Paarl factory. Complete plants are built by our engineering staff which are delivered and commissioned anywhere in Southern Africa.

MAIN ADVANTAGE

The system handles high fouling waters with relative ease.

THE MEMBRATEK MODULE

Based on an overseas concept, the Bakke Membratek System was modified for South African conditions and improved to the extent that it is now considered superior to imported conventional R.O. plants. The module design carries South African and EEC patents.

The R.O. modules have a 100% local content and were developed particularly for water with high fouling characteristics. Fouling agents such as organics, silica, iron and manganese can, to a large extent, be removed from the membrane surface by intermittent sponge ball flushing. The more exposed membrane surface facilitates cleaning, thereby minimizing the troublesome pretreatment stage needed in conventional R.O. plants.

Modules consist of cellulose acetate type membranes in tubes made up of polymer discs housed in aluminium, which reduces the cost of the tubular system to a level competitive with conventional spiral membrane systems. Each module contains 19 tubular membranes which are factory assembled and tested. Membranes are also replaced at the factory and old modules are exchanged for reconditioned ones as the need arises.

Pilot work on secondary sewage effluent indicates a membrane life of at least three years without any prefiltration for the R.O. stage. Total dissolved solids (TDS) reduction of 90% at a volume recovery of 75% have been obtained on a 12 month pilot run at Port Elizabeth Municipality. Comprehensive analysis of the product water indicates a quality better than SABS potable standards.

THE MEMBRATEK MODULE SPECIFICATION

1. SALT REJECTION	90 - 98% - 2 000 mg/l Na Cl 98 - 98% - 2 000 mg/l Na_2SO_4
2. MEMBRANE AREA	1,75 m^2 per module
3. INITIAL FLUX	700 - 1 000 l/m /d
4. DESIGN FLUX	500 - 600 l/m /d (at 40 bar 20 C and 1 000 mg/l Na Cl)
5. CLEANING	Reverse flow at 60 - 600 minute adjustable cycles using sponge balls for each row of modules
6. PRESSURE DROP	1 bar per module at 1m/sec velocity (7,6 l/m through 12,7 mm ø pipe x 1m/sec)
7. LINEAR VELOCITY	0,50 - 2,00 m/sec
8. MEMBRANE MATERIAL	Cellulose acetate (Tubular Membrane)
9. MEMBRANE PROPERTIES	pH range 3 - 6,5
10. RECOVERY RATES	± 70% at 5 000 TDS, - 85% at 1 000 TDS (Na Cl)
11. MEMBRANE LIFE	2 - 5 years depending on water quality

APPLICATIONS FOR TUBULAR REVERSE OSMOSIS

With the shortage of good quality water in most parts of the country, and the rising cost of water, it is becoming viable to purify and re-use various water supplies rather than discharge them. Listed hereunder are some of the desalination uses of tubular reverse osmosis:

1. High scaling waters can be desalinated to prevent scaling up of nozzle orifices, pump glands, pipes and other equipment that is in contact with water.
2. Effluent discharge can be re-used in industrial applications such as electroplating shops, etc.
3. Brackish water in remote areas can be purified well within potable standards.
4. Municipal feedwaters can be cleaned sufficiently for use in the electronics industry.
5. Because the membrane removes all bacteria, viruses, etc., it can be used for pharmaceutical water purification.
6. The system is also suited to purify secondary sewage effluents to both industrial and potable standards as tests by competent authorities have proved (the CSIR - NIWR and P.E. Municipality).
7. Ion exchange demineralisation is made more cost effective on waters with a high TDS. Up to a 97% saving on regenerant chemicals can be realised.
8. Systems that need high quality water such as boilers and heat exchangers, can be supplied by a Tubular Reverse Osmosis System, while at the same time the waters can be recycled through the system.

FACTS AND FIGURES — MEMBRATEK TRO

1. **The Difference between TRO and RO**
   There are two major differences between tubular reverse osmosis and the more commonly encountered spiral wrap or hollow fibre techniques. The first is the tubular system's ability to handle high fouling waters without fouling the membrane irreversably. The technology is best suited to difficult waters such as high hardness waters in systems where scaling creates problems. The other major difference between our technology and other membrane systems is the minimal amount of pretreatment our systems require. Because fouling is not a problem, only cartridge type coarse filtration is used in conjunction with acid dosing and chlorination if needed.

2. **Energy consumption**
   The only electrical energy used is for driving the pump motors. Very little is used for instrumentation and controls. The total consumption ranges between 1,5 - 3,0 kwh/m^3 of product water, depending on the feedwater quality and the size of the system.

3. **Membrane replacement cost**
   Membrane replacement costs between 10 and 20 cents per m^3 water produced depending on the membrane life which can vary between 2 and 5 years.

4. **Experience**
   Apart from laboratory types tests on various waters/effluents and our local (Pearl) pilot testing the following pilot tests have been performed (starting from the most recent):

Location	Water Type	Remarks
(a) Grootvlei (ESCOM)	Cooling Tower	Considerable reduction of hardness and TDS.
(b) Port Elizabeth	Secondary Sewage	Water produced to potable standards.
(c) ERPM	Acid Mine Water	Seeded slurry with high recoveries.
(d) Bellville	Secondary Sewage	Water produced to potable standards.
(e) Vaal Reefs	Vaal River water	High quality process water obtained.

Brackish water with a high TDS (3000 - 5000 TDS in the case of the plant purchased by the Department of Community Development) can be desalted by our systems.

SCOPE OF SUPPLY

Apart from the hardware listed hereunder the following are also part of the scope of supply:

- Delivery and insurance.
- Installation
- Commissioning
- Training of supervisory staff and operatives.

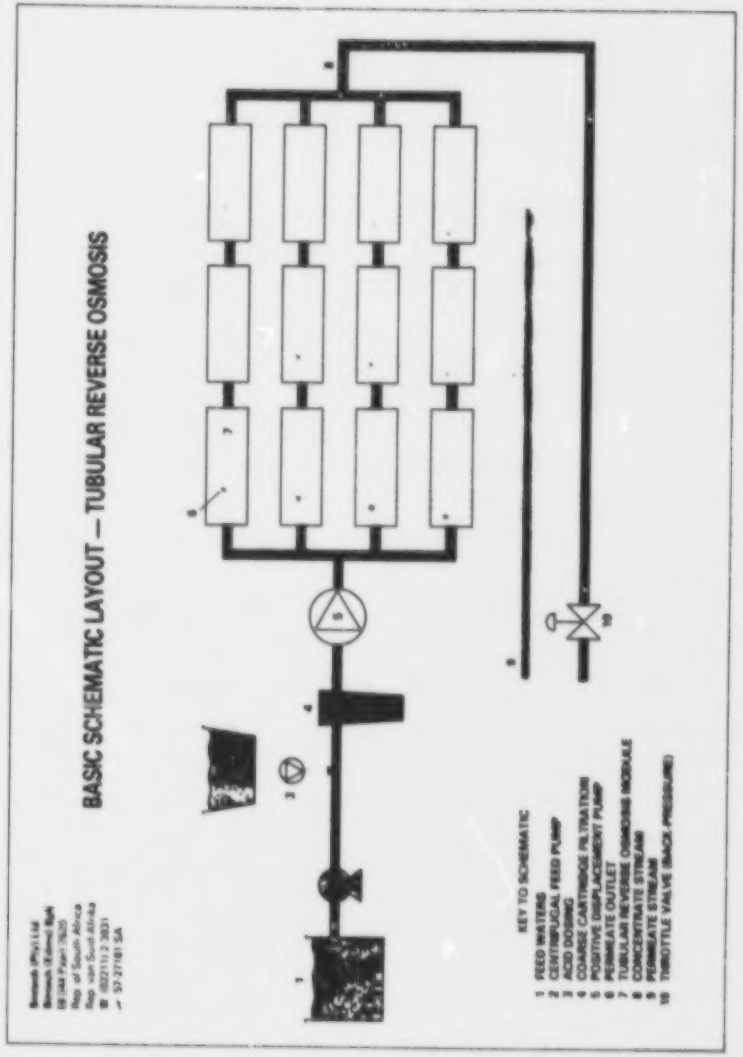
1. **Instrumentation and Control**
   Pressure is controlled at the feed water inlet for low pressure while high pressure controllers are located after the pumps and on the outlet stream. Temperature measurement and control along with pH measurement and control also protect the membranes from out of specification feed waters. Along with high permeate conductivity measurements and excessive power consumption all the above parameters if exceeded (or out of specification) cause the motors driving the pumps to "trip-out". The permeate conductivity measurement includes a feed conductivity measurement and a percentage rejection measurement for comparing data. Also included are flow meters on feed, product and reject streams. On some systems both rotameters and digital readout flowmeters are used depending on the degree of sophistication of the particular plant. A spongeball reverse flow system is included which incorporates a timer that can be set to activate the reverse flow mechanism, as the cleaning cycle demands.

2. **Power**
   Small plant utilise either 250v or 380v while larger plants normally run on 380v or 550v.

3. **Cleaning In Process**
   A C.I.P. tank (sometimes also doubling as a feed tank) is included. Cleaning is done approximately once per fortnight and involves circulating a citric acid and/or detergent mixture through the system for 2 - 4 hours, and then returning the mixture to the C.I.P. tank if it is separate from the feed tank.

4. **Pumps and Motors**
   On small plants positive displacement pumps are used which require a 0,8 to 2 bar feed. Larger plants use multistage centrifugal and/or positive displacement pumps depending on the design configuration. Pumps are either belt drive or direct drive, the motor also being supplied.

5. **Plant Configuration**
   The mechanical part of the plant consists of the Tubular Reverse Osmosis Modules, the support racking, inter-connecting pipework and valves, the feed tank (usually stainless steel), the acid dosing tank and acid dosing pump, in line coarse cartridge filters (100 - 300 microns), and permeate manifolding. The plant should be sited in a covered area with a floor that can hold at least one ton per square meter. Fittings (pipes) to and from the plant can be standardised to the users requirements. Modules are fitted into racks which contain 72 modules, the modules being 2,5 metres in length. These racks can be stacked on top of each other depending on area constraints. The space required by a 100 m^3/day plant is approximately 20 square metres x 3 metres high while a 1,000 m^3/day plant will require approximately a 100 square metres x 4 metres high.



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THE WORLD'S FIRST LARGE SEAWATER REVERSE OSMOSIS DESALINATION PLANT AT JEDDAH, KINGDOM OF SAUDI ARABIA

by

Abdullah Al-Gholaikah[1], Nabil El-Ramly[2],
Isam Jamjoom[3], and Ralph Saston[4]

ABSTRACT

Traditionally, coastal urban centers in arid regions have had to rely on distillation as the means of desalting seawater. A new reality is now available as exemplified by the current installation of a large reverse osmosis plant to desalt highly saline Red Sea water to supply municipal water needs at Jeddah, Saudi Arabia.

The Saline Water Conversion Corporation of the Kingdom of Saudi Arabia awarded a competitively bid contract to Fluid Systems Division of UOP Inc. for the design, fabrication, construction, and two-year operation and maintenance of a seawater reverse osmosis desalting plant with a production capacity of 12,000 m^3/day.

This paper presents a comprehensive review and description of the design, logistics and installation aspects of the plant together with an evaluation of delivery times and capital and operating costs of reverse osmosis vis-a-vis multiflash distillation for seawater desalination.

BACKGROUND INFORMATION

Jeddah

The City of Jeddah, situated on the coast of the Red Sea, is the largest port and most important commercial center in the western region of the Kingdom of Saudi Arabia. It serves as the port of entry for the hundreds of thousands of pilgrims who annually visit Mecca Almukaramah from all over the world.

Jeddah covers an area of about 190 million square meters and is the most densely populated city in the Kingdom. The resident population of Jeddah has constantly been increasing, especially during recent years, as a result of the ambitious industrialization and development programs undertaken by the Government. The population increased from around 40,000 in the mid-forties to about 160,000 in the mid-sixties. The 1974 Population and Housing Census shows that Jeddah had about 565,000 people at the end of 1974. Assuming an annual population growth rate of 10 percent during the past four years to take into account the large influx of foreign workers, Jeddah's population will be over 800,000 persons by the end of 1978.

Jeddah's climate is subtropical with hot, humid summer and warm winter months with occasional scanty rainfall between November and February. The average annual rainfall is a little less than four inches (10 cm) per year.

Water Supplies and History of Desalination Applications

The City of Jeddah is located in an arid region and has always been plagued with water supply problems. Because of the importance of water, it always has been necessary to develop new water resources. Consequently, many pioneering and imaginative water supply schemes were conceptualized and implemented during the city's long history. It is, therefore, not surprising that the first seawater conversion plant to provide a sizable city with its drinking water needs was installed in Jeddah.

Toward the end of the Nineteenth Century, it was decided to import a distillation apparatus that had just been developed in Europe. In 1907, this new invention was purchased from the United Kingdom and installed in Jeddah. Despite the many operating and technical problems associated with that apparatus, known in Jeddah as the

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Kendase (condenser), the local inhabitants, through ingenious maintenance and repair schemes, managed to keep it in operation until 1934 when it was replaced by a larger plant made up of two distillation units.

Because of the increase in water demand, especially created by the increase in the number of pilgrims, it was necessary to operate the two units well above their rated capacity and, therefore, many operating problems were encountered. Nevertheless, this plant continued to provide the City with its drinking water until about 1960 when it was dismantled, partly because of inefficient operation but mainly because a water pipeline had been constructed to bring water from wells and springs in Wadi Fatima, about 86 km east of Jeddah. Wadi Fatima water was subsequently augmented by water from Wadi Khuleys, some 100 km north of Jeddah.

Although water transportation from Wadi Fatima and Wadi Khuleys is still providing Jeddah with fresh water in an amount ranging between 15 and 20 mgd (68800 – 76700 m^3/d), with the great increase in industrialization and the consequent increase in population, these sources were found inadequate and the need to supplement fresh water supplies was imminent. Accordingly, in 1965, after careful and detailed studies of local and technological factors, it was decided to embark on an ambitious desalination program with far-reaching ramifications. The supervision of the implementation was first carried out by Saline Water Conversion Office (SWCO) a department of the Ministry of Agriculture and Water. In recognition of the benefit and importance of this program to the Kingdom, a Royal Decree was issued in 1974 to establish an independent government agency, the Saline Water Conversion Corporation (SWCC), to be in charge of the desalination programs in the entire Kingdom. His Royal Highness, Prince Mohamed Al-Faisal, an internationally recognized desalting pioneer, was named the first Governor of that agency.

The Need – Water Supply/Demand Balance

Table 1 lists the seawater desalination and power projects, in operation or under construction in Jeddah, that have been contracted for by SWCC. The seven projects indicated in this table can be categorized into two groups.

The first group includes the four major and permanent projects, Jeddah I through Jeddah IV. These are dual-purpose plants, with combined capacity of 830 megawatts of electricity and 86 million gallons per day (322,000 m^3/day) of desalted water, that have been planned in relation to the long-range increase in water and power demands. (See Figure 1.) The construction of these permanent installations is being staged in four phases to minimize under-utilization of installed capacity during early years and thereby optimize capital allocation over time. Of course, in staging the four Jeddah phases, consideration was also given to such aspects as the availability of local construction labor, the impact of these large projects on the world desalination industry, operation and maintenance constraints, and other economical and technological factors.

The second group includes the remaining three projects in Table 1, which are relatively small and may be regarded as being of an urgent or temporary nature. These were undertaken, in relation to short term deficiencies in the supply/ demand balance, to alleviate temporary unsatisfied demands as depicted in Figure 1. The seawater reverse osmosis plant described in this paper falls under this group of projects. As a result, its procurement, design, lead-time, mode of operation and other considerations were influenced by its temporary and urgent role.

PLANT PROCUREMENT

Near the end of June, 1977, major reverse osmosis membrane suppliers were invited by the Ministry of Agriculture and Water, Kingdom of Saudi Arabia, to bid on a temporary 12,000 m^3/day seawater reverse osmosis desalination plant to augment the supply of potable water to the City of Jeddah. The tender document, transmitted via telex, required that the plant be supplied in the shortest possible time and requested that tenders be submitted by July 7, 1977. Upon receipt of tenders, discussions were held in Coronado, California, between the bidders and the Ministry's Engineer, VBB (Vattenbyggnadsbyran) of Sweden. On July 19, 1977, a letter of Intent/Order to Commence was awarded to Fluid Systems Division of UOP Inc. for a total lump sum of 105.30 million Saudi Riyals for plant construction and 16.45 million Saudi Riyals for two years of operation and maintenance.

SCOPE AND REQUIREMENTS

Scope of Supply

Equipment and Construction: The scope of supply includes the complete design, supply, erection, testing and maintenance of the plant from a seawater pump well to a 400 millimeter diameter water main, excluding the connection of the pump well to the seawater pipe for the disposal of the reject. The contract includes all pertinent civil works, air conditioning, power generation, seawater pretreatment, reverse osmosis desalination equipment, post treatment, and storage of all chemicals needed for six months of operation at design capacity.

TABLE 1

SEAWATER DESALINATION AND POWER PLANTS OPERATING OR UNDER CONSTRUCTION BY SWCC IN JEDDAH

	Approximate Operating Year	Number of Desalination Units	Design Capability		Desalination Supplier	Desalination Process	Approximate Contract Value Million US$
			Power MW	Water MGD			
Jeddah I	1970	2	50	5	Aqua-Chem	MSF	9
Gas Turbine	1974		20	–			
Temporary	1975	3		0.2	Krupp	MSF	
Jeddah II	1978	4	80	10	Sasakura	MSF	182
Jeddah Sea Water	1978	9*		3.2	UOP	RO	30
Jeddah III	1979	4	200	20	Weir Westgarth	MSF	428
Jeddah IV	1982	10	500	50	SOGEX	MSF	718

*One of the nine units is stand-by. The plant also has three second stage units.

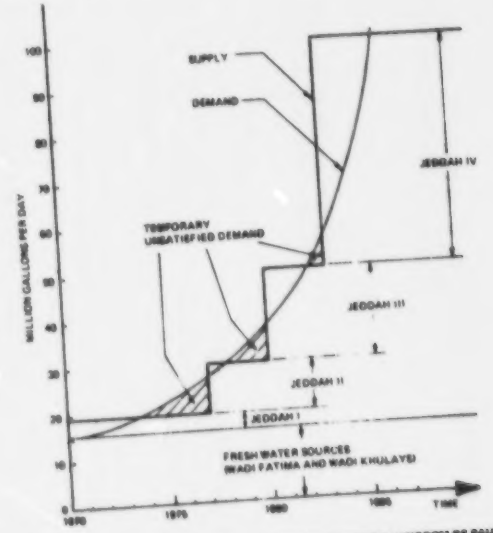


Figure 1. AN ILLUSTRATION OF WATER SUPPLY/DEMAND BALANCE JEDDAH, KINGDOM OF SAUDI ARABIA

Operation and Maintenance: The contract requires operation and maintenance of the whole plant for a period of two years. This includes all supplies and chemicals, except fuel.

Capacity Requirement and Guarantees

It is specified in the tender that the plant shall maintain the full capacity of 12,000 m^3/day in case of any single breakdown of mechanical equipment, such as pumps, chemical dosing, reverse osmosis units, etc. Furthermore, there should be sufficient capacity to ensure design capacity during normal maintenance. In other words, full load and capacity factors are required. Water production is contractually guaranteed, including provision for a schedule of monetary allowances to the owner in the event of stipulated failure to provide the guaranteed amounts and quality of water during the O&M period.

Mobility Requirements

Because of the temporary nature of the plant, the tender document stated that the plant must be sufficiently mobile so that it could be dismantled and moved to other sites after two years of operation. Accordingly, it was specified that the number of reverse osmosis units should be as few as possible, but not less than six, and the units should be able to operate independently of each other. Seawater pretreatment, however, was required to be regarded as a separate plant with a stand-by line. Extensive pretreatment to increase water recovery was discouraged.

Delivery Time

To minimize delivery time, it was required that all equipment should be of such configuration that it could be packaged in containers suitable for air-freight. Furthermore, preference was expressed for factory assembled units to minimize erection work on site.

Water Characteristics

Table 2 lists the specific characteristics of feed and product water.

General Design Requirements

- All parts shall be resistant to corrosion or be protected from it.
- Equipment shall be designed for an ambient temperature of 40°C, and a black bulb temperature of 60°C.

TABLE 2

WATER CHARACTERISTICS

Property	Seawater	Product Water After Conditioning
Temperature	32°C (Max)	–
pH	~ 8	~ 8.5
Lime Saturation Point	–	~ 8.5
TDS mg/ℓ	41,200	< 1,000
Chlorids, Cl, mg/ℓ	22,000	< 600
Sulfate, SO_4, mg/ℓ	2,960	20
Total Hardness, mEq/ℓ	148	1.4 – 2.8
Permanent Hardness, mEq/ℓ	145.5	–
Temporary Hardness, mEq/ℓ	2.5	1.2 – 1.6
Calcium, mEq/ℓ	26	1.0 – 1.8
Magnesium, mEq/ℓ	122	
Total Iron, Fe, mg/ℓ	0.2	
Silica, mg/ℓ	0.4	
Plugging Index, %	91 – 96	
Turbidity	0.5 – 0.5 as SiO_2	0.3

- Electrical equipment shall be 60 Hertz and the insulation shall be of Class 156(F) or higher. Electric motors shall be totally enclosed.
- Diesel engines and electric motors shall not be used continuously to more than 90 percent of the site rating.
- Mechanical ventilation and air conditioning areas designed for human beings shall be cooled to 26°C, and areas for equipment as needed.
- It shall be possible to use the brine for back-washing of sand or dual-media filters.
- The plant shall be equipped with the necessary instrumentation and automatic regulation devices to shut the plant down in the event the feed had not been adequately pretreated.
- The plant shall be founded on a sulphate-resistant concrete slab.
- Chemical sludge and reject (brine) shall be discharged into the sea near the plant.

PLANT DESIGN

Design Concept

To allow for maximum flexibility and reliability, and to permit later use of complete sections of the plant at other locations, the design concept chosen was to provide, as much as is practical, independent parallel operating trains. Commonality of components was employed to the maximum extent to further increase reliability and ease of maintenance.

Plant Description

The plant layout is shown in Figure 2, and the process flow diagram is given in Figure 3. These drawings should be referred to while reading the following description.

Seawater is supplied through a pipe type intake. Water is withdrawn from the ocean and conveyed through an underwater pipeline to a concrete inlet well. Water is then lifted from the seawater intake well to a splitter box by means of three low speed vertical pumps, two operating and one stand-by.

From the splitter box, the feed water flows to three 32-foot diameter (9.75 m), gravity flow, dual media filters. Filter media are composed of anthracite coal and sand. Each dual media filter is divided into three individual compartments to facilitate back-washing while maintaining the required full capacities.

The filtered water exits through the underdrain of the dual media filters into a concrete clearwell. Water is then transported from the clearwell by three pumps, again two operating and one stand-by, to a pipeline header in the building which houses the reverse osmosis units for distribution to individual units. The pumps lifting the seawater from the clearwell are identical to the pumps which lift the water from the seawater intake well.

The reverse osmosis plant is made up of first and second stage units. The plant includes nine first stage units, eight operating and one stand-by, and three second stage units. The nine first stage units are fed by individual pipelines from the distribution header. Each stream is treated prior to desalting.

Pretreatment consists of acid and phosphate addition, followed by filtration. Acid is injected into each stream to adjust the feed water pH to approximately 6.4. Also, at approximately the same injection point, sodium hexametaphosphate is added at the rate of 2 mg/ℓ to inhibit scale formation. After chemical treatment has been accomplished, each feed stream is filtered in cartridge type filters to promote chemical mixing and to remove suspended solids to protect the high pressure pumps. Cartridges are constructed of 25-micron mesh size.

The pressure of each of the nine feedstreams is then boosted by two multi-stage vertical turbine pumps, operating in parallel. Each of the two parallel pumps is directly driven by a 425 hp diesel engine. Each pump has a capacity of 500 gallons per minute (2726 m^3/day), at a discharge pressure of 1000 psi (6900 k Pa). Thus, the feed flow to each of the nine first stage units from the combined parallel operating pumps is 5432 m^3/day.

The first stage units will be run at 38.5 percent recovery. Thus, each of the nine first stage units will be producing 1663 m^3/day. This results in a combined output from the eight operating first stage units of 13,300 m^3/day.

The permeate from the first stage units flows to a common collection header. The permeate can either be routed directly to the post-treatment system or split for partial flow to the second stage units. The system's performance, either using or not using the second stage, is discussed later in this paper.

Each of the three second stage units is capable of producing 2315 m^3/day of product water from a feed of 2726 m^3/day (600 gpm). Thus, the second stage units will operate at 85% recovery. The concentrate from the second stage units will be recycled through the first stage units. One feed pump, operating at a pressure of 600 psi, is used for each of the second stage units. These feed pumps are identical to the parallel operated feed pumps on the first stage units. Also, they are driven by identical diesel engines as those for the first stage.

The combined product water output from the first and second stage units is collected in a permeate header which flows to a final permeate holding tank. In the final section of the pipeline header before entering the permeate tank, lime is added to the permeate to stabilize the product water and raise the pH to approximately 7.5. Also, near the same injection point as the lime, the product is sterilized by the addition of chlorine at approximately 2 mg/ℓ as Cl_2.

The stabilized water is then lifted from the permeate holding tank by three pumps, again two operating and one stand-by, and transported to the pipeline which goes to the City of Jeddah.

Seawater Supply

The seawater inlet is provided for under a separate contract between SWCC and a Saudi contracting firm,

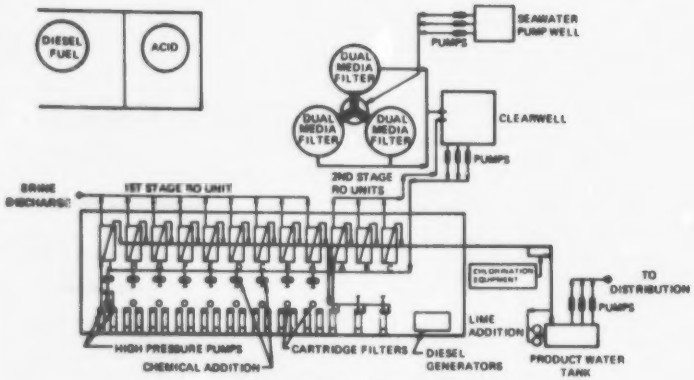


Figure 2. PLANT LAYOUT 3.2 MGD SEAWATER RO PLANT JEDDAH, KINGDOM OF SAUDI ARABIA

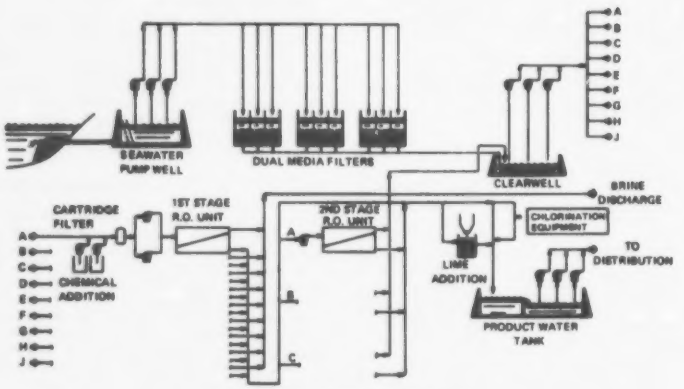


Figure 3. FLOW DIAGRAM 3.2 MGD SEAWATER RO PLANT JEDDAH, KINGDOM OF SAUDI ARABIA

Mapher Corp. It is basically a concrete inlet well, connected to the Red Sea by an underwater pipeline. The open end of the inlet pipeline is to be 6 meters below meanride and extend approximately 2 meters beyond a coral reef shelf. At the end of the coral reef, the bottom of the sea slopes abruptly downward to approximately 50 to 60 meters. Appearance of the water is very clear. Water flows through the intake pipe into the concrete well in which trash and fish screens are placed to prevent intrusion of this type of matter into the reverse osmosis inlet.

Pretreatment Equipment

The chemical pretreatment equipment is composed of acid storage and injection pumps, hexametaphosphate storage and injection pumps, and cartridge filters.

Fouling of the membrane can originate from impurities in the feedwater, such as small amounts of iron and manganese, and from scaling caused by carbonate or non-carbonate hardness. The effects of iron and manganese can be greatly reduced by pH control and filtration. Another benefit of acid addition is the removal of sufficient bi-carbonate from the feed, thereby avoiding the occurrence of calcium carbonate scale on the membrane surface.

Nine acid addition systems, complete with feedback control for pH adjustment of feedwater to the reverse osmosis plant and with required interlocks for safe plant operation, are provided. Also provided are nine sodium hexametaphosphate addition systems for scale inhibition, and nine stainless steel cartridge filters.

The pH control loop will measure pH after the cartridge filters and will be used as a signal for simple on-off control of the acid injection pump. Extended time high pH will be interlocked for individual unit shut down. Care is exercised in the acid piping to assure anti-siphon conditions.

Reverse Osmosis Units

The nine first stage reverse osmosis units are each composed of 56 Fiberglass pressure tubes (Model 56FRP-6) 160 mm diameter by 6.5 m long. (See Figure 4.) These pressure tubes are piped in parallel. Each tube contains six TFC™ Model 1501PA spiral wound high pressure elements with polyamide membrane resulting in a total of 336 membrane elements for each first stage unit. One of the units is shown in Figure 4 which is 7 meters long by 3 meters wide by 3 meters high.

Each of the three second stage units is composed of 56 FRP pressure tubes identical to those of the first stage. But, these units are piped in a configuration such that water flows through a three-pass system composed of 32 tubes in the first pass, 16 in the second pass and 8 in the third pass. This means that the second stage units are piped as a 32-16-8 array.

The plant uses Fluid Systems' polyamide thin film composite membrane element, Model 1501 TFC. The element is spiral-wound 6-inch in diameter and 40-inch long. It has a design permeate flow output rating of 1600 gal/day at 400 psi net driving pressure at 25°C. This requires an applied pressure, depending on temperature and ocean water salinity (and corresponding osmotic pressure) of 800 to 860 psi for a system operating at 30% product water recovery. The salt passage, for design purposes is 1.1% (98.9% rejection) based on chloride ion transport.

The design flow rates for the first and second stage units are given in Table 3. The last entry of this table gives the total permeate from the plant when all of the first and second stage units, except the one stand-by first stage unit, are operating, under such a situation, the overall recovery from seawater intake to final permeate will be 27.8%.

TABLE 3

MAJOR FLOW RATES*

Stream	Rate of Flow	
	m^3/d	gal/min
(1) Seawater intake	43,882	8,010
(2) First stage feed (8 units)	43,086	8,800
(3) First stage permeate (8 units)	13,300	2,440
(4) Second stage feed (3 units)	8,177	1,600
(5) Second stage permeate (3 units)	6,945	1,376
(6) Total permeate (3) - (4) + (5)	12,086	2,216

*Design conditions corresponding to a situation when all the first and second stage units, except the stand-by first stage units are operating.

Modes of Operation

During the initial operation of the first stage units, it is expected that the permeate TDS will be between 850 and 900 ppm while operating at a pressure of approximately 860 to 870 psi. (See Figure 5.) With passage of time, however, it is anticipated that the TDS of the permeate from the first stage will gradually increase. As indicated in Figure 5, at some time during the first two years, the TDS of the first stage permeate may exceed the specified limit of 1000 ppm. If and when this happens, the second stage units will be employed.

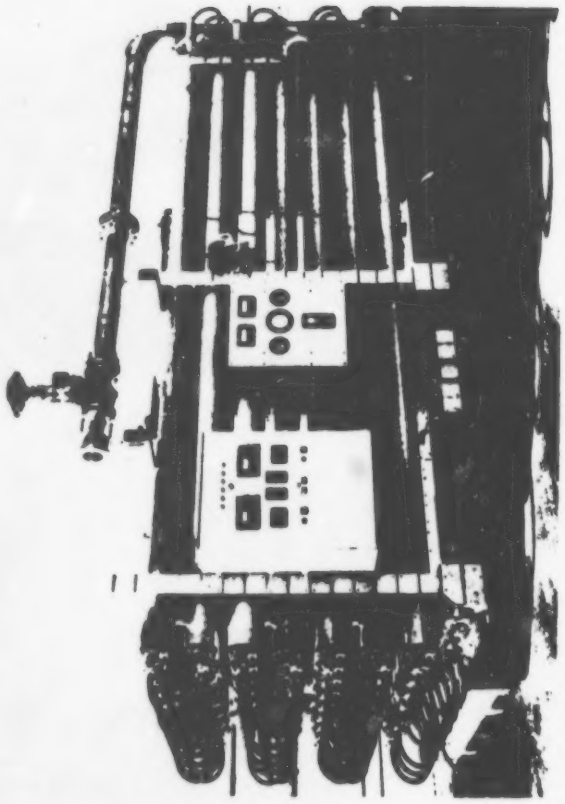


Figure 6. 1982 m^3/DAY SECTION OF THE 13,200 m^3/DAY SEAWATER RO PLANT, JEDDAH, KINGDOM OF SAUDI ARABIA

The product water quality of the second stage units will be in the range of 50 to 100 ppm TDS, depending on the quality of the feed to the second stage (i.e., the quality of the permeate from the first stage). With full plant operation, it is possible to produce a blended feed from the output of both the first and second stage units of less than 1,000 ppm TDS, even if the quality of the output from the first stage units deteriorates so that the TDS goes as high as 2,000 ppm.

Thus, the second stage units are incorporated into the design to ensure that the plant will meet the water quality requirement of the contract. This assurance, however, has resulted in an available overcapacity during the early period of plant operation. As indicated in Table 3, with eight operating first stage units, the output is calculated to 13,300 m^3/day, which is 1,300 m^3/day above the capacity requirement. Since the second stage units operate at 85% recovery, it was necessary to oversize the first stage units.

There is still another benefit that stems from the first stage units being oversized to allow for full plant capacity while operating the second stage units at 85% recovery. If the output of the first stage units is increased by only 3% (raising the net pressure by 12-15 psi or 1 atm) the required output of 12,000 m^3/day can be achieved by operating seven of the first stage units rather than eight. Thus, in reality, the plant might actually have two complete stand-by first stage units. The projected first stage, second stage, and blended product water quality as affected by time are presented in Figure 5.

ERECTION AND INSTALLATION

The major contract for this project was awarded to Fluid Systems Division of UOP Inc. and as indicated earlier, it included the erection and installation of all equipment. Two other minor contracts were also awarded by SWCC. They covered the construction of the seawater intake, and transportation of equipment from San Diego to Jeddah. At the same time, arrangements proceeded for the total organization of the project and the selection of subcontractors.

Procon Incorporated, a UOP subsidiary, acted as construction manager. Fluid Systems Division, as the prime contractor, employed locally available skills wherever possible. Civil work and electrical and mechanical installation subcontracts were awarded to Saudi firms who performed their work under the supervision of the prime contractor's field engineer and staff.

As with any project of this size and relatively short delivery schedule, some problems and delays were

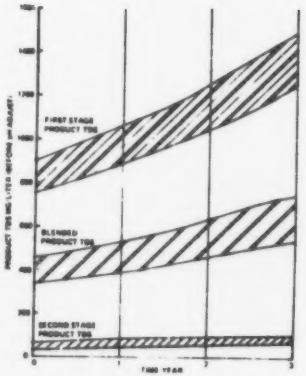


Figure 5. VARIATION OF PERMEATE QUALITY WITH TIME JEDDAH, KINGDOM OF SAUDI ARABIA

inevitably encountered. They included: sea wall problems, site erosion, compaction, and delayed construction of the intake. It was necessary to change the transportation mode from air to ship. All problems were resolved within a reasonable time.

The reverse osmosis rack assemblies were fabricated and tested at Fluid Systems' facility in San Diego, prior to shipment to Jeddah. SWCC personnel verified the condition of the equipment upon arrival. Figures 6 and 7 are photographs of the completed plant taken during the final stage of its construction.

COSTS AND MSF COMPARISON

Capital Costs

The breakdown of the capital costs of the plant is indicated in Table 4. The table shows local construction and installation costs amount to about 26 to 30% of total installation cost.

To compare the capital cost of seawater reverse osmosis with multistage flash, please refer to Table 1 in which the actual contract prices of the three multistage flash plants are listed (contracted for at about the same time as this reverse osmosis plant for installation in Jeddah. Assuming a credit of $500 per kilowatt of electrical capacity, the cost

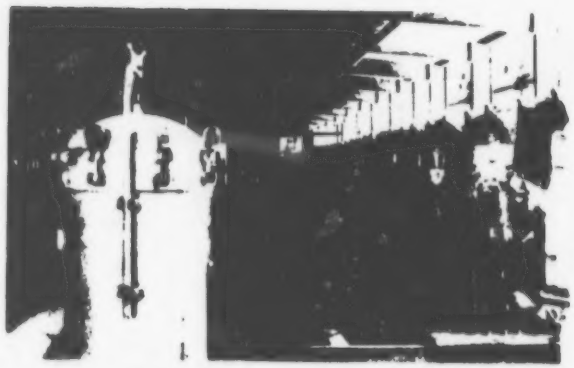


Figure 6. 3.2 MGD JEDDAH SEAWATER RO PLANT, INTERNAL VIEW

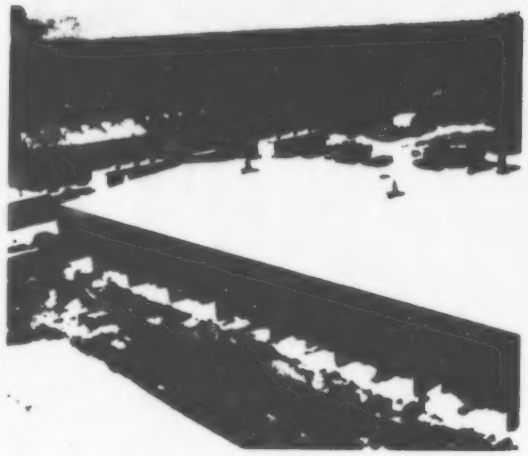


Figure 7. 3.2 MGD JEDDAH SEAWATER RO PLANT, EXTERNAL VIEW

per gallon per day of installed capacities of the Jeddah multistage flash plants would be as follows:

Jeddah II	$14.2
Jeddah III	$16.4
Jeddah IV	$ 9.4

These figures are to be compared with a $9.4 cost per gallon per day capacity for the reverse osmosis plant. It should be noted also that the reverse osmosis plant is only 3.2 mgd as compared to 10 mgd (Jeddah II), 20 mgd (Jeddah III), and 50 mgd (Jeddah IV). Taking the economy of size into account, the capital cost of reverse osmosis is undoubtedly more competitive than MSF. Furthermore, as indicated in Table 4, the reverse osmosis plant capital cost includes $2 million worth of electric generating capacity of about 6.6 MW that were not credited to the reverse osmosis plant. The owner's stipulation requiring that the plant be supplied in light, self-contained sections also significantly increased the capital cost.

The delivery time periods were one third to one fifth of those normally required for MSF plants.

TABLE 4

CAPITAL COST SUMMARY

Item	Cost Saudi Riyals
Filters	4,942,833
Electrical Equipment and Diesel Generators	3,828,843
Piping, Valves and Materials	16,908,203
R O Pressure Tube Stacks and Membrane	30,086,496
Pumps, Diesels and Motors	16,205,341
Pretreatment Skids and Storage Tanks	1,066,400
Control Panels and Instruments	720,048
Miscellaneous Hardware, Structures, Bolts, Gaskets, Paint, Grout, etc.	3,564,236
	79,121,000
Civil Work	19,250,000
Electrical and Mechanical Installation	7,000,000
	105,371,000

Energy Cost

One of the most important factors in operating costs is energy. Reverse osmosis is a relatively low user of energy, compared to distillation. Assuming a performance ratio for multistage flash of 10 pounds of fresh water per 1000 Btu and a fuel to steam efficiency of 80%, one million Btu will be needed per 1,000 gallons (3,785 m^3) of product water for a multistage flash plant.

Making the extremely conservative assumptions indicated below for a reverse osmosis plant that is similar to the upper limit values of the plant described in this paper, it will only require 1/2 million Btu for the production of 1000 gpd of fresh water using reverse osmosis, or only half of the requirements for multistage flash.

first stage recovery factor	30.5%
second stage recovery factor	85%
first stage pressure	1000 psia (6890 k Pa)
second stage pressure	500 psia (3450 k Pa)
combined pump/motor efficiency	70%
fuel to energy efficiency	30%

To demonstrate that the above assumptions are realistic, it is to be noted that the guaranteed value of fuel consumption for the plant described here is actually 500,000 Btu per 1000 gallons (3.785 m^3) of product water.

CONCLUSION

Experience to date with the design, construction and installation of this first large reverse osmosis system for the desalination of seawater has been consistent with expectations. Employment of local skills in Saudi Arabia was encouraging and satisfactory. Actual cost data accrued to date supports the contention that reverse osmosis is significantly less costly than multistage flash both in terms of capital and operating costs, even when compared to large dual purpose MSF plants. It has been demonstrated that seawater reverse osmosis systems can be erected with very short lead times compared to MSF. In summation, seawater desalination using reverse osmosis is a reality with excellent prospects for further improvements.

EDITORIAL NOTE

An earlier version of this paper was presented at the Sixth International Symposium on Fresh Water from the Sea, European Federation of Chemical Engineering, Las Palmas, Gran Canaria, Spain, September 1978.

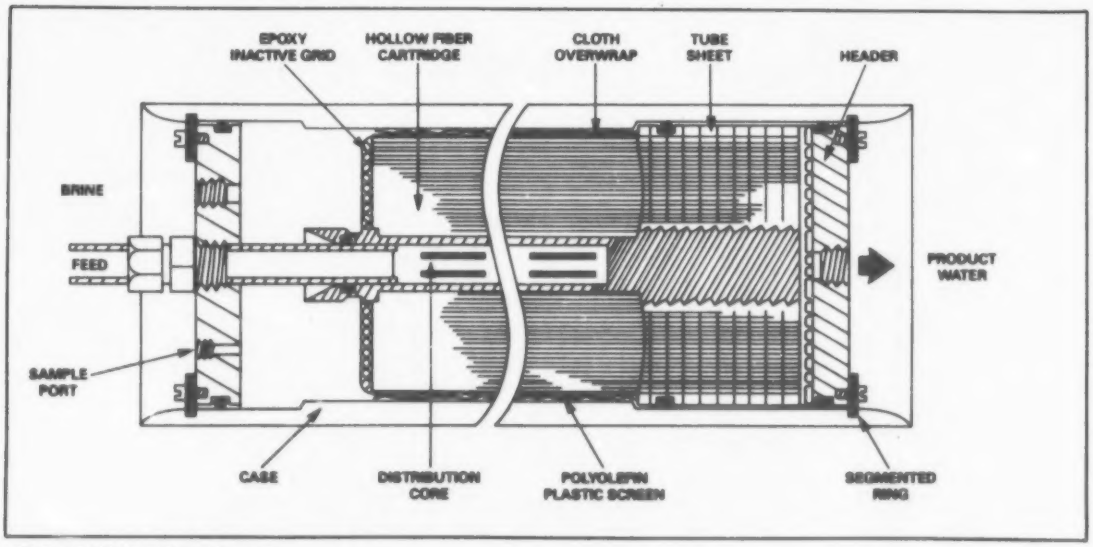
INTRODUCTION

The DOWEX* RO-4K Permeator is a water purification module which operates on the principle of reverse osmosis to remove dissolved solids from water. Construction of the Permeator is shown in Figure 1.

Feedwater is pumped under pressure into the distribution core, where it bathes the exterior of thousands of hollow fiber membranes. If the feedwater is pressurized above its natural osmotic pressure, product water having considerably lower dissolved solids will pass through the membrane walls and into the product water line. The reject, or brine, containing most of the dissolved solids in a concentrated form, is collected through the brine outlet.

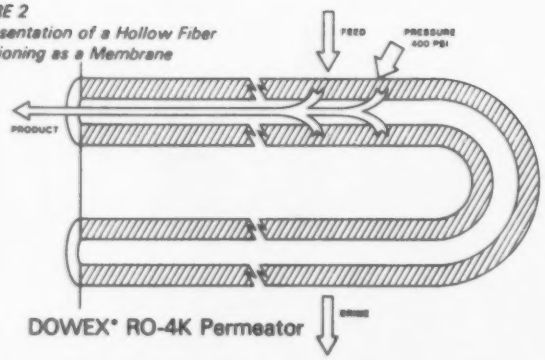
This Permeator is rated at long-term productivity of 4000 gallons per day. The 4000 gallons per day represents a theoretical extrapolation from initial test data. Initial productivity will be significantly higher, but the actual long term productivity of each permeator is influenced by a variety of factors, including feedwater temperature and pressure, dissolved solids concentration, and the presence of possible foulants or scalants in the feed. These effects, and others, will be discussed later in this manual. In general, greater than 90% of the dissolved solids will be removed.

FIGURE 1
DOWEX RO-4K
Reverse Osmosis Permeator



* Trademark of The Dow Chemical Company

FIGURE 2
Representation of a Hollow Fiber Functioning as a Membrane



DOWEX* RO-4K Permeator

REVERSE OSMOSIS

Reverse osmosis can be described as the separation of water from dissolved solids by application of a pressure differential across a membrane which is permeable to water, but not to the dissolved solids. The applied pressure differential must be sufficient to overcome the forces tending to keep the water and dissolved species together.

The hollow fibers contained in the DOWEX RO-4K Permeator can be visualized independently to show how they function as membranes (Figure 2). Feedwater containing dissolved solids flows over the outside of the hollow fiber. An applied pressure differential of up to 400 psi forces water through the semi-permeable walls of the hollow fiber. The dissolved species (brine) remain behind. The permeated water (product water) flows out the open end of the fiber. The incoming water has been physically separated into two streams, generating no additional pollutants.

In theory, no chemicals need be added to effect this separation, in actuality, some chemicals are required for control of pH, iron fouling, scale control, or biological growth. These and several other factors cause differences in performance of various membranes which can be of economic significance in long-term operation.

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CONSTRUCTION OF THE DOWEX RO-4K PERMEATOR

The DOWEX RO-4K Permeator consists of the following components as shown in Figure 1.

1. Case — made of filament-wound fiberglass with epoxy binder. It is designed to enclose the fibers in the pressurized compartment.

2. End plates (headers) — enclose the open ends of the fiberglass case. They are held in place by segmented rings. Sealing is provided by O-rings, and end plates may be removed by first removing the segmented rings.

   One end plate contains the product water port. The second end plate contains both the feedwater port and brine port.

3. Feedwater distribution core — allows feedwater to bathe the entire hollow fiber bundle. It is a slotted, hollow PVC tube, with a screen outer wrap. The core also adds extra strength to the hollow fiber bundle.

4. Tube sheet — an epoxy compound which secures the open ends of the hollow fiber membranes. It separates the high pressure feedwater and brine from the product water. Sealing against the case is provided by an O-ring.

5. Hollow fiber bundle — a compact bundle of thousands of longitudinally aligned fibers which surrounds the feedwater distribution core. Both ends are secured by epoxy resin, and the bundle is encased in a cloth overwrap and a polyolefin screen.

The hollow fibers which make up the membrane in the DOWEX RO-4K Permeator are cellulose triacetate (CTA). (U.S. 3,532,527)

Cellulose acetate is produced with different degrees of acetylation (different ratios of acetate to hydroxyl functionality). Some membranes use a polymer with a degree of acetylation of 5:1 (one hydroxyl to five acetate groups). The CTA polymer used in the DOWEX RO-4K Permeator is essentially completely acetylated.

The performance of reverse osmosis membranes is somewhat affected by the degree of acetylation. In general, membranes with higher acetate functionality exhibit better salt rejection, and also are more resistant to biological and chemical degradation.

The membrane in the DOWEX RO-4K Permeator must be kept wet to prevent structural changes. This is common with most membranes. Also in common with most other membranes, the rate of production of product water will decrease with time due to a phenomenon called "compaction" (see Glossary). The effects of compaction are discussed on page 8.

SYSTEMS USING DOWEX RO-4K PERMEATOR

DOWEX RO-4K Permeators must be installed in properly constructed and sized systems. Feedwater quality will dictate pretreatment requirements, which are discussed below. Figure 3 is a schematic flow diagram of the reverse osmosis portion of a water treatment system.

Treated low pressure feedwater enters the feed side of a high pressure pump and is pumped through the reverse osmosis permeator. The operating pressure is developed by pumping against a back pressure regulating device on the brine side. Concentrated brine from the permeators is discharged through this back pressure regulator to a disposal system. Multistage centrifugal pumps are preferred due to minimum pressure pulsations. Positive displacement pumps require some means of controlling high pressure fluctuations.

Product water low in dissolved solids is collected from the appropriate port in each permeator. This water may be used either as it comes from the permeator or it may require further treatment, depending upon its intended use. For staged systems brine-side pressure losses may be determined from Appendix VI.

FIGURE 3

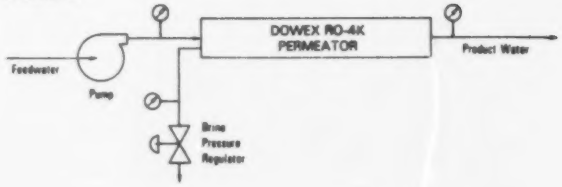


FIGURE 4

REVERSE OSMOSIS WATER ANALYSIS

Sample Identification _____

Specific Conductance _____ micromho/cm _____ pH _____

Feed Source _____

CONSTITUENT _____ RAW FEED (ppm) _____

Ca	CO_3
K	HCO_3
Mg	SO_4
Mn	Cl
Na	F
Fe	NO_3
Ba	SiO_2 (soluble)
Sr	SiO_2 (colloidal)
OH	Other Ions

T.D.S. (by _____ method)

Total Alkalinity (as $CaCO_3$)

Total Hardness (as $CaCO_3$)

Turbidity (JTU)

Bacteriological analysis — standard plate count

Temperature

Silt density index or plugging factor

Remarks _____

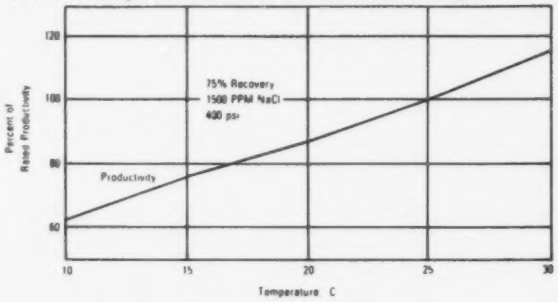
_____

_____

Analysis by _____

Date _____

FIGURE 5 Temperature Effects of DOWEX RO-4K Permeator



FEEDWATER

Feedwater quality is important in reverse osmosis systems because it can affect the performance and life of the permeators and the ultimate quality of the product water. Feedwater pretreatment may be required for reliable performance. A FEEDWATER ANALYSIS is required for determining the pretreatment requirements.

Figure 4 lists the minimum information required in a feedwater analysis. In addition to this, it is often desirable to determine levels of organic matter such as organic acids, alcohols, etc. since their presence can affect performance.

Certain feedwater characteristics can affect the performance of a reverse osmosis permeator through physical or chemical interactions with the membrane.

1. **Hydrogen Ion Concentration** expressed as pH — should be between pH of 4.0 to 7.5 for optimum performance. The higher the pH (and temperature), the shorter the membrane life. CTA hollow fibers will tolerate pH levels outside the recommended range, but at the expense of long-term performance. When feedwater is highly alkaline, pH should be adjusted to a maximum of 7.5. Low feedwater pH must be adjusted to a minimum of 4.0.

2. **Feedwater Temperature** should normally not exceed 30°C (86°F) or be lower than 0°C (32°F). In common with other membrane processes, reverse osmosis permeation varies greatly with temperature. Feedwater temperatures higher or lower than the rated temperature of 25°C (77°F) will give, respectively, greater or lesser product water production than rated productivity. To help estimate productivity, Figure 5 shows the percent of rated productivity obtained with different feedwater temperatures. Please consult a Dow representative if operation above 30°C is anticipated.

FIGURE 6 Percentage of Rated Productivity as a Function of NaCl Concentration at Various Recoveries, 400 psi, 25°C

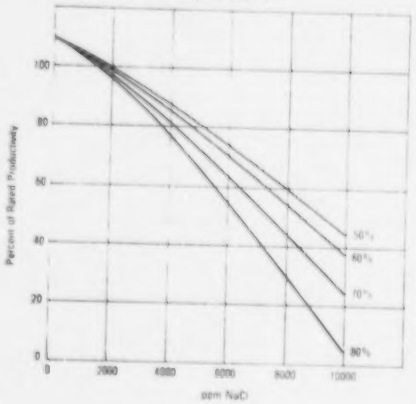
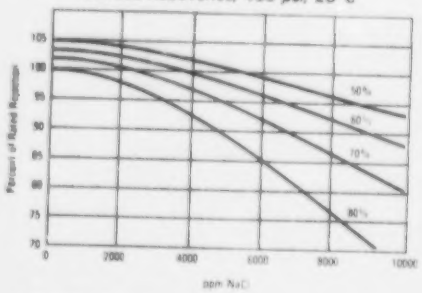


FIGURE 7 Percentage of Rated Rejection as a Function of NaCl Concentration at Various Recoveries, 400 psi, 25°C



See Figure 8 for rated passage for various ions.

3 **Total Dissolved Solids**—can affect performance in three ways. First, the concentration of total dissolved solids can affect the productivity as shown in Figure 6 due to osmotic effects. Second, some effects on rejection are also observed, as shown in Figure 7. Third, the species making up the total dissolved solids affect overall rejection due to differences in the ability of the membrane to reject them. Figure 8 shows the relative percent rejection of a number of dissolved species.

4 **Suspended Solids**—can cause deterioration of performance if not removed from the feedwater. Adequate prefiltration must be provided to ensure continuous high productivity. In general, prefiltration to five microns will be adequate. In cases where significant quantities of colloidal solids or solids of less than five microns are present, product water rates will drop as the hollow fiber bundle becomes plugged. Additional means of suspended solids removal must be used, such as polyelectrolytes or filter aids.

5 **Iron**—can reduce productivity of reverse osmosis systems by causing buildup of insoluble hydrated complexes on the membranes. In all cases, the trivalent (Fe^{+3}) form must be present in order to cause such buildup. In most cases, it must be removed in the pretreatment scheme, but sometimes the addition of sodium hexametaphosphate is sufficient to complex the iron. Iron can be removed by passage of the feedwater through green sand or ion exchange resin beds, but at the expense of ion exchange resin life.

6 **Calcium Carbonate**—can precipitate in the permeator to cause scale formation. Even if the concentration of calcium carbonate in the feedwater is low enough to be soluble under those conditions, as reflected by a negative Langelier Index (see Appendix II) scale formation may occur due to the higher concentration of solids in the brine from the permeator. In some cases, the expected concentration of hardness (as $CaCO_3$) can be calculated for the brine and checked for Langelier Index to determine scaling tendency. (see Appendix II) in many cases, however, it is better to concentrate feedwater in the laboratory to simulate the brine and check for scale formation. Both temperature and pH have an effect on the tendency for scale formation; lower pH and lower temperature will limit scale formation. Acidification of the feedwater must be to a pH that results in a negative Langelier Index in the brine. Ion exchange softening or lime soda softeners followed by acidification also can effectively prevent scale formation.

7 **Calcium Sulfate** (gypsum)—as saturation levels are approached, due to either initial feedwater quality or when saturation levels are obtained at given recoveries, saturation must be controlled either through ion exchange softening or addition of up to 20 ppm sodium hexametaphosphate (see Appendix V). Precipitation of gypsum, if not controlled, will eventually cause deterioration of performance. Barium and strontium sulfates must be similarly controlled.

8 **Chlorine**—may be present in some feedwater. The CTA membrane in a DOWEX RO-4K Permeator is resistant to attack by dissolved chlorine levels sufficient to control growth of most problem organisms (up to 1 ppm). Levels up to 5 ppm can be tolerated for shorter exposure.

All reverse osmosis membranes are subject to fouling due to growth of bacteria and "slime" in untreated feedwater. Organisms may locate in any reverse osmosis module and feed on nutrients found in feedwater. For this reason, it is often desirable to chlorinate feedwaters to control such growth in the modules as well as in pipes and storage facilities.

FIGURE 8

REAGENT	REJECTION %	PASSAGE %
NO_3^-	85	15
Cl^-	95	5
SO_4^{-2}	97	3
PO_4^{-3}	99	1
HCO_3^-	90	10
Ca^{+2}	98	2
Na^+	95	5
Fe^{+2} and Fe^{+3}	98	2
Mg^{+2}	97	3
K^+	95	5
TDS	95	5
Cl_2	NIL	—
Colloidal Solids	100	—

In order to estimate the expected passage of these ions under other conditions, refer to FIGURE 7. The TDS may be substituted for NaCl concentration. Passage listed above for ions may be modified by Percent of Rated Passage from FIGURE 7.

* Note: Empirical only. Variation is expected in mixed salt solutions due to pH dependence, common ion effect, and the necessity for electric neutrality.

PERFORMANCE

The performance of DOWEX RO-4K Permeators will vary with the temperature and quality of the feedwater, and with the operating pressure. Effects of temperature and water quality were discussed in the preceding section. Figure 9 illustrates the effects on productivity and rejection of operating pressures less than 400 psi.

Figure 10 will show expected performance changes with variation of conditions.

FIGURE 9 Pressure Effects of DOWEX RO-4K Permeator

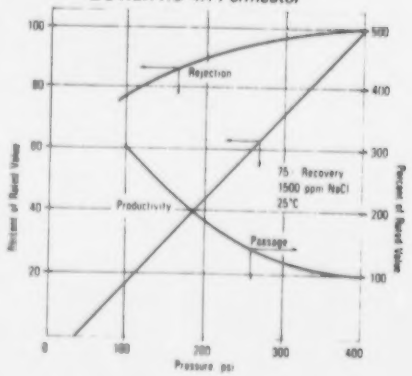


FIGURE 10 Performance at Selected Conditions of DOWEX RO-4K Permeator

FEEDWATER QUALITY	FEEDWATER FLOW	TEMPERATURE	PRESSURE	PRODUCT WATER QUALITY	PRODUCT WATER FLOW
1500 ppm TDS	3.7 gpm	25°C (77°F)	400 psi	150 ppm TDS	2.8 gpm
5000 ppm TDS	2.8 gpm	25°C (77°F)	400 psi	700 ppm TDS	2.0 gpm
1500 ppm TDS	3.2 gpm	20°C (68°F)	400 psi	150 ppm TDS	2.4 gpm
1500 ppm TDS	2.1 gpm	25°C (77°F)	300 psi	200 ppm TDS	2.0 gpm
5000 ppm TDS	2.0 gpm	30°C (86°F)	400 psi	110 ppm TDS	2.3 gpm

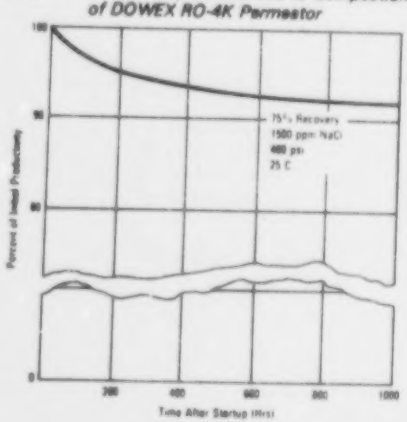
OPERATION

General

DOWEX RO-4K Permeators may be operated in series, parallel, or in a combination of the two. When systems are operated in series (brine from first is feed for second), product water recovery is usually lower in each stage than with single-pass parallel operation.

Series operation is used primarily to guarantee flow in excess of the minimum brine-side flow rates needed to minimize boundary layer effects. For DOWEX RO-4K Permeator an arithmetic average brine flow ½ (feed flow + final brine flow) of 3-8 gpm is recommended. See Appendix VI for data on module pressure drop vs brine-side flow rate.

FIGURE 11 Productivity Decline Due to Compaction of DOWEX RO-4K Permeator



Startup & Storage

DOWEX RO-4K Permeators must be flushed for at least 24 hours when first installed if product water is to be used for human consumption to remove contaminants from the module. Flushing should be at operating pressure, with product water flow rates of at least 1.0 gpm. If product water is not for human consumption, flushing for several hours should remove most residual formaldehyde. For all uses product water should be tested to determine that contaminants have dropped to acceptable levels so that flushing may be terminated.

When DOWEX RO-4K Permeators are to be stored or maintained on stand-by for periods of more than three days they should be drained and refilled with a 0.5 weight percent aqueous formaldehyde solution to protect against microbial growth in the module.

Compaction

All reverse osmosis membranes are subject to declines in productivity independent of feedwater or pretreatment precautions. This decline is due to compaction of the membrane structure under the stresses of pressure encountered during operation. The degree and rate of compaction vary, with feedwater temperature and transmembrane pressure being the most significant influence.

Because compaction affects the ultimate capacity of a system to generate purified water, it is very important that it be taken into consideration in sizing a system.

To assist in sizing treatment systems using DOWEX RO-4K Permeators, Figure 11 shows productivity drop due to compaction for the particular stated conditions.

INSTALLATION OF DOWEX RO-4K REVERSE OSMOSIS PERMEATORS

General

The DOWEX RO-4K Permeator will contain a 0.5 weight percent formaldehyde solution for preservative. The DOWEX RO-4K Permeator must not be allowed to freeze. It must be protected at all times from extremes of temperature. Care should be taken when removing the DOWEX RO-4K Permeator from its packing box to avoid severely scratching the fiberglass pressure case.

Dimensions and capacities are shown in Figure 12. Permeators can be mounted either horizontally or vertically, but provision must be made to secure them and prevent undue vibration.

Feedwater

The feedwater port is tapped ½" female NPT. It will accept a variety of adapters for operation at high pressures. Galvanized and black iron fittings are not acceptable due to their associated corrosion problems.

Brine

The brine port is tapped ¾" female NPT. Adapters may be used for lines capable of withstanding the pressures to be encountered. Brine can be discharged as waste or recycled through a second bank of Permeators if desired. Galvanized and black iron fittings must be avoided.

Product

A ½" NPT female port is in the product end plate. Product water will be discharged at less than 75 psig. If it is desired to feed the product water into a pressurized water system (greater than 75 psig), appropriate tanks and pumps are necessary.

Precautions

1. Do not allow pressure of the product water to exceed that in the brine by more than 75 psig. Pressure differentials greater than this may cause internal damage due to local overpressures. This situation results most often when feedwater pressure drops quickly in system failures or shutdown.
2. Do not subject permeators to temperatures less than 0°C (32°F) or more than 30°C (86°F). Protect from freezing.
3. Do not operate permeators above 450 psig. Product pressure must not exceed 75 psig.
4. Do not damage the fiberglass pressure case. Such damage may lower the margin of safety under pressure. If modules appear to be damaged on arrival, notify the nearest Dow Sales Office immediately.
5. At full rated productivity, the average brine flow rate must be maintained between 3 and 8 gpm. In normally operating systems, the percent recovery of individual permeators should not exceed 60%.

(6.) At full rated productivity, the average brine flow rate must be maintained between 16 and 42 gpm. (See Appendix VI)

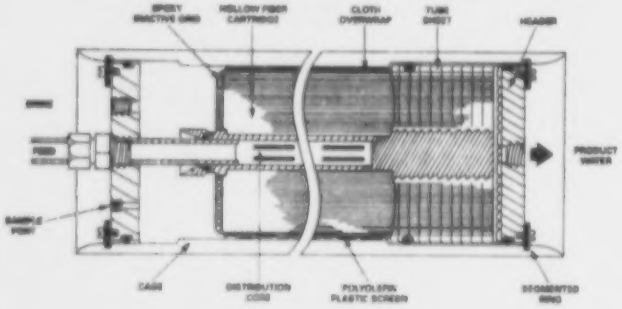
FIGURE 12 DOWEX RO-4K Reverse Osmosis Permeator

PRODUCT INFORMATION

Membrane	Cellulose triacetate hollow fibers
Configuration	Shell-and-tube
Dimensions (case length)	48 in. (121.9 cm.)
(case diameter)	6¼ in. (15.9 cm.)
Connections (feed)	½ in. NPT
(product)	½ in. NPT
(brine)	⅝ in. NPT
Shipping Weight	86 lb. (39.1 Kg.)
End Plates (feed)	PVC
(product)	304 Stainless steel
End Plate Retainers	304 Stainless steel
Pressure Case	Filament-wound fiberglass/epoxy
Feed tube O-ring	Buna N-114
Tubesheet and end plate O-rings	Buna N-365

Productivity* (design)	4000 gpd (0.63m³/hr.)
Salt Rejection*	90% minimum
Operating Pressure	0 — 400 psi (0 — 27.6 Bars)
pH Range	4.0 — 7.5
Chlorine Tolerance	1.0 ppm maximum

*At test conditions of 400 psi, 75% recovery, 29°C, and 1500 ppm NaCl



MAINTENANCE

Monitoring

Adequate means of monitoring process streams is important in all unit operations. Some means of monitoring the critical feedwater characteristics is necessary to assure proper operation of the water treatment system. Following is a list of operational limitations which should be monitored. Certain feedwaters may require additional monitoring as defined by the manufacturer.

Cl_2 (free)	≤1.0 ppm in feed
oxidants	≤1.0 ppm as free Cl_2 in feed
temperature	≤30°C (86°F)
pH	≥4.0; ≤7.5
pressure	
(feed and brine)	≤450 psig
(product water)	≤75 psig
suspended solids	≤1.0 JTU (Jackson Turbidity Units) ≤4.0 SDI (Silt Density Index)
feed source	must not vary by more than 10% from the individual system design basis in parameters which would have a negative impact on module performance

Records

Operational records must be maintained which record at least the following:

1. Feedwater quality and flow
2. Necessary chemical additives, their addition rates and monitored levels
3. Product water quality and flow
4. Brine flow and quality
5. Associated temperatures and pressures
6. Cleaning schedules, if required

Testing

Used properly, within the operational limitations, permeators should provide usable product water for many years. During this time, the combined productivity and rejection of the modules should be tested regularly. If significant changes in either occur, when compared to a previous test, then individual permeators should be tested.

Conductivity of feed, brine and product from each permeator should indicate if any are possibly defective. If no single permeators are defective, then the following checks should be made:

1. The feedwater conductivity may have increased to levels higher than anticipated;
2. pump rates may have decreased;
3. feedwater pH may have drifted outside the recommended range of 4.0-7.5, causing the membrane to partially deteriorate;
4. system operating pressure may have changed;
5. solids may have accumulated in the permeators due either to insufficient pretreatment or improper operation.

Disassembly

Normally, DOWEX RO-4K Permeators should NOT be disassembled in the field. Damage to the hollow fibers can occur due to physical shock or drying out. The module must not be disassembled by persons not specifically authorized by Dow.

Storage and Handling

DOWEX RO-4K Permeators have been tested to assure safe performance under recommended conditions for installation and operation. General guidelines for safe operation are listed below:

1. **Pressure**: The pressure case components of the DOWEX RO-4K Permeator are designed for a maximum operating pressure of 480 psig, with an adequate margin of safety. The reverse osmosis system should be designed to provide pressure protection to prevent exposure to pressures in excess of 480 psig.

   Safe operation of the DOWEX RO-4K Permeator depends upon proper installation of the end plates and support rings. These plates should not be removed or altered in the field.

2. **Storage Protection**: Permeators as shipped contain a 0.5% solution of formaldehyde for protection against biological growth. The formaldehyde should be thoroughly flushed from the permeator before the product water is collected for use.

   Because of the stability of the DOWEX RO-4K Permeator, the system can be designed for continuous or intermittent addition of chlorine to the feedwater. This makes it unnecessary to periodically shut down to sterilize the system. If the DOWEX RO-4K Permeators are shut down for periods of more than three days they should be filled with a 0.5 weight percent formaldehyde solution.

   Freezing may impair the performance of DOWEX RO-4K Permeators. In shipping, handling, operations and storage, the Permeators should be protected against freezing.

3. **Chemicals**: Operation of the pretreatment system and storage protection of the modules will involve use of toxic chemicals such as chlorine, acid, and formaldehyde. Conventional safety practices should be followed in handling these materials.

As with any other product, membrane devices must be used and disposed of in accordance with established and acceptable practices.

Many potential uses for these and other membrane products fall under requirements or restrictions imposed by various Governmental agencies. The user of these membrane devices must establish that their use is permitted under all applicable governmental regulations and statutes.

The disposal of these devices must take into consideration potential effects of not only the device itself, but also of any chemical, biological, or other agent or agents which may be associated with the device as a consequence of its use. Disposal must conform with applicable legislative requirements and governmental regulations.

If any questions arise concerning operation, performance, appropriateness or disposal of these membrane devices which is not provided for in this booklet, please contact the nearest Dow Chemical U.S.A. sales office.

APPENDIX I

Glossary

Average brine flow — the arithmetic average of the feedwater and final reject flowrates ½ (feed rate + brine rate)

Brine — (concentrate; blowdown; reject) — normally, the waste stream from reverse osmosis which contains most of the dissolved solids in the feed in a concentrated form.

Cellulose triacetate — (CTA) — a modified cellulose wherein all available reactive sites have been acetylated.

Compaction — tightening of a membrane structure due to compressive stress of operating pressure.

Feedwater — the influent water to the module.

Hydrolysis — chemical reversion of cellulose acetate back to cellulose by removal of acetate groups occurring most rapidly at very high or low pH.

Osmotic Pressure — pressure required to prevent spontaneous flow of solvent (water) into a solution when separated by a semi-permeable membrane.

Polyelectrolyte — water soluble polymers containing ionizable groups as part of their structure; often useful in causing agglomeration of fine suspended solids.

Productivity — the measurement of rated output, expressed in volume 24 hour day under a given temperature, pressure and salinity.

Product water — (permeate) — the water permeating the membrane surface of the composite module, collected at a port provided on the module end-plate.

Recovery — an expression of the feed converted into product; i.e.,

$$\frac{\text{feed rate} - \text{brine rate}}{\text{feed rate}} \times 100$$

Reverse osmosis — forced flow of solvent (water) from a solution through a semi-permeable membrane by means of pressure in excess of the osmotic pressure.

Salt rejection — defines the product quality, i.e.,

$$\frac{\text{feed concentration} - \text{product concentration}}{\text{feed concentration}} \times 100 = \text{salt rejection}$$

TDS — Total Dissolved Solids, expressed as parts per million (ppm)

APPENDIX II

Langelier Index Determination

Langelier Index Determination:

Ca ppm as $CaCO_3$ _____ Temp. °F _____

"M" Alkalinity as $CaCO_3$ _____ pH _____

Total Solids _____

(ppm Ca x 2.5 = ppm Ca as $CaCO_3$)

p Ca _____ pCa: Locate ppm value for Ca as $CaCO_3$ on the ppm scale. Proceed horizontally to the left diagonal line down to the pCa scale.

p Alk _____ pAlk: Locate ppm value for "M" alk as $CaCO_3$ on the ppm scale. Proceed horizontally to the right diagonal line down to the pAlk scale.

"C" _____ Locate ppm value for total solids on the ppm scale. Proceed horizontally to the proper temperature line and up to the "C" scale.

Sum pHs _____

Actual pH _____

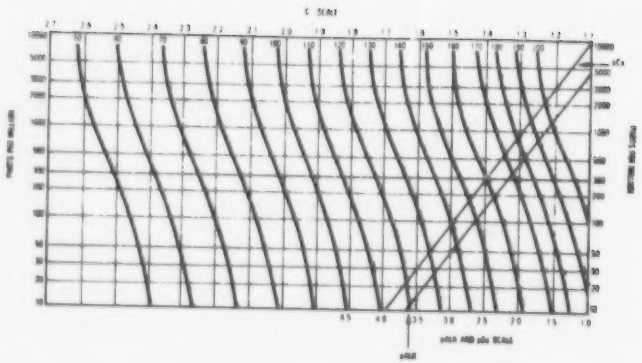
Difference _____ = Saturation Index. (Actual pH – Sum pHs) Positive number indicates scaling.

EXAMPLE:

Temperature = 140 °F
Ca Hardness = 200 ppm
M Alkalinity = 160 ppm
Total Solids = 400 ppm
pH = 7.80

p Ca = 2.70
p Alk = 2.80
C at 140F = 1.68
Sum = pHs = 6.78
Actual pH = 7.80
Difference = +1.04

= Saturation Index



APPENDIX III

Empirical Estimation of Scaling Tendencies of Brine from R.O. Modules

S = T.D.S. of feed
H = Calcium hardness of feed, as ppm $CaCO_3$
A = Total alkalinity at untreated pH as $CaCO_3$
K = Alk/CO_2 ratio at untreated pH from graph
C = CO_2 level in untreated water, as ppm CO_2 = A/K
R = Desired recovery ratio
$= \frac{\text{Product-water flow rate}}{\text{Feed water flow rate}}$
K_1 = Alk/CO_2 ratio at desired pH from graph
X = Change in alk. and CO_2 units due to pH adj.
$= \frac{A - CK_1}{K_1 + 1}$
C_1 = CO_2 level in feed after pH adj.
$= C + 0.9X$
A_1 = Alk. of feed water after pH adj.
$= A - X$
C_2 = CO_2 level in brine
$= \frac{0.9C_1}{1 - R}$
A_2 = Alk. of brine
$= \frac{0.9A_1}{1 - R}$
K_2 = Alk/CO_2 ratio in brine
$= A_2/C_2$
P_2 = pH of brine from graph at K_2
H_2 = Calcium hardness of brine
$= \frac{0.9H}{1 - R}$
S_2 = T.D.S. of brine
$= \frac{0.9S}{1 - R}$
P_{sb} = Scaling pH of brine from Langelier Index Appendix II

NOTE: If $P_{sb} > P_2$ then brine will not scale. If $P_{sb} < P_2$ then scaling is indicated and either pH must be lowered or recovery must be reduced.

This estimation should be used as a guide — not as absolute. If P_{sb} and P_2 are close (say, within 0.5 units) actual tests should be made of the scaling tendency, or as noted above, pH should be lowered, or lower recovery should be accepted.

APPENDIX IV

Determination of Acid Required to Reduce pH to Desired Level

A = Total alkalinity of untreated water, as ppm $CaCO_3$

K = Alkalinity: CO_2 ratio at untreated pH from graph

C = CO_2 level of untreated water, as ppm CO_2
$= A/K$

K_1 = Alkalinity: CO_2 ratio at desired adjusted pH from graph

x = H_2SO_4 required to adjust pH, as ppm H_2SO_4
$= \frac{A - (CK_1)}{0.90\,K_1 + 1.02}$

S = H_2SO_4 required to adjust pH, as lb. per 1000 gal. feedwater
$= \frac{x}{120}$

M = HCl required to adjust pH, as lb. (100% basis) per 1000 gal. feedwater
$= .745\,(S)$

APPENDIX V

Computation of $CaSO_4$ Solubility

(a) = Ca^{++} (ppm as ion_____ x 2.5 = _____ ppm as $CaCO_3$)
(b) = Na^{+} (ppm as ion_____ x 2.18 = _____ ppm as $CaCO_3$)
(c) = Mg^{++} (ppm as ion_____ x 4.1 = _____ ppm as $CaCO_3$)
(d) = SO_4^{--} (ppm as ion_____ x 1.04 = _____ ppm as $CaCO_3$)
(e) = Cl^{-} (ppm as ion_____ x 1.41 = _____ ppm as $CaCO_3$)
(f) = HCO_3^{-} (ppm as ion_____ x .82 = _____ ppm as $CaCO_3$)

NOTE: (a)+(b)+(c) = (d)+(e)+(f)
If not within 10%, the analysis is incorrect or incomplete

If (d) is less than (a)

(g) = [(a)−(d)] .02 = _____
(h) = (b) (.02) = _____
(i) = (c) (.02) = _____

If (a) is less than (d)

(g) = [(d)−(a)] .02 = _____
(h) = $[(b)\left(1-\frac{(d)+(a)}{(b)+(c)}\right)]$ .02 = _____
(i) = $[(c)\left(1-\frac{(a)}{(b)+(c)}\right)]$ .02 = _____

(j) = (g)+(h)+(i)

(k) = "y" from curve (k) at "x" = (j) = _____
(l) = "y" from curve (l) at "x" = (j) = _____
(m) = "y" from curve (m) at "x" = (j) = _____
(n) = (k)(g)/(j) = _____ (o) = ((l)(h)/(j) = _____ (p) = (m)(i)/(j) = _____

(q) = (n)+(o)+(p)

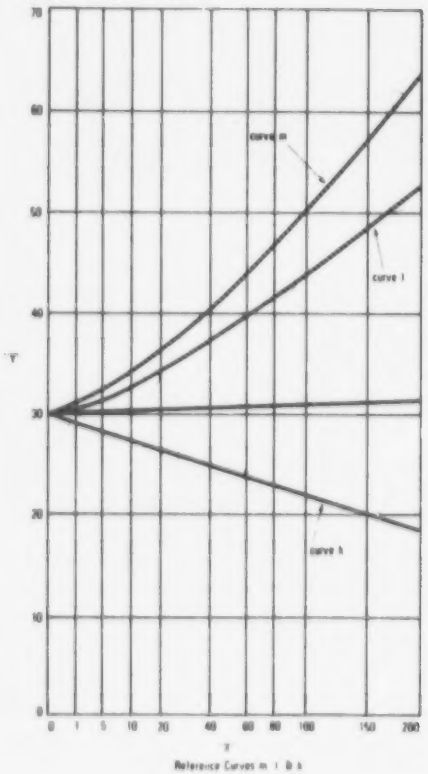
(r) = $\frac{(g)}{50(q)}$ = _____ % of saturation

If (d) > (a) r = $\frac{2(g)}{q}$ = _____ % of saturation

If (a) > (d) r = $\frac{2(d)}{q}$ = _____ % of saturation

(s) = 100−(1.26)(r) = _____ % of maximum recovery

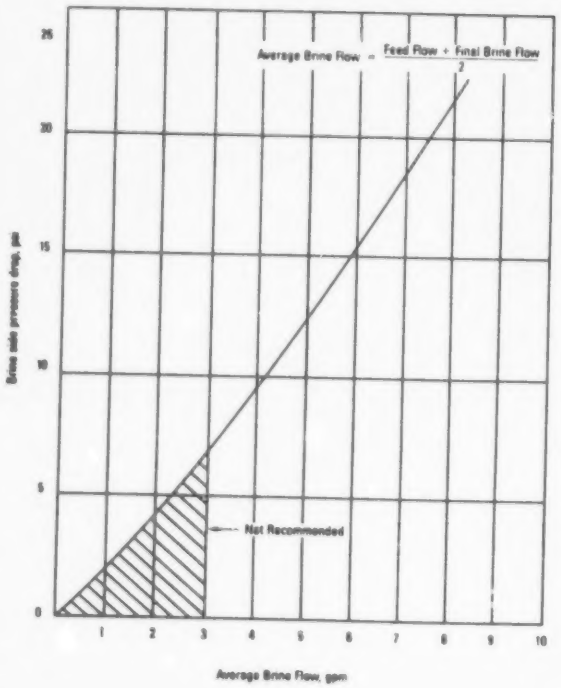
Appendix V (cont.)



Reference Curves m, l, & k

APPENDIX VI

Pressure Drop vs. Average Brine Flow For DOWEX RO-4K Permeators



APPENDIX VII

Test for Determining Silt Density Index

Equipment

1. Millipore* Filter Pad Holder with a 0.45 micron filter disc
2. 500 ml. graduated cylinder
3. Stopwatch
4. Dull tweezers

Procedure

1. Unbolt the filter holder, wet it, and place a 0.45 micron filter on the back-up plate using the dull tweezers
2. Place the "O" ring properly and then replace the top half of the filter holder and bolt loosely
3. Connect apparatus to the feedwater line (minimum 30 PSIG) in a vertical, downflow position and open the needle valve a crack
4. Loosen two adjacent filter holder bolts, tilt the apparatus and bleed out all trapped air, then retighten bolts and adjust the pressure to 30 PSI while starting the stopwatch
5. Immediately run the flow into the graduated cylinder and measure the time required to collect 500 ml, maintaining a pressure of 30 PSIG during the run. Mark the time (t) and keep the watch running
6. Repeat step 5 immediately after 5, 10 and/or 15 minutes of total elapsed time. Mark the collection times (t_5, t_{10}, t_{15})
7. Close the sample valve and disconnect the apparatus after the 15-minute reading. Remove the filter disk and place it in a plastic bag for later examination.

Calculations

1. Calculate the ratios $R = t/t_5$, t/t_{10} and/or t/t_{15}
2. Estimate % P_{30} at the selected time(s) from the following equation: % $P_{30} = (1-R) \times 100$
3. Estimate the Silt Density Index, SDI, from the following equation

$$SDI = \frac{\% P_{30}}{\text{Elapsed Time (minutes)}}$$

The 15-minute index will generally be the lowest of the three and should be used for filter sizing purposes.

*Millipore is a registered trademark of Millipore Corporation, Bedford, Mass.

CHAPTER 16

ELECTRODIALYSIS AND ELECTRODIALYSIS REVERSAL (EDR)

- Suppliers of EDR Systems 708
- Information on EDR 708
- Comments 709
- References 710
- WILLIAM E. KATZ (1977) Electrodialysis: The First Twenty-Five Years 712
- Desalting High Salinity Brackish Water Using 10-Stage EDR, D. R. BROWN and K. D. McELHINNEY (1981) 713
- DAVID ELYANOW, et al. (1981) The Determination of Supersaturation Limits in an EDR Unit with Aliphatic Anion Membranes 717
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- JONES, R.A. (1982) Electrodialysis (ED) and Electrodialysis Reversal (EDR) 761
- SCHUTTE, C.F. (1983) Desalination: A South African Perspective, Chapter 7, Electrodialysis 775
- IONICS, AQUAMITE Brochures 789
- GARLING, R.A. (?) Evaluation of Electrodialysis for Process Water Treatment for In Situ Mining 795

Electrodialysis and electrodialysis reversal (EDR) have been described by SCHUTTE (1983), an excerpt of whose report is inserted here. C. F. Schutte is a senior advisor to:

WATER RESEARCH COMMISSION
Post Office Box 824
Pretoria 0001
South Africa
(012) 48-5461
Telex: 30464

During 1984, Mr. Schutte left on sabatical to further his studies for 1-2 years in the U.S.A. and if he has not yet returned, he can be reached through the above address for further comment.

SUPPLIERS OF EDR SYSTEMS

There are two main suppliers of EDR process systems in the world, Ionics, Inc. and Asahi Glass Co., Japan.

IONICS, INC.
65 Grove Street
Watertown, MA 82172
(617) 962-2500
Telex: 922473
Bill Katz
Ark W. Pang
Floyd H. Meller

Ionics is represented in South Africa by:

PROCESS SYSTEMS (PTY) LTD.
Box 10142
Johannesburg 2000
(011) 802-4230
Ralph A. Jones

ASAHI GLASS CO. LTD.
1-2 Marunouchi 2-Chome
Chiyoda-Ku, Tokyo, Japan

Asahi Glass Co. Ltd. is represented in South Africa by:

MAGCENT (PTY) LTD.
Box 681
Bedfordview 2008
(011) 53-9328
Telex: 420987

INFORMATION ON EDR

The most informed information on EDR, apart from the comprehensive literature including SCHUTTE (1983), JONES (1982), and GARLING (?), KATZ (1977), BROWN and McELHINNEY (1981), ELYANOW, et al. (1981) and OWRT (1979) inserted below.

MELZER and VAN DEVENTER (1983) reported testwork of two ED units of 2 m^3/d and 130 m^3/d product flow for water recovery from cooling water blowdown at an ESCOM power station in South Africa. Their paper estimates the capital and operating costs for an EDR plant to concentrate effluent from a 3,600 MW power plant into 20% of the volume, and a further reduction to 2% of the initial volume by evaporation.

These documents provide a good idea as to the capabilities and cost of EDR. In addition, a brief description of an EDR plant at the Kriel power station, South Africa, is provided in Appendix I.

Individual experts who may be available to provide additional information include the vendor contacts:

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COMMENTS

1. The largest EDR plant to date is the 24,000 m^3/d desalination plant on the Tigris River, Iraq, which comprises six aquamite 100 modules by Ionics teating brackish water. Feedwater runs 1,800 mg/l TDS which will be reduced to 30-50 mg/l prior to polishing.

2. It is clear that significant recoveries and brine concentrations can be achieved using EDR. However, the cases cited do not demonstrate EDR ability to treat minewater or mill tailings solutions with, say, 1,500 mg/l $CaSO_4$. Certainly, it has been found that gypsum concentrations well in excess of saturation (2,000 mg/l) can be tolerated in EDR concentrates without foulding if anti-scaling agents are used, even up to 400% of saturation which would be about 8,000 mg/l $CaSO_4$. However, that would allow only 80% recovery from a minewater feed containing 1,500 mg/l $CaSO_4$. Consequently, there is a questionmark as to how applicable EDR is for that type of solution.

3. At East Rand Proprietory Mines Ltd. (ERPM), at test demonstration EDR plant was installed by the South African representative of Ionics. During a visit to another installation at this site, it was noted that the pretreatment facility at the EDR pilot plant was significantly larger than the EDR unit itself.

   No data or information were provided on the pilot test results which were not yet complete at the time of the RANDOL tour. These would provide an insight into the potential applicability of EDR to AMD treatment. The following individuals will eventually be able to release information on this test program:

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4. A paper by G. A. Garling (date unknown) on an evaluation of electrodialysis for process water treatment for in situ mining of uranium in Wyoming is inserted below. For the particular solution testes, EDR appears highly suitable, bearing in mind that the feed contained 363 mg/l $SO_4^{=}$, and the brine was concentrated to 1,656 mg/l SO_4, 2,384 mg/l HCO_3, and 1,884 mg/l Cl^-. In this case, uranium was concentrated from 9.15 mg/l to 21.4 mg/l--a recovery of about 80% into the brine which could prove useful for further concentration. Although highly promising as a tool for in-situ leach wellfield restoration, this case is not a satisfactory test for highly scaling $CaSO_4$ solutions. The only really good test of that known is the ERPM minewater pilot test noted above.

5. A visit to the EDR installation at Kriel power station as described in Appendix I was convincing as to the maturity of EDR technology. These units can be installed rapidly and cleanly to result in a functional plant. The Kriel plant, which consists of two aquamite 100 modules, i.e., 8,000 m^3/d capacity, was erected and operating in a period of 12 weeks. In this case, however, the EDR duty is relatively light. Regional water at about 250 mg/l TDS is demineralized to around 40 mg/l TDS to take the load off the ion exchange polishing plant.

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Electrodialysis
The First Twenty-Five Years

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One morning in February of 1952, the front page of the NEW YORK TIMES carried a two-column headline announcing the demonstration by a small company in Boston of a radical new method of desalting sea water and brackish water. The new method used electricity to move salts and minerals through special plastic membranes. The company was Ionics and the process was called electrodialysis. That demonstration — twenty-five years ago — has had far-reaching effects on the technology and development of water desalting. Today — in a few minutes — let us mark that anniversary by noting some of the consequences of that demonstration for users and developers of saline water equipment of all types. Our interest in the past lies primarily in what it can teach us for the future — the next 5, 10, and 25 years. Accordingly, these remarks will conclude with a listing of some challenges facing the saline water industry today, in the form of projections for the future, founded in our mutual experience to date.

For the moment, let us return to some important results of that 1952 demonstration.

First, electrodialysis in 1952 demonstrated the startling new idea that a practical desalting method could be based on a physical principle other than the boiling of water and the condensing of steam.

Second, the use of synthetic polymeric membranes in electrodialysis enlisted for the first time the prodigious ingenuity, energy, and techniques of the polymer chemist in the mainstream of water desalting research. This alliance has had major benefits in the fields of electrodialysis, reverse osmosis, and ion exchange, and no doubt in the future will yield further improvements and new processes — yet unnamed.

Third, the news of the new technology had been previewed to a delegation of senators and congressmen in 1951. Within a few months Congress passed the first Saline Water bill, reasoning that if a small company could make such a breakthrough on $100,000 of private money, imagine what a few millions in government support could do!

Fourth, electrodialysis had especially low costs on brackish waters. The availability (for the first time) of a process to treat brackish waters stimulated a whole new market — and led in the next two decades to a careful cataloguing of the inland brackish water resources of a large portion of the world. Any salty well or river became a potentially useful water resource — for the first time.

In the decade following 1952, a series of important pioneer brackish water projects were realized using electrodialysis equipment.

1) The first commercial sale of a brackish water unit was made to Arabian American Oil (ARAMCO) in 1954 to supply water to an exploration crew. ARAMCO has recently purchased modern electrodialysis equipment for their Community Water Supplies in Dhahran and other key population centers.

2) The first municipal use of electrodialysis — appropriately enough — was in 1955 by the Bahrain Petroleum Company for their community of Awali on Bahrain. This unit plus expansions and upgradings has served Awali continuously for more than 20 years.

3) A number of other units went into service in the 1950's and early 1960's in several Middle Eastern countries to supply fresh water for oil production camps, military installations, beverage bottling, fresh water production, and industrial applications. Thus the new technology has been used in the development of Middle East water supplies for almost a quarter century — and the technological feedback from those early units has made a long-term major contribution to the success of electrodialysis.

4) The City of Coalinga, California, became the first municipality in the U.S. in 1958 to treat a part of their water supply by desalting (electrodialysis).

5) In 1962, the Town of Buckeye, Arizona, became the first U.S. community to treat all of its municipal water supply by desalting — again electrodialysis. Buckeye was followed later in the 60's by Port Mansfield and Dell City, Texas, and later by Siesta Key, Florida; Gillette, Wyoming; Sanibel, Florida; and the Foss Reservoir in Oklahoma.

Summarizing, by the end of the 1960's, it was already generally demonstrated and accepted through the technology of electrodialysis that any brackish water source could be turned into fresh water, and that municipalities, industries, resorts, bottlers, and military installations could reliably operate such equipment.

Worldwide installed membrane desalting capacity aggregated about 5,000,000 gallons per day on January 1, 1970. Capacity began to increase rapidly in the 1970's, aided by a major marketing and technological push from reverse osmosis, and, more recently, by a very basic improvement in electrodialysis — namely, the development of polarity-reversing electrodialysis equipment.

Today, as we meet in San Diego at least two electrodialysis and two basic reverse osmosis configurations are competing in several market areas for shares of a rapidly expanding market. This vigorous commercial and technological competition has been a prime factor in the broadening of the market and in the improvement of the processes.

Our successes — all of our successes — of the past are not the issue. The question is where do we all go from here? In the next 25 years.

Perhaps many of us could agree on the following prognostications:

1) There will be substantial penetration of membrane processes into the market for desalting sea water and diluted sea waters.

2) Some radical new type of particulate pretreatment is needed and will be developed — perhaps using membranes. Polarity reversal ED has eliminated the requirement for acid and polyphosphate pretreatment for most waters — and relaxed the demands on particulate pretreatment — but the pretreatment area is still the biggest problem in the membrane field. All membrane processes have outrun — in my opinion — most conventional pretreatment processes. It is time for the pretreatment element of the system to take a great leap forward.

3) There will be a continuation of the trend to smaller intermembrane spacings in spite of the cleaning and pretreatment problem.

4) High recovery systems (90% or more) will become standard.

5) Operation of large and small desalting plants will be made simpler through the use of microprocessors and related data processing techniques. As a related development, software or technology transfer will become an integral part of desalting equipment applications — better manuals, better training, better background information.

6) There will be continued progress on the longevity of materials.

7) There will be progress on the use of thermally driven ion exchange or membrane systems because of the relatively low cost and wide availability of thermal energy.

8) The relative cost of new sources of water will rise at least as fast as the cost of new sources of energy — and in water-scarce areas even faster than the cost of energy — thus providing the economic market demand for further growth and progress in the desalting industry.

9) There will be a continuation of the trend by consultants, owners, and operators, to choose higher capital cost designs to gain lower O&M costs and greater reliability.

10) More than anything else — the progress in our industry will go to those processes and those suppliers who can deliver plants of demonstrated reliability. We have heard clear and authoritative statements of this need by speakers from Saudi Arabia and other countries earlier in this conference. The keyword for the 70's and 80's is reliability.

Those of us who were privileged to be present at the birth of this industry 25 years ago cannot help but view with pleasure the burgeoning advances in technology and the current good health of the industry. With luck, some of us may be able to meet in 2002 — to look back on fifty years of membranes. Whatever happens, the future looks bright — we can all share in it if we continue to work hard, to have faith, and to meet the requirements of the marketplace.

Let us listen well to the users!

And let us continue!

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Desalting High Salinity Brackish Water Using 10-Stage EDR

by
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Demineralization of brackish water using the Electrodialysis Reversal (EDR) process has previously been proven to be reliable and economical for feedwaters with up to 5000 ppm total dissolved solids. This is demonstrated by the fact that of the over 1000 ED units either installed or under construction throughout the world, over 500 are reversal systems with an aggregate capacity of over 150,000 M^3/Day. Paralleling this rapid growth in EDR installations, there have been continuing research and development programs to expand the applicability of the EDR process. One such program has resulted in the development of EDR technology capable of treating high TDS feedwaters with up to 15,000 ppm TDS. This paper will review the design and operation of an EDR installation which has been operating in North Africa since January 1980, producing over 300 M^3/Day (~80,000 GPD) of potable water from a 9700 ppm TDS feedwater.

HISTORY

A unique opportunity to demonstrate this capability arose in 1978 when a Middle East oil company experienced failure of their distillation plant. The location of the plant was at a terminal site located on the coastal fringe of the Sahara Desert in North Africa. As the distillation plant was over 15 years old and the required repairs were too extensive, the company resorted to trucking in water. It was quickly realized that this was unacceptable due to varying and generally poor water quality and exorbitant costs (170 M^3/Day at about \$17/M^3). A quick and reliable solution to the problem was sought. Ionics, Incorporated and other desalting equipment manufacturers were asked to supply tenders to provide a water plant with a production capability of at least 225 cubic meters/day of potable water to World Health Organization Standards.

Two sources of water were available to supply the camp's need. The first being the Mediterranean Sea with a dissolved salt content of about 34,000 ppm and the second a series of wells containing approximately 10,000 ppm TDS. Although the salinity of the well water appeared stable, the fact that the wells were within 4 km of the Mediterranean coast brought some concern of sea water intrusion. Therefore, if equipment was used to demineralize the wells, it would have to be capable of treating feedwaters of up to 15,000 ppm TDS. Based upon their tender, Ionics, Incorporated was awarded a contract to supply and install a plant to demineralize the on site wells. A complete analysis of the raw water is shown on Table A.

PRELIMINARY DESIGN CONSIDERATIONS

Preliminary design focused on four major objectives:

a. Minimize electrical power loadings and consumption.
b. Provide sufficient desalting capability to reduce feedwaters of up to 15,000 ppm TDS to World Health Organization standards for potable water — namely 500 ppm TDS.
c. Control calcium sulfate precipitation. Feed water analyses provided by the customer showed $CaSO_4$ saturation levels of 70 to 100%. Predicted saturation levels in the brine blowdown were 130 to 180%.

TABLE A
WATER ANALYSES

	Design Feed	Actual Feed	Design Product	Actual Product	Actual Brine Blowdown
Sodium	2440	2090	115	79	3694
Calcium	575	652	7	4	1390
Magnesium	430	484	6	4	964
Chloride	3950	3687	186	111	7084
Bicarbonate	154	134	34	25	175
Sulfate	2940	2672	22	19	5000
TDS (Σ ion)	10439	9727	360	242	18307
pH	7.8	7.0	7.7	6.8	7.2
Iron (total)	5	2	0	0	0
Temp. °C	24	25	24	25	25
Langelier Index[3]	1.05	.26	—	—	.92
$CaSO_4$[4] Saturation – %	72	75	—	—	150

All constituents shown as ppm as the ion where appropriate.

d. Provide pretreatment for the removal of up to 5 ppm total iron in the feedwater.

In order for the system to be considered by the purchaser, the electrical demand of the water treatment system had to be less than the excess power available from existing generating facilities located at the camp site. In an electrodialysis system the DC power requirement (W) of the membrane array can be expressed as:

$$W \sim \frac{\text{Flow} \times \text{Change in Salinity}}{\text{Membrane Area}}$$

Thus, maximizing membrane area was an important factor towards reducing power consumption. In addition, minimizing pumping requirements would also reduce power loadings.

When considering the design of the ED system, these factors played a key role in determining which process approach to take — i.e. batch, feed and bleed, or straight-through. In a straight-through design, a sufficient number of stages are provided so that the salinity is reduced to the product level in one pass through the system. In a batch or feed and bleed operation, less stages are used and the partially desalted water is recycled a sufficient number of times to achieve product quality. Thus, the straight-through approach was preferred as the high membrane area per unit volume of production reduced DC power consumption; and the elimination of recycle pumping, besides reducing overall power consumption, substantially simplified the process system thereby improving system reliability.

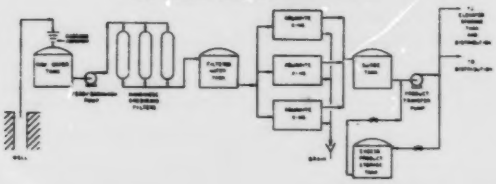
Of course, there are limitations as to how many stages can be put in series before having to resort to interstage pumping. As stages are added, higher fluid pressures must be applied to the inlet of the first stage and/or lower fluid velocities must be maintained in the membrane array. Therefore, the limiting values of these parameters can limit the number of stages which can be used.

Previously, the maximum number of stages used in an EDR system was six stages. This was primarily due to the fact that on lower TDS brackish waters there was little or no demand for having more stages. Computer analyses and internal laboratory testing both indicated that ten stages would be required to provide sufficient desalting capacity for feedwaters with up to 15,000 ppm TDS. They also indicated that the significantly lower fluid velocities would still be safe enough to provide stable, reliable operation. Therefore, the ten stage straight-through approach was the most efficient system and was used as the basis for the ED system design.

As the polarity reversal feature of EDR systems has been shown to effectively control $CaSO_4$ precipitation — without chemical conditioning — at saturation levels of over 150%[1, 2] this was incorporated into the system design. The elimination of hexametaphosphates and acid dosing not only reduces operating costs, but is a distinct advantage for plants located in desolate areas where accessibility to the required chemicals is limited.

If iron bearing waters are allowed to enter an ED membrane array, the iron tends to precipitate onto the membrane surface forming a layer of slime which reduces desalting capacity and increases electrical resistance. The membranes can be effectively recovered by acid washing using the Clean-In-Place system. However, where the iron content exceeds .2-.3 ppm, the required frequency of this cleaning procedure becomes unacceptable and pretreatment for iron removal is required. When considering the pretreatment design to remove up to 5 ppm of iron, systems requiring continuous chemical dosing were eliminated due to operating costs and chemical accessibility. Therefore, the design was based on aeration followed by greensand filtration.

FIGURE A
SYSTEM FLOW DIAGRAM



FINAL DESIGN

The overall flow system is shown in Figure A and consists of the following:

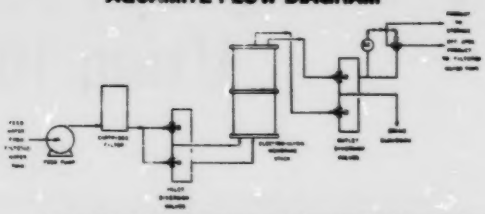
a. Well water is transferred to the plant site through 4 kilometers of 300 mm PVC pipe and is discharged through a natural draft step aerator at a rate of up to 31.8 M^3/hr. (140 gpm). This ensures that adequate oxygen is present in the water for the iron oxidation reaction. The water then flows by gravity into a 320 M^3 (84,000 gallon) holding tank.

b. A low pressure feed/backwash pump then delivers the water to three 122 cm (48 inch) diameter greensand filters operating in parallel. The filters both catalyze the oxidation reaction and filter out the precipitated iron. The effluent is delivered to a 160 M^3 (42,000 gallon) filtered water holding tank.

c. The water then flows by gravity to three Aquamite X-HS units operating in parallel (refer to Figure B). Each Aquamite consists of a skid containing pumps, rectifiers, hydraulic and electrical controls, and two membrane stacks. The stacks are connected in parallel and each contains 10 hydraulic stages connected in series.

d. After passing through a surge tank, the water is transferred to the customer's elevated product water storage tank and then to distribution. An additional 320 M^3 (84,000 gallon) excess product storage tank is provided and, if necessary, can be directly connected to the distribution system through the same transfer pumps.

FIGURE B
AQUAMITE FLOW DIAGRAM



In general, three identical units connected in parallel were used in order to improve system reliability and to increase operating flexibility to more closely match plant production with camp demand. This in turn minimized electrical operating loads. In addition, this allowed the use of the standard Aquamite X unit (with proven reliability from almost 10 years experience) to serve as the basis for the EDR units. The standard skids were then modified accordingly for this application. The stacks were specially built with 2 electrical and 10 hydraulic stages. In addition, newly developed aliphatic anion membranes were used due to their improved electrical efficiency and anti-fouling characteristics.

The plant as ordered called for a complete turnkey installation by Ionics and included all necessary pretreatment equipment, water storage tanks, transfer pumps, EDR units, piping, wiring and the water treatment building to house the EDR units. The entire facility was manufactured, shipped and installed within 10 months from receipt of confirmed purchase order.

OPERATING EXPERIENCE

The entire water treatment facility was commissioned in January, 1980. During the first full year of operation, virtually no operating difficulties with either the EDR units or the pretreatment have been experienced, and the overall operation has been very stable. Table B, which summarizes the operating parameters of the EDR units, shows that they are actually producing more water of better quality with less power consumption than originally designed. Figures C, D, E and F are graphic illustrations of pertinent operating parameters over the year for one of the EDR units and are indicative of the long term system stability.

TABLE B
EDR PERFORMANCE

	Design	Actual
Feed TDS — ppm	10,439	9,727
Product TDS — ppm	360	240
Feed Temp. °C	24	25
Product Cap. — M^3/Day	268	305
(GPD)	70,900	80,600
Recovery — %	40	40
Power Consumption —		
KWH/M^3	9.25	7.66
(KWH/KGAL)	35	29

Note: The above figures are total for 3 units.

FIGURE C
CAPACITY VS. TIME

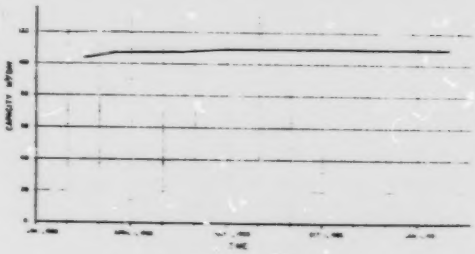


FIGURE D
PRODUCT TDS VS. TIME

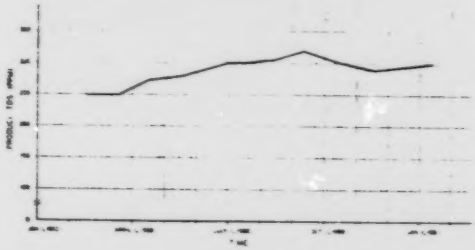
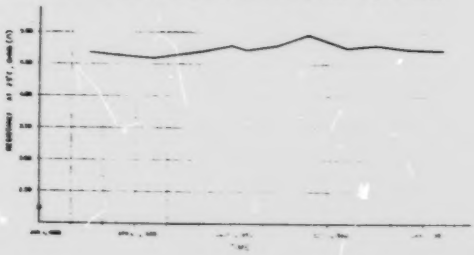


FIGURE E
STAGE I ELECTRICAL RESISTANCE VS. TIME



A number of interesting observations were made regarding the first year's operation:

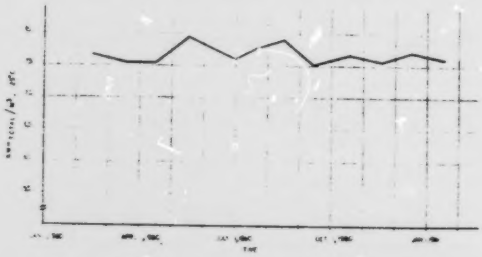
a. After start-up, the dissolved iron level of the well water dropped and stabilized to about 2 ppm. Aeration and retention reduced this to about 1.7 ppm. The greensand filters reduce total iron to 0. Although frequent backwashing is required, filter regeneration with potassium permanganate is done only once very 4–6 months.

b. Immediately after the polarity reversal in an EDR system, a period of flushing occurs where the previous brine compartments flush out with dilute water. During this period the product water is off specification and returned to the feed tank. As the instantaneous throughput is limited by such parameters as stack inlet pressure, this flushing period effectively reduces production capacity, since the unit is producing on spec water only 80–90% of the total operating time. As the duration of this off-spec period is fixed, an effective way to reduce the percentage of off spec time is to reverse polarity less often. One unit has been modified so that reversal occurs half as often as the other two units. This has effectively increased production capacity from approximately 97.7 M^3/Day (25,800 GPD) to 109.8 M^3/Day (29,000 GPD). Figures C, D, E and F represent the operating data from this unit and show that the operation has been very stable. Pending further review of the 18 month operating data, it is planned to modify the other two units accordingly. This will increase total plant production to approximately 330–340 M^3/Day (87,000–90,000 GPD).

c. Figure D represents product TDS over the year. In June, the hydraulic and electrical settings were slightly readjusted to increase production capacity and to increase product TDS from 250 to 300 ppm thereby reducing the corrosive properties of the product water. Since then, product TDS has remained very stable at the 300 ppm level.

d. By plotting the electrical resistance of the membrane array versus time, one can determine if there has been any appreciable loss in membrane capacity. An increase in resistance usually signals a loss of capacity. Of course, increased electrical power will also be required to achieve the same demineralization. As feedwater temperature fluctuation (which does vary from 25 to 28°C) will change the stack resistance, the data has been corrected for a constant 25°C feedwater basis. Figure E represents the electrical resistance of the first electrical stage vs. time. As can be seen, the resistance has been very stable and there has only been a slight increase (~3%) over a period of the year.

FIGURE F
POWER CONSUMPTION VS. TIME



e. Figure F represents the total electrical power consumption versus time. Again, the process stability is evident as power consumption has consistently been in the 7.4–7.7 KWH/M^3 (28–29 KWH/1000 Gal) based on a 25°C feedwater. The aliphatic anion membranes have contributed significantly toward reducing power consumption due to their superior electrical efficiency.

f. The polarity reversal function of the EDR units has effectively controlled calcium sulfate precipitation. There have been no operational difficulties caused by scale formation despite having 140–160% saturation in the brine waste.

g. In addition to the reversal process, the system is kept free of scale accumulation by periodically washing the membrane array with a mild (5%) acid solution. This is accomplished without requiring stack disassembly using the Clean-In-Place (CIP) system. In addition to the conventional CIP system which flushes the entire membrane stack, these units have been fitted with a special CIP system just for the electrode compartments (ECIP). In many applications, the first signs of scale accumulation occurs in the electrode compartments. This then determines the normal CIP frequency even if the main sections of the stack show no signs of scaling.

Therefore, by acid washing the electrode compartments separately, the normal CIP frequency can be substantially reduced. Since the ECIP uses substantially less acid than the CIP, the overall acid consumption is significantly reduced — by as much as 50%. In addition, the ECIP can be performed while the unit is in operation. Therefore, the total system downtime required to perform the CIP's is reduced. ECIP is normally performed for about ½ hour every 3 days. CIP is performed for 1 hour every 15-20 days. Total acid consumption for all three units is approximately 4.6 M^3 (1200 gallons) of 38% HCl per year.

h. These units have been fitted with a new reversal sequence in which the reversal of the inlet and outlet diversion valves and the DC polarities are phased in a specific sequence. This has substantially reduced the off spec duration after reversal thereby increasing production capacity by 8 M^3/D (2100 G/D) per unit. Subsequent testing on another ten stage unit has resulted in a further modification of this reversal sequence allowing for even greater production capacity increases. This new system is now being transferred to conventional EDR units and will result in production capacity increases of about 10% or more with essentially no impact on membrane area requirements or total capital cost.

i. As the salt ions are transferred through the membranes in an ED system, some water molecules are transferred with them. In conventional EDR systems operating on low brackish waters, this amount of water is insignificant. However, on higher TDS applications it can become significant. Membrane selection can become important since different types have varying resistance to this water transfer. The aliphatic anion membranes showed excellent capability at resisting water transfer. However, a different cation membrane with tighter matrix structure would substantially reduce total water transfer. Tests on a subsequent 10 stage unit with the same anion and tighter cation did indeed result in a reduction in total water transfer by 50%.

j. Membrane replacements during the first year's operation totaled approximately 3% of total installed membranes. Based on membrane analyses and the stack resistance data, average membrane life is expected to be at least 10 years.

CONCLUSION

We believe that the performance and stability of operation of these units has demonstrated the ability of electrodialysis reversal systems to successfully and economically treat high TDS brackish feedwater. Also, the ability of EDR systems to successfully operate on high calcium sulfate waters without the need of continuous chemical conditioning of the feedwater has once again been shown.

The fact that these systems are based on standard Aquamite units has another important implication. That is, for applications where the feedwater TDS has substantially increased since the time of unit purchase or start-up, it is relatively simple to convert the units to a larger number of stages, thereby maintaining acceptable product quality.

Finally, high TDS feedwaters can also amplify certain systems dynamics making optimizations and improvements more apparent. Thus, development of the 10 stage EDR process has actually resulted in many systems improvements for conventional EDR systems. As additional high salinity plants (which are now either planned or under construction) come on line, additional design improvements for both salinity and standard brackish water units will undoubtedly result. This extra bonus helps confirm the need for continued development and refining of water desalting technology.

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The Determination of Supersaturation Limits In An EDR Unit With Aliphatic Anion Membranes

by
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I. SUMMARY

Test work done as part of the Office of Water Research and Technology (OWRT) Contract #14-34-0001-9510 "Parametric Test of an Electrodialysis Reversal System with Aliphatic Anion Membranes", had as one of its objectives the determination of upper limits of calcium sulfate supersaturation on the performance of an EDR unit with aliphatic anion membranes. For test purposes, an Ionics EDR system was installed at the OWRT Roswell Test Facility and Operated using simulated Alamogordo water[1] (approximately 42 EPM% calcium sulfate) and progressively higher recoveries.

The determination of supersaturation limits for calcium sulfate in the operation of an EDR unit became of special interest when the Office of Water Research and Technology selected EDR as the process to be demonstrated in a proposed brackish water demonstration plant at Alamogordo, New Mexico, under Public Law 95-84, Desalting Demonstration Plant Program. Although this project has not been authorized and only feasibility studies have been completed to date, the desire to achieve high product recoveries on the high calcium sulfate waters anticipated as feedwater to the proposed Alamogordo plant, resulted in a need for field studies to support future design work. Accordingly, OWRT sponsored field tests under a contract with Ionics, Inc. to explore more fully the limits of calcium sulfate supersaturation permissible in the concentrating stream of an EDR unit, with or without chemical additives, as well as the most recently developed aliphatic anion membranes. The OWRT facility at Roswell was chosen as a location for these tests using simulated Alamogordo feedwater since adequate test facilities and laboratory service could be more readily supplied at Roswell.

The EDR stack which was tested consisted of primarily aliphatic AR 204 SXZL anion membranes together with small section containing various types of test membranes. These test sections were meant to serve as a screening function to determine the optimum membrane for resistance towards calcium sulfate scale. Tests were started with zero chemical feed, 100% calcium sulfate saturation, and a Langelier Index of 1.7 in the waste stream. Recoveries were increased for several more tests until scaling occured in the skid piping and stack at a Langelier Index of 2.45 and calcium sulfate saturation of 230%. The scale was predominantly carbonate. Acid injection into the brine stream to a Langelier Index of approximately 2.0 was tried next, resulting in severe gypsum scaling in the piping, seizing of the brine recirculation pump, and little to moderate gypsum scaling of the membranes. The calcium sulfate level at this point was roughly 245% of saturation. After cleaning the EDR unit with a 24 hour 5% hydrochloric acid soak and several rinses the unit was restarted with both acid and sodium hexametaphosphate (SHMP) fed into the brine stream. This allowed trouble-free operation at recoveries up to 93.5% and calcium sulfate saturation levels of 440%. Stack inspection showed adequate performance by all membrane types, with the AR 204 RXZL singled out as the potentially least scale prone membrane.

The economics of acid and SHMP were considered and, based on Roswell chemical consuption, the cost for operation of a 2 MGD facility at Alamogordo was estimated at $.005/K gal. product for sulfuric acid and $.0045/K gal. product for SHMP for a total of $.0095/K gal.

In conclusion, using acid and SHMP together with EDR, it may be economically and physically feasible to operate at $CaSO_4$ saturation levels of 440%, thereby allowing high recoveries on difficult to treat waters without resorting to expensive lime, lime soda, or ion exchange pretreatment.

II. DESCRIPTION OF THE ELECTRODIALYSIS REVERSAL SYSTEM AT THE ROSWELL TEST FACILITY

The Electrodialysis Reversal (EDR) system at the Roswell Test Facility consists of an Ionics AQUAMITE X EDR plant containing the following components:

1) An hydraulic/electrical skid containing feed and brine pumps, a 10 micron filter, pressure regulating valve, a DC rectifier, reversal valves, and associated control and monitoring equipment.
2) A membrane stack containing 450 cell pairs in 3 electrical and 6 hydraulic stages and using Ionics' Mark III-4 spacers, CR 61 CZL-386 cation membranes, and predominantly 204 SXZL aliphatic anion membranes. Thirty-six cell pairs of other anion membranes are inserted in test sections in the first and sixth hydraulic stages. These test sections consist of 5 cell pairs each of 204 RXZL, developmental 304 RXZL and 304 SXZL, and 3 cell pairs of 103 PZL anion membranes.
3) An instrument cabinet for the monitoring and recording of feed, product, and brine conductivities, and for monitoring the electrical energy to the rectifier in kilowatt-hours.
4) Composite samplers to catch representative samples for either short-term runs (30 min.) or long-term runs (ca. 150 hrs).
5) Feed, product, and electrode water meters to obtain production and recovery data.
6) CIP tank — which is used with the brine recirculation pump for routine chemical clean-in-place procedures.

Feed water to the EDR unit is composed of a blend of facility well water (6000 ppm) and Roswell city water (approx. 900 ppm) to produce a roughly 42% gram equivalents per million (epm) calcium sulfate 1830 ppm water analagous to Alamogordo water.[1] Blending is accomplished in the same room as the EDR unit. The North well water is filtered through 10μ cartridge filters before blending to prevent sand from entering the system. Flows of the two streams are adjusted to maintain a nearly constant conductivity of roughly 2680 μmhos/cm in the blend.

After blending, the feed water is generally dechlorinated by thiosulfate injection and enters a 4000 gallon feed tank. Level controls close a 2½ inch motor operated valve (MOV) when the feed tank is nearly full. Contacts on the MOV shut down the well pump to prevent it from pumping against the closed valve. On low level, the low level controller opens the MOV, starting flow to the tank and contacts within the MOV start the well pump, thus maintaining the proper feed blend.

The EDR unit works as follows:

The feed stream is pressurized to 80–100 psig and passes through 10 micron polishing filters and a pressure regulating valve which maintains the filtrate at a constant pressure as the filters become plugged. The feed then splits into three streams — dilute, brine makeup and electrode. The predominate portion of the feed becomes the

dilute stream and travels through the diluting cells of the stack, where this stream becomes progressively demineralized until it exits the stack as the product stream. A smaller part of the feed is used as brine makeup water which combines with the brine recycle at the suction end of the brine pump to become the concentrate stream. This stream is pressurized to 60–80 psig and travels through the concentrating cells of the ED stack becoming progressively more concentrated until finally exiting the stack, where a portion goes to waste as brine blowdown and the remainder is recycled. The rate of brine blowdown is slightly greater than the rate of brine makeup due to a small amount of water transfer between the dilute and concentrate streams. The recovery of the ED unit can, therefore, be simply adjusted by changing the brine makeup flow rate.

At zero or low brine makeup, almost all of the brine stream is recirculated resulting in the buildup of high brine concentrations and, therefore, very high recoveries.

The electrode stream is the third stream taken off of the feed and is used to flush the electrodes of gases which are formed as part of the electrochemical reactions which occur in these compartments. The electrode waste stream is generally very close in composition to the feed except for pickup of oxygen, chlorine and hydrogen gases, and pH changes. Since this stream can generally be reused or fed from an alternate source, the electrode flow is monitored separately from the dilute stream by an electrode rotameter and water meter.

Polarity reversal in electrodialysis results in the concentrate and dilute cells changing identity, thus flushing out potential scale seed crystals and foulants from the former concentrating cell. Motor operated valves are used to switch these flows at the inlets and outlets of the stack. At reversal, the product becomes progressively more saline, since the product cells are now changing to concentrate cells. At a set conductivity, a controller will signal a motor operated valve to turn, diverting this "off-spec product" back to the feed tank. As the dilute stream replaces the concentrate stream in the dilute cells (which were concentrate cells before reversal), the off-spec product improves until the conductivity controller diverts the product back to product storage.

Figure one is a system diagram of the Roswell EDR unit as used in these tests and Figure two is a photograph illustrating the layout of the major components.

III. DESCRIPTION OF TESTS

The test program outlined here was performed as part of OWRT Contract #14-34-0001-6510, "Parametric Tests of an EDR System with Aliphatic Membranes". This paper deals only with the phase of this test program which has as its objective the determination of limits on the ability of an EDR system with aliphatic anion membranes to operate at relatively high recoveries on high calcium sulfate waters without extensive pretreatment. Previously, the highest percentage of calcium sulfate supersaturation which had been achieved with an EDR unit was approximately 150 percent at Dell City, Texas. The range above 150% calcium sulfate had not been explored, and there were preliminary indications that aliphatic test membranes were more scale resistant. A test program, therefore, was suggested to systematically determine the limits of calcium sulfate supersaturation with this new membrane system and was carried out during 1980 at the Roswell Test Facility.

The test program originally called for the operation of an EDR test unit at progressively higher recoveries until irreversible scaling occurs. At that time, membranes were to be replaced as necessary and tests repeated with acid and/or SHMP addition. Initially, the program was projected to operate 75 hours at 100% and 133% calcium sulfate saturation, 150 hours at 166% $CaSO_4$ saturation, and 300 hours at each subsequent increase of 33% $CaSO_4$ saturation. The actual series of tests varied somewhat from design in that much higher levels of supersaturation were obtained with chemical addition than had originally been planned. The resultant series of tests may be grouped into three phases: tests at up to 233% $CaSO_4$ with ZERO CHEMICAL FEED, a test at 233% $CaSO_4$ with acid addition to the concentrate stream, and tests at 233% to approximately 440% $CaSO_4$ with acid and sodium hexametaphosphate addition to the concentrate stream.

The design basis of these tests called for a simulated Alamogordo feed water (1780 mg/L TDS) which was blended

TABLE 1

CALCULATED ALAMOGORDO (KAISER REPORT) BLEND USING 743 mg/l

ROSEWELL CITY WATER & FACILITY NORTH WELL

	CITY WATER (1/4/80 Analysis)	NORTH WELL (2/20/80)	4.62 City: 1.0 Well BLEND	KAISER REPORT ANALYSIS
Na	30	1000	203	210
K	—	100	18	3
Ca	126	788	244	225
Mg	36	243	72	94
Cl	35	2393	455	298
SO_4	272	1834	550	690
HCO_3	244	250	245	260
pH	7.55	6.99	—	7.5
SiO_2	14.6	—	—	15
Fe	—	.43	—	2.5
TDS	743	6611	1787	1788
EPM % Ca	59.6	37.4	44.4	39.9
EPM % SO_4	53.2	34.8	40.5	42.7

FIGURE 1

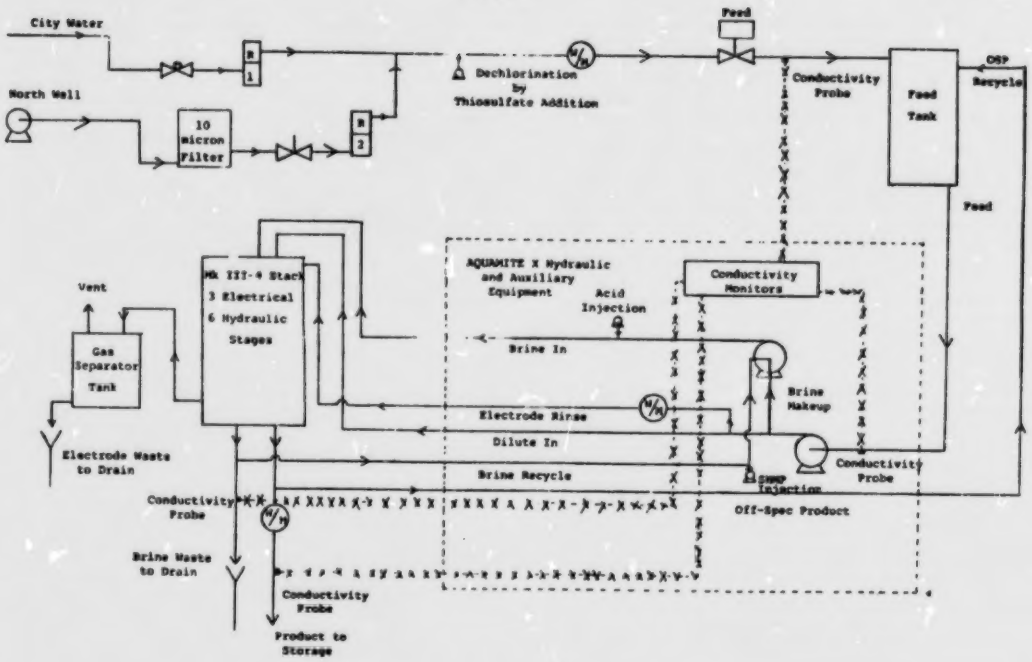
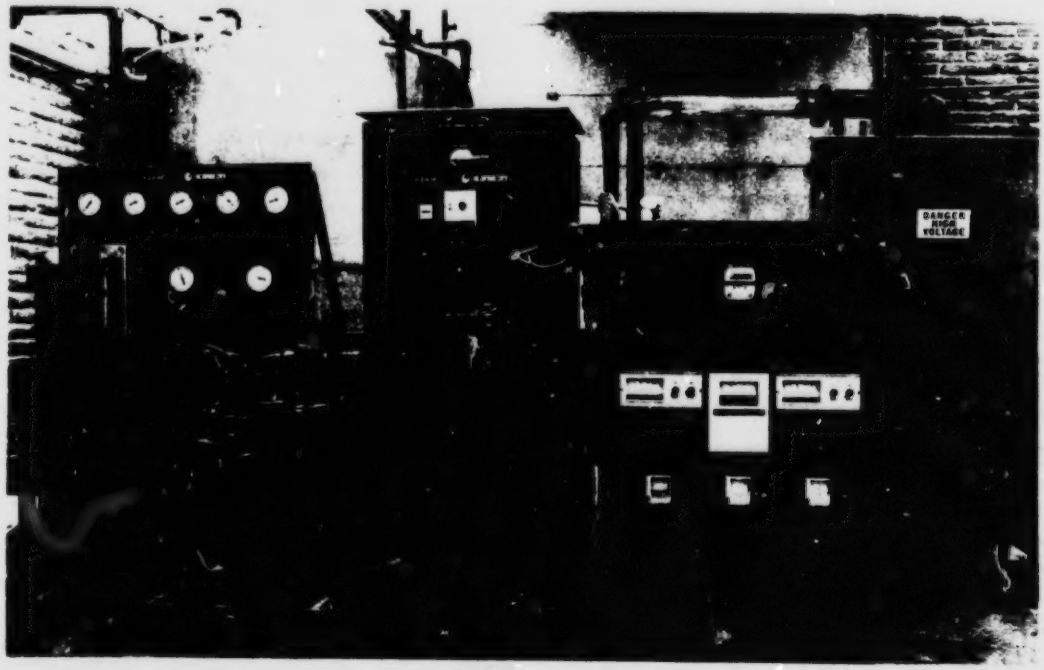


FIGURE 2



from Facility North well and Roswell city waters. Some typical analyses for these two sources are included in Table 1, and Table 2 shows the original estimates for simulated Alamogordo waste composition. The design production and product TDS were 95M³/day (25,000 gpd) and 200 mg/L, respectively.

The actual operation of the EDR plant allowed for some variation in product TDS, production, and recovery from design setpoints, since each of these variables is dependent on a number of factors.

Rather than try to compensate for these factors, the tests were run, as nearly as possible at set dilute flow, brine makeup flow and stack voltages. Table 3 lists the average values of these settings for each test. As can be seen from this table, dilute flow was kept essentially constant. The brine makeup flow determined the system recovery for each test and was adjusted for the recovery calculated to produce the desired percentage calcium sulfate saturation. Voltage settings were changed only where low temperatures or higher recoveries resulted in lower percentage demineralizations than desired.

Table 4 outlines the duration and resultant % $CaSO_4$ saturation, recovery, and production for the plant settings given in Table 2.

The test duration is measured between the first and last loggings or between the weekly short-term composite sampling for two-week runs and does not include the total unit running time. Before the unit is logged, the system is run for roughly 3 hours to assure steady state operation. As the unit is logged in, the composite samplers are readied and long-term composites are taken of the feed, product, and blowdown streams. Logs of the important operating parameters are taken at least twice daily and these data are used in subsequent unit performance calculations. The long-term samples are taken for conductivity measurements before the final logging, and short-term composites are taken throughout positive and negative polarities during the final logging for full laboratory analysis.

IV. DISCUSSION OF RESULTS

FEED ANALYSIS SUMMARY

The Alamogordo parametric test feed analyses are summarized in Table 5. The mean value for the feed total dissolved solids was 1829 mg/L. On the average, the feed was higher in sodium, chloride, and calcium and lower in magnesium, sulfate and bicarbonate than the Alamogordo analysis. Significant variations were observed in feed composition and TDS, even though the blend was regularly adjusted for desired conductivity. This was primarily due to large variations in feed water quality, possibly resulting from part of the Roswell Test Facility product occasionally returning through the city water interconnections. The blend feed TDS/conductivity ratio is thus seen to vary from a high of .72 to a low of .626, thus making conductivity control of TDS rather inaccurate. As might be expected, the low TDS/conductivity ratio corresponds to a higher sodium chloride ratio than the higher TDS/conductivity values.

BRINE ANALYSIS & RECOVERY DATA

Table 6 summarizes the brine waste analyses for the Alamogordo parametric tests. The progression of 33% increases in calcium sulfate saturation could not precisely be met due to the large feedwater composition variations mentioned previously. One does, however, see a general progression in calcium sulfate saturation and Langelier Index (except for acid addition cases) from Test 1 at 101% to Test 7 at an average of 440% calcium sulfate saturation. The first week of Test 5 is an exception to this because of a combination of lower calcium and sulfate feed concentrations and incorrect brine make-up setting. The low calcium sulfate figure for the second week of Test 5 with acid addition is a result of this being a 5½ day composite sample rather than the usual 30 minute composite. At high levels of saturation, the longer term composite samples tend to precipitate out and, therefore, give lower waste concentrations. The 30 minute composite was not taken in this case, due to North well pump failure.

Some comparisons between short and long-term recoveries may be seen in Table 7. Considering that the long-term data is derived from conductivity measurements and TDS to conductivity ratios, the correlation is quite good.

The brine TDS and, thus, the calcium sulfate saturation levels are seen in Tables 6 and 7 to increase rapidly at high recoveries. The 93–94% recovery in Test 7 was the highest recovery possible with this apparatus, due to physical limits of electro-endosmotic water transfer and cross-leak. There is a possibility that a few percentage points higher recovery could be obtained with flatter components that have not been exposed to scale, due to lower cross-leakage.

Salt and scale trapped between membranes and spacers after stack disassembly tend to promote excess cross-leakage and leakage to the outside. The exterior leakage is the prime cause of poor correlation between water meter readings and water analyses in Table 8 for the last three tests. Avoidance of scaling conditions, better cleaning or flatter components could have avoided most of this effect.

One major result of the data in Table 6 is to place the parameters of Test 5, approximately 89% recovery, 240% calcium sulfate saturation, and 2.45 Langelier Index as the conditions where calcium sulfate and calcium carbonate precipitation become problematical. An additional, extremely important result is the demonstration of an average of 440% calcium sulfate saturation in Test 7, with acid and SHMP addition.

DEMINERALIZATION PERFORMANCE

A summary of the demineralizer data for the Alamogordo phase parametric tests is given in Table 8. Data is listed here on recovery, production, fractional demineralization, energy consumption, stack resistance corrected for temperature, composite current efficiency values, and total dissolved solids concentrations for feed, product, and waste. The subjects of feed water analysis and water recovery have been covered previously; the fractional demineralization, energy consumption characteristics, and net production are discussed in the following.

The product water salinity and fractional demineralization for the Alamogordo tests can be seen to average 234 mg/L TDS and 87.3% respectively. This value of product TDS is somewhat higher than the design value of 200 mg/L; however, the fractional demineralization is only slightly below the design value of 88.8%. The reasons for the fluctuation of product TDS for these tests are primarily due to feedwater TDS and temperature variations. The degree of demineralization is rather easily controlled by varying the rectifier output voltage, but since it was desired to keep voltage settings relatively constant, the product TDS was allowed to vary within limits.

The product water production during the first five tests was seen to vary between 27,200 and 22,600 gallons per day. This is slightly above the 25,000 GPD design. The small decrease in production between tests one and five is primarily due to a lengthening in the time the unit produces below specification product water after reversal. As the concentration of the waste stream increases, there is an increase in the time necessary to fully wash it out during reversal. The lower productivity during the tests with chemical feed is primarily due to exterior leakage problems mentioned previously. Starting out with fresh components, one would expect production values closer to those in Test 5 with zero chemical feed. One would expect some further decline in production at the higher recoveries of Tests 6 and 7, although this is not reflected in the data.

The energy consumption can be seen to generally increase with an increase in recovery. Energy is found more nearly proportional to brine salinity than to recovery. One might expect this, as current efficiency is largely a function of the concentration gradient across the membrane. The energy consumption versus brine TDS is graphically depicted in Figure 3. Here one sees the metered energy consumption range from 2.0 KWH/1000 gallons at 73% recovery to 4.0 at 93.8% recovery. The instantaneous energy consumption values are calculated from the actual stack voltage and amperages with an efficiency factor of 94% and temperature corrected to 70°F. The energy consumption using this value is seen to increase at a significantly lower rate, from 2.1 KWH/KGAL at 73% recovery to 3.6 at 93.8% recovery. This is primarily due to correction for the declining temperature during the last tests. Water losses due to stack leakage also have contributed approximately 5% to the power consumption in the last tests because of lower productivity. The increase in energy consumption with increasing brine salinity is found using Figures 4 and 5 to be due to a reduction in current efficiency with increasing waste total dissolved solids. Figure 4 shows that stack resistance decreases with increasing waste concentration, thus tending to reduce energy consumption. The drop in efficiency in Figure 5 tends to over-power this effect since the energy consumption is inversely proportional to the efficiency squared.

The efficiencies of Figure 5 are termed composite efficien-

FIGURE 3

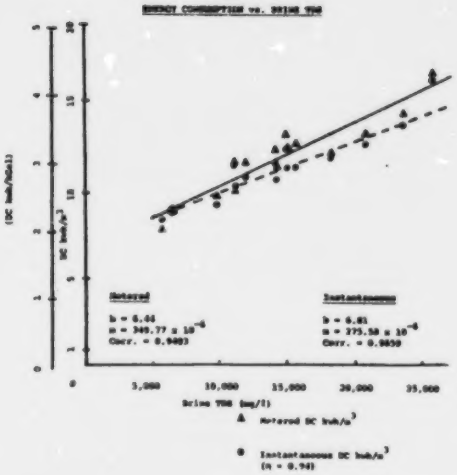


FIGURE 4

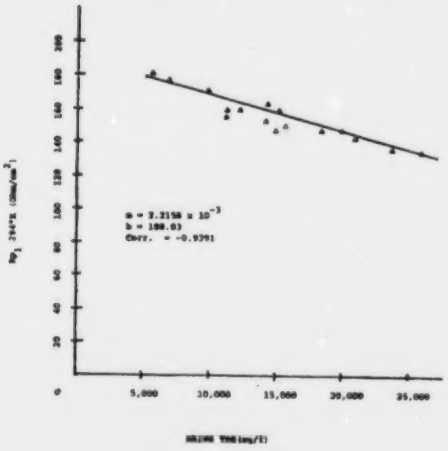
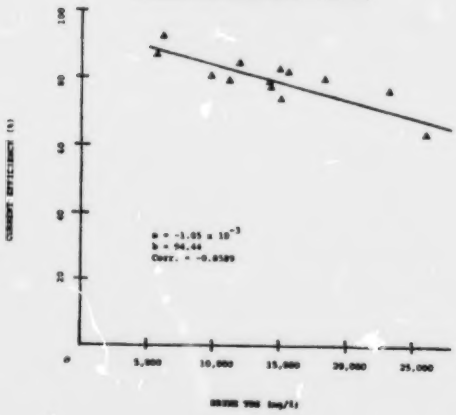


FIGURE 5



cies, since they are based on composite samples, net production, and steady state amperage readings. Because these steady state readings are higher than the average amperages and since reversal effects are included, these values are significantly lower than steady state values. The main utility of these efficiencies values is in establishing comparisons and trends between the different recovery cases. Except for one spuriously high reading, the efficiencies tend to decrease nearly linearly with increasing brine TDS.

SUMMARY OF OPERATING EXPERIENCE

The Alamogordo phase tests were started on July 28, 1980 beginning with a two-day test at 100% calcium sulfate saturation to establish a baseline. Testing progressed as planned through to Test 4 at 200% calcium sulfate when a high voltage drop was detected across one cell pair of the E.D. stack. Upon disassembling the stack, this problem was found to be caused by a minor misassembly. Inspection revealed no traces of scale or any other problems and thus testing was continued again under the same conditions.

On August 22, the North well pump failed and Test 4 was suspended until a new pump was installed. Well pump failures due to clogging with sand or improper wiring delayed testing two other times during Test 5 with no chemical addition and during Test 6 with acid and SHMP addition.

Test 4 was restarted on August 28 operating at 220% calcium sulfate and Test 5 was started on September 4. During Test 5, some scaling was observed in the tubing entering the membrane stack. At the end of Test 5 the stack and hydraulic piping were inspected. Scaling was found both in the E.D. stack and in the brine recirculation loop. The scale on the membrane was easily acid soluble evolving gas in the process, and thus predominantly carbonate. Analysis of scale from the brine pump indicated a ratio of two parts carbonate to one part sulfate.

At this point it was decided to inject sulfuric acid into the brine stream to reduce the Langelier Index from 2.45 to roughly 2.0. Test 5 was repeated using acid injection.

Tuesday morning, October 21, the unit was found to have shut down around midnight October 20/21. Investigation showed that the brine pump would no longer turn, and had probably caused the shutdown by activating the low pressure switch. The stack was flushed out and the pump was opened for inspection. The pump was very heavily scaled (⅛–¾" deposit) on all parts. The impeller apparently had bound at the suction race way and at its base. The pump seal was clogged by a white paste and was replaced. No scale was observed in the clear plastic piping on the stack inlets and outlets.

A stack inspection showed zero to moderate scaling which did not easily dissolve in hydrochloric acid, and was presumed to be primarily sulfate. Analysis of scale from the brine pump at Roswell Test Facility showed a composition of 26.8% calcium, 73.1% sulfate, and less than 1% carbonate.

Testing was resumed on November 7, repeating Test 5 at roughly 250% calcium sulfate and using a roughly 10–15 ppm SHMP injection into the brine stream in addition to the acid injection. No additional problems with scaling occurred and testing progressed through Test 6 at 354% $CaSO_4$ saturation and on through Test 7, run at maximum recovery (zero brine make-up), averaging 4[illegible]% $CaSO_4$ saturation.

The results of field observation may be summarized as follows:

OCTOBER 1, 1980 — Operation without chemicals resulted in precipitation and scale formation in both membrane stack and hydraulic equipment at 233% $CaSO_4$ supersaturation. Scaling was predominantly carbonate type scale. None of the various membranes could be rated any better or any worse than any other membrane; e.g., Stage 1 showed loose scale in all cells, but none of the various types of membranes were scaled internally or damaged. In the sixth stage, there was no loose scale, but all the various types of membranes showed a trace amount of internal scale. Stage 2 showed general loose scale as in Stage 6.

OCTOBER 25, 1980 — Operation with addition of acid in the brine stream resulted, again, in precipitation and scale formation in the membrane stack and hydraulic equipment, at 233% $CaSO_4$ supersaturation. Scaling, however, was predominantly sulfate type rather than carbonate. There was some evidence that the RXZL formulation of both the 204 and 304 series of membranes showed

less scaling tendency than either the SXZL and standard PZL. It is important to note that all of the single test membrane new insertions made at the October 1 inspection were not scaled, indicating the possibility of previous carbonate seeding in the original test section when operating without acid.

DECEMBER 17, 1980 — Operation with both acid and SHMP in the brine stream resulted in trouble-free operation (and, without necessity of CIPs) up to the maximum calcium sulfate supersaturaton limits physically attainable with this type of unit. Stack inspection showed that the single membrane insertions made at the October 1st and 25th inspections were all scale-free (with the exception of the 304 RXZL which showed only a trace amount of internal scale) and, therefore, there is a good possibility that successful operation is feasible with all various types of the test membranes except, possibly, the 304 RXZL type

The 204 RXZL membranes (both original and new insertions) showed no trace of scaling whatsoever in both test sections and, therefore, would be considered top candidate for continued and long-term testing.

Stack inspection results are summarized in Table 9 for the various test sections and Table 10 for the main body of the stack, which is made up of SXZL membranes.

ECONOMIC ANALYSIS OF CHEMICAL ADDITION TO THE EDR BRINE STREAM AT ROSWELL

The chemical usage data from these tests were analyzed with regards towards operating costs for a 2MGD demonstration plant.

The enclosed Table 11 summarizes the chemical consumption during the Alamogordo Phase parametric tests at Roswell. Costs are based on the unit costs given in the Kaiser Alamogordo report, page 44, and are adjusted by a factor of 1.137 to correct for one year's inflation.

It should be noted that the chemical consumption and costs are based on usage per thousand gallons of product water in order to facilitate comparison. In actuality, both acid and SHMP are added to the concentrate stream alone. Since a relatively small amount of concentrate is wasted compared to production, very small quantities of chemical are required. Additionally, it should be noted that unlike many other processes which require a negative Langelier Index in the concentrate stream, acid was added to the concentrate stream in these tests to reduce the Langelier Index to roughly +2.0 (pH ≅7.0). this requires only minor quantities of acid when compared with treating a feed water to produce a negative Langelier Index in the concentrate stream.

The foregoing discussion explains the reason for the relatively low average chemical consumptions of .180 lbs. of 66° Be sulfuric acid per thousand gallons product and 0.149 lbs. of sodium hexametaphosphate per thousand gallons product water, and average chemical costs of $.005/K gal. product for acid and $.0045 for SHMP, The net impact on operations and maintenance for a 2 MGD demo plant would be $19/day for both acid and SHMP, or $9/day (30 lbs./day) for SHMP alone and $10/day (360 lbs./day) for acid.

V. CONCLUSIONS

The following conclusions may be drawn as a result of the data presented in the previous section:

1. The Langelier Index limit for EDR systems with zero chemical feed appears to be approximately +2.4, where carbonate scale formation occurs on both system piping and membranes.
2. The calcium sulfate saturation limit for EDR with zero chemical feed or with sulfuric acid addition appears to be between 220 and 250%. At roughly 250% calcium sulfate saturation, gypsum deposition on the brine piping becomes intolerable and some gypsum scale deposition occurs on the membranes.
3. Using acid addition to a Langelier Index of +2.0 in the brine stream and sodium hexametaphosphate addition, trouble-free operation was demonstrated to an average of 440% calcium sulfate saturation for 300 hours. Higher levels of supersaturation may be obtainable, but are as yet uncertain.
4. The effect of SHMP on calcium sulfate saturation has been established during these tests, but the requirement for sulfuric acid addition in addition to SHMP is questionable. Tests are planned using SHMP injection alone to prevent carbonate and sulfate scale.
5. The AR 204 SXZL anion membrane as well as all the test membranes performed adequately at high levels of calcium sulfate saturation. The AR 204 RXZL anion membrane was singled out as potentially that most resistant to calcium sulfate scaling. Full stack tests are planned in the future.

Many brackish waters in the United States and throughout the world contain sufficiently large concentrations of calcium sulfate such that potential water recovery is severely limited by calcium sulfate supersaturation. It is hoped that this work done as part of OWRT contract #14-34-0001-9510 has extended this limit so that reasonable recoveries will now be possible on waters previously requiring expensive lime softening or ion exchange pretreatments.

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TABLE 2

	ESTIMATED BRINE WASTE USING KAISER ALAMOGORDO FEED (1780 TDS)					ESTIMATED BRINE WASTE USING ROSWELL SIMULATED ALAMOGORDO FEED (1787 TDS)					KAISER FEED	SIMULATED ROSWELL BLEND
$CaSO_4$ Saturation %	100	133	166	200	233	100	133	166	200	233	31.3	28.6
Recovery %	70.6	78.1	83.5	85.5	87.5	73.2	79.9	84.0	86.7	88.6		
TDS mg/l	5568	7400	9211	11065	12887	6113	8108	10106	12148	14154	1780	1787
Concentration (mg/l as ion):												
Na	634	840	1044	1252	1456	663	875	1087	1304	1518	210	203
Ca	726	969	1209	1454	1696	860	1145	1430	1721	2006	225	244
Mg	298	396	493	593	691	249	330	412	495	577	94	72
K	10	13	16	19	22	62	83	103	124	145	3	18
Cl	946	1259	1569	1886	2198	1580	2100	2620	3151	3673	298	455
HCO_3	777	1028	1276	1529	1778	801	1057	1313	1575	1834	260	245
SO_4	2175	2894	3604	4332	5047	1897	2519	3141	3778	4402	690	550

TABLE 3

PLANT SETTINGS FOR ROSWELL ALAMOGORDO PARAMETRIC TESTS

TEST	DILUTE FLOW M^3/hr (GPM) (Average)		BRINE MAKEUP M^3/hr (GPM) (Average)		AVERAGE TEMPERATURE (°C)	°K	VOLTS STAGE 1	STAGES 2 & 3
1	9.77	(21.5)	3.05	(6.71)	(23.1)	296.1	107	81
2	9.81	(21.6)	1.92	(4.23)	(24.7)	297.7	107	82
3	9.81	(21.6)	1.39	(3.07)	(23.8)	296.8	108	87
4	9.77	(21.5)	0.95	(2.1)	(23.7)	296.7	107	95
5	9.81	(21.6)	0.31	(0.69)	(22.5)	295.5	114	93
Acid Add'n to Brine Stream								
5 (Repeat Acid Add'n)	9.77	(21.5)	0.26	(0.57)	(21.1)	294.1	118	92
Acid & SHMP Add'n to Brine Stream								
5 (Repeat Acid & SHMP Add'n)	9.77	(21.5)	0.26	(0.58)	(18.9)	291.9	118	93
6	9.77	(21.5)	0.15	(0.33)	(16.9)	289.9	118	96
7	9.81	(21.6)	0	0	(15.4)	288.4	125	110

TABLE 4

Contract No: 14-34-0001-9510

TEST DESCRIPTION — ALAMOGORDO PHASE PARAMETRIC TESTS

TEST #	WEEK	%$CaSO_4$ SATURATION	RECOVERY BY ANALYSIS	PRODUCTION (KGPD)	M^3/DAY	DURATION HOURS
No Chemical Addition						
1		100.6	72.97	(27.0)	102.2	42.7
2		115.0	76.70	(26.8)	101.4	46.6
3		102.9	83.42	(27.2)	102.9	137.3
4 —	1	198.0	86.04	(27.2)	102.9	21.0
—	2	220.5	86.12	(26.2)	99.2	185.3
	Avg.	209.3	86.08	(26.7)	101.1	Total 206.3
Acid Add'n to Brine Stream						
5 —	1	245.8	88.66	(25.6)	96.9	165.3
—	2	156.2[1]	86.77[1]	(25.3)	95.7	129.7
	Avg.	201.0	87.72	(25.4)	96.3	Total 295.0
Acid & SHMP Add'n To Brine Stream						
5 —	1	290.75	89.14	(23.2)	87.6	142.6
—	2	211.8	89.41	(22.4	84.8	144.0
	Avg.	251.28	89.28	(22.8)	86.3	286.6
6 —	1	361.35	89.99	(22.6)	85.5	114.7
—	2	345.88	90.42	(23.5)	88.9	43.4 (140.2)[2]
	Avg.	353.62	90.21	(23.0)	87.2	254.9
7 —	1	455.5	93.06	(23.1)	87.4	141.3
—	2	424.59	94.10	(23.1)	87.4	164.0
	Avg.	440.05	93.58	(23.1)	87.4	305.3

[1]Based on long-term analysis, some precipitate in sampler.
[2]96.8 hrs. prior to well pump failure, 43.4 hrs. after restart.

TABLE 5

FEED ANALYSIS SUMMARY — ALAMOGORDO BLEND — PARAMETRIC TESTS

CONTRACT NO: 14-34-0001-9510

TEST #	WEEK	SODIUM	POTASSIUM	CALCIUM	MAGNESIUM	CHLORIDE	SULFATE	BICARBONATE	TDS	pH	COND.	TDS/COND.	%$CaSO_4$	Langelier Index
1		250	–	312	66	475	491	218	1712	7.48	2540	.674	23.1	0.47
2		237	–	308	66	439	485	268	1693	7.35	2351	.720	21.8	0.45
3		215	–	252	71	422	614	232	1406	7.30	2580	.700	30.3	0.40
4 –	1	222	–	240	71	418	579	234	1754	7.50	2560	.685	28.2	0.56
–	2	225	–	252	80	446	607	238	1848	7.65	2700	.684	29.3	0.74
(5) –	1	297		196	61	500	461	249	1764	7.75	2660	.663	30.7	0.75
5 –	1	230		244	75	479	564	230	1812	7.6	2720	.666	27.4	0.64
–	2	255		304	63	470	464	230	1699	7.5	2600	.653	21.8	0.46
Acid Add'n														
5 –	1	240		236	75	421	605	229	1806	7.5	2654	.680	28.4	0.51
–	2	255		304	63	470	464	230	1699	7.5	2600	.653	21.8	0.44
Acid & SHMP														
5 –	1	245		260	75	489	607	227	1906	7.55	2790	.683	29.8	0.60
–	2	313	2	200	61	505	436	163	1760	6.85	2810	.626	19.5	-0.40
Acid & SHMP														
6 –	1	250	3	384	80	507	888	244	2356	7.35	2890	.815	48.1	0.41
–	2	246	2	270	92	500	647	244	2001	7.10	2780	.710	30.8	0.12
Acid & SHMP														
7 –	1	244	2	265	79	496	600	234	1920	7.38	2820	.681	29.7	0.24
–	2	303	1	190	62	560	413	198	1729	7.20	2740	.631	18.5	-0.06
MEAN ALL ANALYSES		252.0		238.8	71.4	478.6	560.7	225.2	1829	7.37	2678	.683	27.0	0.36
σ ALL ANALYSES		28.8		47.0	8.7	47.8	114.1	24.5	164	.24	134	.045	7.0	0.31
KAISER ALAMOGORDO FEED		210	3	225	54	298	650	260	1788	7.5			39.8	0.42

Note: All concentrations in mg/l as ion

TABLE 6

WASTE ANALYSIS SUMMARY — ALAMOGORDO PHASE PARAMETRIC TESTS

TEST #	WEEK	SODIUM	POTASSIUM	CALCIUM	MAGNESIUM	CHLORIDE	SULFATE	BICARBONATE	TDS	pH	COND. (µS/cm²)	% $CaSO_4$ Saturation	Langelier Index
1		663	–	815	244	1436	1930	566	5,564	7.78	7,360	100.6	1.74
2		720	–	931	287	1524	2270	763	6,495	7.82	8,035	115.0	2.00
3		1010	–	1463	438	2292	3580	986	9,789	7.70	11,050	182.9	2.17
4 –	1	1350	–	1624	450	2747	3860	1159	11,180	7.80	13,180	198.0	2.38
–	2	1368	–	1784	511	2900	4260	1154	11,957	7.80	14,000	230.5	2.42
(5)[1] –	1	1686	–	1403	426	3155	3390	1161	11,302	7.97	14,180	181.3	2.47
5 –	1	1755	–	1925	693	3853	4410	1537	14,273	7.8	17,560	227.8	2.56
–	2	2080	–	1965	620	4165	4750	1430	15,010	7.65	18,270	231.1	2.39
ACID ADDITION													
(Repeat)													
5 –	1	1871	–	1952	576	3456	5050	1257	14,165	7.27	15,920	245.8	1.93
–	2[2]	1740[2]	–	1343[2]	458[2]	3385[2]	3950[2]	954[2]	11,222[2]	7.35[2]	14,420[2]	156.2[2]	1.92
ACID & SHMP ADD'N													
(Repeat)													
5 –	1	1710	–	2326	706	3874	5620	1357	15,593	7.13	17,640	390.8	1.85
–	2	2375	15	1885	547	4760	4500	878	14,960	6.87	18,830	211.8	1.11
6 –	1	2700	18	2927	888	5716	7200	1505	20,955	6.86	24,020	361.4	1.69
–	2	2000	18	2767	827	4610	6620	1493	18,335	6.89	21,400	345.9	1.69
7 –	1	2500	23	3644	1032	5855	8400	3064	23,738	7.30	24,970	433.5	2.24
–	2	3300	26	3609	1192	7374	8075	2416	25,992	7.05	28,230	424.6	2.16

[1] Incorrect brine makeup flow used for Test (5); Readjusted following week for Test 5
[2] Test cut slightly short; long-term composite analysis given—scaling in sampler gives low results for TDS and % $CaSO_4$ saturation.

TABLE 7

COMPARISON BETWEEN LONG AND SHORT-TERM OPERATION

TEST	SHORT-TERM RECOVERY %	SHORT-TERM FRACTION DEMIN.	LONG-TERM RECOVERY %	LONG-TERM FRACTION DEMIN.	LONG-TERM TDS mg/l by ANALYSIS FEED	PRODUCT	BRINE	LONG-TERM TDS by CONDUCTIVITY FACTORS mg/l FEED	PRODUCT	BRINE
1	72.97	85.28	72.85	85.35	1712	252	5,654	1631	239	5,366
2	76.70	86.18	79.28	85.11	1693	234	6,495	1699	253	7,059
3	83.42	87.65	83.00	85.83	1806	223	9,769	1659	235	8,611
4 – Wk 1	86.04	89.17	86.64	88.31	1754	190	11,190	1596	194	10,689
Wk 2	86.12	88.15	85.27	86.15	1848	219	11,957	1855	257	11,103
5 – Wk 1	88.76	87.09	88.15	86.42	1812	234	14,273	1679	228	12,477
Wk 2	89.98	87.23	90.18	85.84	1699	217	15,010	1660	235	14,739
Acid Add'n to Brine Stream										
5 – Wk 1	88.66	87.49	89.34	86.52	1806	226	14,165	1818	245	15,008
Wk 2	–	–	86.77	85.98	–	–	–	1690*	237*	11,222*
Acid & SHMP Add'n to Brine Stream										
5 – Wk 1	89.14	87.51	89.30	86.17	1906	238	15,593	1851	256	15,167
Wk 2	89.41	88.86	87.71	86.40	1760	196	14,960	1647	224	11,798
6 – Wk 1	89.99	87.86	89.44	86.51	2356	286	20,955	2209	298	18,390
Wk 2	90.42	86.46	88.71	84.91	2001	271	18,335	1915	289	14,685
7 – Wk 1	93.06	84.79	93.28	83.36	1920	292	23,738	1791	298	22,512
Wk 2	94.10	88.03			1729	207	25,992			

*Actual Analysis

TABLE 8

Contract No: 14-34-0001-9510

OPERATIONAL SUMMARY — ALAMOGORDO PHASE PARAMETRIC TESTS

Alamogordo Test	Recovery By Analysis Percent	Recovery Water meter Percent	Production m^3/day (Gal/day)	DC kwh/m^3 Instantaneous[1] (DC kwh/1000 gal.) (0.94% Rect. Eff.)		kwh/m^3 (kwh/1000 gal) Metered AC to Rectifier		Rp_1 294°K (Average)	Current Efficiency Percent	Feed TDS mg/ℓ	Product TDS mg/ℓ	Brine TDS mg/ℓ	% $CaSO_4$ in Brine Waste	Percent Demin.
1	72.97	70.87	102.2	(27.0)	0.563	(2.13)	0.528	(2.00)	180.08	86.82	1712	252	5,654	100.6	85.28
2	76.70	79.3	101.4	(26.8)	0.605	(2.29)	0.605	(2.29)	176.91	92.36	1693	234	6,495	115.0	86.18
3	83.42	82.81	102.9	(27.2)	0.626	(2.37	0.658	(2.49)	170.75	80.34	1806	223	9,769	182.9	87.65
4 - Wk 1	86.04	87.64	102.9	(27.2)	0.697	(2.64	0.679	(2.57)	159.85	79.0	1754	190	11,190	198.0	89.17
Wk 2	86.12	83.8	99.2	(26.2)	0.729	(2.76)	0.787	(2.98)	159.09	84.5	1848	219	11,957	220.5	88.15
Avg.	86.08	85.72	101.1	(26.7)	0.713	(2.70)	0.734	(2.78)	159.47	81.75	1801	205	11,574	209.3	88.66
5 - Wk 1	88.76	88.03	100.3	(26.5)	0.719	(2.72)	0.771	(2.92)	163.92	77.10	1812	234	14,273	227.81	87.09
Wk 2	89.98	88.25	99.2	(26.2)	0.761	(2.88)	0.843	(3.19)	159.27	73.79	1699	217	15,010	231.17	87.23
Avg.	89.37	88.14	99.7	(26.4)	0.740	(2.80)	0.808	(3.06)	161.60	75.45	1756	226	14,642	229.49	87.16
Acid Add'n															
5 - Wk 1	88.66	88.11	96.9	(25.6)	0.779	(2.95)	0.835	(3.16)	152.41	78.82	1806	226	14,165	245.8	87.49
Wk 2	86.77	86.69	95.7	(25.3)	0.771	(2.92)	0.787	(2.98)	155.71		1690[3]	237[3]	11,222[3]	156.2[3]	85.96[3]
Avg.	87.72	87.40	96.3	(25.5)	0.790	(2.99)	0.811	(3.07)	154.06		1748	232	12,694		86.74
Acid & SHMP Add'n															
5 - Wk 1	89.14	80.24	87.6	(23.2)[3]	0.761	(2.88)[3]	0.861	(3.26)[3]	149.13	81.78	1906	238	15,593	296.15	87
Wk 2	89.41	78.22	84.8	(22.4)[3]	0.843	(3.19)[3]	0.890	(3.37)[3]	147.62	82.31	1760	196	14,960	211.8	88.86
Avg.	89.28	79.23	86.3	(22.8)	0.816	(3.09)[3]	0.877	(3.32)[3]	148.08	82.05	1833	217	15,277	251.28	88.19
6 - Wk 1	89.59	84.80	85.5	(22.6)[3]	0.856	(3.24)[3]	0.901	(3.41)[3]	142.06	95.06	2356	286	20,955	336.35	87.86
Wk 2	90.42	87.22	88.5	(23.5)	0.803	(3.04)[3]	0.822	(3.11)[3]	147.82	79.77	2001	271	18,335	345.88	86.46
Avg.	90.21	86.01	87.2	(23.1)	0.843	(3.19)[3]	0.861	(3.26)[3]	144.94	87.42	2179	279	19,645	353.62	87.16
7 - Wk 1	93.06	87.3	87.4	(23.1)[3]	0.930	(3.52)[3]	0.977	(3.70)[3]	135.91	72.27	1920	252	23,738	455.5	84.79
Wk 2	94.10	84.7	87.4	(23.1)	0.975	(3.69)[3]	1.133	(4.29)[3]	134.10	63.15	1729	207	25,992	424.59	88.03
Avg.	93.58	86.0	87.4	(23.1)	0.954	(3.61)[3]	1.057	(4.00)[3]	135.01	67.71	1825	250	24,865	440.05	86.41

[1]Corrected to 294°K using factor of 2.4579 x $(1.01129)^T$. T = °F

[2]Based on long-term sample—some precipitation in brine composite sampler.

[3]Tests run after Nov. 7, 1980, had high leakage resulting in moderately lower production and higher energy consumption.

DE/mgd

TABLE 9

MEMBRANE STACK FIELD OBSERVATIONS - TEST SECTIONS

MEMBRANE TYPE Stage 1	Qty. Memb.	INSPECTION AFTER ZERO CHEMICALS October 1, 1980 Type & Degree of Scale	Qty. Memb.	INSPECTION AFTER ACID ONLY October 25, 1980 Type & Degree of Scale	Qty. Memb.	INSPECTION AFTER ACID & SHMP December 17, 1980 Type & Degree of Scale	COMMENTS
103 PEL	3	Moderate to Heavy Loose CO_3	1 2	Moderate Internal SO_4 Light Internal SO_4 Includes Oct. 1 insertion	3	No scale - Includes Oct. 1 & Oct. 23 Insertions.	New insertions did scale.
304 SXEL		Moderate to Heavy Loose CO_3	2 3	Light Internal SO_4 No scale includes Oct. 1 Insertion	3 2	Moderate Internal SO_4 No scale - Oct. 1 and Oct. 25 Insertions	Increased Internal scale—new insertions did not scale.
304 SXEL	5	Moderate to Heavy Loose CO_3	5	No scale includes Oct. 1 Insertion	5	Trace Internal SO_4 Includes Oct. 1 and Oct. 25 insertions	All membranes have begun to scale (slightly)
204 SXEL	5	Moderate to Heavy Loose CO_3	1 3 1	Moderate Internal SO_4 No scale includes Oct. 1 Insertion Light Internal SO_4	5	No scale Includes Oct. 1 and 25 Insertions	No scale present
204 SXEL*	63	Moderate to Heavy Loose CO_3	50% 50%	Light to Moderate No scale— Includes Oct. 1 Insertion	-	General moderate Internal SO_4— Oct. 1 and Oct. 25 Insertions not scaled	Significant Increase in scaling—new sections not scaled
Stage 6							
103 PEL	3	Trace Internal CO_3	2 1	Light Internal SO_4 Trace Internal SO_4 Oct. 1 Insertion	1 2	Moderate Internal SO_4 No scale Oct. 1 and October 25 Insertions	Slight increase in internal scaling but new insertions did not scale
304 SXEL	5	Trace Internal CO_3	4 1	Trace Internal SO_4 No scale Oct. 1 Insertion	3 2	Light Internal SO_4 No scale Oct. 1 and and Oct. 25 Insertions	Increased internal scale— new insertions did not scale
304 SXEL	5	Trace Internal CO_3	4 1	Trace Internal Scale SO_4 No scale Oct. 1 Insertion	5 -	Trace Internal SO_4 (Less than in Stage 1) Includes Oct. 1 and Oct. 25 Insertions	New insertions have begun to scale (slightly). No new scale in old membranes
204 SXEL	5	Trace Internal CO_3	5	No scale— Includes Oct. 1 Insertion	5	No scale— includes Oct. 1 and Oct. 25 insertions	No scaling present
204 SXEL*	51	Trace Internal CO_3	-	General light Internal SO_4 Oct. 1 Insertions not Scaled	-	General trace to light Internal SO_4 — Oct. 1 and Oct. 25 insertions not scaled	No increase in scaling

* In Main Body of Stack—Included for Comparison

TABLE 10

MEMBRANE STACK FIELD OBSERVATIONS

Main Body of Stack – (204 SXZL)

INSPECTION AFTER ZERO CHEMICALS October 1, 1980	INSPECTION AFTER ACID ONLY October 25, 1980	INSPECTION AFTER ACID & SHMP December 17, 1980	COMMENTS
STAGE 1 – Moderate to heavy loose scale CO_3	50% anion membranes light to moderate internal – SO_4	General moderate internal SO_4	Increased amount of scale
STAGE 2 – Moderate to heavy loose scale CO_3	General moderate internal SO_4	General light to moderate internal SO_4	Decreased amount of scale
STAGE 3 – General trace internal CO_3	General light to moderate internal SO_4	General trace internal SO_4	Decreased amount of scale
STAGE 4 – General trace internal CO_3	General moderate internal SO_4	General light to moderate internal SO_4 (same as Stage 2	Decreased amount of scale
STAGE 5 – General trace internal CO_3	General light internal SO_4	General light internal SO_4	No increase
STAGE 6 – General trace internal CO_3	General light internal SO_4	General trace to light SO_4	Decreased amount of scale

TABLE 11

CHEMICAL CONSUMPTION & PROJECTED COSTS

ALAMOGORDO PARAMETRIC TESTS

TEST	RECOVERY %	(Lbs. CHEMICAL/K GAL. PRODUCT) Kg CHEMICAL/M³ PRODUCT 66° Be H_2SO_4		SHMP		COST (ZK GAL. PRODUCT[1]) $/M³ PRODUCT H_2SO_4		SHMP		TOTAL COST	
Acid Feed Only											
5 Wk 1	88.7	(.113)	0.014	—	—	($.0032)	$0.0008	—	—	($.0032)	$0.0008
Wk 2	86.8[2]	(.181)	0.022	—	—	($.0051)	$0.0013	—	—	($.0051)	$0.0013
Average	87.7[2]	(.147)	0.018	—	—	($.0042	$0.0011	—	—	($.0042)	$0.0011
Acid & SHMP											
5 Wk 1	89.1	(.131)	0.016	(.0140)	0.0017	($.0037)	$0.0010	($.0042)	$0.0011	($.0079)	$0.0021
Wk 2	89.4	(.213)	0.026	(.0165)	0.0020	($.0060)	$0.0016	($.0049)	$0.0013	($.0109)	$0.0029
Average	89.3	(.172)	0.021	(.0153)	0.0018	($.0049)	$0.0013	($.0046)	$0.0012	($.0095)	$0.0025
6 Wk 1	90.0	(.213)	0.026	(.0171)	0.0020	($.0060)	$0.0016	($.0051)	$0.0013	($.0111)	$0.0029
Wk 2	90.4	(.283)	0.034	(.0112)	0.0013	($.0079)	$0.0021	($.0034)	$0.0009	($.0113)	$0.0030
Average	90.2	(.248)	0.030	(.0142)	0.0017	($.0070	$0.0043	($.0043)	$0.0011	($.0113)	$0.0030
7 Wk 1	93.1	(.116)	0.014	(.0158)	0.0019	($.0032)	$0.0008	($.0047)	$0.0012	($.0079)	$0.0021
Wk 2	94.1	(.189)	0.023	(.0147)	0.0018	($.0053)	$0.0014	($.0044)	$0.0012	($.0097)	$0.0026
Average	93.6	(.153)	0.018	(.0153)	0.0018	($.0042)	$0.0011	($.0046)	$0.0012	($.0088)	$0.0023
MEAN CHEMICAL CONSUMPTION											
Tests 5-7 Mean		(.180)	0.022	(.0149)	0.0018	($.0050)	$0.0013	($.0045)	$0.0012	($.0095)	$0.0025
σ		(.058)	0.007	(.0021	0.0003	($.0016)	$0.0004	($.0006)	$0.0002	—	—

[1]Basis: 66° Be H_2SO_4 — ($55/ton) $61.67/metric ton. SHMP — ($30/100 lbs.) $661/metric ton.
Costs from Kaiser Alamogordo Report increased by 1.137 factor derived using ratio of "Chemical Week", December 1980 & December 1979 cost indices to adjust for inflation.

[2]Test 5, Acid Feed Only, Wk 2 data is from long-term analysis, since unit was shut down before the regular sample could be obtained.

IONICS

IONICS, INCORPORATED

FOR MORE INFORMATION CALL OR WRITE:

Head Office

IONICS, INCORPORATED

65 Grove Street, Watertown, Massachusetts 02172

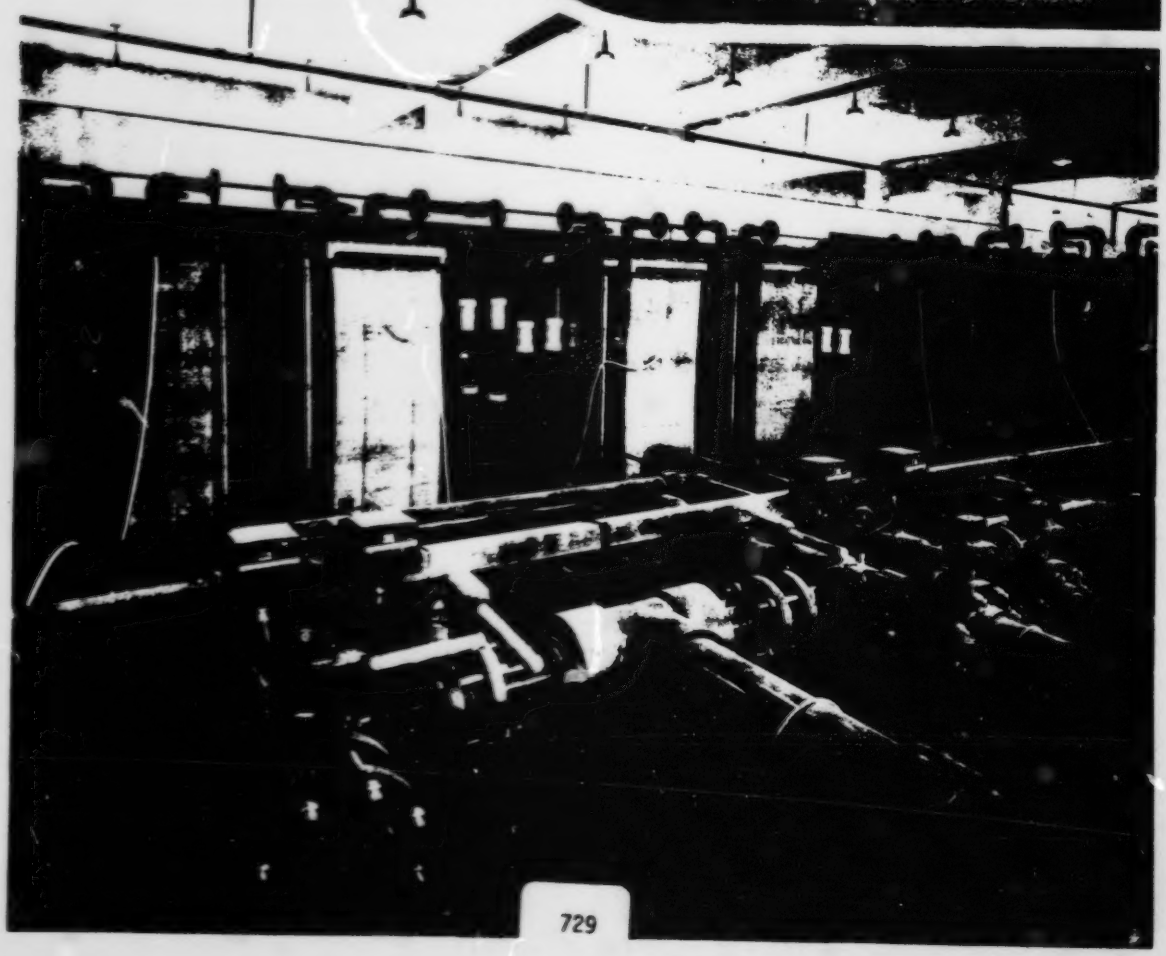
Telephone: (617) 926-2500 Telex: 922473

40-50¢/1000 gal desalt H_2O

WATER RESEARCH CAPSULE REPORT

ELECTRODIALYSIS TECHNOLOGY

Technology Transfer
Office of Water Research and Technology
U.S. Department of the Interior



SIGNIFICANCE

THE RAPIDLY increasing need for fresh water for municipal, industrial, and agricultural uses in the United States has resulted in withdrawal of fresh water at a rate of approximately 360 billion gallons per day, almost three times the rate of three decades ago. The projections for future water requirements indicate that increasing supplies of high-quality water will be required to meet the world's future needs. The problem and needs can generally be summarized as follows:

- Adequate quantities of ground or surface water are not always available when or where they are required.
- Those supplies which are available are often contaminated or are of a higher than desirable salinity.
- Recycling or reuse of water is a desirable objective to augment natural supplies and to conserve both resources and energy.

Electrodialysis is one of the major desalting processes now in use in over 600 plants throughout the world providing about 42 million gallons per day (mgd) of purified water from brackish water sources for both municipal and industrial uses. Electrodialysis installations are operating in communities, industries, hospitals, hotels, and a variety of other locations providing potable water from brackish sources.

Electrodialysis is an ion transfer process using ion selective membranes and small quantities of electrical energy to remove or concentrate dissolved salts in water. ED offers several unique advantages over classical desalting technology. Salt can be removed to specified levels rather than total salt removal, as in distillation, which often requires some mineral replacement for taste enhancement or corrosion control. Also, the electrodialysis process can adapt to changing mineral content of either feed-water supply or desired product water. Energy requirements for the electrodialysis process are in direct relation to the quantity of salts removed. Therefore, as salt removal requirements increase, so do energy costs.

Several aspects of electrodialysis such as improved components and high temperature operation are under development to expand the economic usefulness of this process to higher salinity levels including sea water desalting.

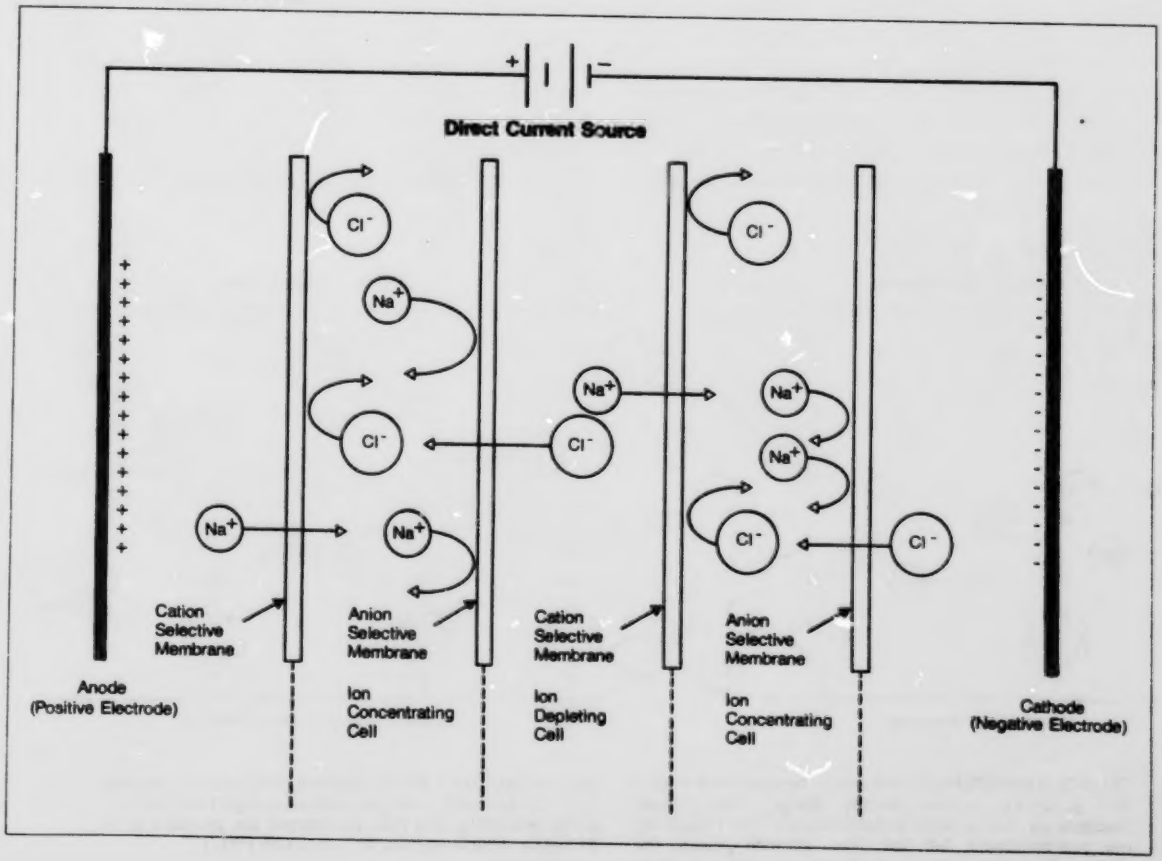
THE PROCESS

ELECTRODIALYSIS is an electro-chemical separation technology with the capability to reduce or concentrate ionized minerals or salts in water solution. The type of energy used to perform the separation process is direct current electricity. The separation media are two types of plastic sheets, called membranes, which have the capability of selectively transferring either positively or negatively charged particles, called ions, in solution. Ions are electrically charged atoms or chemical groups.

Commercial units consist of at least one pair of electrodes and several hundred "cell pairs" of membranes and water flow spacers to achieve the required water production rate of the system. A single cell pair consists of four elements as shown in Figure 1:

- Cation selective membrane
- Ion depleting cell
- Anion selective membrane
- Ion concentrating cell

FIGURE 1.
BASIC ELECTRODIALYSIS SYSTEM



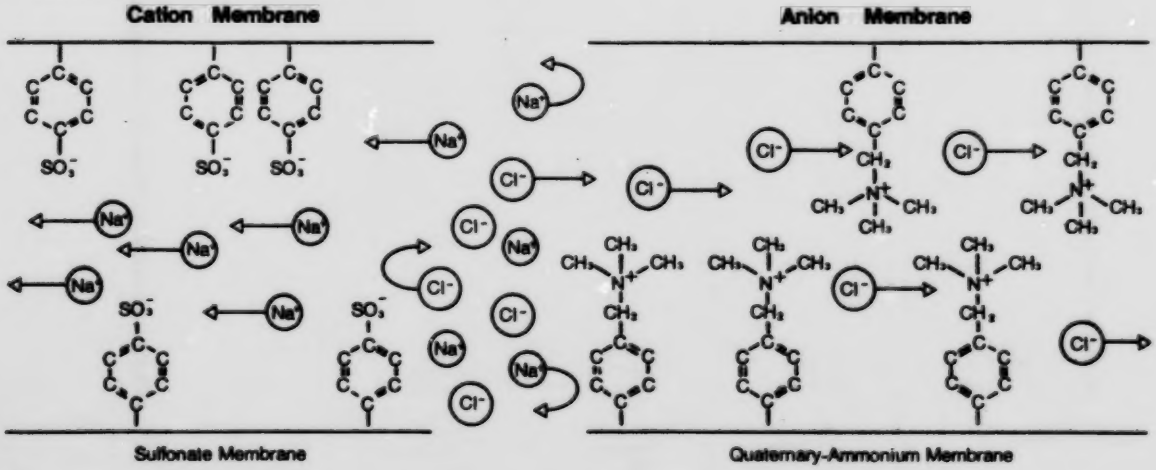
With multiple membranes and water passages located between a pair of electrodes it can be seen that alternating passages contain ion concentrating or ion depleting solution. The two flow paths are isolated and the ED process operates with a continuous flow of water through each cell. The reduction in concentration of ions in the depletion passage is a direct function of the amount of direct electric current applied and the flow rate of the water through the cell.

The electrodialysis membranes are designated as anion permeable (negative ion transfer), or cation permeable (positive ion transfer). Typical anions are: chloride, sulfate, nitrate, and bicarbonate. Cations include: sodium, calcium, and magnesium. The anion permeable membrane is an inert organic molecular structure having fixed positively charged groups in place in the membrane. Normally, this is a quaternary amine type of group. The structure of the cation permeable membrane is similar except that a fixed negative charge is in place such as a sulfonate group. Under the driving force of an impressed direct current electrical field, positively charged cations will move in the direction of the negative electrode (cathode) until they are repelled by an anion membrane. Negatively charged anions will move toward the positive electrode (anode) until repelled by a cation membrane. Ions in solution of positive charge will electrically transfer through the cation membrane by means of the fixed negative charge groups. In like manner, negative ions will transfer through the anion membrane by means of the fixed positive charge groups. Negative ions in solution will be repelled by the negative fixed charges of the cation membrane with the opposite case being true for the anion membrane.

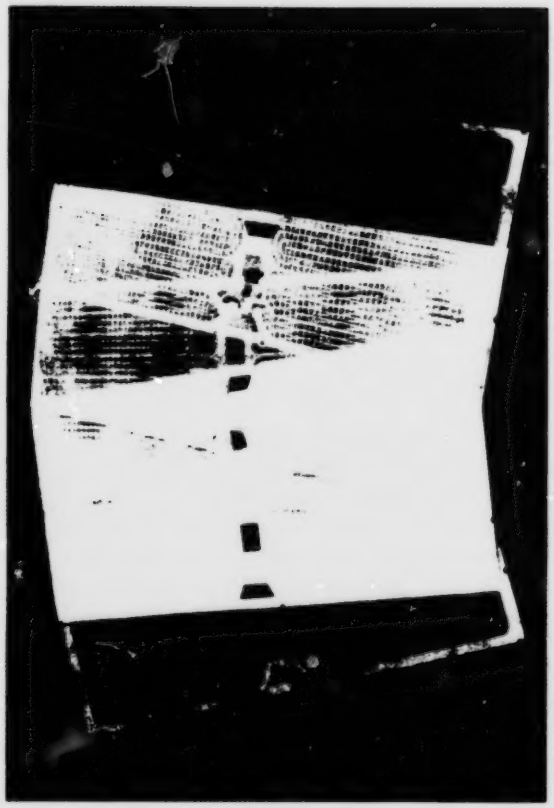
An electro-chemical membrane cell can be constructed to remove and concentrate ions in water passages between membranes utilizing the selective transfer and rejection functions of the membranes along with a direct electric current as shown in detail in Figure 2. Water will exit from an electrodialysis cell, called a membrane stack, as two streams: a purified stream and a concentrate stream. In water desalting applications, the purified stream is the product while the concentrate goes to waste. The ratio of product to waste is normally controlled through concentrate recycle.

The removal of minerals from water by the electro-

FIGURE 2.
SELECTIVE MEMBRANE STRUCTURE



CHARGED MEMBRANES discriminate between ions in solution according to their electric charge. Two charged membranes are shown schematically. The negatively charged membrane (left) has fixed sulfonate groups. The sulfonate membrane allows positive ions, such as sodium (Na^+), to pass, but it blocks negative ions, such as chloride (Cl^-). The positively charged membrane (right) has the opposite selectivity. The positive charges are provided by a derivative of the quaternary ammonium ion (NH_4^+).



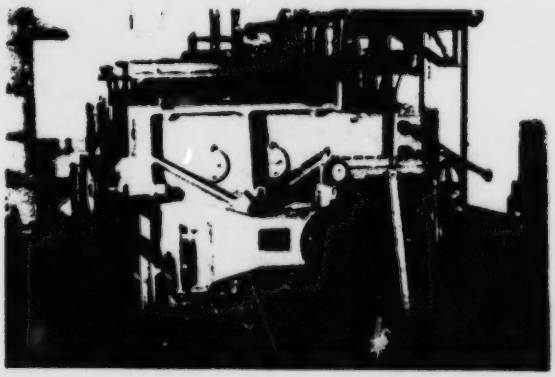
dialysis process is a function of the amount of electric current applied. The process becomes more efficent with increasing temperature up to the present commercial limit of about 110°–160°F. Process efficiency is enhanced by hydraulic turbulence in the water passage areas to aid in the transfer of ions. Process inefficiencies can be caused by scaling or fouling of membrane surfaces. Membrane efficiency also depends on the construction and materials used to manufacture the membrane since there are many different types of membranes for differing applications.

Addition of chemicals, such as acid, to the membrane stack may be required to avoid fouling of the membrane surfaces. Chemicals may also be added to improve stack operation and efficiency. This is accomplished by increasing the electrical conductivity of the water which reduces power requirements.

A special technique called polarity reversal has been developed to overcome membrane scaling and fouling problems without the addition of acids or other chemicals. This process reverses the electrical polarity of the electrodes three or four times per hour. At the same time, automatic valves reverse stream flow so that the depleting and concentrating flow paths are interchanged. This reversal causes ions to flow in the opposite direction breaking up scale forming concentrate layers at membrane surfaces. Colloids carrying electrical charges are also removed from the membrane and carried off in the waste stream. Most of the electrodialysis systems installed today use the polarity reversal system.

Certain materials, when present in the feedwater, should be removed by pretreatment. Iron or hydrogen sulfide above 0.3 ppm, manganese above 0.1 ppm, and free chlorine should be avoided. These elements along with turbidity in excess of 2 JTU are normally controlled by means of standard aeration, filtration or ion exchange techniques. These limitations apply to water desalting and their control are generally essential to maintain optimum operation and cost performance.

In food processing and chemical applications of the electrodialysis process, special membrane considerations may be required. The application of electrodialysis for industrial process use, other than water purification, should be evaluated on a case by case basis.



PERFORMANCE

DESALTING of brackish water at ambient temperature is the main commercial application of the electrodialysis process. Results of operation of two electrodialysis plants, one a 3 MGD standard electrodialysis plant and the other a 100,000 GPD electrodialysis polarity reversal plant, now operating in the United States are described in this section.

Standard Electrodialysis Plant

FOSS RESERVOIR in western Oklahoma had been idle for ten years because of the high mineral content of the impounded water. High concentrations of calcium and magnesium sulfates made this water too highly mineralized for practical domestic use. Bids were taken by the Foss Reservoir Public Works Authority on membrane plants for the purpose of demineralization of this water. On the basis of lowest evaluated cost, a 3 MGD standard electrodialysis plant was installed.

Tables 1 through 3 show actual performance data for this plant during the first year of operation. Total solids in the feedwater was 1,960 ppm with product water reduced to a salinity of 300 ppm total dissolved solids. Pretreatment consisting of coagulation and softening for the reduction of hardness and suspended solids is used. Sulfuric acid is used to reduce the pH of the brine and electrode rinse streams to prevent precipitation in the electrodialysis stacks.

TABLE 1.
FIXED AVERAGE ANNUAL OPERATION AND MAINTENANCE COSTS—
3MGD DEMINERALIZATION PLANT—DOLLARS PER YEAR

Membrane or Replacement Element	$ 8,676
Stack or Module Parts	-
Pump Parts	-
Labor - Plant O & M	33,129
Labor - Membrane Replacement	3,071
Carbon Replacement* *	8,449
Total Fixed O & M	$53,416

* Prepared from first-year operating records of the Foss Reservoir demineralization plant.
* * Sinking Fund to be applied toward purchase of carbon when necessary.

TABLE 2.
VARIABLE PRETREATMENT QUANTITIES

	Year Total	Quantity/1000 Gallons
	1975 Actual Amount	1975 Actual Amount
Gallons Pretreated-Year	277,346,136	277,346,136
Raw Water Pumps	53,480 kwh	.1928 kwh
Lime	273,350 lb	.9856 lb
Alum	53,638 lb	.1934 lb
Polyelectrolyte	1,907 lb	.0069 lb
Sodium Aluminate	-	-
Chlorine	3,842 lb	.01255 lb
Sulfur Dioxide	96 lb	.00033 lb
Sulfuric Acid	-	-
Miscellaneous Cost	-	-
Load Factor	17.7 %	-

* Prepared from first-year operating records of the Foss Reservoir demineralization plant.

TABLE 3.
VARIABLE DEMINERALIZATION QUANTITIES

	Year Total	[illegible]
	[illegible]	[illegible]
Gallons Produced-Year	194,142,295	194,142,295
Electrical Energy	1,106,608 kwh	5.70 kwh
Wastewater	82,203,839 gal (30.0% feed)	300 gal/1000 gal. pretreated
Sulfuric Acid	88,817 lb	.45749 lb
Sodium Hex.	1,624 lb	.0084 lb
Caustic	1,210 lb	.0062 lb
Soda Ash	800 lb	.00030 lb
Filter Cartridge	$2,880	$.0360
Chlorine	2,438 lb	.01255 lb
Muriatic Acid	8,840 lb	.0027 lb.
Load Factor	17%	-

* Prepared from first-year operating records of the Foss Reservoir demineralization plant.

Electrodialysis Polarity Reversal Plant

THE ADVANTAGES of polarity reversal can best be shown by an application where both standard electrodialysis and polarity reversal systems were used. Dell City, Texas is a location where this comparison has been demonstrated. Raw well water ranges from 2,500 to 3,000 ppm total dissolved solids with a high calcium sulfate content (approximately 78% of theoretical saturation). The product water is required to have less than 500 ppm total dissolved solids for general human consumption.

Dell City water was first treated with a standard electrodialysis plant starting in 1967. This 70,000 GPD unit was operated for nine years and ultimately replaced by a 100,000 GPD electrodialysis polarity reversal unit. The standard ED plant, fed with acid and sodium hexametaphosphate, produced good water but operation and maintenance costs were high. The high calcium sulfate content of the feed-water resulted in scaling which shortened membrane life.

The electrodialysis polarity reversal system uses no chemical feed or pretreatment. Operation and maintenance costs are significantly reduced and all system parameters are close to original design levels after two and one-half years of operation.

TABLE 4.
PACKAGED DEMINERALIZATION PLANTS—TYPICAL COST RANGES (IN U.S. CENTS PER 1000 GALLONS OF PRODUCT WATER)

Conditions	Case 1	Case 2
Feed Water TDS (ppm)	1,500	3,000
Product TDS (ppm)	150	300
Operating Costs		
Electric Power (2 ¢/KWHr)	12-16	22-24
Labor (at $4.00/hr.)	3-7	3-7
Cleaning Chemicals	1	1
Totals	16-24	26-32
Maintenance Costs		
Membrane Replacement	9-12	11-14
Filter Cartridges	4	4
Misc. Parts Replacement	3-5	4-6
Labor (at $4.00/hr.)	3-7	3-7
Totals	19-28	22-31
Capital Equipment		
Cost decreases with increase in installed daily capacity:		
Typical Range: $0.55 to $2.00 / gallon of installed capacity		

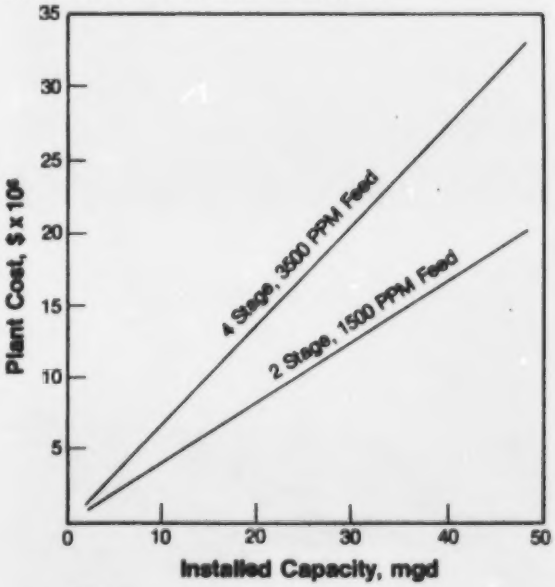
ECONOMICS

ATTRACTIVE operating and maintenance costs for desalting lower salinity brackish waters balance relatively higher capital costs for electrodialysis desalting systems. Electrodialysis generally provides the most economic treatment for waters in the range of 1000 to 3500 ppm total dissolved solids (TDS). Typically, two and one half kilowatt hours of electrical energy are required for each 1000 ppm of TDS removed from each 1000 gallons of product water. Pumping power adds about two and one half kilowatt hours per 1,000 gallons of product.

General operating cost data for ED systems are shown in Table 4. These costs are typical for medium-sized plants treating several hundred thousand gallons per day. The principal value of this table is to show the approximate proportion of costs for such factors as electric power, labor, membranes, and so forth.

Capital equipment costs vary with plant size and range from about $0.55 to $2.00 per gallon per day of installed capacity. Figure 3 shows estimated installed costs for large plant installations in the United States.

FIGURE 3.
INSTALLED COSTS FOR LARGE ED SYSTEMS



75°F
500 PPM Product.
50% NaCl Feed.
Costs are April, 1977 $ For
A Plant Installed in a Building
(Included) in the Southwest U.S.A.

APPLICATIONS

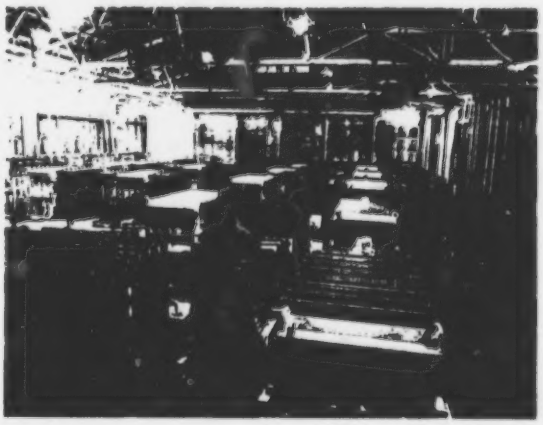
ELECTRODIALYSIS has several unique features which make it suitable for a wide variety of process applications. The most developed application is for the desalination of brackish water. It has many other excellent and effective uses in various facets of the food and chemical process industries.

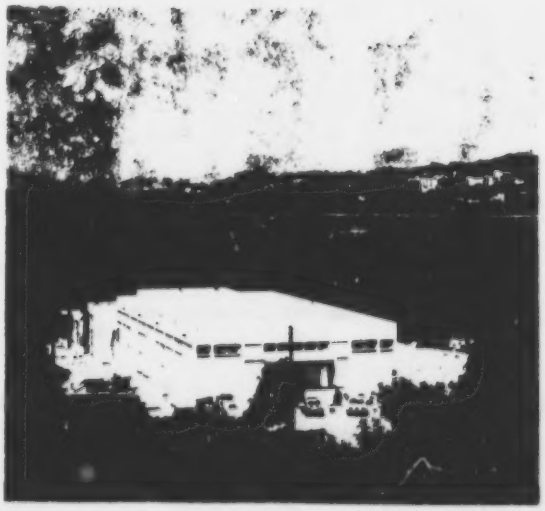
Brackish Water Desalting

AT THE PRESENT time, ED is one of the most effective processes for desalting water with mineral content in the range from 1,000 to 3,500 ppm total dissolved solids. Special considerations relative to raw water pretreatment, maintenance, water chemistry, and waste concentration can extend this range.

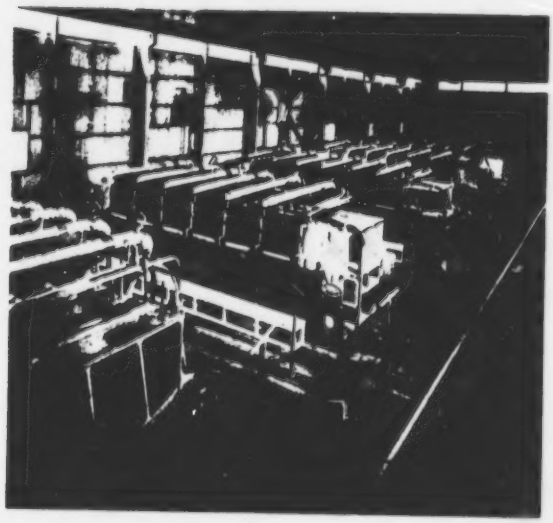
In 1970, ED desalting plants were producing approximately five million gallons per day of purified product water. By 1977, this figure had grown to 42 million gallons per day. Advances in the technology of the ED process and expanding markets have created this dramatic rise in process application. Many of the most recently installed plants have been supplied as packaged demineralization systems. These units are constructed and tested at the factory for ready installation at the field site. Equipment of this type ranging in production capacity from 15,000 to approximately 1,000,000 gallons per day can be supplied. Plants of larger sizes are custom designed to fit the specific conditions of application. Information about many of the ED brackish water desalting plants is given in the annual Desalting Plant Inventory Report published by the U.S. Department of Interior, Office of Water Research and Technology.

Large ED plants ranging from three to five million gallons per day have been installed in many parts of the world. The raw feed water for these plants ranges between 1,200 to 2,200 ppm of total dissolved solids. The product water is generally purified to less than 500 ppm total dissolved solids which is the current drinking water standard. Typical examples are the three million gallon per day electrodialysis plant at Kashima, Japan and the four million gallon per day plant on the island of Corfu, Greece.





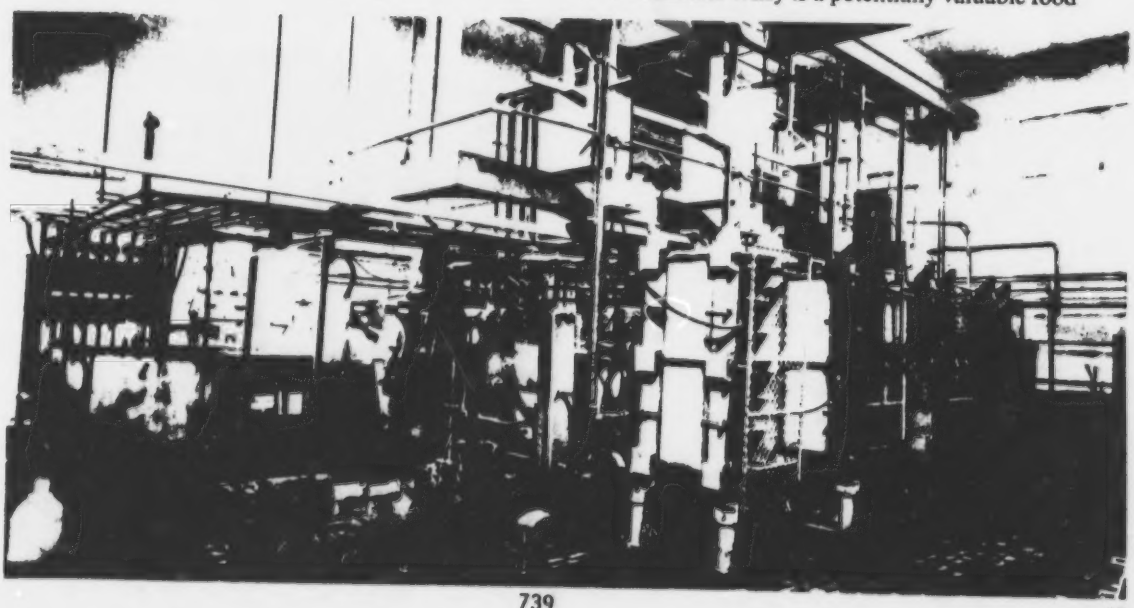
Industrial Applications



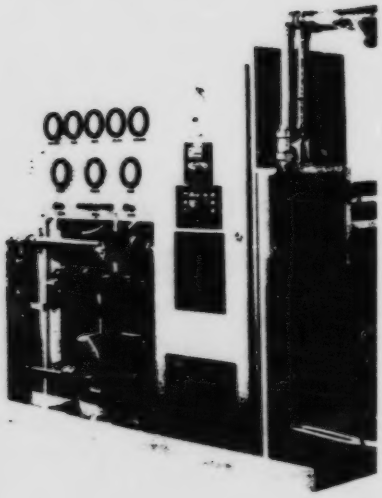
IN ADDITION TO water desalination, electrodialysis and related electromembrane processes have been used for a wide variety of industrial and chemical process applications. These range in scope from the purification of by-product food materials through preconcentration of salt prior to crystallization, to recovery of chemicals from by-product or waste solutions.

In Japan, ED is used as a preconcentration process for the recovery and purification of table salt from sea water. The process has two distinctive advantages; first, the energy requirements for ED concentration of sodium chloride from 3% to approximately 20% is less than the energy requirement for conventional evaporation; and secondly, ED selectively concentrates sodium chloride while leaving other salts for discharge in the waste stream.

Whey is produced as a by-product in the manufacture of cheese. Whey is a potentially valuable food

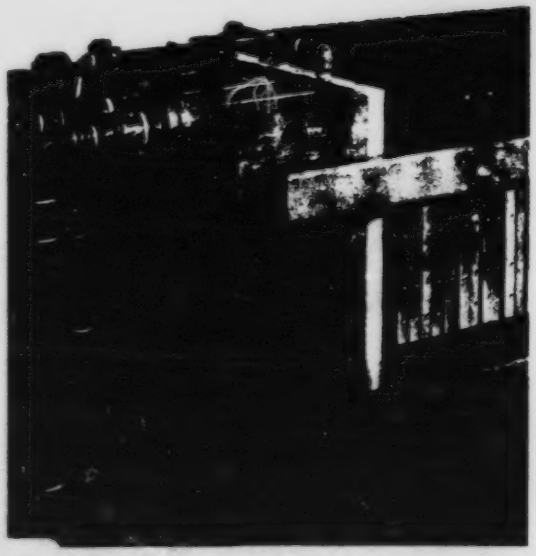


product because it contains large quantities of protein and milk sugar. The contaminant limiting its wide-spread use for human consumption is moderate amounts of dissolved salts. These salts can be effectively and economically removed by ED or the transport depletion process. Modified ED systems can also be used to remove or adjust acid concentration in certain types of whey rendering it more viable for wide-spread food product use. Partially demineralized whey products are widely used in infant foods, ice cream and frozen deserts, baked products, and, many other products where milk protein and sugar are desirable ingredients.

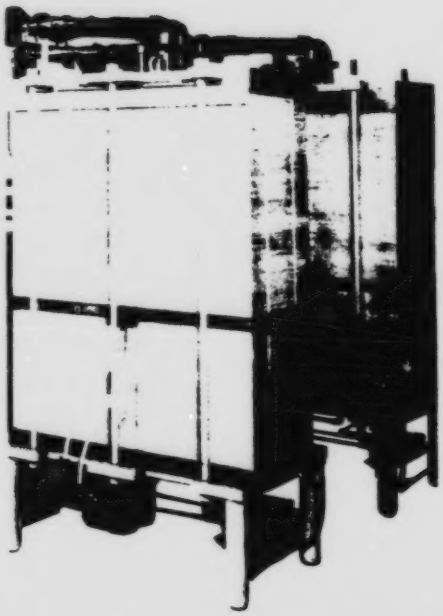


The metal finishing industries offer excellent prospects for the use of ED systems for both pollution control and recovery of otherwise lost chemicals. In most electroplating operations, the parts which have been plated with the desired metal are rinsed with high purity water as a final step. The nature of this operation is that trace quantities of the metal bearing chemicals are lost in the dilute rinse water. ED can both remove these metals which might be toxic if released to the environment as well as recover and reconcentrate them for nearly direct reuse in the electroplating bath. Although the application of electromembrane technology in this field is still in demonstration stages the prospect for broad-scale application and use is excellent.

One of the important facets of air pollution control is the removal of sulphur bearing gases from the environment. Sulphur dioxide recovery from stack gases by means of caustic soda scrubbing is commonly used. The sodium salts which are generated by this procedure can be processed in electromembrane cells to split the by-product salts that are generated reforming caustic soda for reuse and generating sulphuric acid as a by-product.

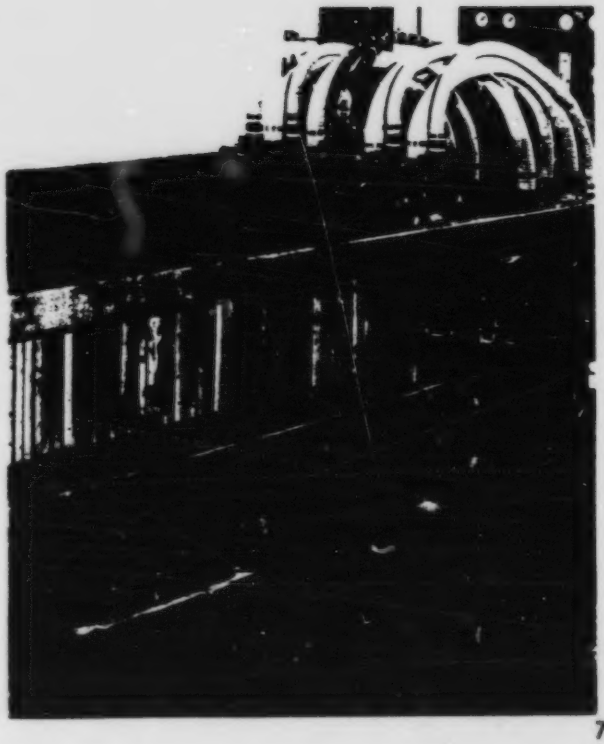


The production of high purity water for use in boilers as well as other chemical and manufacturing process applications can be enhanced with membrane technology. Electrodialysis is being applied as a pre-demineralizer for removal of the bulk of naturally occurring water minerals prior to polishing by ion exchange. ED has economic advantages over ion exchange which make it an ideal candidate for this



type of service. The cost of electrical energy for removing minerals by electrodialysis is substantially less than the cost of chemicals for the regeneration of ion exchange resins. Since ED does not require regenerant chemicals, a substantially lower quantity of waste chemicals must be discharged into the environment. Membrane systems for the removal of as much as 90% of the minerals in water prior to ion exchange demineralization are now in successful use.

Although electromembrane technology has been in commercial use for approximately 25 years, it is still in some respects at an early stage of technical development and demonstration. Future improvements in ED are expected to result in substantial reductions of electric power requirements and broader application to the chemical process industries. Development of membranes and stack components compatible with higher operating temperatures (greater than 160°F) will definitely enhance the application of ED. New membrane types with greater ion selectivity and better electrochemical properties will also expand the use of the process. As more application experience is gained, better system reliability and greater versatility with respect to process application is being developed. Because of its ability as a continuous and efficient process for the separation and removal of ionized components from solution, ED and its related electromembrane processes can be expected to solve many problems in water supply, pollution control, and chemical process fields.



ELECTRODIALYSIS DESALINATION SYSTEM For Boiler Feed Water

12,000m³/day

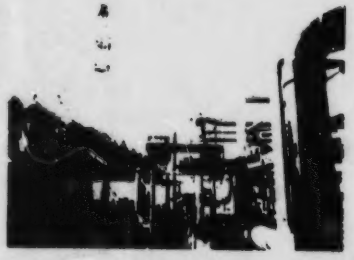
MA...
B...
HELVETIA HSE, RIETFONTEIN, GERMISTON
TEL 53-9328/9 TELEX 4-20967

ASAHI GLASS

The Kashima South Joint Power Plant provides power, steam and purified water to the huge Kashima industrial complex. Abundant water is available from nearby Lake Kasumigaura. However, the lake is often contaminated by water from the adjacent Pacific Ocean. Desalination equipment was needed to remedy this situation.

In 1975, an Asahi Glass Company electrodialysis desalination plant was installed. With a throughput of 2,000 m^3/Day, it was the largest plant of this type in Japan.

In 1978, Asahi delivered another desalination plant to the same complex, this one with a throughput of 12,000 m^3/Day. It is used to pre-treat boiler water.



ASAHI'S DESALINATION PROCESS

Figure 1 shows the principle of the electrodialysis desalination process using ion exchange membranes. Selectivity is achieved because the cation exchange membrane (CM) passes only cation (Na^+) and the anion exchange membrane (AM) passes only anion (Cl^-). Combined with the electrodialysis technique, ions are thus removed from salt-contaminated water. The process involves alignment of ion exchange membranes in individual stacks.

The desalination system was designed for optimum operational efficiency depending on the salt concentration in the raw water, product water, rate of water processing, and so on.

Table 1 shows three types of desalination systems. With the one-pass continuous type system, the rate of water processing depends on the rate of water circulation through the electrodialysis stacks. The number of stacks (in series) used depends on the water's salt concentration.

In the feed and bleed system, the rate of water processing is lower than the rate of water circulation. There is a feedback line to return some of the dialysed water to the raw water feed line.

The third system is operated in a batch mode, which is only practical for a small-scale operation. The Kashima South Joint Power Plant requires desalination from 800 to 160 ppm in a chloride ion concentration, at a rate of 12,000 m^3/Day. Therefore, the feed and bleed type of system is utilized.

Figure 1: Principle of the multi-cell electrodialysis process

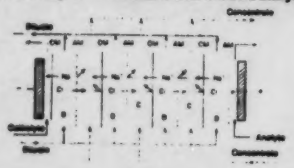


Table 1: Versions of the electrodialysis desalination system

Item / Version	Batch system	Feed and bleed system	One-pass continuous system
Flow chart	Circulation; Filter water; Desalinated water	Desalinated water; Raw feed water	Raw water to sequentially passed across the electrodialysers in cascade connection. (Ratio of feed water = Ratio of circulation water through tank.)
	The whole volume of solution in tank is replaced after completion of the desalination.	Desalinated water is removed from the system at the same concept rate as raw water is fed to the system. (Rate of feed water < Rate of circulation water.)	
Production capacity	Suitable for small scale plant	Suitable for medium to large scale plant	Suitable for large scale plant
Degree of desalination	High desalination rate	Lower efficiency with large desalination rate	High efficiency through larger number of stacks required in series with larger desalination rate
Tank capacity	Large	Small	Small
Pump capacity	Large	Small	Small (adjusted to the actual size of the system)
Connection to other processes	Intermittent	Continuous	Continuous
Operational condition	Substantial change from large to small current in stack	Constant	Constant

OUTLINE OF THE PROCESS

Figure 2 is a flowsheet of the electrodialysis desalination process. The primary filtrate obtained by passing raw water through an existing pretreatment unit, is treated through a fully-automatic backwash-type and filter unit, and then, it passes through a cartridge-type safety filter unit to remove suspended contaminants.

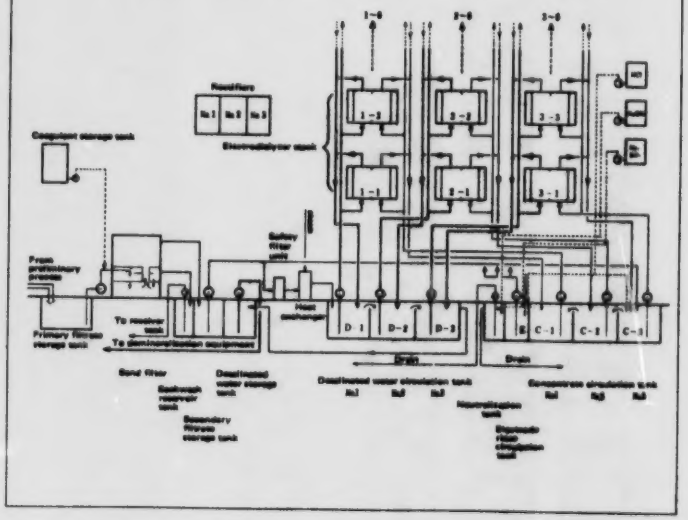
The secondary filtrate thus produced is fed to the first-stage electrodialysis stacks via the first-stage desalinated water circulation tank. After partial desalination, it is fed to the second-stage electrodialysis stacks. After this, it passes through the third-stage electrodialysis stacks for continuous desalination.

When the processed water reaches the desired desalination in the desalinated water storage tank, it is fed to the water demineralization equipment. The feed rate to the equipment is automatically controlled, depending on consumption of the demineralized water.

This system is designed in three electrodialysis stages, each comprising six parallel electrodialysis stacks for continuous desalination to an arbitrary conductivity level. The system may be partially operated – a single stage, for example.

The secondary filtrate is warmed to above 25°C for more efficient desalination and is partially fed to the stacks as the concentrate for circulation. In this process, pH adjustments can be made, if necessary, by adding a small volume of hydrochloric acid. The secondary filtrate is also partially fed to the electrode rinse circulation tank. After pH adjustments and addition of a small quantity of reducing agent, it is circulated through the electrode compartments. A small drain from the electrode compartments is neutralized, if necessary, and then put into disposal.

Figure 2: Flowsheet of an electrodialysis desalination process plant installed at the Kashima South Joint Power Plant



ION EXCHANGE MEMBRANES AND ELECTRODIALYZER STACKS

1. Ion exchange membrane "Selemion"

The electrodialysis plant mentioned above uses the ion exchange membranes "Selemion CMV" and "Selemion AMV". The following table specifies the properties of these membranes.

Membrane type	Strongly acidic cation permeable membrane (Na^+-type)	Strongly basic anion permeable membrane (Cl^--type)
Thickness (mm)	0.11 ~ 0.15	0.11 ~ 0.15
Bursting strength (kg/cm²)	3 ~ 5	3 ~ 5
Specific resistance (Ω-cm)	180~240	170 ~ 230
Resistance per Unit Area (Ω-cm²)	2.0 ~ 3.5	2.0 ~ 3.5
Transport No. T-Na / T-Cl	0.91 <	0.93 <

2. Electrodialyzer stacks

The electrodialyzer stacks are the up-to-date "DW Series" specifically designed for water production.

	DW-III	DW-IV
Size of fitted membrane	86 x 112 cm	112 x 112 cm
Effective membrane area	0.423 m²	0.918 m²
Standard number of fitted membrane pairs	200 pairs	300 pairs
Electrode material	Ti-Pt plate	Ti-Pt plate

FEATURES OF THE ELECTRODIALYSIS PROCESS

This process is the most suitable desalination of water of lower salt concentration, such as the industrial water available at the Kashima Industrial Complex. The reasons for this are:

1. The recovery rate of water is so high that the loss of raw water is usually less than 10%.
2. The salt concentration in the desalinated water may be arbitrarily adjusted while being able to cope with rises of the salt concentration in raw water.
3. Comparatively simple pre-treatment.
4. Installation and running costs are cheap for desalination of raw water with a salt concentration ranging from hundreds to thousands ppm.
5. Available at high temperatures.
6. The water demineralization system can be loaded less often, resulting in lower resin reconditioning costs.
7. Asahi's inexpensive ion exchange membranes have a high reputation worldwide for quality and are readily available in any quantity.

Because of these features, the electrodialysis process will find wider applications in the future: preliminary desalination of feed water before it passes to the demineralization equipment for boiler water production, desalination of flush or waste cooling water, production of drinking water from underground or sea water by desalination.

SPECIFICATIONS OF ELECTRODIALYSIS DESALINATION SYSTEM

Basic requirements for the design

1. Quality of the raw feed water:

The primary filtrate water from the existing electrolytically formed aluminum hydroxide injection coagulation filter unit may be fed to this system.

- Chloride ion concentration: 800 ppm
- Turbidity: Less than 1 ppm
- COD: Less than 5 ppm
- pH: Approx. 7
- Temperature: 15 to 30°C

2. Quality and output of the desalinated water:

- Chloride ion concentration: Less than 100 ppm
- Output of the desalinated water: 12,000 m³/Day

3. Type of desalination system:

Feed and bleed system with 3 stages of electrodialysis, each comprising 8 stacks in parallel.

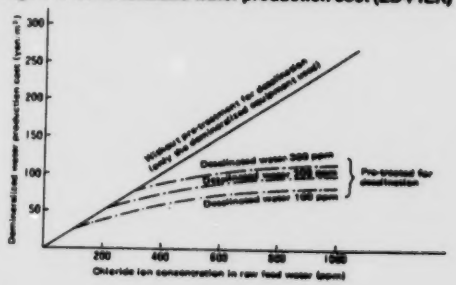
4. Hardware specifications:

- Filter assembly - 1 full automatic backwash-type sand filter unit
  - 1 safety filter unit
- Warming device - 1 unit
- Desalination unit - 18 electrodialyzer stacks of Model DW-IV (400) with 7,344 pairs of ion exchange membranes CMV/AMV and a set of accessories, such as pumps and tanks.
- Mode of operation - full automatic
- Electric facilities - 3 thyristor rectifier units
  - 1 control center
- Drain-neutralization facilities - 1 set

RUNNING COST OF THE DESALINATION PROCESS

Figure 3 gives a few examples of the curve that may be used to calculate the running cost of the desalination process, depending on different chloride ion concentrations in the raw feed water. As indicated in this figure, higher chloride ion concentrations in the raw feed water justify combined use of the electrodialysis desalination system since running cost is lower than only using the water demineralization equipment.

Figure 3: Demineralized water production cost (ED+IER)



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ELECTRODIALYSIS USED FOR DESALINATION OF WASTE WATER IN AN ESCOM POWER STATION

J. MELZER* and D. VAN DEVENTER**, Escom

Paper to be presented at Symposium on Desalination : New Developments and Industrial Application CSIR Conference Centre, Pretoria 27 October 1983

The concentration of cooling water blow-down, with the aim to reduce its volume to achieve "zero liquid discharge" from the power station, has been tested in an electrodialysis pilot plant and the results are reported. Experimental data such as water recovery, desalting ratio, electrical consumption, calcium sulphate saturation, feed water pretreatment, utilization of chemicals, and other operational and maintenance aspects are discussed. The economical evaluation of a full-size electrodyalisis plant for a 3 600 MW power station is presented.

1. INTRODUCTION

Escom is implementing the concept of "zero liquid discharge" in order to avoid the outflow of pollutants from its power stations. In a coal fired power station which is operating on "wet-evaporative cooling" with a high production of cooling water blow-down, and "wet ashing" with a high absorbance capacity of water within the ash, the balance between the effluents produced and consumed is easily achievable. This is not so in a power station operating on "wet-evaporative cooling" and "dry ashing", which requires only about half the quantity of water for ash conditioning, compaction, and dust suppression. This would be the case in two of the new power stations - Tutuka and Lethabo, where the excess of effluents will have to be treated in a concentration plant in order to reduce their volume to a magnitude to suit the absorbance capacity of the ash.

Table 1 contains a simplified effluent balance for a power station with a generating capacity of 3 600 MW, operating on evaporative cooling. In the case of wet ashing, the effluent production is balanced with its consumption, whereas in the case of dry ash disposal, there is an excess of about 5 900 m^3/d of effluents.

Different technologies for the concentration of the effluents have been considered, including evaporation, reverse osmosis and electrodialysis. This paper will deal with electrodialysis only.

From Table 1 it appears that the excess of effluents of 6 910 m^3/d can be related completely to the cooling water blow down. Fortunately enough, the feed to the ED plant can be supplied from the cooling water side-stream treatment plant. This is a conventional plant within Escom power stations and is treating a partial flow of the circulating cooling water in a lime process for partial dealkalization and softening of the water which is afterwards recarbonized by using CO_2 containing stack gases.

A simplified flow diagram containing the integration of the effluent concentration plant with the cooling water system and the side-stream treatment is given in Figure 1.

2. ELECTRODIALYSIS (ED) PILOT PLANTS AT GROOTVLEI POWER STATION

Two pilot plants have been operated at the Grootvlei Power Station in order to test the treatability of cooling tower blow-down in the ED process, the operational parameters and plant performance, the pretreatment requirements and the costing aspects. The ED pilot plants were one of U.S. Ionics and the other one of the Japanese Asahi Glass companies. The last one has been commissioned only in August 1983 and conclusive results will be achieved later this year.

The Ionics ED plant consists of two units which will be named here I-2 and I-130, with 2 m^3/d and 130 m^3/d respectively of product water flow-rate under specified operating con''tions. This project of

treatment of the cooling water blow-down with the two Ionics ED pilot units has been carried out jointly with the Water Research Commission. Unit I-2 has been commissioned in July 1982 and has been in operation until 25 May 1983, for a total of 4 785 hours. It has been operated first as an independent unit in order to establish operational parameters for the full size concentration plant. After that it operated as a second stage ED unit being fed with the brine (reject) from the first stage ED, this being the I-130, in order to establish extreme values for water recovery, $CaSO_4$ saturation levels etc. The ED unit I-130 was commissioned in February 1983 and test work is still going on. Until 6 September 1983 it has been operating for a total of 4 356 hours.

When operating independently, both units, I-2 and I-130 showed similar performances and characteristics and therefore we will refer further on to I-130 as a first stage operation and to I-2 as a second stage operation.

The Ionics ED have normally vertical membrane stacks, with continuous, non recirculating, tortuous path flow, with electrical current reversal, and are named shortly EDR. Both units, I-2 and I-130 have 4 hydraulic and 2 electrical stages each.

3. PRETREATMENT

The initial pretreatment procedure was as follow:

3.1 Chlorination to a residual of 2 mg/l chlorine before the carbon filter.

3.2 In line coagulation with a dosage of 2 mg/l slightly anionic polyelectrolyte, Dow Separan NP-10.

3.3 Multimedia filtration (CPT) (sand, anthracite, garnet) for turbidity removal.

3.4 Activated carbon filtration (ACF) for dechlorination and partial organic removal.

3.5 Precision cartridge filtration.

During the initial period of operating the Unit I-2, the requirements for the pretreatment have been established and optimized. It was found that due to the side-stream treatment, satisfactory removal of suspended matter is achieved by passing the water through the multi-media filter, without the addition of polyelectrolyte. The activated carbon filter was found superfluous and has been bypassed. Initially the hypochlorite has been fed upstream of the MMF, continously, and the traces of residual free chlorine removed by the ACF, but organic fouling occurred on the membranes, and thereafter shock chlorination in the filtered water storage tank has been introduced. This was a partial improvement only and further changes in the chlorination practice might be required.

Hydrochloric acid addition has been found unnecessary when operating under normal conditions i.e. after the feed water to the EDR unit has been properly dealkalized, softened and recarbonated in the side-stream treatment plant.

Sodium-hexa-meta-phosphate (SHMP) addition has been found necessary only to the brine stream of the I-2 unit when operating as the second stage process where $CaSO_4$ saturation levels higher than 150 % are reached.

4. TEST RESULTS FOR NORMAL OPERATING CONDITIONS

Under normal operating conditions, the feed to the Unit I-130 was the product from the cooling water side-stream treatment plant and multimedia filtration and chlorination. The reject from this unit was fed to the second stage unit I-2 where SHMP was added into the brine stream. I-130 was operating on 80 % water recovery and I-2 on 50 %. The flow scheme and the water analyses of the different streams are given in Figure 2 and Table 2.

Operational data for the period 8 May 1983 to 14 May 1983 with daily average values are given in Table 3 and Figure 3. The operating

conditions might be called normal, because there was no reduction in the performance of the plant during this period, although there were significant variations in the salt content in the feed water to I-130 from 1 100 to 1 752 mg/l TDS and to I-2 from 4 171 to 7 588 mg/l TDS, as well as in the $CaSO_4$ concentration levels in both units.

5. TEST RESULTS AT HIGH $CaSO_4$ CONCENTRATIONS

Figure 4 summarises the period between 19 March 1983 to 6 April 1983 during which very high $CaSO_4$ saturation levels have been experienced in the brine stream of Unit I-130 of 200 % and up to 350 % for about seven consecutive days without any addition of antiscaleant (SHMP). No performance reduction of the plant during or after this period has been detected.

6. TEST RESULTS DURING FAULTY PRETREATMENT

During the whole month of July the pilot plant has operated on low grade feed water containing high bicarbonate alkalinity and high turbidity, because of the cooling water side-stream treatment and the recarbonation plant have been out of commission for different length of time. Consequently the feed water was untreated cooling water. A spot sample of 14 July 1983 showed an alkalinity content of 120 mg/l as $CaCO_3$ instead of about 50 mg/l. This happened more than once before, but not for so long a period. Also the suspended matter contained in the cooling water could not be filtered out sufficiently in the MMF as this has been operating without in-line flocculation, and consequently a turbidity of nearly 1.2 FTU has been monitored after the 10 micron filter, instead of one third of it. In addition to this, the MMF has been completely bypassed during 23 July 1983 to 24 July 1983 after being backwashed, due to an operators mistake.

This accumulation of mishappenings was a very fortunate occasion to test the pilot plant under prolonged adverse operating conditions. This period is summarized in Figure 5. It can be seen that the plant performance declined, the product water flow rate dropped from above

130 to less than 110 m^3/d during constant pump discharge pressure and constant water recovery ratio. Also at constant voltage applied to the stack, a decrease in the current density was monitored, in both electrical stages. Probing with voltmeter showed an increase in the voltage drop across groups of cellpairs. The above symptoms indicated a continous build-up of solids within the stack.

Three CIP-cleaning in place, have been performed during 20 to 22 July 1983, one clean each day, and after each cleaning operation which lasts less than one hour, operation was resumed. Only after the third cleaning, the performance seemed to be restored when the flow rate and the amperage started rising, but soon after, they dropped again. The conclusion was that the solids accumulated in the stack can not be removed by CIP and consequently the stack has been opened and dismantled for inspection on 4 August 1983.

Heavy scaling was evident in the first hydraulic stage. In addition, most of the membranes and spacers of the stack were covered with slime. All the components of the stack were manually cleaned, and a number of damaged membranes as well as some spacers which have been damaged during the opening of the stack, have been replaced. After the stack has been reassembled, a thourough CIP has been carried out - first with 5 % HCl and afterwards with a mixture of 5 % NaCl plus 5 % NaOH at pH of 10,2. The plant was recommissioned and after the 9 August 1983 it was found that its performance has been restored back to normal.

7. ECONOMICAL EVALUATIONS

Assuming an effluent balance as given in Table 1 and taking into consideration the test results on the EDR pilot plant, the effluent concentration plant for a 3 600 MW power station can be conceptualized as containing two stages - electrodialysis to reduce the volume to 20 %, and evaporation, to further reduce the volume to 2 % of the initial value. A schematic water and salt balance for the two concentration stages is given in Figure 6.

The economical evaluation is given in Table 4. The capital investment is R5 200 000, total operating cost is R441 000/ year. The PV-present value calculations for 30 years operation show a nett gain of R180 000. The overall cost of the recovered water is 35 cents/m^3, incidentally the same as the raw water of the same quality.

8. CONCLUSIONS

Although experimental work is still in progress, the following can be concluded in regard to the concentration of the cooling water blow-down at the Grootvlei Power Station by the EDR process.

8.1 The pretreatment of the feed water to the EDR plant as accomplished in the cooling water side-stream treatment i.e. dealkalization/softening plus recarbonation, followed by multi-media filtration and adequate chlorination, are sufficient for a continuous normal operation. No active carbon filtration is required

8.2 No addition of acid or antiscaleant to the feed or to the brine stream is required when operating at a $CaSO_4$ saturation level below 150 % in the brine stream. This corresponded to 80 % water recovery.

8.3 Feed water salt concentration might vary within broad limits in terms of TDS, as experienced - from 1 100 to 1 800 mg/l or more provided the $CaSO_4$ concentration in the brine does not exceed that saturation level.

8.4 At constant water recovery, the increase in feed salinity resulted in higher current density, hence higher current consumption per unit product volume, and in lower desalination ratio.

8.5 At higher water recovery rates and at higher saturation levels of $CaSO_4$ concentrations, antiscaleants have to be added to the brine stream. The antiscaleants tested, SHMP, Calgon Cyanomer P70 gave inconclusive results, and more work will have to be done on this.

8.6 The plant can operate satisfactory with improper pretreatment provided the upset conditions last hours and not days and consequently a CIP might be necessary to re-establish the plant performance. In case where the side-stream treatment is operating but not the recarbonation, acid addition to the brine stream might be required.

8.7 Normally CIP is required once a month on a prescheduled, preventive basis.

8.8 In case of prolonged operation with a nontreated feed water, scaling of the membrane stack occurs and this is easily identified by monitoring the reduction in the flow of water, build-up of pressure, reduction in the current density (amperage), the voltage drop through groups of cellpairs, reduction in desalting. In such cases the opening of the stack and the manual cleaning of the membranes as well as CIP have to be carried out in order to re-establish the performance characteristics of the plant.

8.9 The operating experience on the EDR plant at Grootvlei Power Station was positive enough to consider its application at the Tutuka and Lethabo Power Stations for the concentration of the cooling water blow-down.

9. ACKNOWLEDGEMENT

The autors wish to thank the Water Research Commission and the Electricity Supply Commission for permission to present this paper.

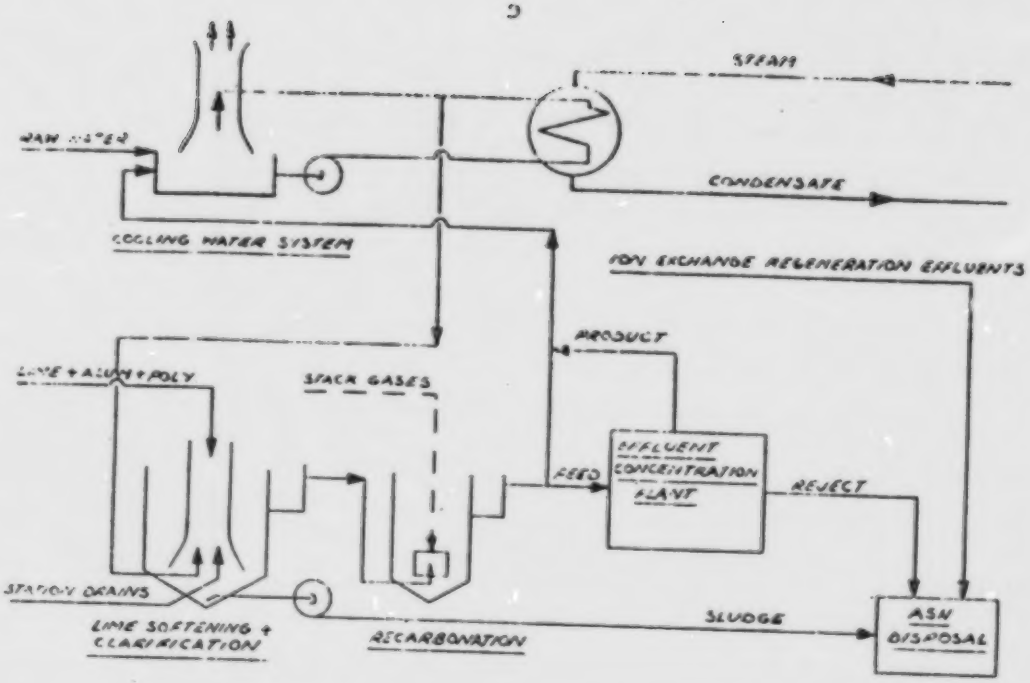

FIG. 1 COOLING WATER SIDE-STREAM TREATMENT, BLOW-DOWN CONCENTRATION AND EFFLUENT DISPOSAL

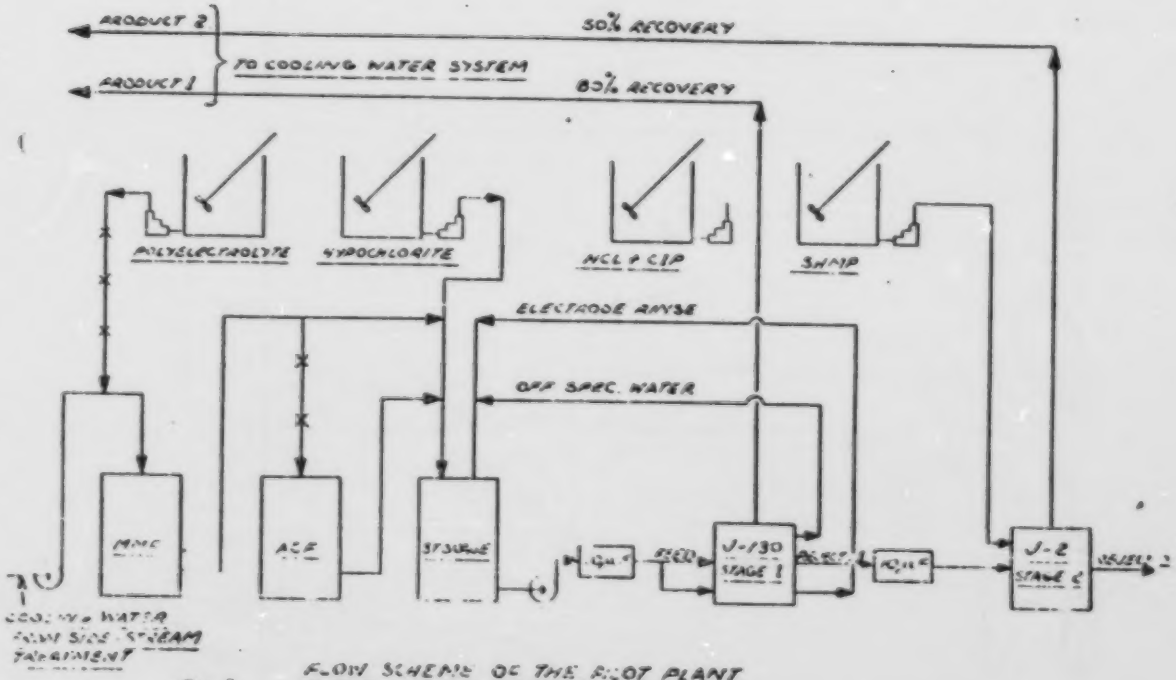

FIG. 2 FLOW SCHEME OF THE PILOT PLANT OPERATING IN TWO EDR STAGES

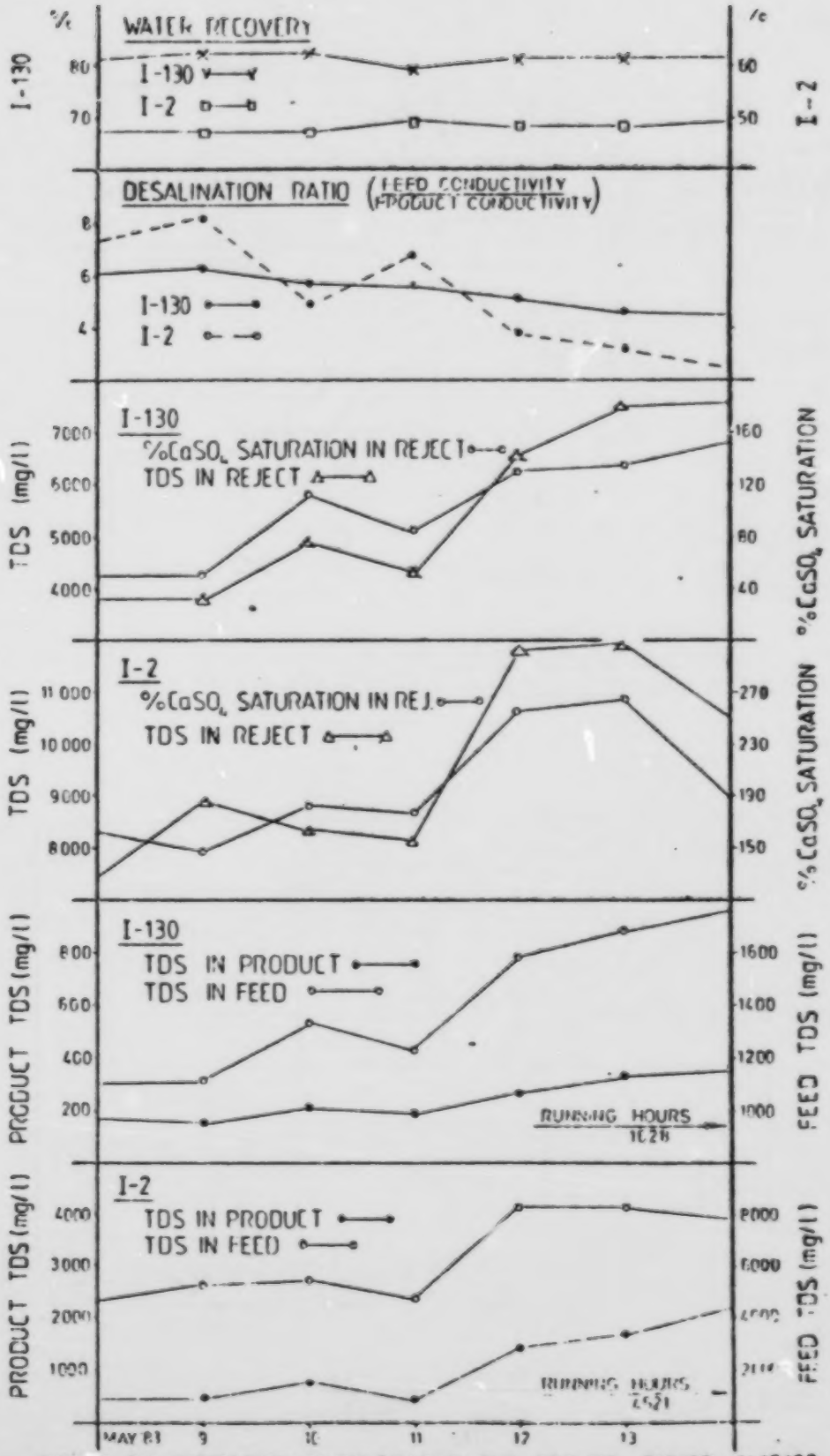

FIGURE 3: OPERATION RESULTS FOR THE PERIOD 9/5/83 - 14/5/83

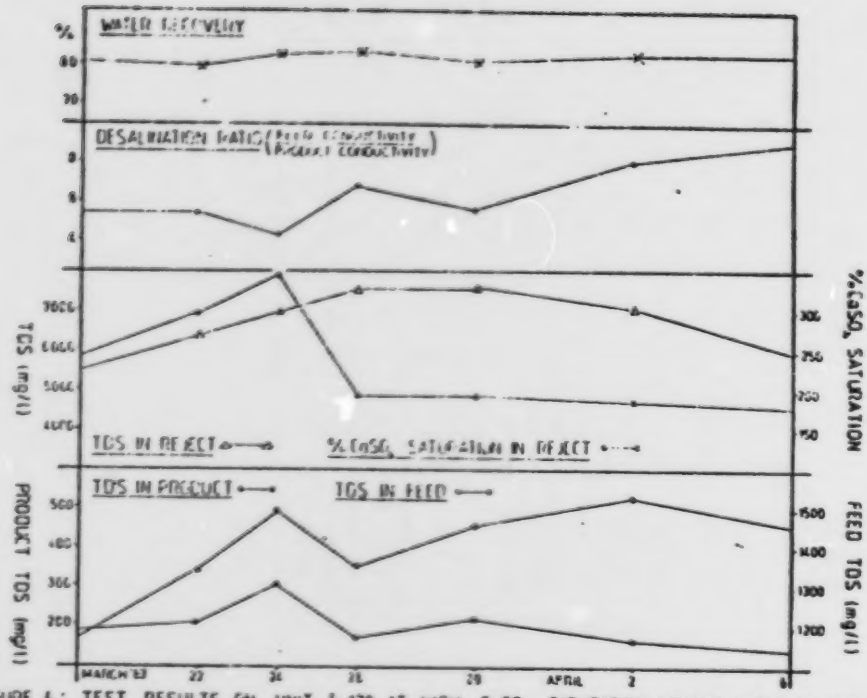

FIGURE 4: TEST RESULTS ON UNIT I-130 AT HIGH CaSO4 SATURATION LEVELS WITHOUT ANTISCALEANTS

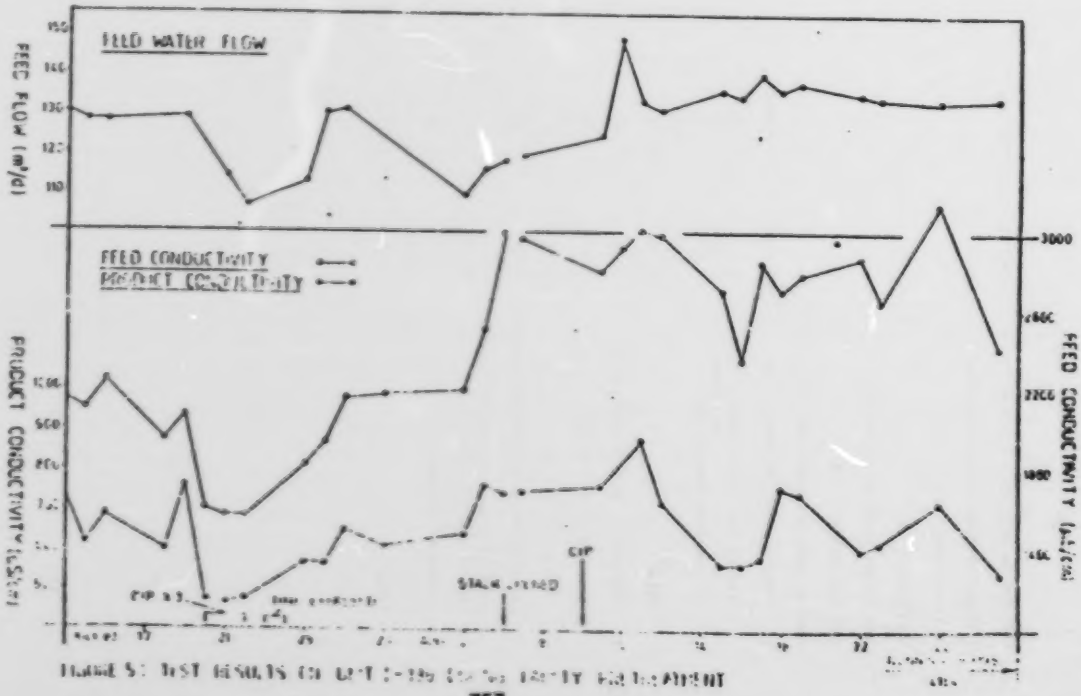

FIGURE 5: TEST RESULTS ON UNIT I-130 [illegible] PRETREATMENT

TABLE 1

EFFLUENT BALANCE FOR A 3 600 MW COAL FIRED POWER STATION OPERATING ON EVAPORATIVE COOLING AND ON "WET" OR "DRY" ASHING

Operating Conditions:

Load factor, 80 %

Coal calorific value, 24 MJ/kg

Coal ash content, 20 %

Cooling water concentration, 20 cycles.

	"WET ASHING"	"DRY ASHING"
1. PRODUCTION OF EFFLUENTS, m^3/d		
Cooling water blow down, as such	6 370	6 370
as sludge	1 500	1 500
Ion exchange regeneration	400	400
TOTAL	8 270	8 270
2. CONSUMPTION OF EFFLUENTS, m^3/d		
Absorbed in bottom ash	530	400
Absorbed in fly ash	3 170	1 580
Absorbed in water treatment sludge	380	380
Recovered in cooling water side-stream dealkalization	4 190	-
Excess of effluents	-	5 910
TOTAL	8 270	8 270

619011

TABLE 2

WATER ANALYSES OF SPOT SAMPLES OF 11 MAY 1983

COMPONENT		I-130			I-2	
		FEED	PRODUCT	REJECT	PRODUCT	REJECT
Turbidity	(F.T.U.)	0,28	0,20	0,9	0,21	1,3
Colour	(Hazen Units)	5	5	5	5	5
Total dissolved solids (mg/l)		1184	219	3760	608	6940
pH		7,3	7,0	7,3	6,9	7,3
Conductivity	uS/cm	1756	346	4124	915	7317
Total alkalinity	(mg $CaCO_3$/l)	62	26	134	31	23
Total hardness	(mg $CaCO_3$/l)	320	42	1080	124	2100
Calcium hardness	(mg $CaCO_3$/l)	252	30	870	96	1740
Magnesium hardness	(mg $CaCO_3$/l)	68	12	210	28	360
Chloride	(mg Cl/l)	116	22	360	23	725
Sulphate	(mg SO_4/l)	630	117	2234	385	3942
Sodium	(mg Na/l)	237	60	790	143	1290
Potassium	(mg K/l)	29	3	97	7	194
Silica	(mg SiO_2/l)	9	8	10	9	12
Oxygen absorbed from N/80 $KMnO_4$ after 4 hours at 27 °C (mg O_2/l)		3,5	1,4	4,0	3,8	5,9
Chemical oxygen demand (mg O_2/l)		13	4	43	31	86
Langelier index		-0,38	-1,89	+0,30	-1,62	0,84
$CaSO_4$ saturation	%			73		140

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TABLE 3

OPERATIONAL DATA WITH DAILY AVERAGE VALUES FOR THE PERIOD 8 MAY 1983 TO 14 MAY 1983

	UNIT	I-130							I-2						
		08/5/83	09/5/83	10/5/83	11/5/83	12/5/83	13/5/83	14/5/83	08/5/83	09/5/83	10/5/83	11/5/83	12/5/83	13/5/83	14/5/83
Feed conductivity	uS/cm	1 507	1 523	1 826	1 678	2 180	2 300	2 400	4 584	5 200	5 410	4 721	8 300	8 305	7 987
Feed total dissolved solids	mg/l	1 100	1 112	1 333	1 225	1 591	1 679	1 752	4 171	4 732	4 923	4 296	7 553	7 558	7 268
Product conductivity	uS/cm	251	247	324	304	434	510	550	630	640	1 130	700	2 250	2 637	3 310
Product total dissolved solids	mg/l	141	158	207	195	278	326	352	403	410	723	448	1 440	1 688	2 118
Brine conductivity	uS/cm	4 200	4 150	5 410	4 721	7 180	8 250	8 300	8 118	9 800	9 177	8 917	13 000	13 092	11 460
Brine total dissolved solids	mg/l	3 823	3 777	4 923	4 296	6 534	7 508	7 553	7 387	8 918	8 351	8 114	11 830	11 914	10 429
Desalination ratio (conduct)		6,0	6,1	5,6	5,5	5,0	4,5	4,4	7,3	8,1	4,8	6,7	3,7	3,1	2,4
Stack voltage - 1st stage	V	144	143	143	144	142	142	141	68	69	66	68	62	62	63
Stack amperage - 1st stage	A	7,2	7,1	8,5	7,0	10,8	11,4	12,2	1,5	1,9	2,0	1,7	2,0	2,6	2,5
Stack voltage - 2nd stage	V	133	132	133	134	132	132	131	62	59	55	60	50	49	50
Stack amperage - 2nd stage	A	3,0	3,1	4,4	3,7	5,8	6,6	7,1	0,8	0,9	1,1	0,8	1,5	1,6	1,5
Electrical power-stack only	KWh/d	34,5	34,2	43,3	34,1	55,2	59,8	63,6	3,6	4,4	4,6	3,9	4,2	5,7	5,6
Electrical power stack + pumps etc.	KWh/d	289	289	291	299	288	300	300	16,3	15,3	17,7	17,5	9,8	19,7	19,6
Running hour per day	h	24	24	24	24	24	24	24	24	24	24	24	24	24	24
Feed flow rate (rotameter)	m^3/d	167	162	160	166	165	168	170	4,6	4,5	5,0	4,8	3,6	4,8	6,0
Water produced (rotameter)	m^3/d	135	133	131	131	133	136	138	2,1	2,1	2,3	2,3	1,7	2,3	2,9
Water reject (rotameter)	m^3/d	32	29	29	35	32	32	32	2,5	2,4	2,6	2,6	1,9	2,6	3,2
Water recovery	%	80,8	82,1	81,9	78,9	80,6	80,9	81,2	46,5	46,5	46,9	48,6	48,3	48,2	49,2
Specific power consumption (stack)	KWh/m^3	0,27	0,27	0,33	0,28	0,41	0,44	0,46	1,67	2,08	1,97	1,68	2,45	2,45	1,93
Specific power consumption (total)	KWh/m^3	2,14	2,17	2,22	2,28	2,16	2,21	2,17	7,49	7,21	7,56	7,48	5,68	8,41	6,73
Feed water temperature	°C	28	29	29	24	30	29	32	28	27	28	23	30	29	26
Feed turbidity after uF	NTU	0,44	0,41	0,55	0,48	0,45	0,55	0,55	-	-	-	-	-	-	-
$CaSO_4$ saturation (brine)	%	50	50	113	83	129	133	148	161	148	185	176	244	264	187

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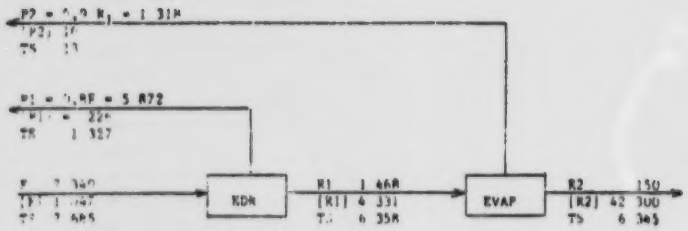

F feed water from cooling water side-stream treatment, m^3/d

[F] salt concentration in feed, TDS mg/l

TS total salt, kg/d

P1 recovered water from EDR, m^3/d

P2 recovered water from evaporation, m^3/d

R1 reject (brine) from EDR, m^3/d

R2 reject from evaporator, m^3/d

FIGURE 4 WATER AND SALT BALANCE FOR A TWO STAGE CONCENTRATION SCHEME

TABLE 4

ECONOMICAL EVALUATION OF THE EDR PLANT

CAPITAL INVESTMENT	R		5 [illegible]
OPERATING COST		%	
Chemicals (chlorination, CIP)	R	11,3	50 [illegible]
Other consumables (membranes etc.)	R	49,9	220 [illegible]
Electricity	R	11,6	51 [illegible]
Labour including maintenance	R	27,2	120 [illegible]
Total operating cost	R	100,0	441 [illegible]
Operating cost, per unit product	R/m^3		0,229
WATER CREDIT			
Recovered water quantity, with 226 mg/l TDS	m^3/d		5 87[illegible]
Recovered water quantity	m^3/y		1 926 3[illegible]
Recovered water value, at 0,35 R/m^3	R/y		[illegible]
PV PRESENT VALUE CALCULATIONS			
PV operating cost	R		1[illegible]
PV total, capital and operating cost	R		1[illegible]
PV credit for recovered water	R		1[illegible]
PV nett saving	R		180 [illegible]
Cost of recovered water, overall	R/m^3		0,34[illegible]

BASIS FOR CALCULATIONS:

1. Feed water is cooling water at 20 concentrations, after side-stream treatment, and contains 1 047 mg/l TDS.
2. EDR water recovery is 80 % and the product contains 226 mg/l TDS.
3. Cost of electricity within the power station is 1,65 c/KWh.
4. Electrical power consumption is 1,2 KWh/m^3 product for the EDR plant plus 0,4 KWh/m^3 product for the transfer of the different water streams to and from the EDR plant.
5. Cost of Vaal water, containing 226 mg/l TDS is 35 c/m^3.
6. The cost of cooling water side-stream treatment is not included.
7. PV present value calculations are based on 30 years life span of the plant, 14 % discount rate and 12 % inflation rate.
8. EDR plant is operating 24 h/d, 365 d/y at 90 % availability.
9. EDR membrane replacement is 20 % per year.

ELECTRODIALYSIS (ED) + ELECTRODIALYSIS REVERSAL (EDR)

by

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Written for presentation at
The S A Institution of Chemical Engineers Symposium

"LIMITING LIQUID DISCHARGES FROM LARGE
INDUSTRIAL FACILITIES"

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SUMMARY

Electrodialysis is a process that has been available for the demineralisation of brack and waste water streams since the early 50's. The development of polarity reversing electrodialysis in the early 70's made the process far more economically competitive owing to the reduced feed pretreatment requirements, increased water recovery rates and improved tolerance to fouling. Advances in engineering with respect to automation, materials of construction and improved ion exchange membrane characteristics allowed the process to compete industrially on a large scale during the last decade. Electrodialysis Reversal has been demonstrated as a technically viable and competitive process for the limitation of discharges from industrial complexes and is poised to become applied on an even wider scale during the 80's.

ELECTRODIALYSIS (ED) + ELECTRODIALYSIS REVERSAL (EDR)

1.0 INTRODUCTION

Despite the fact that S A engineers and chemists made a major contribution to the advancement of Electrodialysis (ED) technology during the 1950's (1) comparatively little work was done in S A since then, apart from small scale research work at the CSIR and NIWR. Technological advances of the reverse osmosis (RO) process naturally led to this process becoming widely accepted for desalting purposes and by 1974 the total installed water desalting capacity of RO overtook ED. (2)

The birth of RO and its sustained growth naturally created severe competition for the classical undirectional ED process. Under competitive pressures the leading ED firm situated in the U S A concentrated on technical innovation as a means of improving its share of the desalting market. Manual polarity reversal was known to remove scale buildup on ion exchange membrane surfaces (1). This fundamental principle was extended by full automating the reversal of polarity and the sequential changeover of concentrate and diluting streams, thus establishing the first fully symmetrical membrane reversal process - now called electrodialysis reversal (EDR) (3).

Indeed the application of this technique can be regarded as a major breakthrough for electrodialysis as it resulted in several important commercial benefits.

- Ability to operate at traditional recoveries (±75%) without any chemical feed.
- Ability to operate at high recoveries (±90%) with relatively small amounts of chemical addition.
- Longer membrane life
- Reduced pretreatment requirements
- Improved resistance to membrane fouling
- Wider range of technological applications.

Prior to examining the potential that EDR has for limiting liquid discharges from large industrial facilities it will be useful to examine briefly the principles of electrolysis, electrodialysis and electrodialysis reversal.

2.0 PRINCIPLES OF ELECTROLYSIS, ED + EDR

Most common inorganic salts when dissolved in water will dissociate into cations and anions. Figure 1A illustrates the dissociation of sodium chloride in water. In figure 1B a d.c. potential has been applied across the electrodes immersed in the solution, thereby causing the anions to move toward the positive electrode and the cations to move toward the negative electrode. This is the well known principle of electrolysis which is widely applied in the manufacture of chlorine.

2 / ...

If membranes having selective permeability to cations and anions respectively are introduced between the two electrodes to form three water-tight compartments (figure 2A), followed by the application of a d.c. current across the electrodes, then the central compartment will be demineralised (figure 2B). Na^+ ions from compartment A cannot pass through the anion membrane into compartment B and likewise Cl^- ions from compartment C cannot pass through the cation membrane into compartment B. However, both Na^+ and Cl^- ions can pass through the cation and anion membranes respectively giving rise to the demineralisation in the central compartment, and concentration in the two end compartments.

Figure 3 respresents a multicompartment unit similar in principle to the commercial ED stack. Letter 'A' designates the anion membranes, letter 'C' the cation membranes, the +ve sign the anode and the -ve sign the cathode. Clearly the principle of operation of the multicompartment cell is similar to that previously illustrated in figure 2. In the case of ED the process continues indefinitely with the diluting and concentrating compartments performing the same function for the entire life of the installation. The first slide gives a clearer picture of the process which in this particular case shows the brine recycle loop.

Shown in slide 2 is a view of the most widely used commercial membrane stack - the Ionics Mark III. Electrodialysis membrane stacks exist today designed and assembled with the membranes stacked in either the vertical or the horizontal position. Differences in both membrane thickness and spacer flow patterns exist. One configuration which has seen limited use by Japanese and European suppliers is the thin membrane (± 0,2 mm) and the "sheet flow" spacer type. The other design which has been dominant over the past decade was developed in the U S A. In this configuration the tortuous path spacer with thicker more durable membranes (± 0,5 mm) are used. The latter design achieves a uniform hydraulic flow distribution across the face of the membrane and has thus proved the more successful in a variety of desalting applications. The third slide shows an exploded view of a cell pair which consists of a cation membrane, an anion membrane and two tortuous path spacers.

In EDR, when the d.c. polarity is reversed the direction of the flow ofions also reverses. The reversal takes place at regular preset intervals which is normally between 15 and 30 minutes. The stream which was the concentrate now becomes the dilute and vice versa. Automated changeover valves ensure that the product and brine streams do not contaminate each other at reversal. After the reversal the concentrations of both compartments are changing and are not at their steady state levels. For an interval of 1-2 minutes off-spec product is either recycled or wasted.

3 / ...

In both the case of ED and RO, which are unidirectional processes, there is a tendency for constituents which are capable of forming slimes and precipitates to be deposited at the membrane solution interface. Over a period of time this can seriously affect the membrane desalting performance.

However, in the case of EDR any tendency for scale buildup will be extremely short lived and after reversal scale and film will be purged away from the surface, dramatically improving the performance. The principle of scale removal is synonomous to the reversing heat exchangers used in the cryogenic industry for removal of carbon dioxide and water scale from low temperature surfaces.

Because the EDR process has this self cleaning characteristic it has emerged as a rapid growth desalting process and is now gaining ground in the treatment of different quality waters. By the last quarter of 1982 the EDR installed or contracted capacity has grown to over 250 000 m^3/day in a period of 8 years.. EDR has been commercially competitive for desalting waters with a TDS between 250 and 12 000 ppm. Further improvements in membrane technology and cell stack design are underway to widen the range of applications for both higher and lower TDS wastes.

3.0 EXISTING APPLICATIONS

3.1 General

EDR is certainly not the panacea to every industrialist's effluent problem. However, it can go a long way in solving a variety of problems where it is usually a partial rather than a total solution to eliminating waste discharges.

When reviewing any potential applications for EDR it is important that not only the process stream in question is examined, if this is a composite of streams emanating from several sources. Often the most cost effective solution could lie in the treatment of any one or more of the separate streams rather than the overall combined stream.

3.2 Boiler Feed Water Preparation

In this regard EDR is fulfilling a useful role for the predemineralisation of boiler feed water.

Demineraliser wastes from conventional ion exchange plants are not only composed of a concentration of the salts that were in the original feed, but in addition contain the salts of the neutralised regeneration chemicals which are often 3-5 times greater by weight than the original salts in the feed.

4 / ...

By introducing EDR as a primary demineralising step the effluent salt load will be reduced significantly. However, on waters with a TDS higher that 300 ppm the capital and operating costs of the EDR plant can be justified on the savings in regeneration chemicals alone, without inclusion of credits arising from reduced mineral discharge. This is particularly true when considering new demineralisation facilities or the extension of existing facilities which have become a bottleneck as a result of the deterioration of the feedwater quality or increased demand.

3.3 Whey Desalination and Lactose Removal

The growth of the cheese manufacturing industry and the progressive tightening of restrictions on the disposal of whey, motivated dairies to seek new outlets for products which could be recovered from whey. Owing to the nutritional value of whey it can be used as animal feed for limited local markets. Normally transport costs prohibit its consumption further afield and excess whey was discarded.

Whey is a dilute solution containing salt, lactose, protein and fat. The salt (or ash as it is commonly referred to) can be removed using an electrodialysis stack similar to that used in water desalting. This salt removal is only a partial solution to recovering and producing deashed whey. The total process normally involves solids concentration, pH adjustment and clarification, electrodialysis followed by spray drying to produce a free flowing saleable product of high nutritional value. Deashed whey is used as a major component in infant food formulaes.

3.4 Groundwater restoration for In-situ Mining

In the USA where in-situ mining of uranium has been practised, increased emphasis has been placed on improving water conservation as well as restoration of aquifier waters. A commercial sized EDR plant has been used for pilot restoration work (8) where it has proven its ability to treat waters with both high calcium bicarbonate and sulphate levels in the feed. Despite relatively high levels of both these components in the feed and the supersaturation of calcium sulphate in the brine loop, scaling was minimised due to polarity reversal while cleaning was easily and effectively done using a standard clean in place circuit.

5 / ...

General data taken from the report by Garling (8) (figure 5) shows the demineralisation potential of EDR for this typical mine water. Following the successful demonstration for this application, a further commercial sized plant of 1000 m^3/day has been installed for aquifier restoration in Texas.

3.5 Calcium Sulphate Concentration above supersaturation

At the same time work was undertaken at the OWRT test facility in New Mexico where a commercial sized EDR plant, the Aquamite X was used to desalt a high $CaSO_4$ bearing brine stream.

It has been demonstrated that EDR could be used without any chemical addition up to the point where scaling occurred, at a $CaSO_4$ saturation of 230% and a Langelier Index of 2.45. Above these limits it was found necessary to introduce sodium hexameta phosphate (SHMP) and acid into the brine stream. Trouble free operation has been shown over a 5000 hour test period with water recoveries of up to 93,5% and $CaSO_4$ saturation levels of 440%.

The commercial possibilities for the treatment of S A minewater is a natural extension of the success already gained. This applies to all underground waters whether these be from coal, gold or uranium and where the waters are notably high in sulphates due to the oxidation of pyrite. Undoubtedly careful attention needs to be given to the pretreatment of these waters prior to demineralising with EDR.

3.6 Desalting of Sewage Effluent

In September 1982 the first commercial sized EDR plant for desalting water arising from the Municipal Sewage Treatment plant was commissioned at Dubai. The effluent is blended with city water in the first of four maturation ponds, thus reducing the oxidation requirements at the inlet of the subsequent chlorination stage. After chlorination, carbon slurry and ferric sulphate is added upstream of two clarifiers. The overflow from the clarifiers passes through two filters in series containing sand and activated carbon before reaching the EDR feed tank. This is certainly the most complex of any pretreatment system used in conjunction with EDR.

The feedwater with a TDS in excess of 2000 ppm is reduced to a salinity of approximately 600 ppm. Longer term operating results over varying load conditions will be compiled in the future. Start up analysis is shown in figure 6.

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4.0 POTENTIAL APPLICATIONS

To cover all potential applications for EDR and to give a broad outline of each is beyond the scope of this paper. However, I will mention only a few and would gladly answer questions on these or other related subjects.

a) Cooling Tower Blowdown (7)
b) Boiler Blowdown
c) Plating Bath effluents (5)
d) Concentration of metallurgical plant effluents to produce a concentrate suitable for recovery and a product water suitable for recycle (5)
e) Concentrating dilute saline streams.
f) Reduce nitrogen (NH_4) loading from fertilizer factories (6)
g) Removal of organic acids.

The example given above demonstrate the wide variety ofpotential applications for ED and EDR. A good account is given in the references (5) and (6) by Messrs Schoeman and Botha.

5.0 LIMITATIONS OF EDR

Many industrial effluents are unique and may contain components which could reduce the efficiency of EDR. It is recommended that the Iron (Fe^{++}) and Manganese Mn^{++}) levels be kept below 0,3 and 0,1 ppm respectively. Aromatic based anion resins require a zero residual chlorine level although aliphatic resins will operate over long periods at chlorine levels of 0,3 ppm and can be shock chlorinated at levels up to 10 ppm for control of biological growth.

6.0 CONCLUSIONS

EDR minimises slime or inorganic salt scale by utilising polarity reversal and where unpredicted scaling cannot be controlled or removed by the "clean-in-place" circuit the stacks may be disassembled for individual cleaning of the membranes. As EDR is suitable for concentrating salts from dilute solutions it can be used to reduce effluent volumes prior to final disposal or it may be used to recover both water and potentially valuable materials.

Electrodialysis Reversal has been demonstrated as a technically viable and competitive process for the limitation of discharges from industrial complexes and is poised to become applied on an even wider scale during the '80s.

7 / ...

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PRINCIPLE OF ELECTROLYSIS

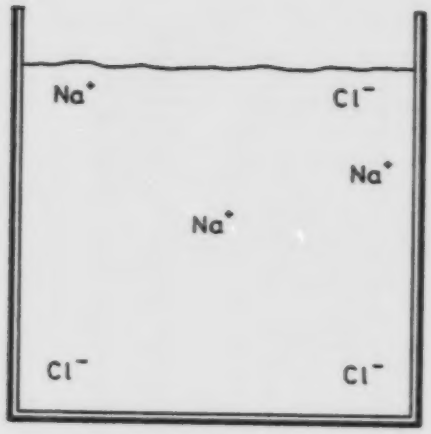


FIGURE 1A.

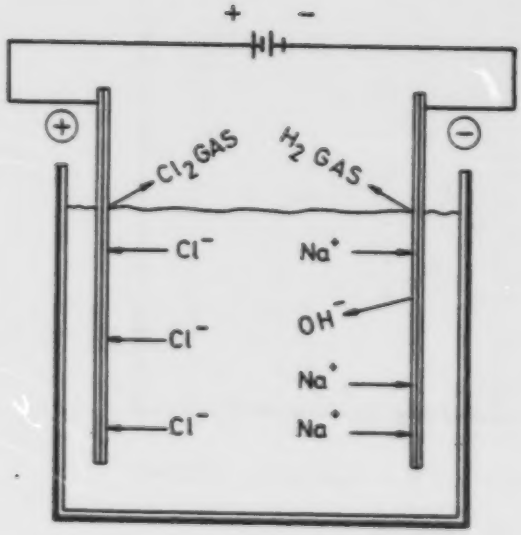


FIGURE 1B.

PRINCIPLE OF ELECTRODIALYSIS

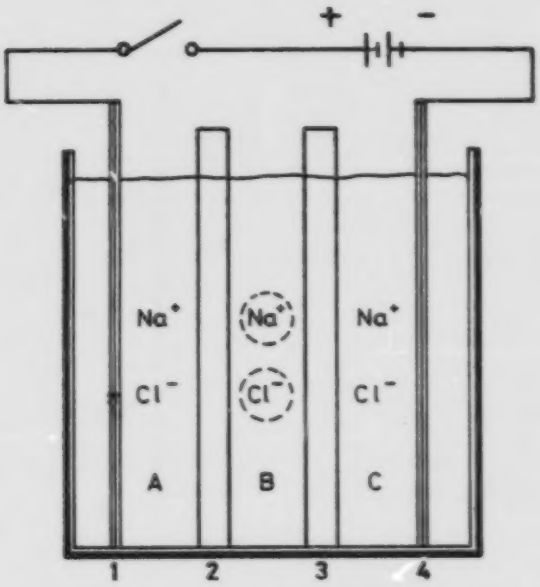


FIGURE 2A (NO CURRENT FLOW)

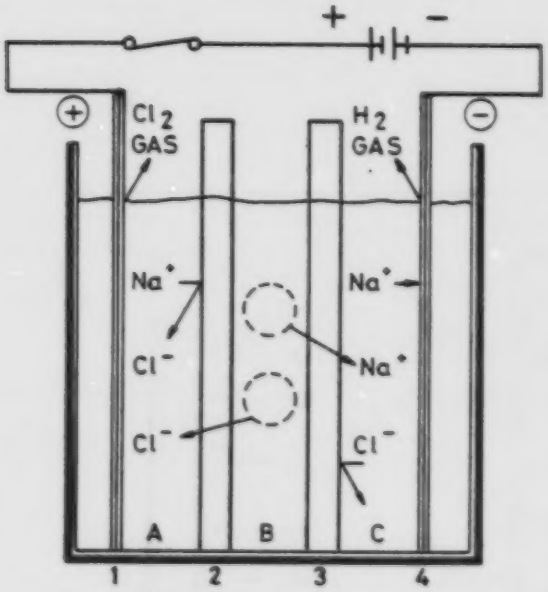
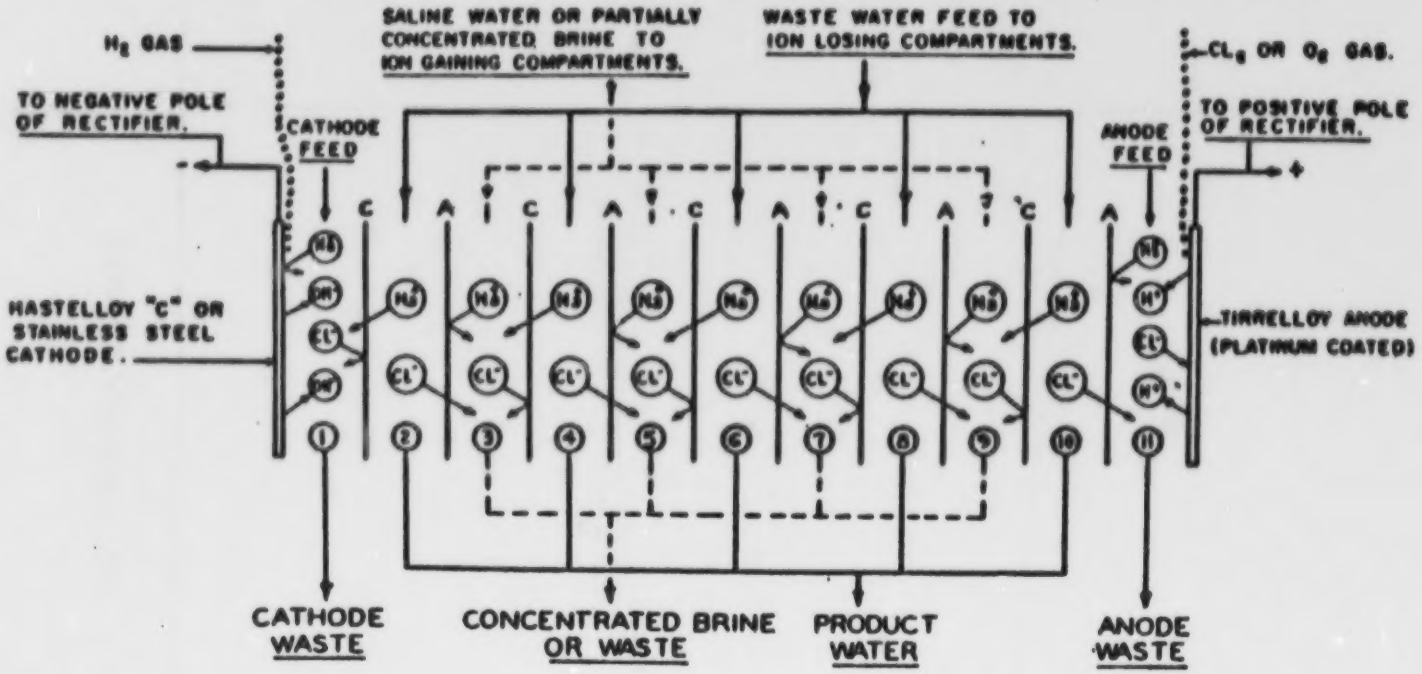


FIGURE 2B (CURRENT FLOW)

1 ANODE
2 ANION MEMBRANE
3 CATION MEMBRANE
4 CATHODE

Figure 3

BASIC ION AND WATER FLOW IN ELECTRIC MEMBRANE STACK



LEGEND:

C---CATION MEMBRANE

A---ANION MEMBRANE

(7)--COMPARTMENT NUMBER (SEE TEXT)

(Na^+)--ANY CATION (POSITIVE ION) LIKE SODIUM.

(CL^-)--ANY ANION (NEGATIVE ION) LIKE CHLORIDE.

EDR - X + Y STREAMS

FIG 4

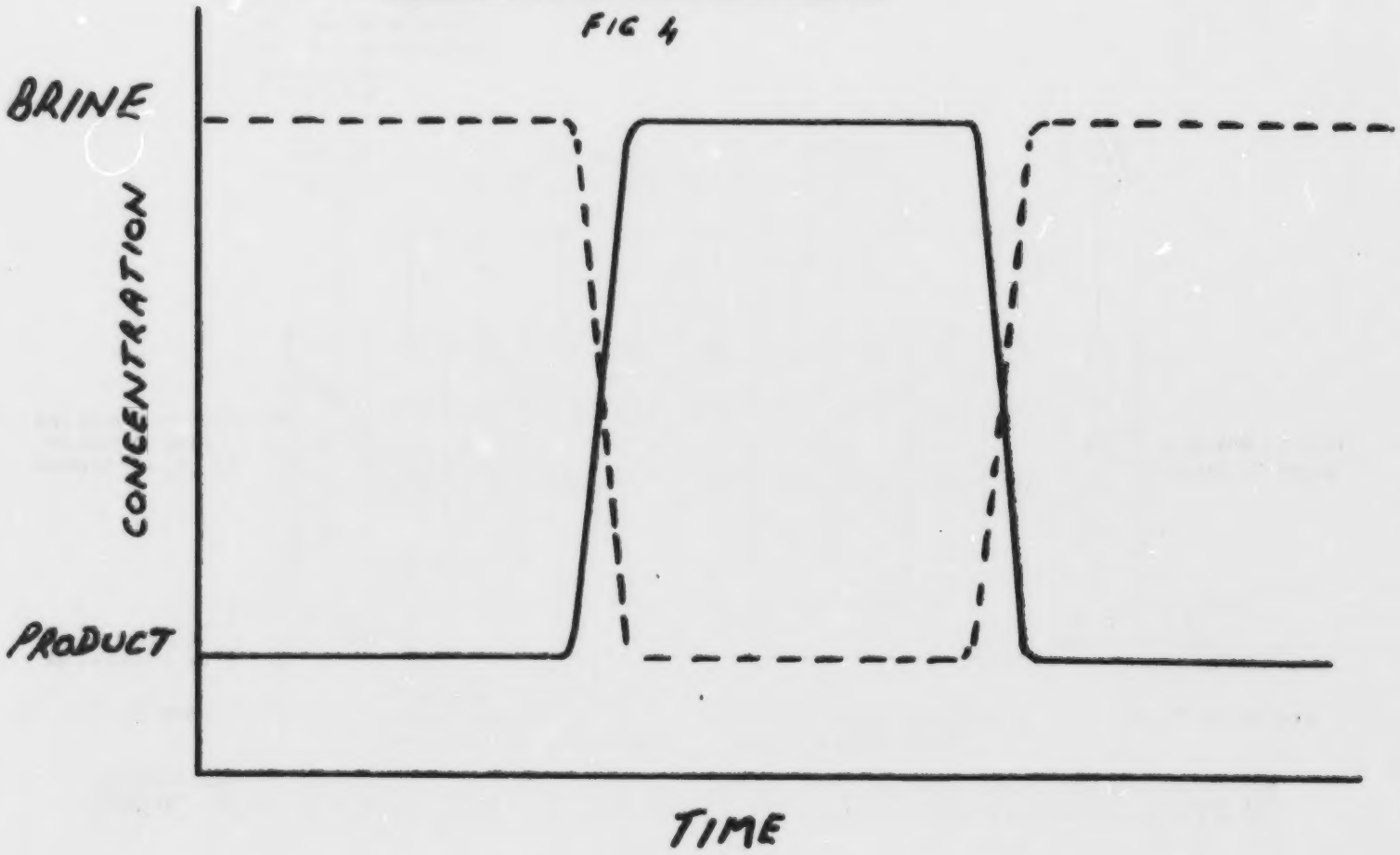


TABLE 5

EDR TEST/ANALYTICAL MEANS

PARAMETER	FEED	BRINE	PRODUCT	REJECTION
Major Parameter	mg/1	mg/1	mg/1	
HCO_3^-	573	2 384	106	81,5%
Cl^-	432	1 884	61	85,9%
$SO_4^=$	363	1 656	23	93,7%
Ca^{++}	191	826	16	91,6%
Na^+	337	1 464	61	81,9%
Mg^{++}	44	208	6	84,6%
K^+	20	88	2	90,0%
Traces				
As	,022	0,104	0,009	59,1%
Ba	0,15	0,23	<0,1	>50 %
NO_3+NO_2	1,9	8,0	0,44	76,8%
Se	0,11	0,19	0,02	81,8%
U	9,15	21,4	1,80	80,3%
Radiometrics	pCi/L	pCi/L	pCi/L	
Ra 226	667	2 904	64	90,4%
Th 230	54	415	10,0	81,5%
Gross α	735	3 294	149	79,7%
Gross β	2 182	4 390	379	82,6%

TABLE 6

DESALTING OF SEWAGE EFFLUENT

DUBAI RESULTS

PARAMETER	RAW	DILUTE FEED	PRODUCT	BRINE
Na	405	395	126	976
Ca^{++}	100	88	18	274
Mg^{++}	83	77	19	225
Cl^{-}	704	700	191	1822
HCO_3''	348	41	40	90
SO_4''	162	284	50	794
TDS (SUM)	1802	1585	444	4181
TDS (GRAV)	1736	1684	464	4456
pH	7,6	6,1	6,3	6,3
TOC	12,9	6,8	5,5	6,8
Fe^{++}	0,09	0,04	0,02	0,09

DESALINATION: A SOUTH AFRICAN PERSPECTIVE

C.F. SCHUTTE

ELECTRODIALYSIS

7.1 Introduction

Desalination by electrodialysis (ED) is based on the fact that most dissolved salts in water are ionic in nature and that these electrically charged ions are attracted by opposite electrical charges. To utilize this phenomenon to desalinate water, membranes which will allow cations or anions - but not both - to pass are placed alternately between the electrodes. By this arrangement concentrated and diluted solutions are formed in the spaces between alternating membranes.

The present day electrodialysis industry came into being in the 1950's when sheet membranes made from ion-exchange resins were used to demonstrate the desalination of brackish waters. A significant event in the early days of the ED industry was the construction of an 11 Ml/d plant for desalinating underground mine water in the Orange Free State. However, before the plant was fully operational the need to desalt the water fell away and the project was stopped.

Since 1945 when the first ED unit was sold up to 1975 installed ED capacity totalled almost 100 Ml/d. In the early 1970's the Electrodialyses Reversal (EDR) process was developed and from 1975 onwards very few conventional ED plants were installed. EDR is inherently less prone to scale formation and other fouling (than conventional ED) since scale is dissolved and fouling material flushed from the system when the polarity (and the flow direction) are reversed.

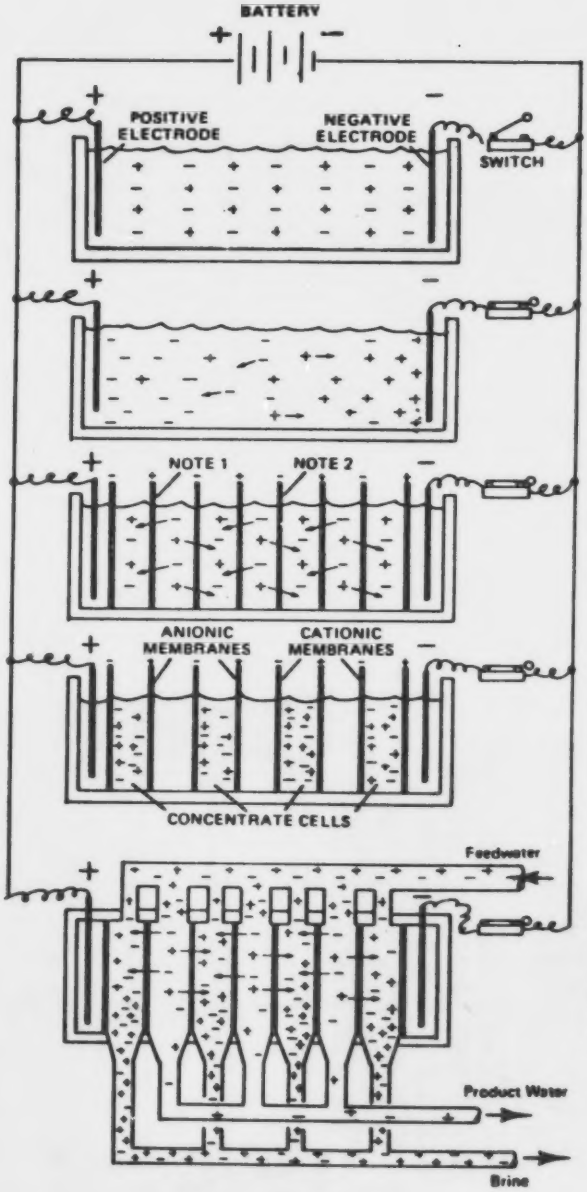
7.2 Operating Principles

The EDR flowsheet utilizes a standard ED array of alternating cation and anion membranes. It operates on the same basic principles as the standard electrodialysis unit, except that both the product and the brine cells are identical in construction. At intervals of 3 to 4 times per hour, the polarity of the electrodes is reversed and the flows are simultaneously switched by automatic valves so that the product cell becomes the brine cell and the brine cell becomes the product cell. The salts are thus transferred in opposite directions across the membranes after polarity reversal.

Figure 7.1 gives a schematic illustration of the process (USAID 1980) and figure 7.2 shows the basic components of an electrodialysis unit (USAID 1980).

Following the reversal of polarity and flow, the product water is discharged until the cells and lines are flushed clean and the desired water quality is restored. This takes approximately 1 to 2 minutes. The reversal process aids in breaking up and flushing out scale, slimes, and other deposits in the cells. This automatic cleaning action eliminates the need to continuously add acid and/or polyphosphate to prevent scale formation in the electrode compartments. Scaling and fouling are also prevented by in-place automatic chemical cleaning systems with solutions containing sodium hydroxide, hydrochloric acid, sulfuric acid; or sodium chloride.

When polarity reversal and in-place cleaning are insufficient, and scaling does occur the stacks must be disassembled, cleaned, and reassembled. The individual spacers and membranes can be soaked in appropriate cleaning solutions and are rugged enough to be hand-scrubbed if necessary. In many cases when stack disassembly is necessary, only a portion of the membranes need to be cleaned. The membranes to be cleaned can usually be identified by taking resistance measurements on individual membranes, or groups of membranes while the unit is operating. The reversal of flow and polarity in the stacks greatly extends the intervals between the rather time-consuming job of stack disassembly and reassembly. The overall result is reduced maintenance time.



Many of the substances which make up the total dissolved solids in brackish water are strong electrolytes. When dissolved in water they ionize; that is, the compounds dissociate into ions which carry an electric charge. Typical of the ions in brackish water are Cl^{-1}, Na^{+1}, HCO_3^{-1}, Mg^{+2}, SO_4^{-2}, and Ca^{+2}. These ions tend to attract the dipolar water molecules and to be diffused in times, fairly evenly throughout a solution.

If two electrodes are placed in a solution of ions, and energized by a battery or other direct current source, the current is carried through the solution by the charged particles and the ions tend to migrate to the electrode of the opposite charge.

If alternately fixed charged membranes (which are selectively permeable to ions of the opposite charge) are placed in the path of the migrating ions, the ions will be trapped between the alternate cells formed.

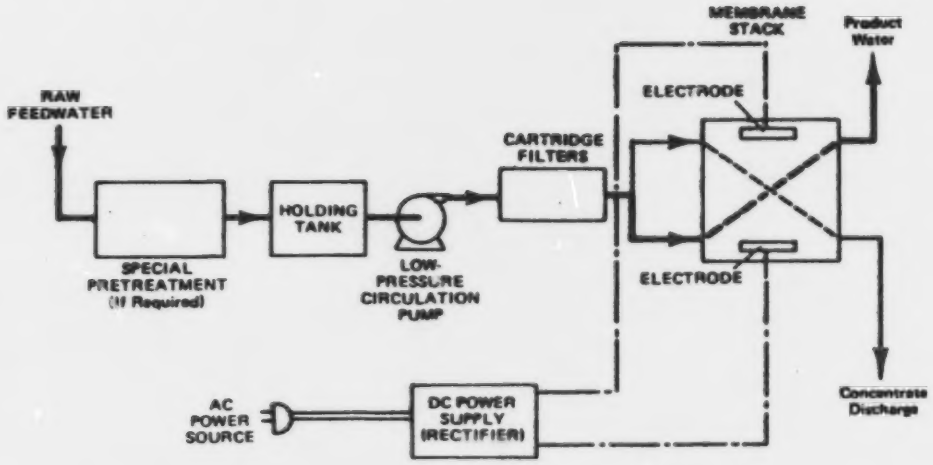
Note 1: A positively fixed charge (anionic) membrane will allow negative ions to pass, but will repel positive ions.

Note 2: A negatively fixed charge (cationic) membrane will allow positive ions to pass, but will repel negative ions.

If this continued, almost all the ions would become trapped in the alternate cells (concentrate cells). The other cells, which lack ions, would have a lower level of dissolved constituents and would have a high resistance to current flow.

The phenomenon illustrated above is used in electrodialysis to remove ions from incoming saline water on a continuous basis. Feedwater enters both the concentrate and product cells. Up to about half of the ions in the product cells migrate and are trapped in the concentrate cells. Two streams emerge from the device: one of concentrated brine and the other with a much lower concentration of TDS (product water).

FIGURE 7.1 Movement of ions in the electrodialysis process.
(USAID 1980)



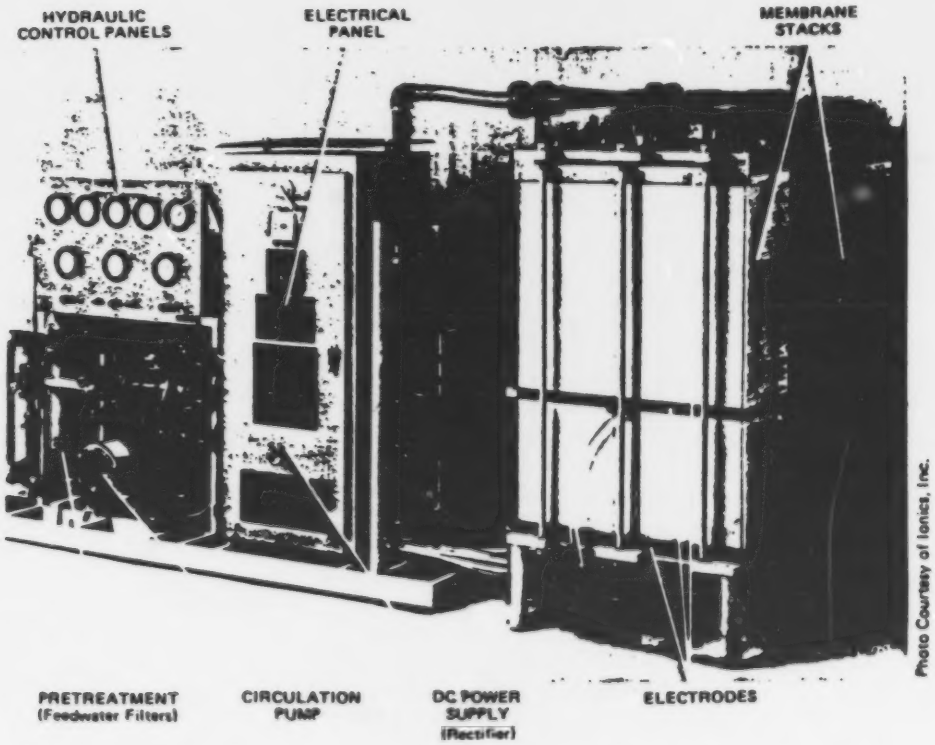


FIGURE 7.2 Basic components of an electrodialysis unit.
(USAID 1980)

7.3 Elements of an EDR Unit

7.3.1 Pretreatment

The requirements for pretreatment in electrodialysis are somewhat less stringent than for reverse osmosis due to the nature of the process. The electrodialysis reversal process reduces the necessity for chemical pretreatment for many applications, but removal of suspended solids, iron and manganese is still critical to avoid fouling and/or other problems with the system. Pretreatment may still be necessary to produce feed water with : Iron 0,3 mg/l; Manganese 0,1 mg/l; Turbidity 2 JTU; H_2S 0,3 mg/l; no free chlorine. (New types of membranes are tolerant to small quantities of chlorine).

Pretreatment is often necessary to prevent microbiological growth on the inner surfaces of the membrane stack. As in the reverse osmosis process, these surfaces provide a place for them to metabolize in the feedwater. A chlorination-dechlorination step is used if the problem is of sufficient magnitude otherwise, the organic slimes are removed in a cleaning step. The dechlorination step is necessary to protect the membranes from continuous exposure to free chlorine.

7.3.2 DC Power Supply

This is usually a rectifier which converts the alternating current to a direct current electricity supply.

7.3.3 Membrane stack

The stack includes the electrodes, membranes, spacers and necessary plumbing.

(i) Membranes : The membranes are flat sheets, usually made of a plastic film formed on a fabric backing to provide strength with ion transfer sites added to the membranes to give each type the required selectivity to pass either anions or cations.

Cation membranes generally consist of cross-linked polystyrene that has been sulfonated to produce fixed ionic charges in the membrane. Anion membranes have quaternary ammonium groups fixed in a similar cross linked polymer. A new generation of aliphatic anion membranes are less prone to organic fouling than the older aromatic membranes.

In water the fixed ionic groups ionize to form mobile counter= ions which readily exchange with ions of the same charge in the water solution under an applied direct electric current. Mem= branes come in a variety of sizes, depending on the manufac= turer and the application. A typical full scale size is 46 by 102 cm. The thickness of the membrane depends on the applica= tion. Thicker membranes usually have greater strength, in= creased erosion resistance, and longer life, whereas thinner membranes have lower electrical resistance and hence reduced energy requirements. Typically, membranes are about 0,56 mm thick.

The structure of membranes can also be varied to suit different conditions; for example the water content can be varied making the membrane more or less ion permeable.

The following characteristics are required from an ED membrane: thermal stability; mechanical strength, resistance to chemical and biological degradation; dimensional stability; ionic selectivity; low cost; low resistance.

(ii) Spacers : The spacers separate the membranes and provide a pathway in the cell for the water flow. Cells are made up of two membranes with a spacer between and are stacked with alter= nating concentrate and dilute cells. The number of stacks, stages and electrodes are designed to suit specific circumstan= ces and requirements such as feed water quality and required product quality.

(iii) Electrodes : One pair of electrodes is required for each electrical stage. The electrodes are generally constructed of niobium or titanium with a platinum coating.

7.3.4 Circulation pumps

These are used only for circulation of the water through the stack. The head loss varies with the construction of the stacks, number of stages, etc, but generally a pressure of about 350-500 kPa is required compared to the 1,5-2,5 MPa required for reverse osmosis. Because of the reduced pressures the connecting piping, valves, etc, can be made from standard plastic pipe and fittings at lower cost (compared to stainless steel, etc) and with high resistance to corrosion in a saline environment.

7.4 Process characteristics

7.4.1 Power consumption

Electrical power is used for pumping water through the system as well as for the transfer of ions through the membranes. Overall energy usage is proportional to the amount of dissolved solids removed. Stack power usage amounts to about 0,7 kwh/m^3 product per 1000 mg/l of dissolved solids removed while pump power usage ranges from 0,5 to 1 kwh/m^3 product. Power losses amount to about 5% of total usage.

This gives a total power consumption of
1,3 - 1,9 kwh/m^3 to remove 1000 mg/l of TDS
2,0 - 2,6 kwh/m^3 to remove 2000 mg/l of TDS
3,5 - 4,1 kwh/m^3 to remove 4000 mg/l of TDS
as compared to 2 - 3,2 kwh/m^3 for brackish water desalination by reverse osmosis.

EDR is therefore energywise highly competitive to reverse osmosis for the desalination of brackish waters with TDS concentrations of up to about 2000 - 3000 mg/l.

7.4.2 Dissolved solids removal

A single electrodialysis hydraulic stage can remove from 40 to 60% of the entering total dissolved solids depending on feedwater characteristics. Further removal of dissolved solids requires that two or more stages be used in series. More than one hydraulic stage can be built into one stack and more than one stack can be used in series. Any required level of dissolved solids removal can therefore be achieved by adding hydraulic stages in series, each of which will remove about 40-60% of the incoming TDS to that stage. However, each additional stage will increase capital and operating costs and therefore the plant design usually is a compromise between required product water quality and economic considerations.

The extent to which feedwater is desalinated in each stage depends on the residence time in the stage and the current density. Current densities are kept as high as possible to improve desalination. The actual current flow is limited by the high electrical resistance when the ionic concentration of the water is sharply reduced.

7.4.3 Process efficiency

EDR Desalination of brackish waters with dissolved solids concentrations lower than about 3000 mg/l of dissolved solids can be done on a cost competitive basis compared to reverse osmosis (depending on water quality and ionic composition). Electrodialysis membranes are resistant to chemical and microbiological attack and have average lifetimes of longer than 5 years. The membranes can be cleaned chemically in the stack or can be removed and cleaned mechanically.

The EDR process can achieve very high water recoveries without elaborate pretreatment even with feedwaters containing high concentrations of scale forming substances such as calcium sulphate. It has been demonstrated that an EDR plant can desalinate waters containing calcium sulphate at 250% of the saturation limit without any chemical feed and at higher than 400% with acid and sodium hexametaphosphate addition to the brine side (Elyanow 1981).

Only ions are removed from the feed water and therefore organic material is not removed to any significant extent and thus remains in the product water. In water reclamation applications where organic material in the product is important EDR therefore does not have the same advantage as reverse osmosis which removes most of the organic material in the feed water.

7.5 Applications

Electrodialysis and in particular electrodialysis reversal (EDR) is applied almost exclusively for the desalination of brackish waters for domestic and industrial use. The cumulative installed capacity of 228 EDR plants in 1980 was 150 Ml/d (Techno-Economic Services 1981).

EDR has also found application for the production of low TDS process water such as for printed circuits in the computer industry and also for boiler feed water. In these applications EDR is usually combined with another demineralization process, typically ion exchange to produce very low TDS waters. (Highfield 1980).

Research on the application of EDR for the desalination of cooling water blow down at power stations and for desalination of underground mine waters is currently in progress in South Africa.

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TABLE 11.3

BRACKISH WATER DESALINATION

Reverse osmosis (RO) : Feed 2000 - 5000 mg/l : 80% recovery,
Electrodialysis reversal (EDR) : Feed 1800 mg/l, 3 stages

Plant capacity	3 800 m^3/d		18 900 m^3/d	
	RO	EDR	RO	EDR
Installed equipment cost $\$/m^3/d$	158	328	138	303
Total capital cost $\$/m^3/d$	318	531	254	464
Water cost $\$/m^3$				
Fixed capital charge @ 18%	0,16	0,26	0,12	0,23
Operation and maintenance	0,08	0,07	0,05	0,04
Membrane replacement	0,04	0,05	0,03	0,03
Electricity @ \$0,05 kwh	0,10	0,05	0,10	0,05
Total water cost $\$/m^3$	0,38	0,41	0,31	0,35

Total desalinated water costs for electrodialysis reversal for a 18 900 m^3/d plant vary from $\$0,31/m^3$ to $\$0,42/m^3$ depending on the chemical composition of the feedwater which in turn determines the water recovery possible (80-87%) and the number of stages required for a specific production and desalination duty. The figures given in table 11.3 are for one type of feedwater and a product quality of 500 mg/l TDS.

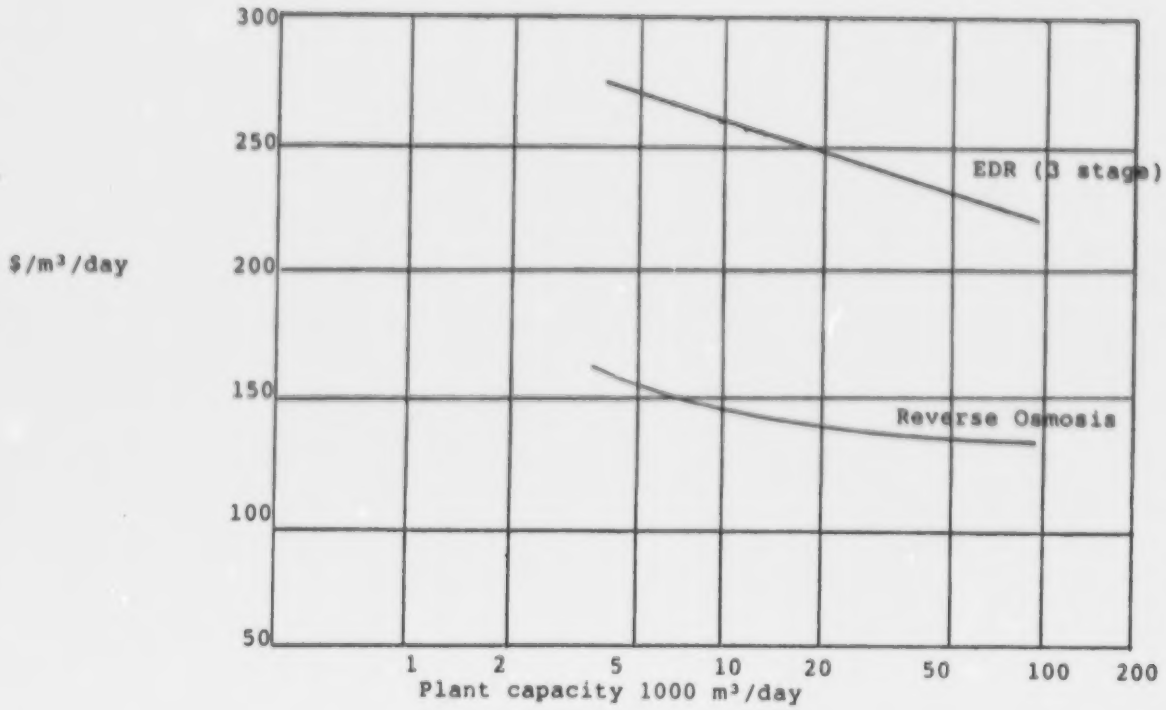

FIGURE 11.3 : CAPITAL COST- BRACKISH WATER DESALTING
(REED 1982)

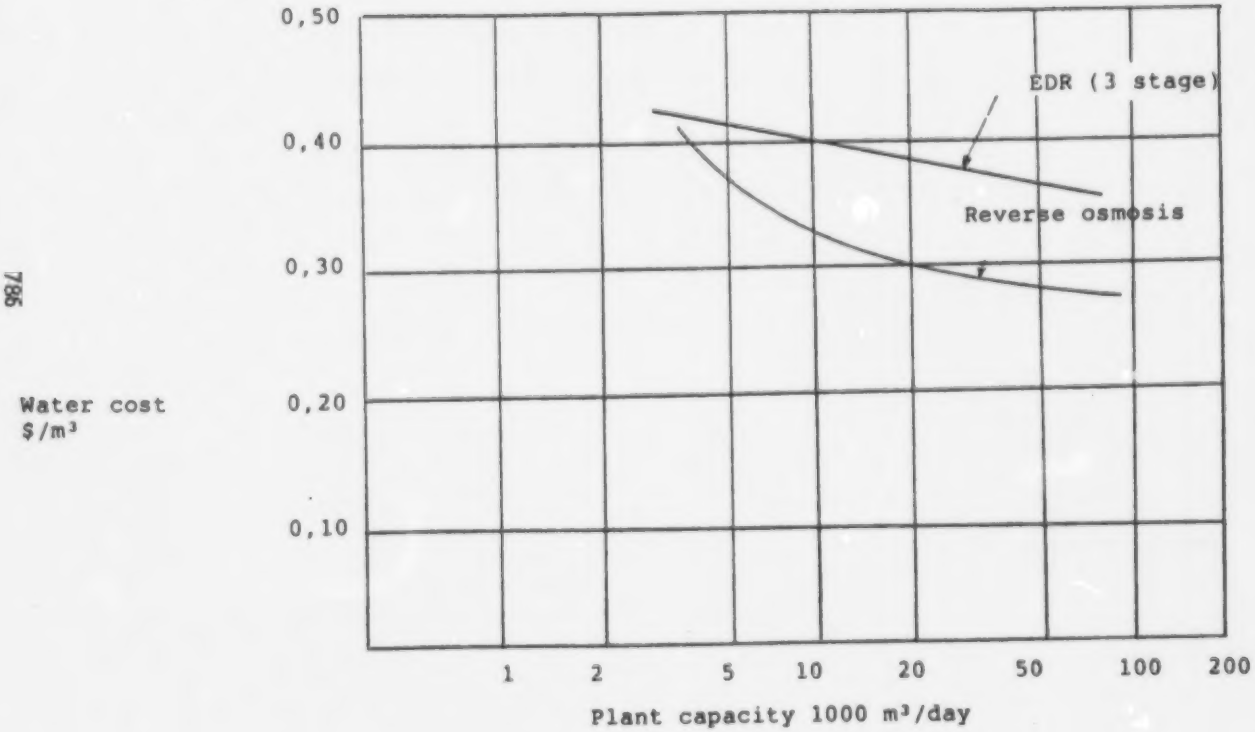

FIGURE 11.4 : WATER COST - BRACKISH WATER DESALTING
(REED 1982)

WARNING

1. Caution should be exercised when using these cost data.
2. These costs are computed for basic desalination facilities in the USA. These costs include no storage capacity and allow for only fundamental feedwater development and brine disposal. If storage capacity is added and/or more complex feedwater or brine facilities are required, overall project costs can significantly increase. This is especially true with brackish water facilities. Construction in locations outside the USA can also add to the overall cost. Actual costs of up to 300% (or more) of those shown on this figure (especially at lower capacities) would not be unusual for projects in many developing areas.

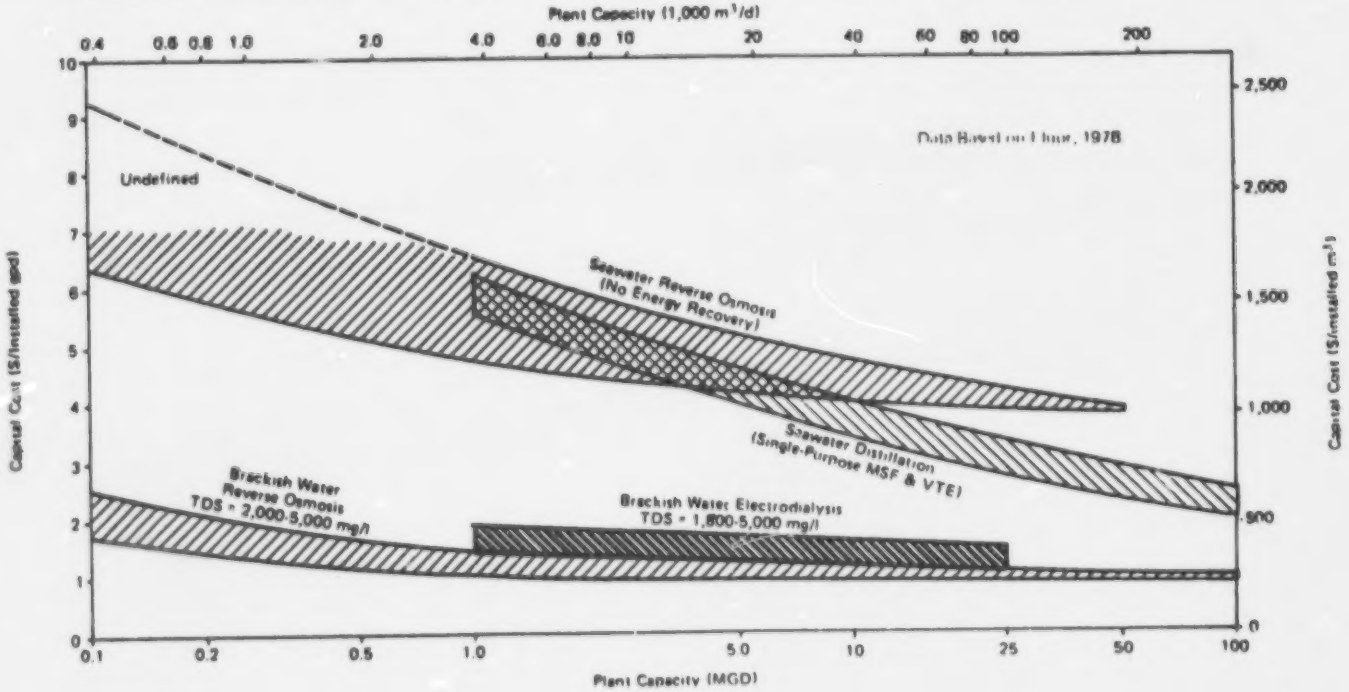

FIGURE 11.1 Generalized capital cost estimates for desalination processes. (USAID 1980)

WARNING

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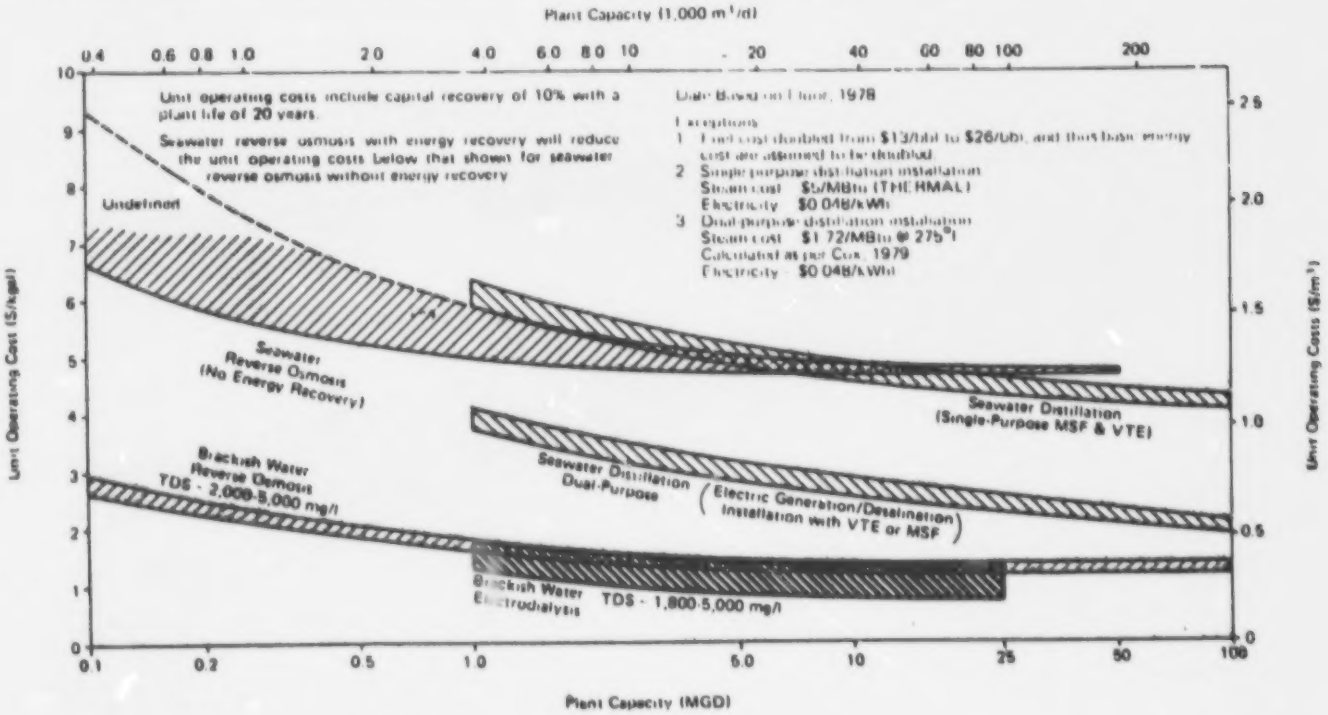

FIGURE 11.2 Generalized unit production cost estimates for desalination processes. (USAID 1980)

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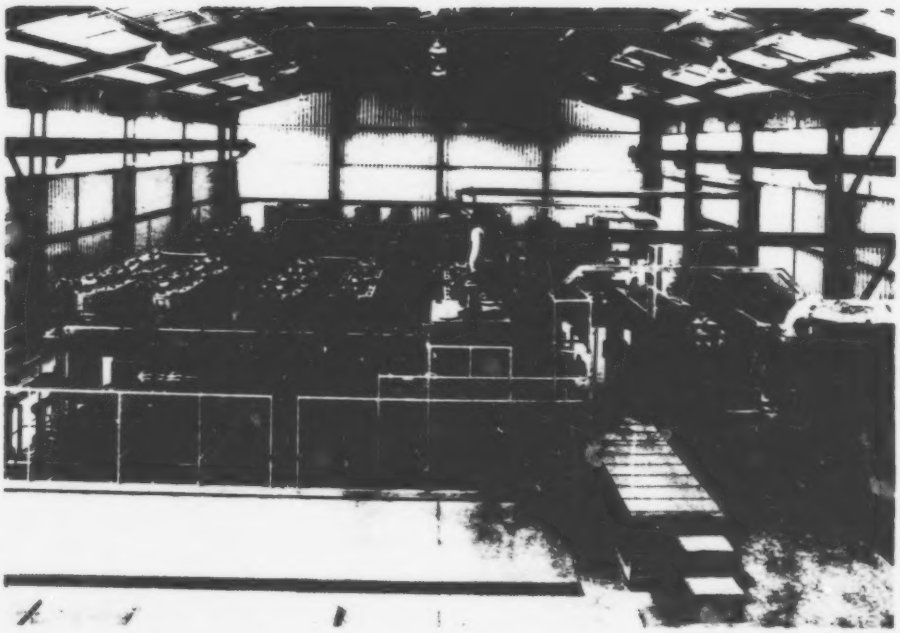
PROCESS SYSTEMS



The Ionics Aquamite 100 Electrodialysis Reversal (EDR) Plant producing predemineralised water for the Escom Kriel Power Station. The plant is the largest of its kind in the southern hemisphere and the largest desalting plant in South Africa.

While EDR is a relatively new technology in South Africa, this process has been used successfully throughout the world for the demineralisation of various waters. The process has also been demonstrated for the demineralisation of cooling tower blowdown at the Grootvlei Power Station where a pilot programme has been underway for over a year. While the process has many advantages over other membrane processes, undoubtedly two of its main features are its resilience to operator error and membrane fouling, both of which determine the cost effectiveness of all membrane processes. These two factors are all too often not quantified during the technical and commercial feasibility of demineralisation processes.

AQUAMITE®

EDR Systems for Water Demineralization

EDR Systems — Electrodialysis Reversal for Reliability in Water Treatment

Ionics, "The Water Company", manufacturers and supplies a comprehensive line of water and wastewater treatment systems and instruments featuring unique technology developed in the Company's laboratories.

Ionics began in the water business with the invention of the ion transfer membrane in 1948 which resulted in the development of the classical ED (electrodialysis) process. In 1954, the ED process was introduced commercially to demineralize brackish waters in Saudi Arabia.

The New EDR (electrodialysis reversal) process was developed in the early 1970's to solve operating and maintenance difficulties encountered when injecting acids and chemicals into the system to control scaling. The elimination of chemical feeds and low-cost automatic operation earned rapid acceptance for the EDR process.

Today, over 500 EDR systems, the largest with a capacity of 24,000 cubic meters per day (6 million gallons), demineralize water for industrial and municipal applications in over 25 countries around the world.

The Aquamite

The Aquamite combines high efficiency membrane stacks with skid mounted modules containing electric power and automatic control systems, low pressure centrifugal pumps and corrosion proof plastic piping. Completely assembled systems are factory tested to meet the requirements of each project resulting in low installation costs, rapid commissioning, and high on-line reliability.

Ionics' total Aquamite spectrum is composed of seven Aquamite systems with production capacities from 2 to 4,000 cubic meters per day (500 to 1 million gallons). Multiple units are used to systems over 4,000 cubic meters per day.

Features

- Fully automatic — simple operation
- Water recoveries up to 95%
- Salt removal up to 99%
- Lowest operating and maintenance costs
  - Zero chemical feed for normal operation
  - Polarity reversal for automatic scale control
  - Proven membrane life up to 10 years
  - Low pressure operation
  - Low electric power
- Feedwater salinities from 100 to 12,000 ppm TDS
- Product water purity to 10 ppm TDS
- Ambient temperatures up to 55°C (131°F)
- Feedwater temperatures up to 45°C (113°F)

Applications

- **Drinking Water**
  - Towns and Villages
  - Hotels and Hospitals
  - Construction and Military Camps
- **Boiler Feed and Cooling Tower Water**
  - Power Plants
  - Refineries
  - Petrochemicals
- **Process Water**
  - Cement Manufacturing
  - Food and Beverage Processing
  - Metals Industry
- **Ultrapure Water**
  - Electronics
  - Pharmaceuticals
  - Biomedical
- **Agricultural Water**
  - Poultry Farms
  - Greenhouses
  - Hydroponics
- **Water Re-use**
  - Municipalities
  - Mining
  - Industry

Ionics Capabilities

- Research and Development — Advanced Membrane Systems
- Design and Engineering — Water Treatment Systems
- Manufacturing — Membranes/Equipment/Systems
- Turnkey Construction — Total Responsibility
  - Water treatment systems
  - Civil Works
  - Electro-mechanical installation
  - Commissioning
- Training — on site/at the factory
- Regional Field Service and Spare Parts Availability

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Process Systems (Pty) Ltd,
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A NEW TECHNOLOGY FOR ESCOM

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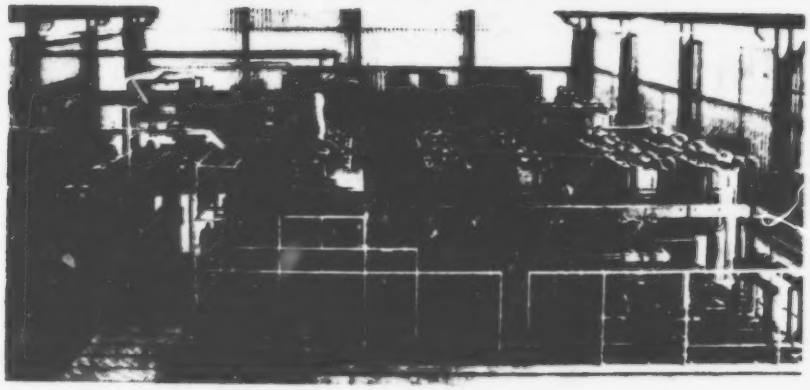


While much publicity has been given to the reverse pumping of the Vaal River, relatively little has been mentioned of yet another project important to the operation of the Kriel Power Station, which is capable of generating nearly a seventh of Escom's electricity output.

Process Systems in conjunction with their principals, Ionics Incorporated of Boston, U.S.A., have supplied, delivered, erected and commissioned an Electrodialysis Reversal (EDR) plant in a record time of 12 weeks. Such a tight programme has only been possible through the co-operative efforts of all the suppliers and subcontractors. The contractor's achievements are further highlighted by the fact that this plant is the largest of its kind in the southern hemisphere and the largest membrane desalting plant in South Africa.

The Kriel Power Station was designed to take water from the Usutu River system which has a much lower salinity level than that of the Vaal River. The Ionics EDR process is being used to reduce the Vaal River salinity to a level lower than that of the Usutu River, thus enabling the station to use its existing demineralisation plant for the production of boiler feedwater. The EDR plant at Kriel Power Station will enable the station to operate at full capacity on Vaal water supply.

While EDR is a relatively new technology in South Africa, this process has been successfully used throughout the world for the demineralisation of brack waters. Escom engineers visited several operating plants overseas to evaluate the suitability of this technology, and a pilot plant programme has been underway at the Grootvlei Power Station for over a year.

The Van Eck power station, operated by SWAWEK in S.W.A., took the lead in the commercial utilisation of EDR a year ago. Like Escom, SWAWEK were faced with a deteriorating water quality due to the prolonged drought in S.W.A. The Van Eck plant has been operating successfully since its commissioning in November 1982.

The technology has tremendous potential in South Africa for numerous applications including:

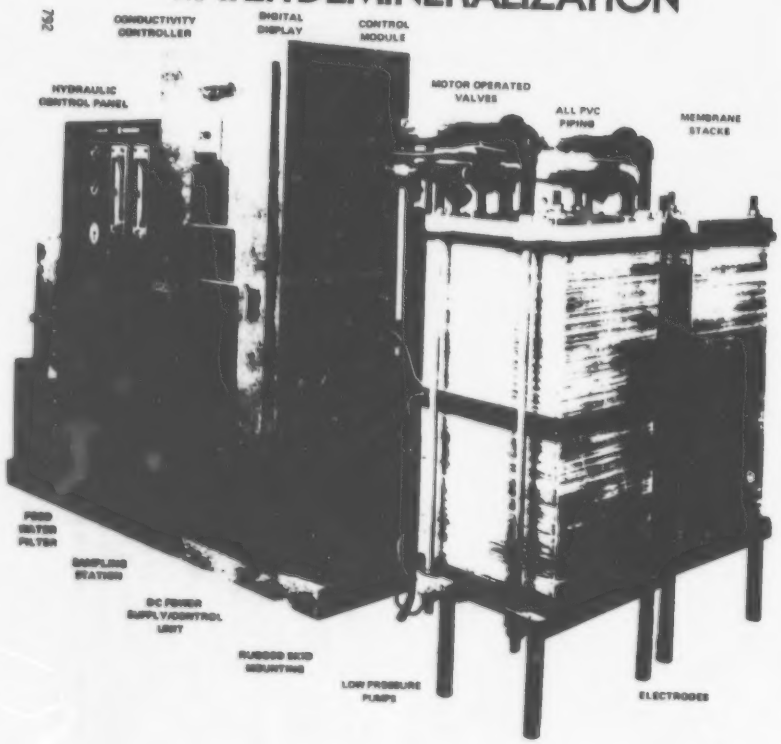
- Pre-demineralisation of Boiling Feedwater.
- Preparation of Potable Water from Brack Water.
- Desalting of cooling tower blowdown, enabling recycle.
- Desalting of mine waters.
- Desalting certain effluents prior to recycle.

While the process has many advantages over other membrane processes, undoubtedly two of its main features are its resilience to operator error and membrane foulings, both of which determine the cost effectiveness of all membrane processes. These two factors are all too often not quantified during the technical and commercial feasibility of demineralisation processes.

Escom has placed another contract with Process Systems for the predemineralisation of Rand Water Board water for Klip Power Station. This new plant is cost effective based on the saving of chemicals used for normal regeneration of the existing ion exchange plant. A further benefit to Escom is the reduction in the amount of effluent leaving the works.

Both the Water Research Commission and the National Institute of Water Research have been instrumental in the introduction of the new technology to South Africa. Through the foresight of these two bodies, evaluation of the technology was in progress a long time prior to the current water problems. Indeed, they can be commended for their efforts in finding yet another of many solutions to the South African water problem.

PACKAGED ELECTRODIALYSIS PLANTS FOR WATER DEMINERALIZATION



The AQUAMITE V employs the proven process of electrodialysis (ED) to provide from 15,000 to 30,000 U.S. gallons per day (USGPD) of fresh water from brackish water, or very pure industrial process water from normal water supplies. In the ED process, the water to be demineralized is pumped at low pressure (30 to 60 pounds per square inch) between special plastic membranes and emerges as pure product water. Within the membrane assembly (called a membrane stack) DC electric current drives the salt and mineral particles, called ions, through the membranes to a concentrated waste water stream.

The AQUAMITE system can operate on feed waters up to 110°F and withstand pH ranges from 1.0 to 13.0. No chemicals are required for normal operation of the plant, thus eliminating the historical economic and operational problems associated with accurate dosing, equipment corrosion and local supply of hazardous and expensive materials.

The AQUAMITE system employs electrical Polarity Reversal in place of continuous chemical feed for control of scaling and membrane fouling substances. This unique process, coupled with occasional use of the Clean-In-Place (CIP) treatment system minimizes membrane stack maintenance problems. Membrane stack cleaning by stack disassembly offers a third maintenance option to maximize plant efficiency under extreme operating conditions.

Widely flexible design options allow the AQUAMITE to provide water over a broad range of product purities and capacities. This flexibility is achieved by staging of the membrane stacks. In general, increasing the number of stages increases product purity and reduces flow. Also, water temperature increases improves salt removal rates (see Operating Specifications table — back page).

The AQUAMITE consists of a membrane stack or stacks and a rugged steel skid containing the DC power supply/control unit, feed water filter, pumps, valves and other hydraulic equipment. An AQUAMITE V-2 has two 18 x 20 inch membrane stacks while the model V-1 has one. The V-2 therefore has twice the product capacity of the V-1 under the same operating conditions. Optionally, an 18 x 40 inch membrane stack may be used. If product water requirements or feed water composition changes, membranes or membrane stacks can be added in the field or staging changes can be made to solve the problem.

The AQUAMITE ED plant is tailored to each individual application while maximizing standard design components. The use of standard designs reduces capital costs and allows for rapid delivery of AQUAMITE units. All PVC piping and bronze pumps give maximum protection against corrosion and product contamination.

Details of feed water characteristics and product water requirements determine recommended membrane stack areas, staging and any special pretreatment requirements. Pretreatment would normally be recommended for waters containing free chlorine, iron over 0.3 ppm, hydrogen sulfide over 0.3 ppm, turbidity above 2.0 JTU, or manganese over 0.1 ppm. A completed "Water Questionnaire" and analysis of your water will enable IONICS to prepare an engineering study for your consideration.

The AQUAMITE unit is typically housed in a structure that will minimize extreme exposure conditions. The engineering drawings provided show layouts and connections so that the skid and membrane stacks can be easily installed. Three hydraulic lines are required: feed water, product water, and concentrate water. A single power connection at the DC power supply/control unit panel completes the installation.

In automatic operation, a low pressure pump introduces feed water through a cartridge filter to alternate passages in the membrane stack in series. Flow through each stage of the unit. DC power is applied though the membrane stack with current and voltage outputs monitored on the digital display. Another low pressure pump circulates concentrate water on a rotate basis to alternate water passages adjacent to the feed water passages in the membrane stack with a calculated fraction sent to waste. The DC power supply and pumps are activated by signals from level controls in the product water storage tank.

At a fixed point in time (about three to four times per hour) Polarity Reversal occurs, automatically reversing the electrical polarity of the stack and by means of motor operated valves reversing the product water, concentrate and electrode streams. This reversal purges membrane and electrode surfaces of scaling and fouling materials which may have deposited during the cycle. Product water purity is continuously monitored with a conductivity controller which automatically diverts "off spec" water to drain in case of system malfunctions. The polarity status of the membrane stack is indicated by lights on the control module.

Automatic controls shut down the unit in case of high temperatures in the DC power supply/control unit or high/low hydraulic pressures.

The following table shows typical operating specifications of the AQUAMITE V-2 (two membrane stacks). The Model V-1 (with a single stack) produces about one half these flows. Actual operating specifications depend on exact feed water composition, temperature, and stack design and are given only with formal quotations based on complete information on your water. To meet specific economic or site requirements, designs can often be adjusted to achieve either lower energy consumption or higher water recovery or greater demineralization.

The table covers waters of assumed 75% sodium chloride type in the most commonly encountered range of 1500 to 3500 parts per million total dissolved solids. Waters of lower total solids can be treated at lower energy consumption, and waters of higher total solids — up to about 7000 ppm — can be treated at greater energy and lower production.

FEED WATER TOTAL DISSOLVED SOLIDS (TDS)	1500 (ppm)		2500 (ppm)		3500 (ppm)	
NUMBER OF STAGES	4	6	4	6	4	6
TEMPERATURE						
65°F — Product Flow (in thousands USGPD)	30	15	30	15	30	15
Product TDS (ppm)	260	120	435	210	610	310
Percent TDS Removal	83	92	83	92	83	91
Percent Water Recovery (Product to Feed Water Quantity)	80	75	80	75	75	74
Electrical Energy Consumption (KW-Hr/1000 US Gal)	8.5	11	12	14	16.5	17.5
80°F — Product Flow (in thousands USGPD)	30	15	30	15	30	15
Product TDS (ppm)	160	75	280	120	380	170
Percent TDS Removal	89	95	89	95	89	95
Percent Water Recovery (Product to Feed Water Quantity)	79	73	78	72	75	72
Electrical Energy Consumption (KW-Hr/1000 US Gal)	8.5	11	12	14	16.5	17
100°F — Product Flow (in thousands USGPD)	30	15	30	15	30	15
Product TDS (ppm)	100	60	170	80	240	130
Percent TDS Removal	93	97	93	96	93	96
Percent Water Recovery (Product to Feed Water Quantity)	79	71	77	70	74	69
Electrical Energy Consumption (KW-Hr/1000 US Gal)	8.5	11	12	14	16.5	16.5

PRODUCT FLOW (max): 30,000 USGPD
FEED FLOW (max): 55,000 USGPD

POWER REQUIREMENTS:
480/460/380/220V. 3φ. 50/60 Hz
35 KVA total connected load

SHIPPING WEIGHT:
AQUAMITE V-1 — 4,500 pounds
AQUAMITE V-2 — 5,800 pounds

SHIPPING VOLUME:
AQUAMITE V-1 — 350 cubic feet
AQUAMITE V-2 — 380 cubic feet

TYPICAL INSTALLATION AREA:
AQUAMITE V-1 and V-2 — 14.5 x 20.5 feet (including maintenance clearance)

OVERHEAD CLEARANCE: 10 feet

CONDUCTIVITY CONTROLLER:
Ranged for application

AUTOMATIC VALVES:
Feed & Reversal Systems —
3 way motor operated PVC ball valves
Electrode Rinse —
Stainless steel solenoid valves

MEMBRANE STACKS:
Electrodes — platinum plated
Cation Membranes — Ionics 18 x 20 inches or 18 x 40 inches
Anion Membranes — Ionics 18 x 20 inches or 18 x 40 inches

PUMPS:
Low pressure centrifugal — all bronze
Feed — 7.5 HP Concentrate — 5 HP

D-C POWER SUPPLY:
20 KVA (max), 3φ, full wave, silicon diode, 5% ripple (max), class H insulation

Edward P. Geschecke.

IONICS

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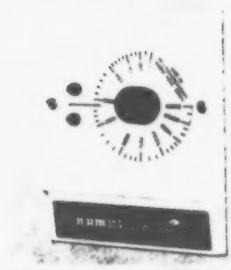
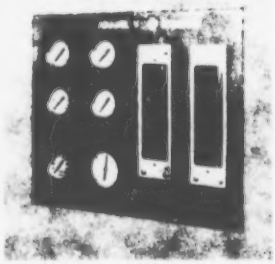
IONICS

ZERO CHEMICAL FEED FOR OPERATION
MEMBRANES STABLE ON HOT FEEDWATERS UP TO 110° F
ONLY TWO OPERATING CONSUMABLES – ELECTRICITY & CARTRIDGE FILTERS
NO HEAT – NO HIGH PRESSURE – NO CHEMICAL REGENERANTS
HIGHEST TOLERANCE TO PLUGGING
POLARITY REVERSAL FOR CONTINUOUS SCALE CONTROL
SINGLE RESPONSIBILITY SUPPLIER
PROVEN MEMBRANE LIFE UP TO 10 YEARS
HIGHEST WATER RECOVERY
LOWEST O & M COSTS
QUIET – COMPACT – AUTOMATIC
PRODUCT WATER PURITY TO 10 ppm TDS
FEEDWATER RANGE: 100 ppm to 7,000 ppm TDS

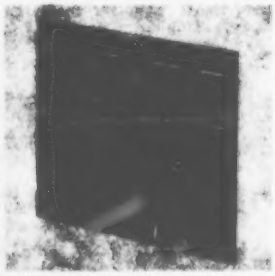

CONDUCTIVITY CONTROLLER

DIGITAL DISPLAY

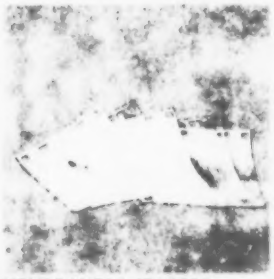

HYDRAULIC CONTROL PANEL

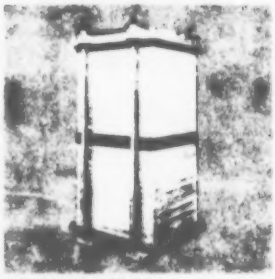
CONTROL MODULE

MOTOR OPERATED VALVES


SAMPLING STATION

LOW PRESSURE PUMP


MEMBRANES & SPACERS


MEMBRANE STACK

EVALUATION OF ELECTRODIALYSIS FOR PROCESS WATER TREATMENT FOR IN SITU MINING

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INTRODUCTION

Since the infancy of in situ uranium mining, a growing number of hydrometallurgical processes have been incorporated into pilot and commercial scale flowsheets. Although initial design efforts were geared toward maximizing uranium recovery and minimizing plant and wellfield flow circuit maintenance, recent emphasis has shifted to improved means of water conservation and aquifer restoration. As mining units approached depletion, evaporation ponds reached minimum freeboard, and state and federal agencies demanded proof of groundwater restoration, processes including mixed bed and conventional ion exchange, reverse osmosis and electrodialysis were adopted by the industry. These units served the additional function of reducing process bleed flows during mining in states where the deep disposal well permitting ice remains unbroken.

This report concerns the use of electrodialysis as an alternative to the more conventional processes used in in situ mining. In addition to a brief history and description of the process, a comparison to reverse osmosis and operational data derived from testing an Ionics, Inc. 1.31×10^{-3} m^3/s (30,000 gallon/day) unit at the Teton-Nedco Leuenberger Research and Development pilot will be presented.

HISTORY

Commercially practicable electrodialysis was contingent upon the development of synthetic ion exchange membranes in 1940's. In 1952, Ionics Inc. demonstrated that the process was amenable to the treatment of salt and brackish water and, in 1954, made their first commercial sale. The following decade saw several major electrodialysis unit sales which were generally targeted for use on private or municipal potable water treatment. Major increases in membrane desalting unit capacities, facilitated by technological advances in the reverse osmosis industry, were noted during the 1970's. The development of polarity reversing electrodialysis equipment which reduced feed pretreatment requirements, increased water recovery rates, and simplified unit operation, kept Ionics Inc. competetive in the water treatment industry. Engineering advances which incorporated automated equipment, non-corrosive construction materials, and improved ion exchange membranes allowed the electrodialysis process to compete in industrial waste treatment among other commercial markets.

PROCESS AND APPARATUS DESCRIPTION

The electrodialysis process utilizes direct electrical current passed across a stack of alternating cation and anion selective membranes in order to achieve an electrochemical separation of ionized materials in an aqueous solution. The membrane stack has the appearance of a plate and frame filter press and auxilliary equipment includes solution pumps, electrically actuated valves, filters, piping and a direct current power source. The ion separation membranes are thin sheets of synthetic cation or anion selective resins. Attaching sulfonate or quaternary ammonium groups to the cross linked copolymer structure determines the ion selectivity of the membrane. The membranes are separated from each other in the stack by non-conductive spacers that house flow channels which route the flow tortuously and parallel to the membranes. Direct electrical current passing perpendicularly to the membranes and solution passages attracts cations toward the cathode and anions toward the anode (Figure 1). As the ions from the feed stream pass through the ion selective membranes, they become concentrated in the adjacent brine channel and are retained there by the combined attractive force of the electrode and the repelling force of the next membrane toward the electrode. Limiting factors on the degree of demineralization possible include chemical solubilities in the brine flow and the current density that will produce an unacceptable degree of polarization (Figure 1). Feed or brine solution treatment with complexing agents or acids has been successfully applied to prevent membrane scaling. Polarization can occur when sufficient current density is applied to dissociate water in the ion depleted region of the diluting compartments near the membrane surfaces. Significant polarization is evidenced by large electrical resistances across cell pairs and notable pH differences between diluting and concentrating streams. Limiting current densities have been increased in U.S. manufactured equipment by utilizing tortuous flow paths of relatively high linear velocities thereby promoting continous solution mixing. Energy consumption is due to separating electrolytes and solutions, oxidation and reduction reactions occurring in electrode compartments, overcoming electrical resistance, conversion from AC to DC power, solution pumping and auxiliary equipment actuation.

A major improvement to the basic electrodialysis process was applied in 1970 which resulted in frequent, automatic cleaning and descaling of membrane surfaces. The process, polarity reversal, incorporates alternating the cathode and anode on a periodic basis while exchanging product and brine flow channels via electrically actuated values. The reversal reduces the potential of stack plugging with $CaCO_3$ (calcite), $CaSO_4$ (gypsum), and colloidal materials and, in most waters, eliminates feed pre-treatment requirements. For approximately two minutes during and following the reversal, off spec. water is flushed to waste or reintroduced to the feed supply. The usual feed treatment on polarity reversing electro-

dialysis equipment (EDR) consists of filtration of particulates exceeding 10 μm (micron).

EDR COMPARED TO REVERSE OSMOSIS (R.O.)

The tool widely adopted by the ISL industry for process bleed reduction and groundwater restoration has been reverse osmosis (R.O.). R.O. units utilize excessive pressure exerted across semi permeable spiral wound cellulose acetate or hollow fiber polyamide membrane elements in order to reverse the natural osmotic process. The net result is similar to electrodialysis in that dissolved solids in feed water are concentrated into a reduced volume and relatively high "clean" water recoveries are noted.

There are several dissimilarities between the processes that suggest significant advantages to the EDR operator. Due to the microscopic pore size of the R.O. membrane, more chemical pretreatment and filtration is required than for the 1 mm flow channels in the EDR stack. Pre-softening or complexing EDR feed is not generally required and the membranes withstand silica scaling. ED membranes can be operated in the pH 1-10 range and exhibit stability to 316°K(110°F). R.O. membranes typically operate only in relatively small pH and temperature ranges. Materials of construction and maintenance costs are reduced for EDR due to the comparatively low feed pressures.

Perhaps the greatest single advantage to the EDR process is the stability and accessibility of the ion exchange membranes. Although ED and RO are similar in that the ion exchange media represents a large proportion of the initial capital cost of the unit, ED is unique because of the long term stability and maintainability of the membranes. Due to the low pressure feed and nature of the process, ED membranes do not suffer from the gradual compaction noted on R.O. membranes, and, as a result have demonstrated working lives in excess of 10 years. Formation of $CaSO_4$ scale that can result in RO membrane failure or plugging, is restricted in EDR operation due to polarity reversal and the commercial stack cleaning circuit. In contrast to R.O. membranes, ED membrane stacks may be physically disassembled and membranes may be individually scrubbed if scaling cannot be controlled or dissolved by the "clean in place" circuit.

Based on recent quotes from both RO and EDR manufactures, capital equipment costs are comparable and range from $175,000 to $250,000 for 1.26×10^{-2} m^3/s (200 gpm) units. Operating costs for EDR units have historically been equal to lower than comparably size RO units (when feed TDS remains below 5000 mg/l) and EDR feed pretreatment costs are typically lower.

PILOT TEST RESULTS

In late 1980, Teton Exploration and Ionics, Inc. initiated an agreement to perform a three month test with a commercially sized EDR unit on the ISL circuits at the Leuenberger pilot project located near Glenrock, Wyoming. An Aquamite V-H 1.31×10^{-3} m^3/s (30000 gallon/day) unit was received, installed, and operating continuously by 2-25-81. The dual stage unit was expected to produce 665 mg/l TDS water from a feed of 2650 mg/l with a product water recovery of ~80%.

Installation of the three ton, two piece unit required skid placement, plumbing unit feed, product and brine lines, and providing a peak 1.26×10^{4} J (35 KVA) power source. Electrical power was provided by the plant three phase diesel generators. Overall dimensions of the unit including reasonable maintenance clearance are 4.27 m (14 ft) x 6.1 m (20 ft) x 3.65 m (12 ft H).

The unit was to be tested on feed solutions comparable to those anticipated during the commercial operation including ion exchange barren effluent, mining zone restoration fluids, and impounded bleed.

Continuous operation began 2/25/81 with a 2.9 g/l TDS feed split from the ion exchange barren effluent stream. Due to the high initial Ca^{++} and HCO_3^- concentrations (0.25 g/l and 1.7 g/l respectively), pH adjustment of the feed flow to pH 5.8 to 6.0 with 35% hydrochloric acid was required to prevent $CaCO_3$(g) precipitation in the brine stream. As feed parameters reduced from the effect of field restoration, CO_2(g), introduced in gaseous form to the feed tank, replaced HCl as the pretreatment chemical.

Pretreatment costs during the test were $0.80/3785 L (1000 gal) for HCl and $0.91/3785 L (1000 gal) for CO_2(g). Although costs were ~14% higher for CO_2 (g) pretreatment, the addition was continued in order to prevent reintroduction of Cl^- ion to the restoring mining zones.

Ionics Inc., testwork indicated that membrane life would not be significantly reduced by feeding elevated levels of free chlorine which allowed recirculation of electrode compartment flows to the feed solution. This reduced brine flow from ~3.5×10^{-4} m^3/s (8000 gallons/day) to ~2.5×10^{-4} m^3/s (5700 gallons/day).

During the evaluation period, 1.25×10^{7} L (3.31×10^{6} gal) were fed at an average TDS of 2.35 g/l, and 1.02×10^{7} L (2.7×10^{6} gal) product at 0.35 g/l TDS and 2.24×10^{6} L (5.8×10^{5} gal) of brine were generated representing a salt rejection of 87.5% and water recovery of 81.5%. Chemical results from the final month of the test are presented in Table 1.

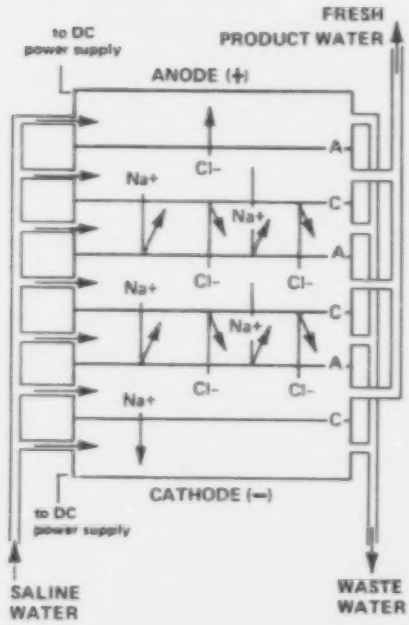
The unit operated 96% of the time available requiring only four cleaning cycles and no stack disassembly. Cleaning downtime was necessitated by operator error in neglecting to maintain flow to the feed tank during polarity reversals. The off specification water generated during the reversals continually enchances raw feed parameters by ~55%.

Routine operating costs averaged $1.02/3785 L (1000 gal) and broke down into pH adjustment chemicals ($0.86/3785 L (1000 gal)) and power requirements ($0.149/3785 L (1000 gal)). Approximately four manhours/day were required for data collection and unit operation and one manhour/day was needed for site analytical work.

A single day, 52,900 L (14000 gal) test was performed on feed from impounded bleed derived from an earlier groundwater restoration sweep. This test was designed to determine the feasibility of reducing water storage volumes by concentrating dissolved solids in a reduced volume and creating a product that met state surface discharge criteria. Test results indicated that the 3.1 g/l TDS feed could be split to provide 78% product water recovery at 0.66 g/l TDS. Additional pre or post treatment of the product to further reduce Ra-226 levels would be required to meet discharge quality.

Analyses performed over the duration of the test period showed a divalent ion rejection of 90.5% and a monovalent ion rejection of 84.8%. Radiometric and detectable trace elements showed feed to product splits equivalent to major constituents (Table 1).

In the Electrodialysis process, water flows between alternately placed cation (C) and anion (A) permeable membranes. A DC current provides the motive force for the ion migrations through these membranes. Salts in brackish water flowing through a "membrane stack" are removed or concentrated in alternate water passages.



In the Electrodialysis Reversal (EDR) system the classical ED process is used. However, at a fixed point in time (about 3 to 4 times per hour), Polarity Reversal occurs, automatically reversing the anode and cathode positions and, by means of motor operated valves, exchanging the "fresh product water" and "waste water" outlets from the "membrane stack". For a brief period (about 1 minute) product water is discarded to allow purging of fouling materials from the "stack".

Maintenance is simplified by controls located on the control panel. A flashing light indicates the need of a filter change. This is also indicated by pressure gauges on the hydraulic control panel.

The automatic Clean-In-Place (CIP) system for periodic (weekly to monthly) chemical flushing of the stack is activated from the control panel and this mode of operation is indicated by a panel light. The CIP system is used to remove stubborn residues from membrane surfaces if they occur. A fail safe system prevents wash water from contaminating product water.

Over the past 20 years, IONICS has learned to build electrodialysis systems to demineralize salty, brackish, hard, alkali, "gyp" or high nitrate waters economically under the widest range of climatic and geographic conditions.

IONICS has installed over 700 commercial electrodialysis plants ranging in size from 500 to 4,000,000 USGPD.

IONICS is the only manufacturer of membrane demineralization equipment that is a fully integrated single responsibility supplier.

IONICS provides a free water analysis of your sample as part of the initial proposal for your AQUAMITE application.

IONICS designs superior scale control systems that are exclusively available with the EDR process.

IONICS has learned to automate the overall AQUAMITE system to maximize on stream time and minimize operator attendance and maintenance.

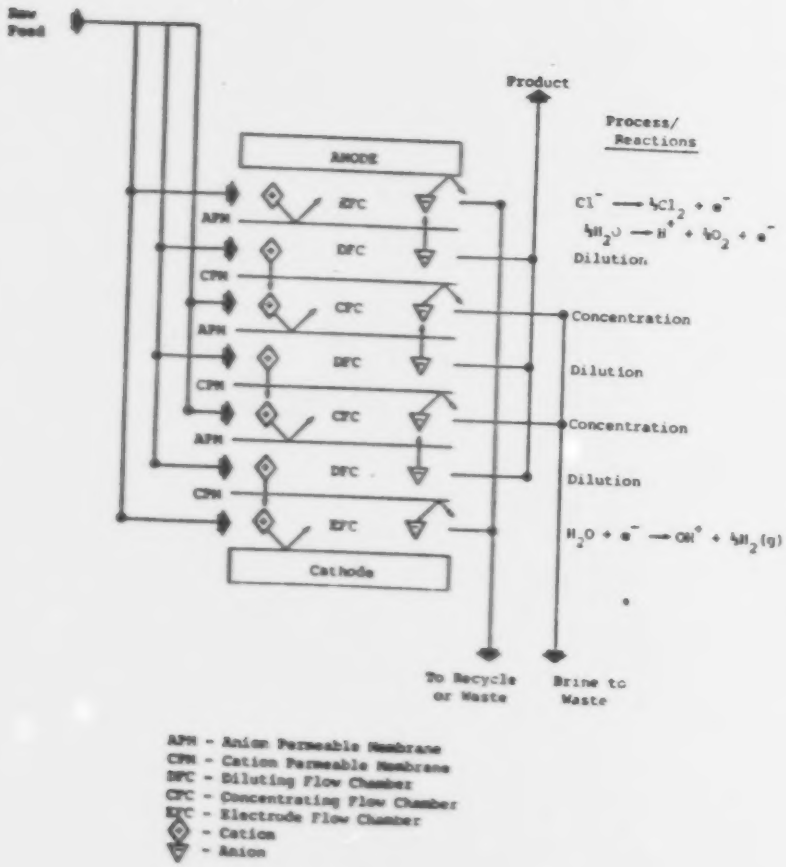
IONICS manufactures and controls the quality of all membranes used in the AQUAMITE units.

IONICS builds equipment with components that stand up in tough applications including long life rugged membranes, corrosion resistant low pressure pumps, plastic piping and fail safe control systems.

IONICS modular AQUAMITE systems are skid mounted subassemblies to simplify field installation and minimize start up time and costs.

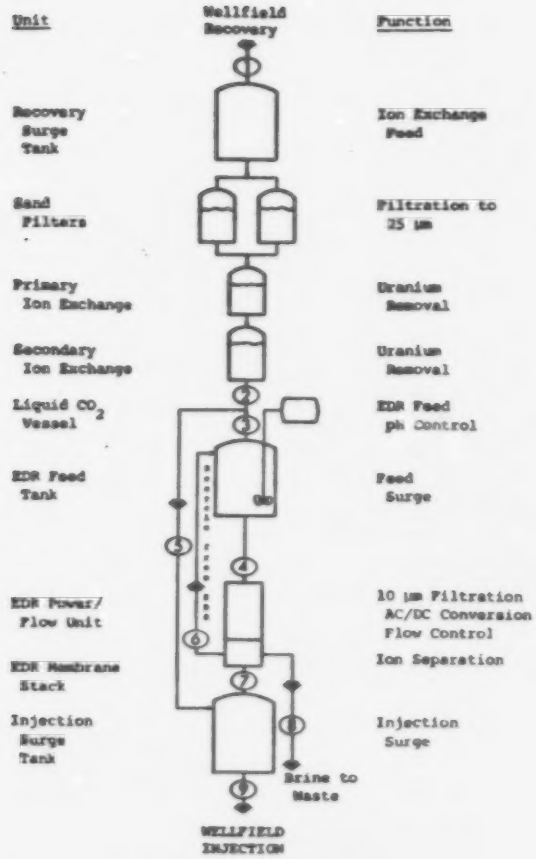
All AQUAMITE units are performance tested prior to shipment to maximize installation and start up efficiency.

IONICS maintains a world wide service organization, available for troubleshooting, start up, training and installation.



APM - Anion Permeable Membrane
CPM - Cation Permeable Membrane
DFC - Diluting Flow Chamber
CFC - Concentrating Flow Chamber
EFC - Electrode Flow Chamber
◇ - Cation
▽ - Anion

FIGURE 1: ELECTRODIALYSIS PROCESS DIAGRAM



TYPICAL FLOW/COND. BALANCE

#	Flow Rate GPM	Solution Conductivity µmhos/cm
1	52.1	1,289
2	52.1	1,289
3	25.4	1,289
4	30.8	1,748
5	26.7	1,289
6	5.4	3,907
7	21.2	182
8	4.2	5,956
9	47.9	856

FIGURE 2 - EDR BASED RESTORATION - FLOW DIAGRAM

TABLE 1
EDR TEST/ANALYTICAL MEANS

PARAMETER	FEED	BRINE	PRODUCT	REJECTION
Major Parameter	mg/l	mg/l	mg/l	
HCO_3^-	573	2,384	106	81.5%
Cl^-	432	1,884	61	85.9%
$SO_4^=$	363	1,656	23	93.7%
Ca^{++}	191	826	16	91.6%
Na^+	337	1,464	61	81.9%
Mg^{++}	44	208	6	84.6%
K^+	20	88	2	90.0%
Traces				
As	.022	0.104	0.009	59.1%
Ba	0.15	0.23	<0.1	>50%
NO_3+NO_2	1.9	8.0	0.44	76.8%
Se	0.11	0.19	0.02	81.8%
U	9.15	21.4	1.80	80.3%
Radiometrics	pCi/L	pCi/L	pCi/L	
Ra 226	667	2,904	64	90.4%
Th 230	54	415	10.0	81.5%
Gross α	735	3,294	149	79.7%
Gross β	2,182	4,390	379	82.6%

CONCLUSION

Based on the results of the three month test period, Teton-Nedco purchased the Aquamite V-H unit for the pilot restoration and decommissioning project. We feel that the EDR process has satisfactorily proven its amenability to HCO_3^- leach ISL water treatment requirements and this and a larger unit have been incorporated into the commercial scale flow sheet. Ease of operation, mechanical availability, capital and operating costs comparable to alternate systems, the units ability to provide >80% water recovery at >80% salt rejection, and the cooperation of the manufacturer were all factors in the decision to use EDR at the commercial level.

The anticipated uses of EDR under commercial operation include:

1) Provision of a source of low TDS process water for Na_2CO_3 makeup, slurry product washing and post elution resin rinsing. The unit feed would be the 0.5 to 2% field overrecovery fluid.

2) Commercial scale wellfield restoration would be accomplished using an Aquamite 20 1.26×10^{-2} m^3/sec. (200 gpm) unit.

3) Process bleed reduction may be attempted by reducing product radiometric levels to a point where the solution is usable for construction water, dust control, drilling, plant washing or, with appropriate approvals, surface discharge.

At this time, the Aquamite V-H unit continues to operate and a "state of the art" pilot scale wellfield restoration is nearing completion.

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ION EXCHANGE

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RANDOL INTERNATIONAL (1980) completed a multi-client report on continuous ion exchange (CIX) and resin in pulp (RIP) systems for uranium recovery. This report was over 2,000 pages long dealing with just that one aspect of ion exchange. Here there is room for a general summary of the principles and main features of CIX systems, their applicability, and to identify the main equipment suppliers, as well as sources of further information and expertise.

Ion exchange is routinely employed to demineralize feedwater for boilers in steam generation for metallurgical use (e.g., acid leach uranium mills use heat for leaching) and for steam-generated power stations. These boiler feedwater demineralizers generally use fixed-bed ion exchange systems employing cation as well as anion exchange resins either in mixed or separate beds. Fixed-bed IX systems operate in a downflow mode and need well-filtered feedwater with the lowest possible suspended solids. IX is generally cost effective compared with other desalination processes at low TDS levels, say 100 mg/l in feedwater, and where ultra high purity water is required.

Ion exchange is employed for desalination as mentioned above or for selective removal (and/or recovery) of one or more ions from a mixed solution. For example, IX has been employed for many years as the preferred way to recover uranium from leach solutions. Earlier vintage plants, e.g., Hartebeestfontein Gold Mining Company Ltd. on the west rim of the Witwatersrand, employs fixed-bed merrygoround ion exchange systems. In more recent times, however, continuous ion exchange recovery systems employing multi-stage upflow fluid-bed systems have been installed at uranium plants. The continuous ion-exchange systems handle larger flowrates in plants that are more compact than the older fixed-bed systems and, most importantly, they can tolerate small amounts of suspended solids in their feed. When the clarification equipment needed in conjunction with fixed-bed systems are taken into account, a well designed, constructed, and operated CIX plant is also more economical than fixed-bed systems. CIX systems have also been installed for uranium recovery from in situ leaching operations, notably in Texas.

For higher grade uranium solutions, the more selective SX process would generally be preferred except where there is concern for the effects of organic entrainment losses on the environment (e.g., Agnew Lake) or its effects on underground wellfield permeability.

For desalination of effluents, for example of acid mine drainage on the Witwatersrand where TDS level rise in Vaal Dam water has become a primary concern, CIX has been considered but apparently rejected in favor of other desalination processes such as R.O. and EDR because:

- At higher salt loads (1,500-2,000 mg/l), EDR and R.O. offers better economics than CIX.

- Ion exchange resin elution and regeneration requires chemical addition. Thus, there are more chemicals in concentrated form to dispose of from IX systems than from membrane processes.

CIX FOR DESALINATION OF MINE DRAINAGE AND TAILINGS EFFLUENTS

HENDRY (1983) makes a valiant case for ion exchange as a desalination tool due to its versatility as a separation, purification, and concentration process capable of shunting ions from one solution to another. He points out that CIX requires only chemical energy to accomplish this and utilizes this energy with efficiencies often close to 100%. He points out that ion exchange offers advantages where useful or saleable chemicals can be recovered in which cases, brine disposal costs would be avoided.

Nevertheless, the advantages described by HENDRY (1983) appear to apply only in special cases. Furthermore, the ion exchange systems advocated in his paper are relatively complicated, involving five separate ion exchange steps which are likely to require special operating skills considering the challenges that the mineral processing industry experiences running even two-step (adsorption and elution) uranium recovery operations. Flowsheets from HENDRY (1983), which employ the innovative NIMCIX ion exchange system are illustrated below for NH_4OH, H_2SO_4 recovery, and for acid mine drainage treatment with recovery of $CaSO_4$ and sodium chloride. Despite this innovative approach to ion exchange processes, which HENDRY (1983) has demonstrated on a large bench scale at the University of Cape Town with support from the Water Research Commission, the Commission and industry have apparently elected to back membrane processes for further mine-site desalination development and demonstration.

Some surprising features of the University of Cape Town work are:

1) HENDRY (1983) proposed the use of gypsum seeding inside a CIX resin fluid-bed contactor allowing 90% water recovery from solutions with 1,750 mg/l TDS. A $CaSO_4$

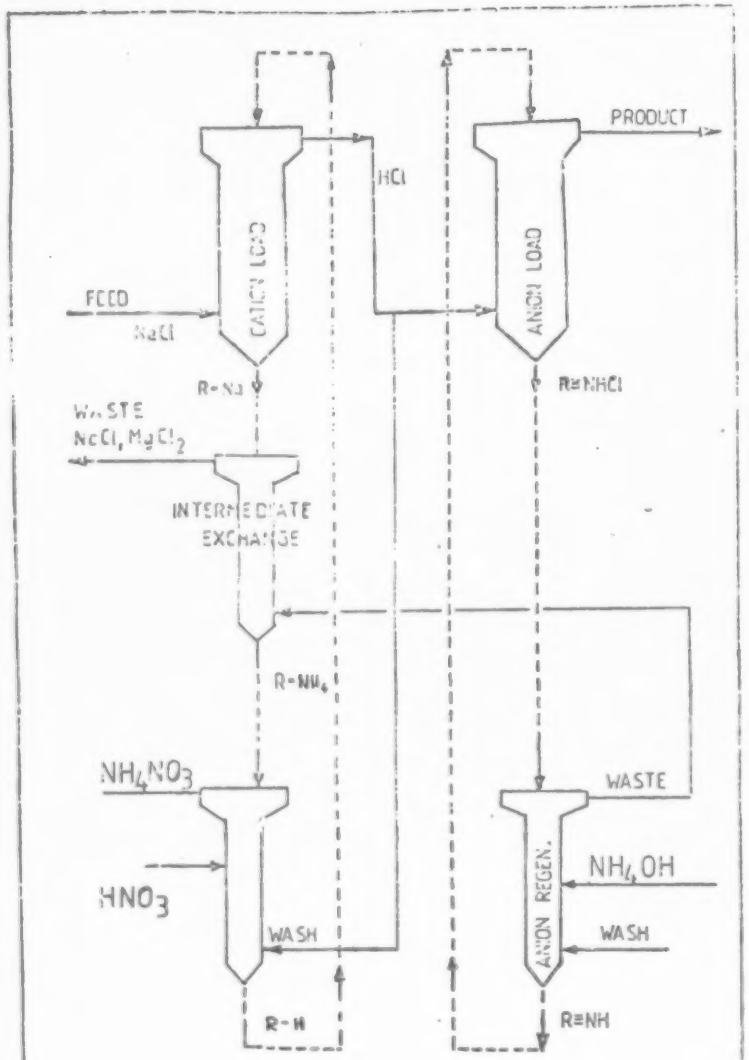


FIGURE 1 FIVE COLUMN SYSTEM WITH NH_4OH RECOVERY

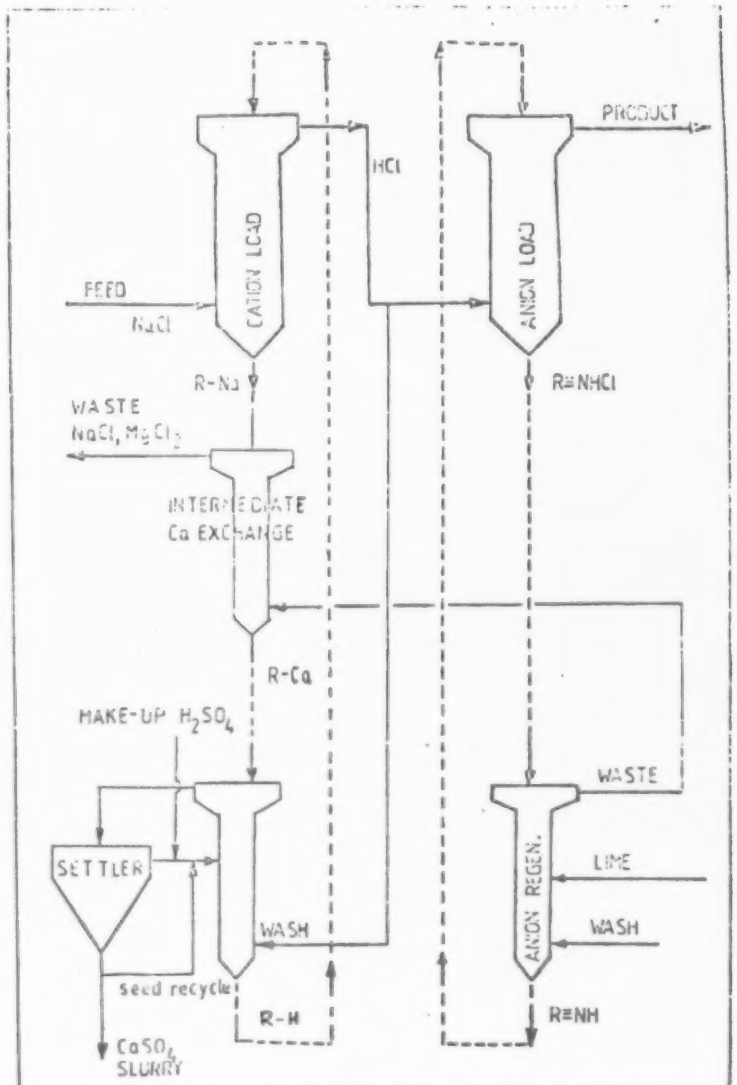


FIGURE 2 FIVE COLUMN SYSTEM WITH H_2SO_4 RECOVERY

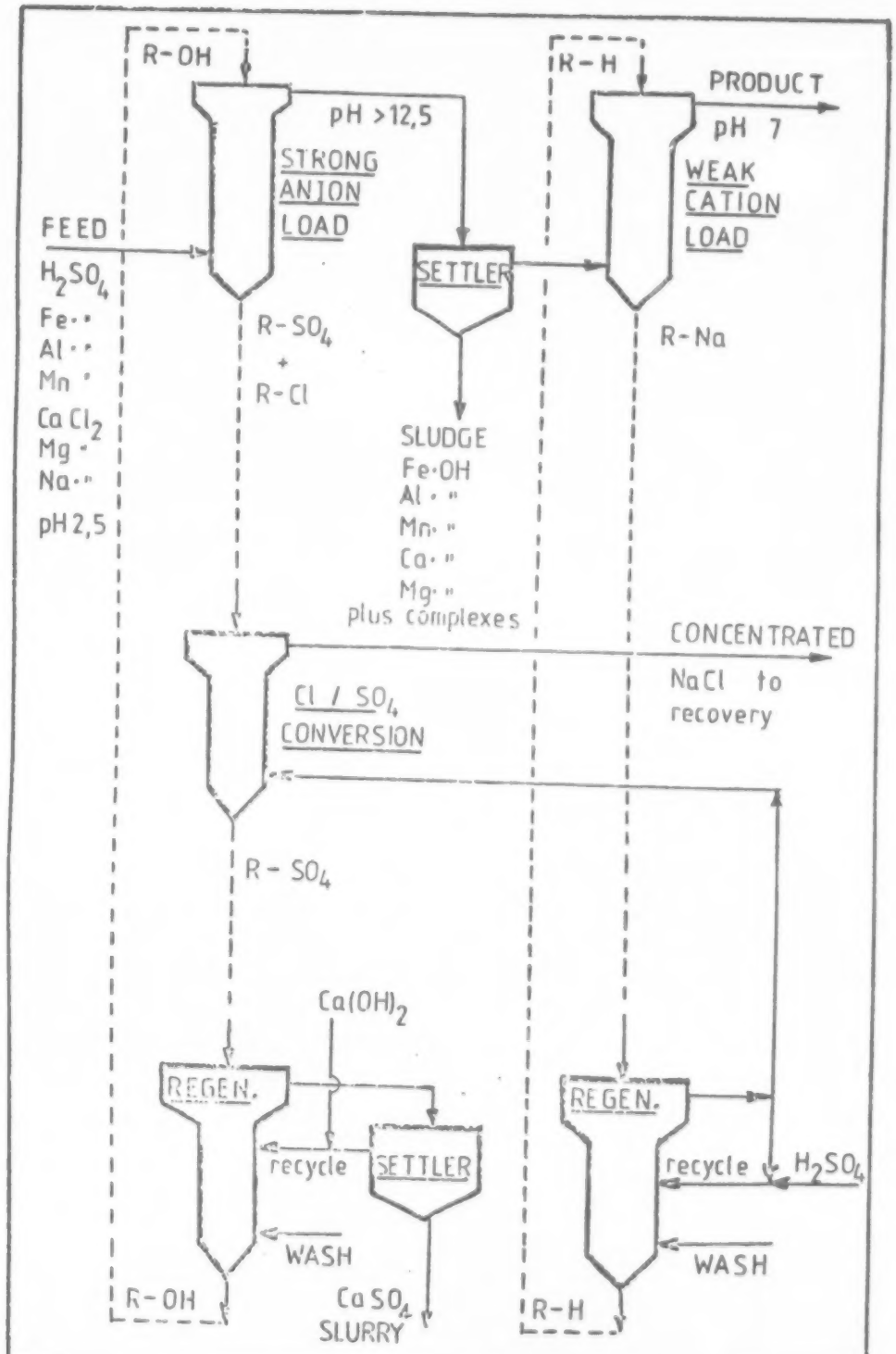


FIGURE 3 ACID MINE DRAINAGE TREATMENT WITH RECOVERY OF SOLID $CaSO_4$ AND SODIUM CHLORIDE.

slurry with 50% solids is removed from the process when the calcium form cation resin is regenerated with H_2SO_4. 92% water recovery from 800 mg/l TDS water has already been demonstrated. In this process, H_2SO_4 and $CaSO_4$ can be recovered using H_2SO_4 and $Ca(OH)_2$ as regenerants.

2) HENDRY (1983) proposed the use of CIX for desalination of high TDS acid mine drainage containing high sulfates as well as high Ca, Mg, Fe, Al, and Mn levels. Strong anion resin exchanges anions for hydroxyl raising the pH to over 12 and thus precipitating almost all of the cations except Na which remains as NaOH. Then, both anion and cation removal is attained with one equivalent of $Ca(OH)_2$ as regenerant costing only RC0.002 (U.S. $0.001) per equivalent, giving a chemical cost of only R0.24/m³ for a 7,000 mg/l water (R1.20/m³ for strong cation/weak anion).

This calculated chemical cost is identical to that incurred if the AMD is simply neutralized using lime. But, it provides a remarkable quality improvement as shown by the results of batch work on samples of AMD tested at the University of Cape Town.

TREATMENT OF AMD WITH STRONG ANION RESIN

	pH	Na	Ca	Mg	Fe	SO_4
Feed	2.8	186	368	488	305	3,425
Product	12.5	186	145	0	0	13

HENDRY (1983) emphasized the early stages of this work and that there are problems relating to resin fouling by "aging" effects of the precipitated metal hydroxides and, particularly, the problem of economically removing the residual NaOH from treated water, especially where Na is high as is usually the case in AMD.

3) In treating treated sewage effluents, the buildup of organic fouling on resin beads was experienced, but this, beyond a certain equilibrium point, did not interfere with ion adsorption by the resin.

Bruce Hendry can be contacted at:

UNIVERSITY OF CAPE TOWN
Dept. of Chemical Engineering
Rondebosch CP
South Africa 7700
(021) 698-548
Bruce A. Hendry
Bill Randall (Ext. 333)

KADLEC and HUBNER (1976) reported an improved technique for brackish water deionization by ion exchange. Their paper was not obtained.

SIROTHERM PROCESS

A second innovative ion exchange desalination process in the SIROTHERM process developed by the CSIRO in Australia and described by BOLTO (1975) and BOLTO, et al. (1982).

The SIROTHERM Process is innovative in that it employs thermal regeneration of the loaded resin, i.e., it overcomes the problem of adding salts to the system for elution of resins and thereby adding more salts for ultimate disposal. It also employs magnetic resin allowing improved kinetics of smaller beads recovered by magnetic filters.

Sadly, the SIROTHERM process appears more suited to NaCl removal than the kinds of salts (e.g., $SO_4^{=}$, Ca^{++}, metal ions Fe^{++}, Mn^{++}, Cu^{++}, etc.) commonly encountered in mine-mill environments.

The SIROTHERM process currently being installed in a commercial-scale municipal supply in a suburb of Perth is described in more detail in Chapter 36 on chloride removal.

More details can also be requested on SIROTHERM from:

CSIRO
Division of Chemical and Wood
Technology
Bayview Avenue
Private Bag 10
Clayton, Victoria
Australia 3168
(03) 542-2244
Telex: 35675
Brian A. Bolto

AMDEL - THE AUSTRALIAN MINERAL
DEVELOPMENT LABORATORIES
182 Wittenoon Street
East Perth, WA 6000
(06) 325-7311
Neville Blesing
Manager

ICI AUSTRALIAN OPERATIONS PTY LTD.
Central Research Laboratories
Newson Street
Ascotvale, Victoria
Australia 3032
(03) 377-2288
Bernie Reichert
Polymer Materials Research Manager

APPLICATIONS OF ION EXCHANGE FOR CONTAMINANT REMOVAL

U.S. EPA (1981) reviewed the use of ion exchange processes for metal removal which would allow wastewater purification and recycling in the metal finishing industry. They also review IX as a means of "end-of-pipe" pollution control and for chemical recovery, again oriented towards the metal finishing industry.

U.S. EPA (1981) acknowledged that although ion exchange processes have been commercially available for many years, widespread interest in their use for metal finishing pollution control has developed only recently. They point out that one reason for the new wave of interest is the broad range of resins available today. They felt that since hydroxide precipitates of metals are "hazardous" wastes, the concentrates produced in IX systems would be more amenable to metal recovery than are hydroxide precipitates. In this latter conclusion, the EPA may be misguided since the small-scale recovery of metals from solutions or precipitates is unlikely to be more than a pipe dream for years to come due to the depressed state of most metal markets and the poor economy of small-scale metal recovery and purification processes. Nevertheless, the EPA has forced the metal finishing industries to treat and dispose of effluents and concentrates and is working hard on the mining and mineral processing industries as well. In some cases, metal chemicals may be recovered in useful form at an improved economy compared with costly disposal procedures.

The U.S. EPA (1980) summary report is available from:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Industrial Environmental Research Lab
Cincinnati, OH 45268

This report includes the following items of general interest:

Table 1 - Selectivity of Ion Exchange Resins in Order of Decreasing Preference

Strong Acid Cation Exchanger	Strong Base Anion Exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Flouride
Potassium	Sulfate
Ammonia	
Sodium	
Hydrogen	

Table 2 - Chelating Cation Resin Selectivities for Metal Ions

Metal Ion	K^m/Ca^*
Hg^{2+}	2,800
Cu^{2+}	2,300
Pb^{2+}	1,200
Ni^{2+}	57
Zn^{2+}	17
Cd^{2+}	15
Co^{2+}	6.7
Fe^{2+}	4
Mn^{2+}	1.2
Ca^{2+}	1

* Selectivity Coefficient for the metal Over Calcium Ions at pH 4

Table 3 - Cost of Commercially Available Resins (1980)

Resin	Cost ($/ft²)
Strong Acid Cation	$ 50-100
Weak Acid Cation	100-150
Strong Bace Anion	150-200
Weak Base Anion	150-200
Chelating Resins	200-250

Table 6 - Chemical Prices (1980)

Reagent	Description	Cost $/Lb.
HCl	Carboys 32% HCl	$0.05
NaOH	Carboys 50% NaOH	$0.075
Hydrated Lime	100 lb. Bags	$0.05
$NaHSO_3$	100 lb. Bags	$0.20
H_2SO_4	Carboys 97% H_2SO_4	$0.05

The examples cited by U.S. EPA (1981) have little or no applicability to mining and mineral processing waste streams. Nonetheless, the need to recycle water and solutions and to treat effluents prior to discharge does affect the mining and mineral processing industry, and ion exchange processes have, in a few cases, been applied usefully.

SLATER, et al. (1978) tested the use of continuous ion exchange for the removal of environmental contaminants from waste streams typical of the mining industry.

A fluidized bed, continuous ion exchange unit was used to treat a synthetic minewater containing 56 mg/l Cu, 3.5 mg/l Ni, 0.3 mg/l Co, 1.0 mg/l Fe, and 20.0 mg/l Ca at pH 4. Strong acid resin, Amberlite 200C was used in the sodium form. After five-minute upflow intervals, the loaded resin was transferred by eluate to the top of an elution column for elution by NaCl. A continuous system was devised. It is not known what the results of these tests were or whether they indicated a cost effective treatment process. The report and further information would be available from:

CANMET
Energy Mines and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1
(613) 995-4194
Gordon M. Ritcey
M. J. Lucas

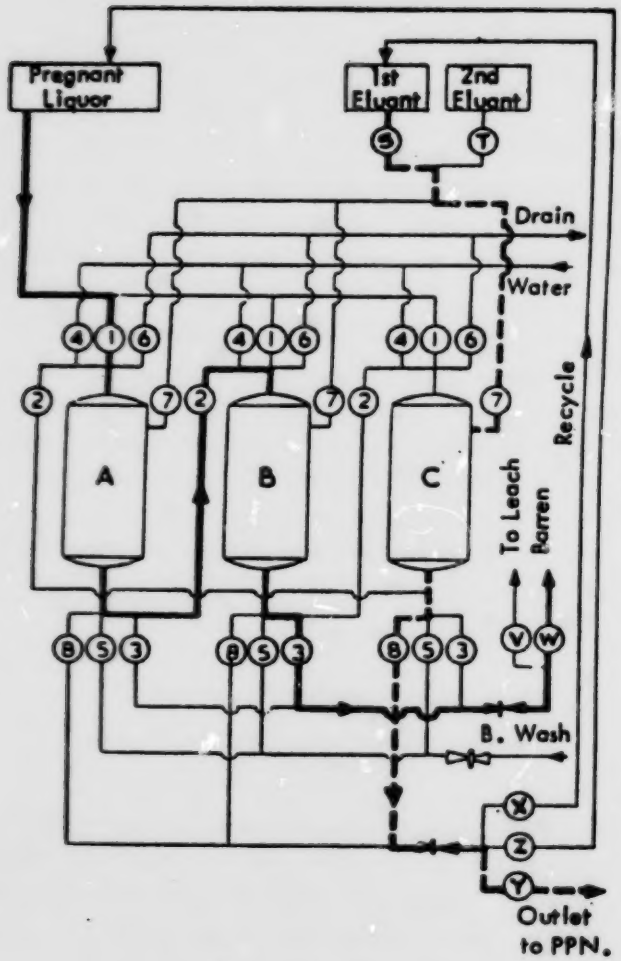
As a result of these tests, no CIX effluent treatment plants have been installed in Canada or elsewhere, although some would like to see further development work in this area.

DIFFERENCE IN PERFORMANCE - FIXED VS. FLUID-BED IX

This report does not have room to accommodate a description or discussion of the various ion exchange process principles or the pros and cons of each. However, one important difference is mentioned between fluid-bed multiple-stage systems and plug flow (downflow fixed-bed) systems. In a counter-current process, the number of stages is a critical factor in the efficiency of the process as is demonstrated by the wellknown McCabe-Thiele diagram. In a plug flow system, as long as solutions are well disributed and channelling avoided, the column acts as an unlimited number of stages. In fluid-bed, multi-stage systems, each stage is assumed to be perfectly mixed, and the system is limited to the number of tanks installed, each acting as a stage. In this sense, the fixed-bed plug flow system should theoretically allow higher loadings of metal ions on the leading edge and the lowest possible levels of ions in the effluent solutions. It is important to distinguish between continuous plug flow systems and two or three-stage merry-go-round fixed-bed systems which effectively present only two stages of adsorption. As mentioned above, continuous plug flow and fixed-bed systems are less tolerant to physical fouling of the IX bed by particulates filtered from the feed solution.

APPLICATIONS OF CIX FOR CONTAMINANT REMOVAL

Ion exchange systems are also employed for the selective removal of undesirable contaminants, e.g., uranium or molybdenum, from process streams. Two examples where effluents are treated by ion exchange prior to discharge primarily to meet discharge premit requirements are the Cotter Corporations's Schwarzwalder minewater at Golden,



THREE COLUMN IX SET FOR URANIUM EXTRACTION
Shown for sake of comparison

Colorado, and Climax Molybdenum Division's tailings effluent treatment plant at Climax, Colorado. These two water treatment plants were installed primarily to remove uranium and molybdenum respectively. The Cotter installation is described in Appendix I trip reports, and also by PALMER, et al. (1984) while GOTT and LAFERTY's (1977) description of the CLIMAX unit is inserted below.

A third large-scale effluent treatment plant employing ion exchange for selective removal of uranium is the Wyoming Minerals Corp. plant that treats Bingham Canyon acid copper mine drainage in Utah. This operation employed Chem-Seps' "Higgins Loops" to treat 1,500 m^3/h (6,600 U.S. gpm) solution containing 6-7 mg/l U_3O_8. This plant was described by RANDOL (1980), and the trip report from that investigation is also inserted below. This trip report is critical of Chem-Seps in that several problems were experienced in this and other plants. It is fair to state, however, that the "Higgins Loop" is a very innovative system, and that if it were to be installed to achieve half a quantum leap forward in terms of specific flow rates rather than the whole quantum leap attempted, this system would undoubtably give rise to fewer mechanical problems.

Several other ion exchange applications for specific removal of contaminants have been installed by Chem-Seps such as nitrates from municipal water supplies and, although these do not refer to mine-mill applications, they are analogous and can be taken into account to demonstrate the practical use of CIX for a wider range of contaminant removal. For example, FICKLIN (1983) reported on the separation of arsenic (III) and arsenic (V) in groundwaters by ion exchange using Dowex strong ion exchange resin. The Dowex IX8 resin 100-200# in acetate form was shown suitable for arsenic removal. More information can be obtained from:

W. H. FICKLIN
U.S. Geological Survey
Box 25046
Denver, CO 80225
(303) 888-3001

WILMOTH, et al. (1979) tested lime neutralization, reverse osmosis, and ion exchange for the removal of arsenic, Cd, Cu, Hg, Ni, Se, Zn, B, and P from mine drainage. All but B and P were removed. They found that although R.O. and ion exchange were slightly more effective overall than neutralization, the chemical requirements and need for subsequent waste treatment offset their advantages.

SYNEX RESINS

Ion exchange can be used for selective recovery or removal of base and heavy metals. Most of the wellknown ion exchange resin suppliers listed below offer a range of metal selective resins for this purpose. Of course, the economics of these processes is

adversely affected by the currently depressed metal markets, but there may be other incentives such as the need to remove contaminants prior to discharge of effluents.

One example of selective IX recovery of ions, e.g., Cu in the presence of Fe from acid solutions (pH2), is available from:

KING INDUSTRIES, INC.
Post Office Box 588
Norwalk, CT 06852
(203) 866-5551
Dr. Leonard J. Calbo

A mixture of 10% active SYNEX DN or DD and SYNEX XB-1 is employed which is eluted with 10-15% H_2SO_4 to recover copper in an eluate suitable for electrowinning.

COTTER CORPORATION - SCHWARZWALDER MINE

The most outstanding application of CIX for minewater treatment encountered so far from a performance point of view is the minewater treatment plant at the Schwarzwalder Mine, Golden, Colorado. Performance of this 500 U.S. gpm plant is described in greater detail in Appendix I. Uranium is reduced from 3-3.5 mg/l U_3O_8 in feedwater to 10-20 ppb U_3O_3 in the product water. In addition, elements such as Cd and copper are reduced to levels of 0.0004 mg/l Cd and 0.005 mg/l Cu and radium from 50-100 p Ci/l to 5 p Ci/l which is remarkably good performance and a breakthrough in effluent treatment technology.

Information on this plant, its design, an its operation can also be requested from:

COTTER CORPORATION
Water Treatment Plant
Ralston Creek Canyon
Golden, CO 80401
(303) 642-3893
Charles Palmer
Site Manager

HIMSLEY ENGINEERING
250 Merton Street
Toronto, Ontario M4S 1B1
(416) 485-4441
Alec Himsley
President

The CIX system employed uses two downflow IX beds in series and a downflow resin elution system. One of the tricks in achieving this exceptional adsorption performance is a step inserted to treat loaded resin between adsorption and elution to react any carbonates (uranium is adsorbed as a carbonate complex in this case). Were it not for this step, CO_2 generated by reaction between carbonates and the acid eluant would cause

channelling in the column which would result in less efficient elution and consequently a less effluent adsorption performance as well.

ION EXCHANGE SYSTEMS

FIXED-BED SYSTEMS - WATER CONDITIONING

Conventional ion exchange systems used in water demineralization prior to use as boiler feed or as a water conditioning step in municipal supply can be obtained from virtually any water treatment equipment supplier. Technology used in this area does not seem to have changed much since the attached description on water conditioning was written in 1970.

There is along list of suppliers of these systems including:

ILLINOIS WATER TREATMENT CO.
4669 Shepherd Trail
Rockford, IL 61105
(815) 877-3041

ROHM & HAAS CO.
Independence Mall West
Philadelphia, PA 19105
(215) 592-3000

CHEMICAL SEPARATIONS CORPORATION
Oak Ridge Turnpike
Oak Ridge, TN 37830
(615) 483-7426
Telex: 557 407

HIMSLEY ENGINEERING LTD.
250 Merton Street
Toronto, Ontario
Canada M4S 1B1
(416) 885-4441
Telex: 06217610

PORTALS WATER TREATMENT SA (PTY) LTD.
Permutit Division
Post Office Box 61188
Marshalltown 2107
(011) 21-0401
Telex: 8-6293
W. Monday
Manager, Industrial Projects

Ultra high purity water is produced using several technologies including the TRIOBED process described by WOLFF and ABRAMS (1979) of the Diamond Shamrock Corporation, Redwood City.

FUNDAMENTALS OF ION EXCHANGE IN WATER TREATMENT

by C. S. Parks and I. M. Abrams, Diamond Shamrock Chemical Company

Brief History

The exchange of ions is a phenomenon universally spread throughout nature. Its utilization by man (for the purification of brackish water) has been given some credibility in the Old Testament, Book of Exodus (Chapter 15, verses 23-25). About 1850, two English agricultural chemists, Harris S. Thompson and John T. Way observed a stoichiometric exchange between ammonium and calcium in soils. In 1876, Lemberg identified crystalline aluminosilicates as the exchangers and showed that the exchange of the cations was stoichiometrically reversible. Various natural minerals, called zeolites were found to have exchange characteristics suitable for the softening of water, which involves the exchange of calcium and magnesium for sodium. In 1904 a German chemist by the name of Gans produced the first artificial aluminosilicates. These artificial zeolites had effective capacities two to three times those of the naturally occurring minerals. Synthesis of these zeolites stimulated the industrial development of water softening.

These inorganic zeolites, though suitable for water softening reactions, are not capable of resisting acids, and therefore cannot be used in the exchange of hydrogen ions. The first acid-proof cation exchange materials were produced between 1923 and 1927 by the sulfonation of coal. Two English chemists, Adams and Holmes, successfully synthesized the first organic ion-exchange resins in 1936, thereby opening the way for complete deionization of water.

Definitions

Ion-exchange resins are by definition insoluble solids containing fixed cations or anions capable of reversible exchange with mobile ions of the opposite sign in the solutions with which they are brought into contact.

When salts are dissolved in water, the various ions which make up these salts dissociate and are free to enter into chemical reactions with other ions. In solution, the salt gives positively charged cations and negatively charged anions. The exchange of desirable cations and anions for undesirable ones by an ion-exchange resin forms the basis for the use of ion exchange as a unit operation in water treatment.

Most ion-exchange resins are made by first forming an insoluble, infusible polymer, then adding active acidic or basic groups by appropriate chemical reactions. The polymer matrix must be physically and chemically resistant to the many conditions imposed upon it both during the production of the ion-exchange resin and in the subsequent use of the product. The majority of commercial ion-exchange resins are based on copolymers of styrene and divinyl-benzene, prepared in bead form. A number of ion-exchange resins are also based on phenol-formaldehyde and epoxy-polyamine condensates. The phenolic-based resins are granular rather than spherical and the epoxy resins can be produced in either bead or granular form.

Special Terms for Ion Exchange in Water Treatment

Two different systems are employed in the U.S. to express the performance of ion-exchange resins. The chemists talk in terms of milliequivalents per milliliter or milliequivalents per dry gram to describe exchange capacity, and equivalents or grams per liter to express concentration of insolution ions. The water treatment engineer speaks in terms of kilograins per cubic foot, grains per gallon and parts per million. To further complicate matters, the chemist works with chemical equivalents whereas the engineer usually converts everything to calcium carbonate equivalents.

In order to work with ion exchange in water treatment, one should become familiar with the system of expressing concentrations and capacities as calcium carbonate equivalents. Ion-exchange resin performance and data (for applications in water treatment) are nearly always presented as calcium carbonate equivalents, particularly in U.S. literature. The use of this system is based upon the existence of

Presented at the 7th Annual Liberty Bell Corrosion Conference

both calcium and carbonate ions in water and the fortuitous circumstance that the molecular weight of the compound is 100. Also, one of the major objects of ion exchange in water treatment is to prevent the deposition of calcium carbonate from water.

Water Analysis for Ion Exchange Calculations

A reasonably accurate water analysis is required to design an ion exchange installation for water treatment. With most natural waters, the analysis can be presented in a form similar to that in Table I.

TABLE I
WATER ANALYSIS FORM

CATIONS		ANIONS	
Alkaline Earth Cations or Total Hardness	Ca^{++} Mg^{++}	Total Alkalinity ALK	OH^- CO_3^{--} HCO_3^-
Alkaline Metal Cations	Na^+ K^+	Total Salts of Strong Acids or TMA	SO_4^{--} Cl^- NO_3^-
Total Dissolved Solids TDS	=	Total Dissolved Solids TDS	=
		CO_2 SiO_2 pH	

It is common practice to state the amount of dissolved impurities as the cations and anions actually determined by analysis. These amounts may be expressed in terms of the ions themselves or as their calcium carbonate equivalents. For ion exchange work it is highly convenient to have all values expressed as calcium carbonate equivalents. Table II lists the factors which are used to convert concentrations as the various ions to concentrations as calcium carbonate ($CaCO_3$). To convert any ion concentration to its $CaCO_3$ equivalent, simply divide 50 (the equivalent weight of calcium carbonate) by the equivalent weight of the ion in question, then multiply the quotient by the part per million concentration as the ion. When a water analysis has been converted to calcium carbonate equivalents, the sum of the total cations must equal the sum of the total anions. This is a convenient way to check the values given in a water analysis.

Water Softening With Cation-Exchange Resins

In a great many industrial, municipal and commercial applications, it is desirable to remove or reduce the hardness of water before it is used. Boiler feedwater, commercial laundries, many industrial processes, and to some extent, cooling water, all require soft water.

The hardness in water is composed of the alkaline-earth cations, calcium and magnesium. The sum of these two is the total hardness. The total hardness is then broken down into two categories, the carbonate or temporary hardness and the non-carbonate or permanent hardness. Temporary hardness is the most common and is responsible for the deposition of calcium carbonate scale in pipes and equipment. The following equation illustrates how this scale is formed:

$$Ca(HCO_3)_2 + \text{Heat} \rightarrow CaCO_3 + H_2O + CO_2$$

Non-carbonate hardness will react with the carbonate alkalinity frequently found in soap and detergent formulations to form insoluble deposits. The following equation illustrates this reaction:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

Soaps react with hardness in water to form insoluble and unsightly scums, particularly the familiar "bathtub ring".

The softening of water by ion exchange is relatively simple, but highly effective. The process consists of passing hard water through a column of cation-exchange resin in the sodium form. The sodium on the resin replaces the objectionable calcium and magnesium ions. Figure 1 illustrates the regeneration and service cycles of a water softener and shows the various ion exchange operations which take place.

The amount of hardness removed by one cubic foot of cation-exchange resin is directly dependent on the amount of regenerant salt used to convert the resin to the sodium form. Table III illustrates the capacities for

TABLE II
CALCIUM CARBONATE EQUIVALENTS

	Symbol	To convert ppm as ion to ppm as $CaCO_3$, multiply by
CATIONS		
Hydrogen	H^+	50.00
Ammonium	NH_4^+	2.78
Sodium	Na^+	2.18
Potassium	K^+	1.28
Magnesium	Mg^{++}	4.10
Calcium	Ca^{++}	2.49
Ferrous	Fe^{++}	1.79
Cupric	Cu^{++}	1.57
Zinc	Zn^{++}	1.53
Aluminum	Al^{+++}	5.55
Chromic	Cr^{+++}	2.89
Ferric	Fe^{+++}	2.69
ANIONS		
Hydroxide	OH^-	2.94
Chloride	Cl^-	1.41
Bicarbonate	HCO_3^-	0.82
Nitrate	NO_3^-	0.81
Bisilicate	$HSiO_3^-$	0.65
Bisulfate	HSO_4^-	0.52
Carbonate	$CO_3^=$	1.67
Silicate	$SiO_3^=$	1.31
Sulfate	$SO_4^=$	1.04
	CO_2	1.14
	SiO_2	0.83

TABLE III

Lbs. NaCl per cu. ft.	Capacity, Kgr/cu. ft.	Lbs. salt per Kgr removed, Average
4	16-18	0.24
5	19-21	0.25
6	21-23	0.27
8	24-26	0.32
10	26-28	0.37
12	28-30	0.41
15	30-32	0.48
20	32-34	0.6
50	36-38	1.35

various regenerant levels of Duolite C-20, a common cation-exchange resin used in water softening.

In order to determine the volume of water which can be softened by one cubic foot of cation-exchange resin, it is first necessary to select the desired regeneration level and its corresponding capacity in kilograins per cubic foot. By way of illustration, let us assume a water which contains 171 parts per million total hardness (as calcium carbonate). Question: How many gallons of this water can be softened per cubic foot of resin? From Table III we see that a capacity of approximately 24 kilograins/cubic foot can be obtained by regeneration with 8 pounds of NaCl per cubic foot. To obtain capacity, we must first convert ppm (as $CaCO_3$) to grains per gallon, as $CaCO_3$. Since 17.1 ppm equals 1 grain per gallon, the water in question contains $\frac{171}{17.1}$ or 10 grains per gallon total hardness, as $CaCO_3$. At the selected regeneration and capacity level (8 lbs. NaCl and 24 kilograins, respectively), each cubic foot of resin will soften $\frac{24,000}{10}$ or 2,400 gallons of water before it requires regeneration.

Ordinary waters containing up to 1500 ppm total dissolved solids are readily softened by conventional techniques, as described above. However, with waters containing between 1500 and 5000 ppm total dissolved solids, somewhat unconventional arrangements of equipment and techniques of regeneration are required. In order to effectively soften waters which contain more than 5000 ppm, it is necessary to employ a weak-acid cation resin in the sodium form. The technique, involving a two-step regeneration, has been called the "CARBO-SOFT" process.

Dealkalization of Water by Ion Exchange

Alkalinity in water can be present as bicarbonate, carbonate, or hydroxide. Bicarbonate alkalinity is by far the most common. When water with carbonate or bicarbonate alkalinity is heated, the alkalinity is broken down to carbon dioxide, as shown by the following reactions.

$$2\ HCO_3^- + \text{Heat} \rightarrow CO_3^= + CO_2 + H_2O$$

$$CO_3^= + H_2O + \text{Heat} \rightarrow CO_2 + 2\ OH^-$$

$$\leftarrow CO_2 + H_2O = = H_2CO_3 \rightarrow$$

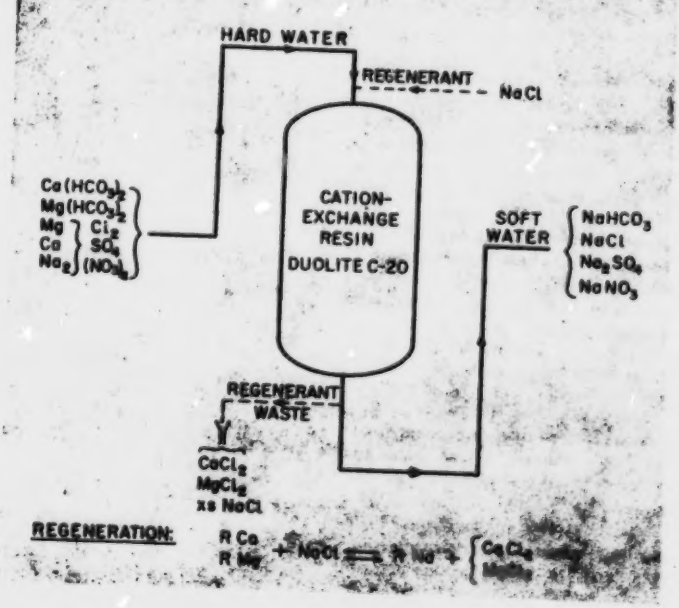
As indicated by the last reaction, carbon dioxide combines with the water to give carbonic acid which can cause corrosion of iron or steel equipment. The corrosion products react further with alkalinity and the deposits can build up in the same manner as calcium carbonate scale.

Alkalinity in raw water can be reduced by several ion-exchange processes. The simplest and most straightforward process is chloride-cycle anion exchange. This process is usually preceded by a water softener. A schematic representation of a chloride-cycle dealkalizer — with the reactions that take place — is illustrated in Figure 2. The resin used in this application is usually a Type 2 strong-base anion exchanger, such as Duolite A-102D.

The use of weakly-acidic cation exchange resin for the dealkalinization of water is becoming increasingly popular with the advent of the new high capacity weak-acid resins (such as Duolite CC-3). These resins simultaneously remove both hardness and alkalinity from waters where the ratio of the total hardness to alkalinity is less than or equal to one. When the total hardness to alkalinity ratio is greater than one, hardness is effectively removed, but "leakage" of hardness is observed. The operation and regeneration of a weak-acid dealkalization unit and degasifier are illustrated in Figure 3.

If the total hardness to alkalinity

FIGURE 1. WATER SOFTENING



ratio is greater than one, there are two arrangements which make it possible to achieve complete removal of both hardness and alkalinity. The first arrangement is illustrated in Figure 4 and is often referred to as a "split-stream" system. In this arrangement, the influent water is divided into two parallel flows. One portion is passed through a sodium-cycle water softener and the other portion is passed through a hydrogen-cycle cation-exchange unit. These two flows are then blended and passed through aerator or decarbonator. The sodium-cycle water softener removes the hardness from the water but allows the alkalinity to be carried forward. The hydrogen-cycle cation unit removes the hardness from the water and also creates some free mineral acidity. When these two flows are blended, the free mineral acidity from the hydrogen-cycle cation unit reacts with the alkalinity from the water softener to produce carbon dioxide and water. The CO_2 can be eliminated by aeration or degasification. The exact amount of alkalinity present in the finished blend from this type of system can be very closely controlled by varying the ratio of flows between the two units.

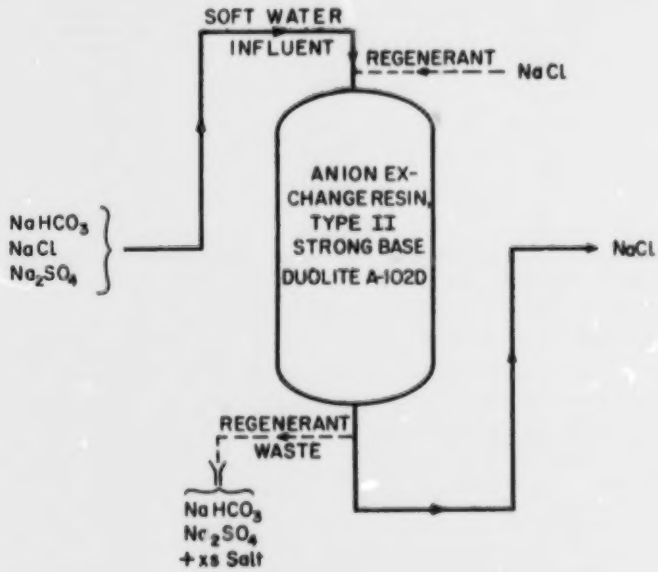
The second means of producing soft, dealkalized water when the hardness to alkalinity exceeds one involves the use of a layered-bed cation unit. This system consists of a single tank ion-exchange unit with a layer of lower density weak-acid resin on a layer of higher density strong-acid resin. The weak-acid resin is regenerated with a mineral acid and the strong-acid resin with sodium chloride. The temporary or carbonate hardness is removed by the weak-acid resin and the non-carbonate or permanent hardness is removed by the strong-acid resin. The effluent from this duo-bed unit is then passed through an aerator or decarbonator for removal of CO_2. The reactions of the individual resins are illustrated in Figure 3 for the weak-acid resin and Figure 1 for the strong-acid resin.

Demineralization with Ion Exchange

Many industries such as manufacturers of electronic components and the public utilities, in their quest for better products and higher output capacities, have found that increasingly larger quantities of extremely high purity water are required for effective operation. Distillation cannot achieve the quantity and quality of water required by such applications. The relative ease and low cost of providing a high purity water by ion exchange has led to widespread use of the process.

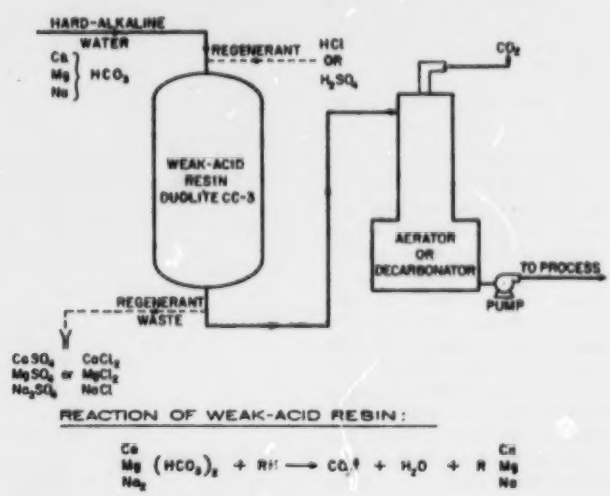
The design and selection of the proper ion-exchange system and the correct type of ion-exchange resins to fulfill the requirements of a particular application is the job of a qualified equipment manufacturer or de-

FIGURE 2. CHLORIDE-CYCLE ANION DEALKALIZATION



REGENERATION: $\begin{matrix} R\,HCO_3 \\ R\,SO_4 \end{matrix} + NaCl \rightleftharpoons R\,Cl + \begin{cases} NaHCO_3 \\ Na_2SO_4 \end{cases}$

FIGURE 3. DEALKALIZATION WITH A WEAK-ACID CATION RESIN



REACTION OF WEAK-ACID RESIN:

$$\begin{matrix} Ca \\ Mg \\ Na_2 \end{matrix} (HCO_3)_2 + RH \longrightarrow CO_2\uparrow + H_2O + R \begin{matrix} Ca \\ Mg \\ Na \end{matrix}$$

FIGURE 4. DEALKALIZATION BY "SPLIT STREAM"

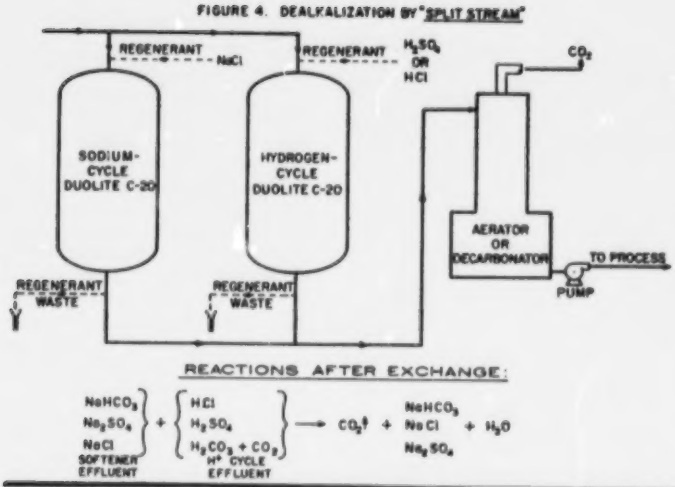


FIGURE 5. DEALKALIZATION BY LAYERED-BED CATION

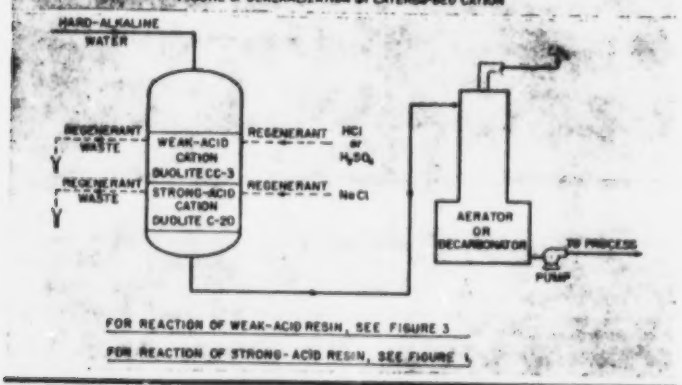
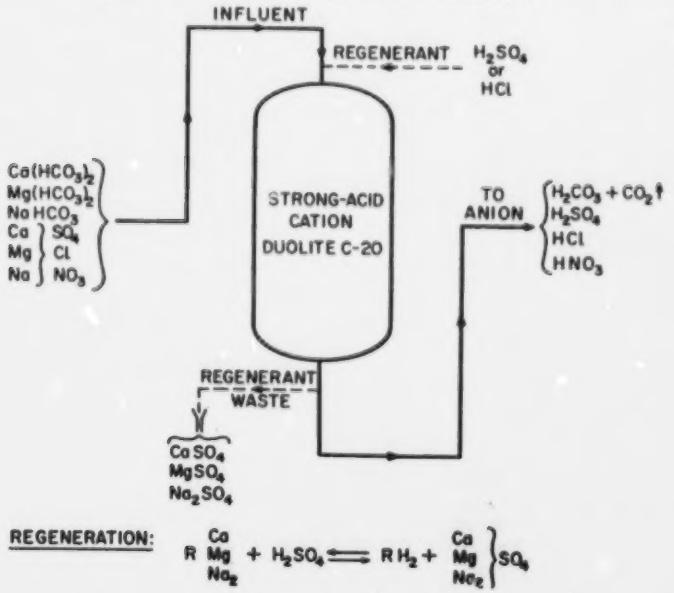


FIGURE 6. HYDROGEN-CYCLE CATION EXCHANGE

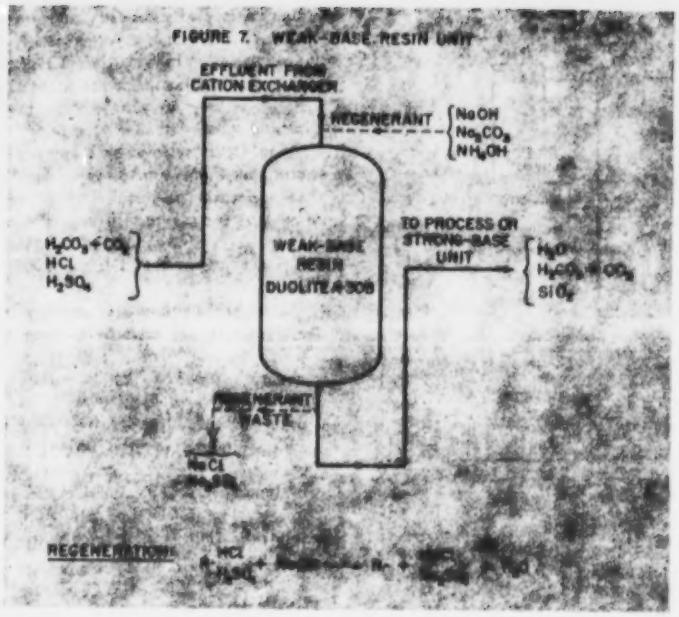


sign engineer. By careful choice of the various ion-exchange resins, it is possible to design many different types of systems to accomplish the same end. Some systems may have high initial capital cost, but low operating expense. Other systems have low capital cost, but higher operating costs. Also the selection of resins and arrangement of equipment will have a direct bearing on the quality of the final effluent from the demineralization system.

Demineralization of water by ion exchange is achieved by passing the water through cation and anion-exchange resins. The cation exchanger in the hydrogen form exchanges hydrogen ions for the positively charged cations in the water. The anion-exchange resin in the hydroxide form exchanges hydroxide ions for the anions in the water. The net result of this operation is replacement of the dissolved salts with water.

These operations can be conducted with the cation and anion exchangers in separate vessels or in a single vessel. Figure 6 illustrates the reactions which occur when a water passes through a column of a strong-acid cation-exchange resin in the hydrogen form. The effluent from such a unit is then carried forward to an anion-exchange resin. This might be either a weak-base or a strong-base resin. A weak-base resin adsorbs the entire acid molecule; that is, if hydrochloric acid (HCl) is put through a weak-base resin, the entire HCl molecule is taken up by the resin, not just the chloride ion. This is illustrated (in reverse) by the equation in Figure 7 which shows the regeneration of a weak-base anion resin. The process consists of a typical acid-base reaction which forms the salt of that acid in water. Since this reaction goes to completion, it is possible to regenerate a weak-base resin with near-stoichiometric amounts of regenerant. In many applications, the weak-base resin is followed by a strong-base anion resin. The spent regenerant from the strong-base anion unit is sufficient to regenerant the weak-base anion resin in most cases.

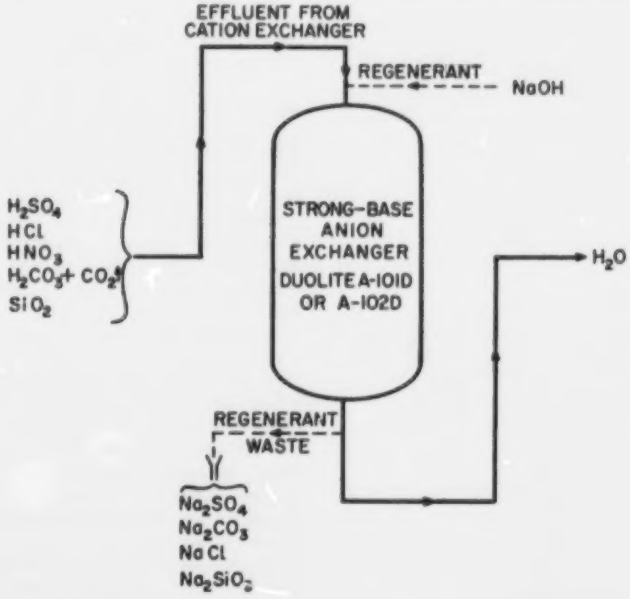
Figure 8 illustrates a typical strong-base anion unit operating in the hydroxide cycle. The mineral acids, carbon dioxide, and silica, which have been created by the cation exchanger, are removed by contact with the strong-base resin in the hydroxide



form. The final product from this unit is demineralized water. With three-bed systems, the strong-base unit removes only the CO_2 and SiO_2 which pass through the weak-base unit.

As mentioned before, it is possible to use many combinations of the various cation and anion-exchange resins to demineralize water. Figure 9 shows some of the various possible combinations and arrangements of ion-exchange resins. It also indicates the conductivity, pH and anticipated silica which might be expected from the various layouts. This illustration alone should further dramatize the need to consult water treatment equipment manufacturers or design engineers when selecting the proper ion-exchange system and resins to do a specific job.

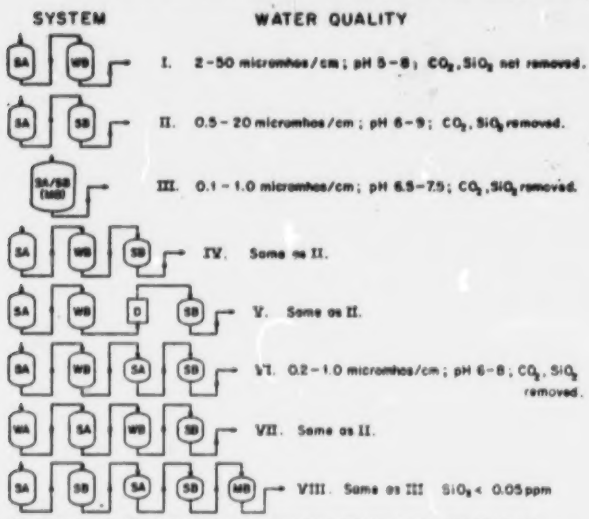
FIGURE 8. HYDROXIDE-CYCLE ANION EXCHANGE (STRONG-BASE)



REGENERATION:

$$R\begin{matrix}SO_4\\Cl\\CO_3\\SiO_3\end{matrix} + NaOH \rightleftharpoons R{\cdot}OH + \begin{matrix}Na_2SO_4\\NaCl\\Na_2CO_3\\Na_2SiO_3\end{matrix}$$

FIGURE 9. FLOW DIAGRAMS OF SYSTEMS USED IN WATER DEIONIZATION



IWC-79-33
Progress Report

OPERATING EXPERIENCE WITH TRIOBED IN THE PRODUCTION OF ULTRA HIGH PURITY WATER

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and

I.M. Abrams, Diamond Shamrock Corp., Redwood City, Calif.

With respect to requirements for ion exchange condensate polishing, the definition of "ultra high purity water" has been changing rapidly during the past decade. Whereas 5 ppb leakage was acceptable in the sixties, 1 ppb became the target in the mid seventies. As we approach the eighties, the target is heading toward 0.1 ppb. This would indeed be a remarkable achievement in a relatively short period of time. Cooperative efforts by resin manufacturers, equipment vendors, and utility operators are promising to reach this target. One such effort involves the development of TRIOBED. This improvement in mixed bed operation and its performance at three power stations in Europe is the principal message of this report.

THE ION LEAKAGE PROBLEM

As pointed out in a 1976 presentation at this conference (1), resins which are completely regenerated to the H/OH forms or to the NH_4/OH forms do not leak ions. By calculations using mass action equilibrium equations, it was shown that sub-ppb leakages could be readily achieved in H/OH operation, but that very high degrees of regeneration and extreme diligence had to be practiced to achieve such very low ion leakage with NH_4/OH operation. For operation beyond the ammonia break, residual sodium in the cation exchanger would have to be less than 0.5%. For chloride leakages below 1.5 ppb, the anion exchanger should contain less than 10.8% residual chloride at pH 8.8 and less than 2% chloride at pH 9.6.

One means of reducing the chloride content of the strong-base resin is to use a two-step regeneration (2). Polyvalent anions readily replace chloride, then hydroxide readily replaces the polyvalent anions. Figure 1 illustrates conversion to the hydroxide form of a Type 1 strong-base anion exchanger (Duolite A-161) from both the chloride and sulfate forms. In the event of a condenser leak, leading to a partial exhaustion of the anion resin with chloride, subsequent leakage of this chloride from the resin could be minimized (especially in NH_4/OH operation) and caustic consumption reduced by a two-step regeneration, for example, with dilute sulfuric acid followed by caustic soda.

It has long been recognized that the principal difficulty in achieving sub-ppb leakage and ultimate quality effluents in mixed bed operations is due to the cross-contamination of resins during

hydraulic separation prior to regeneration. If not completely separated, a minor portion of the cation exchanger contaminates the anion exchanger and is converted to the sodium form on regeneration with caustic soda. Similarly, a portion of the stray anion exchanger is converted to the bisulfate form when contacted with the sulfuric acid regenerant. Thus, incomplete separation subsequently leads to escape of sodium and sulfate ions from the mixed beds.

The problem is particularly aggravated with external regeneration, which is almost universally used by utilities in the U.S. for condensate treatment. The practice of external regeneration and NH_4/OH operation has been a severe challenge to the industry in the attempt to reach the target of sub-ppb leakage.

This challenge has been met in part by some ingenious methods which attempt to remedy the cross-contamination problem in mixed bed operations. These patented methods, such as Ammonex (3), Calex (4, 5) and Seprex (6) have been described adequately in earlier reports and need not be further explained here.

These methods are designed primarily to reduce sodium leakage. Until quite recently the potential for leakage of sulfate was neglected. However, this potential was pointed out by one of us in 1976 (1) and confirmed in England on H/OH condendate polishers (7, 8). The initial sulfate leakage from a freshly regenerated mixed bed in the H/OH cycle is illustrated in Figure 2. This is due to the presence of anion exchanger in the cation resin when the latter is regenerated with sulfuric acid.

THE TRIOBED PROCESS

The process was developed by Dia Prosim in France. The first industrial scale system was installed in Belgium in 1976. About thirty Duolite TRIOBEDS are currently in operation and about thirty more scheduled for startup on the near future. Operating results are now becoming available.

TRIOBED is designed to prevent rather than cure the problem due to cross-contamination in mixed beds. The principle, illustrated in Figure 3, is quite simple. The resin mixture consists of three components: a strong-acid cation exchanger, a strong-base anion exchanger, and an inert resin. The specific gravity and particle size of the three components are designed to separate virtually completely into three distinct layers after ten minutes of backwash and settling. In practice, the layer of inert resin is 10 to 20 cm (4 to 8 inches) in depth.

Either internal or external regeneration can be used. With the former, the inert layer provides a buffer zone to prevent contact between acid and the anion exchanger or between caustic and the cation exchanger. In external regeneration, the inert resin layer serves to prevent carryover of the cation exchanger with the anion exchanger.

TRIOBED Resins

The Duolite TRIOBED ion-exchange resins (Duolite C-26TR and A-161TR), have been optimized to give maximum regeneration efficiency and high resistance to osmotic shock. Experience to date has demonstrated that these resins are capable of achieving sub-ppb leakage for at least three years with little or no deterioration in performance.

Studies were carried out to optimize the particle sizes and densities of the three resins, factors which are necessarily interrelated. Figure 4 shows a plot of the settling rate versus particle diameter of the cation exchanger, the anion exchanger and the inert polymer used in the Duolite TRIOBED process. These studies demonstrated that Duolite C-26TR, with a minimum diameter of 0.7 mm (maximum settling rate of 95 m/h) will separate completely from Duolite A-161TR, which has a maximum diameter of 0.85 mm (maximum settling rate less than 55 m/h). The inert resin (Duolite S-3TR) has a specific gravity intermediate between those of the cation and anion exchangers; its particle size is designed to allow separation from both during backwash and settling. In terms of U.S. Standard Sieves, the Duolite C-26TR is essentially larger than 25 mesh, the Duolite A-161TR smaller than 20 mesh, and the Duolite S-3TR between 22 and 25 mesh.

CASE HISTORIES

1. Kerncentrale EBES, Doel, Belgium

Full-scale testing of the Duolite TRIOBED has been conducted at the Doel Nuclear Power Station near Antwerp, Belgium. Doel 1 and 2 are Westinghouse PWR designs, each with a net electrical output of 392 MW. During construction, the decision was made to control steam generator chemistry with "all volatile treatment" (AVT). As a result, full flow condensate polishers were retrofitted into the systems to cope with anticipated condenser leaks. The original polishers, built by Degremont Sobelco, consisted of precoat (cellulosic) filters to remove "crud", cation exchangers to remove ammonia, and deep mixed beds to remove dissolved salts. (The design is shown schematically in Figure 5.) Because of space limitations, the resin beds were regenerated in the service vessel.

As a result of numerous problems encountered with the initial condensate polisher system (9), the precoat filter was eliminated and the Duolite TRIOBED installed at Doel 1 in January, 1976 and at Doel 2 one year later.

In the original installation, the first cation exchanger vessel contained 14.5 m^3 (512 ft^3) of Duolite C-26C and was operated at a flow rate of 90 m/h (37 gpm/ft^2). The mixed bed, with a diameter of 3.2 m (10.5 ft), contained 5.6 m^3 (198 ft^3) of Duolite C-26C and 7.5 m^3 (265 ft^3) of Duolite A-161TR. It was operated at 110 m/h (45 gpm/ft^2). On conversion to TRIOBED, the Duolite C-26C was replaced by Duolite C-26TR, having a particle size better suited to efficient separation. However, the Duolite A-161C was retained because it was still in good operating condition and had a particle size suitable for TRIOBED. Duolite S-3TR was added to each mixed bed to give the following volumes:

Duolite A-161C:	6.6 m^3	(233 ft^3)
Duolite S-3TR:	1.6 m^3	(56 ft^3)
Duolite C-26TR:	4.8 m^3	(170 ft^3)

The flow rate is 1000 m^3/h (4000 gpm) per TRIOBED. The linear velocity is 108 m/h or 44 gpm/ft^2. The cation exchanger is regenerated with 5% sulfuric acid at a dosage of 1233 kg (16 lbs/ft^3), the anion exchanger with 3.5% caustic soda at a dosage of 900 kg (8.5 lbs/ft^3). The resins are regenerated simultaneously, the caustic soda downflow and the acid upflow, the effluents meeting at the intermediate collector.

Prior to the installation of TRIOBED at Doel 1, the mixed bed actually contributed an estimated 0.45 ppb of sodium to the condensate. From the studies made, it was estimated that sodium

concentration in the steam generator was an average of 23 ppb when the mixed bed polisher was in operation compared to only 12 ppb when not in operation.

A comprehensive study of the TRIOBED operation was made by a team from the CEGB using a mobile unit equipped with very sophisticated analytical instrumentation capable of measuring extremely low sodium and sulfate levels. This study was conducted during the summer of 1977. The results show that the sodium level at Doel 1 falls below 1 ppb even at the beginning of a cycle and goes below 0.1 ppb during much of the working cycle. Similarly, the sulfate leakage falls to about 1 ppb after only a few hours, a result which is all the more remarkable in that the anion exchangers had been in service for 33 months at Doel 1 and 25 months at Doel 2 at the time of monitoring.

Average results

Sodium: At Doel 1, the mean sodium level in the treated condensate during the test period was 0.08 ppb for one of the TRIOBEDS and 0.10 ppb for the other. At Doel 2, the effluent sodium levels of both TRIOBEDS was about 0.25 ppb. The somewhat higher leakage at Doel 2 was probably due to the less centralized position of the intermediate collector in the inert layer.

Chloride: Analyses for chloride in the steam generator indicated levels in the TRIOBED effluents of 0.1 to 0.2 ppb.

Sulfate: Measurements of effluent sulfate did not always check with levels found in the steam generator. However, it can be said that mean values did not exceed 1 ppb and probably fell below this value most of the time.

In general, the tests on the TRIOBED installation at Doel suggested that the leakages (in H/OH operation) were 1/2 to 1/5

of those found with the more convential mixed beds.

2. Interescaut Thermal Power Station, Schelle, Belgium

Early in 1979, the conventional resins in the mixed-bed polisher at Schelle were replaced by TRIOBED resins. The vessel was 2.31 meters (7.6 feet) in diameter and was charged as follows:

Duolite	Volume		Bed Depth	
	Liters	cu.ft.	cm	inches
C-26TR	2,400	85	57	22.4
A-161TR	2,600	92	62	24.4
S-3TR	800	28	19	7.5

The intermediate distributor is centered in the layer of inert resin so that it is equidistant from the cation and anion interfaces after separation.

The condensate is first filtered through AMA cartridge filters (10 mμ) and then through the resin colums at a rate of 305 metric tons per hour, equivalent to a flow of about 75 m/h (30.6 gpm/ft^2). The condensate is treated with 1 ppm NH_3 to give a pH of 9.4.

The resins are regenerated in the working vessel (internally). After separation into three distinct layers by 15 minutes of backwash at 12 m/h (4.9 gpm/ft^2), the resins are regenerated simultaneously, the cation upflow and the anion downflow. The spent regenerants are discharged through the collector buried in the inert resin. The cation exchanger is regenerated with HCl at a dosage of 150 g/l (9.36 lbs/cu.ft.) at a concentration of 10%; the anion exchanger with NaOH, 150 g/l at 4%.

As shown in Figure 6, sodium quickly falls below 1 ppb and levels out at 0.3 ppb. With the cation exchanger in the ammonium form at the end of the cycle and the effluent ammonia at 15 ppb,

the sodium reaches only 1.5 ppb.

Chloride determinations indicated leakage values below 1 ppb at influent levels of 3 to 8 ppb. This is particularly impressive since the cation exchanger was regenerated with HCl.

3. Fawley Power Station (CEGB, UK)

Fawley is a fossil fuel plant. The condensate treatment system, which has been in service since 1974 with standard macroporous resins, was of the same design as those already in use in several British nuclear power stations of the AGR type. The condensate polisher was built by Kennicott Water Treatment Co.

Fawley has four 500 MW units, each equipped with two mixed beds each treating 50% of the condensate. The vessels are 2.286 m (7.5 ft) in diameter and each contained 2.83 m^3 (100 ft^3) of cation exchanger and 2.12 m^3 (75 ft^3) of anion exchanger.

The condensate polishing rate is held constant (by recycle) at 540 metric tons per hour at a flow velocity of 133 m/h (54.3 gpm/ft^2). The condensate was usually treated with 0.2 ppm ammonia and the run stopped at or before the ammonia break (about 10 days). If condenser leakage occurred, a double regeneration was applied.

The resins are externally regenerated in a system which would be considered conventional in the U.S. The resins are transferred hydraulically from the service vessels to the regenerating unit through a 400 meter (1,312 ft) pipe containing several bends.

The cation regeneration/separation tank is 1.83 m (6 ft) in diameter and its collector was at a height which left 10 cm of anion exchanger with the cation exchanger. In other words, it

was designed to transfer most the anion exchanger, but to leave a portion in the cation regeneration vessel.

The resins were separated by backwash at 12 m/h (4.9 gpm/ft^2) and regenerated with 128 g/l (8 lbs/ft^3) of H_2SO_4 at 5% and 96 g/l (6 lbs/ft^3) of NaOH at 6%. The resins are rinsed separately to a conductivity of 50 micromhos/cm and then in the mix/storage vessel to 0.1 micromhos/cm.

The initial resins, used from 1974 to 1979, produced the following ion leakages after five years of service.

Sodium	-	0.2 to 1.0 ppb
Chloride	-	1 to 2 ppb
Sulfate	-	1 to 2 ppb.

It should be pointed out that conditions were quite favorable for low leakage – with H/OH cycles and relatively low ammonia concentration.

With the objective of obtaining experience with the three-resin system, the standard resins were replaced with Duolite TRIOBED resins in March, 1979. The existing system was not otherwise modified. Each of the six mixed beds was charged with 3 m^3 (106 ft^3) of Duolite C-26TR, 2.1 m^3 (74 ft^3) of Duolite A-161TR, and 0.5 m^3 (17.6 ft^3) of Duolite S-37R. The collector was placed to have 72 mm (2.8 in.) of inert resin above it and 106 mm (4.2 in.) below it.

A comprehensive monitoring program was scheduled and the Scientific Services Department of the South Western Region of the CEGB at Bristol has undertaken the difficult task of determining leakage values in the treated condensate. The program provides for investigation of both the H/OH and NH_4/OH cycles.

a. <u>H/OH cycle</u>

The existing conditions in service and regeneration were not changed.

Following backwash, separation of cation and anion resins is virtually complete. It is estimated that the amount of cation exchanger in the anion layer is less than 0.5%. After resin transfer, however, several centimeters of anion exchanger remains in the cation regeneration tank. This is most likely due to turbulence during transfer which results in the migration of a small portion of the anion exchanger to the cation layer. This portion is not transferred to the anion regeneration tank.

Until now, the incomplete transfer of anion resin has had no effect on anion leakage. However, it can be expected that sulfate leakage will increase as the resins age in service. For this reason, attempts are being made to modify the existing plant to minimize turbulence and to transfer the cation resin from the bottom of the separation vessel to the cation regeneration vessel.

The results obtained with TRIOBED are significantly better than those obtained previously. The leakage results to date are as follows:

Sodium - always below 0.1 ppb, and usually in the range of 0.01 to 0.06 ppb;

Chloride - always below 0.1 ppb

Sulfate - below 0.1 to 0.3 ppb

It is also noteworthy that theoretical conductivity is reached only ten minutes after a TRIOBED is put into service. The above leakage levels are reached only 20 minutes after starting the run.

b. NH_4/OH cycle

In conversion to the NH_4/OH cycle, the anion exchanger was first treated with 400 g/l (25 lbs/ft^3) of H_2SO_4 to remove re-

sidual chloride, then regenerated with 400 g/l (25 lbs/ft^3) of NaOH at 6%, then ammoniated with 0.5% NH_3 until the effluent sodium level fell below 1 ppm. The resin was rinsed to a conductivity of less than 20 micromhos/cm.

Significantly, for this test work, the condensate pH was increased to 9.3 to 9.4. During the initial test period, effluent sodium values were below 2 ppb. During a cycle which lasted seven days, very high condenser leakage was experienced during which the condensate contained several ppm of sodium. Even under these adverse conditions, effluent sodium remained below 3 ppb until the end of the cycle.

Chloride leakage remained below 0.5 ppb at all times, even with high levels of condenser leakage. The advantage of the anion sulfate treatment was therefore demonstrated. Sulfate leakage also remained low during NH_4/OH operation (0.2 to 0.6 ppb).

In another cycle, with no major condenser leaks and with a two-week run, similar results were obtained. The tests at Fawley are continuing and full results will be published by the CEGB in due course.

ACKNOWLEDGEMENTS

This report could not have been given without the combined efforts of a number of people. The authors would therefore like to gratefully acknowledge the contributions of the following:

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Mr. G. Mills, CEGB, Fawley Power Station

Mr. A. Ferket, Doel Power Station

Dr. J. Balthazar, Laborelec

Mr. Billast, Schelle Power Station

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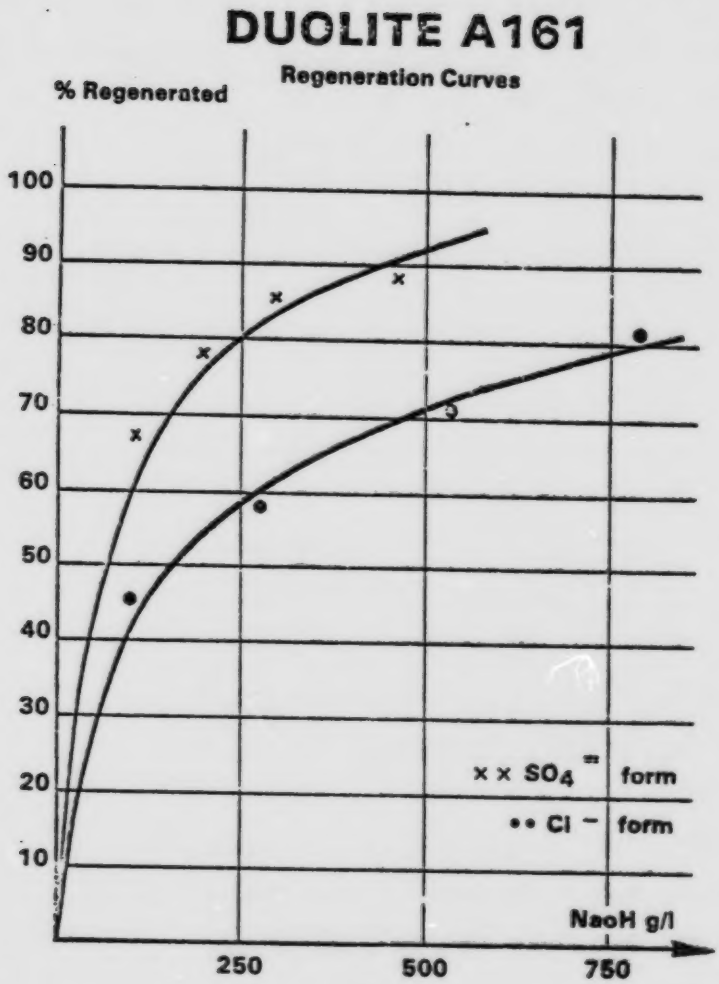

DUOLITE A161
Regeneration Curves
% Regenerated
100
90
80
70
60
50
40
30
20
10
250
500
750
NaoH g/l
× × SO4 = form
•• Cl − form

FIG : 1

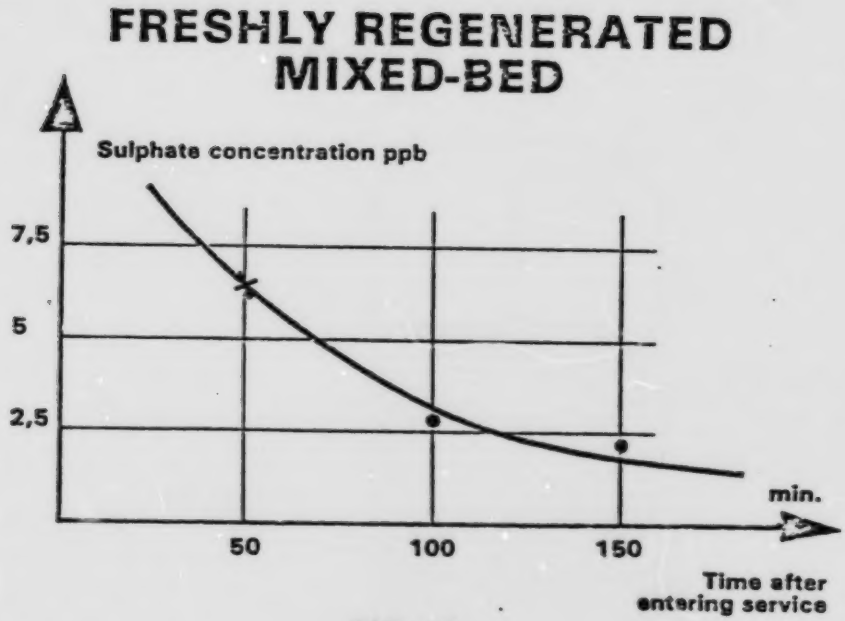
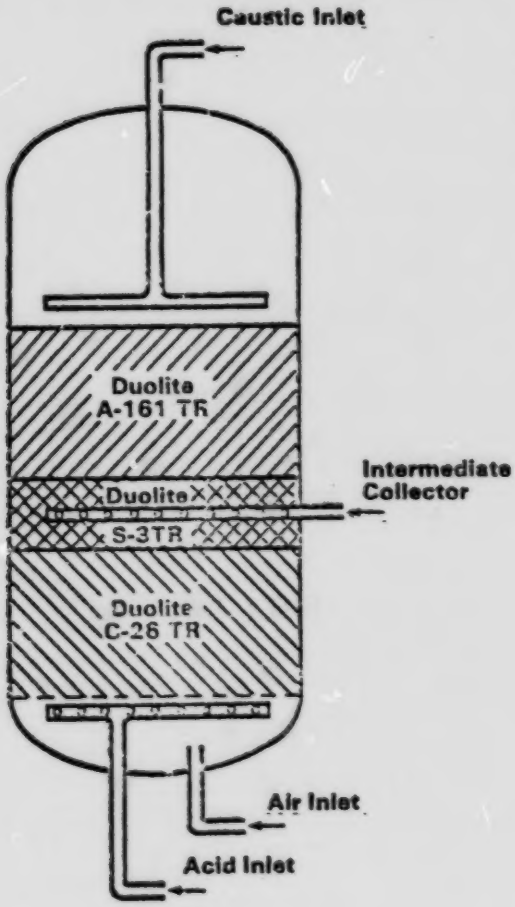

FRESHLY REGENERATED
MIXED-BED
Sulphate concentration ppb
7,5
5
2,5
min.
50
100
150
Time after
entering service

FIG : 2

FIG : 3

TRIOBED AFTER BACKWASH
(INTERNAL REGENERATION)



RATE OF FALL M/H

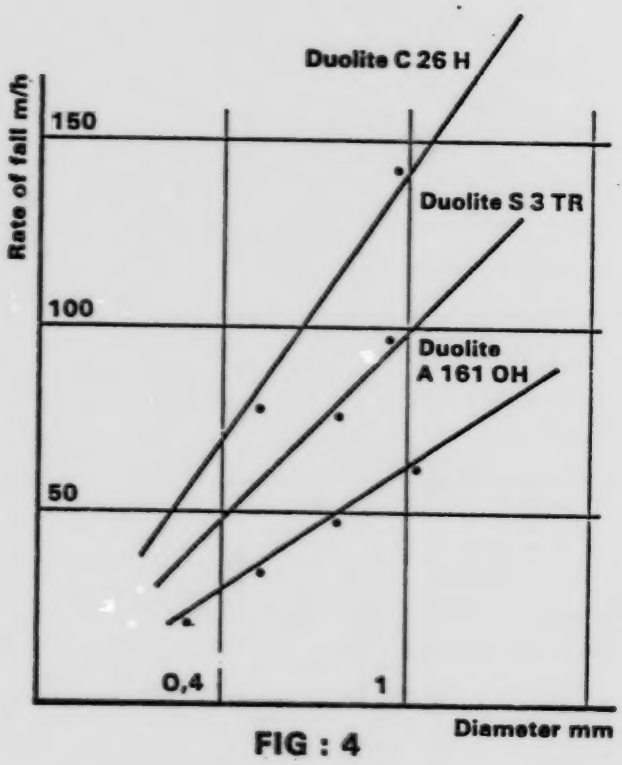


FIG : 4

FIG.: 5

DOEL CONDENSATE POLISHING PLANT

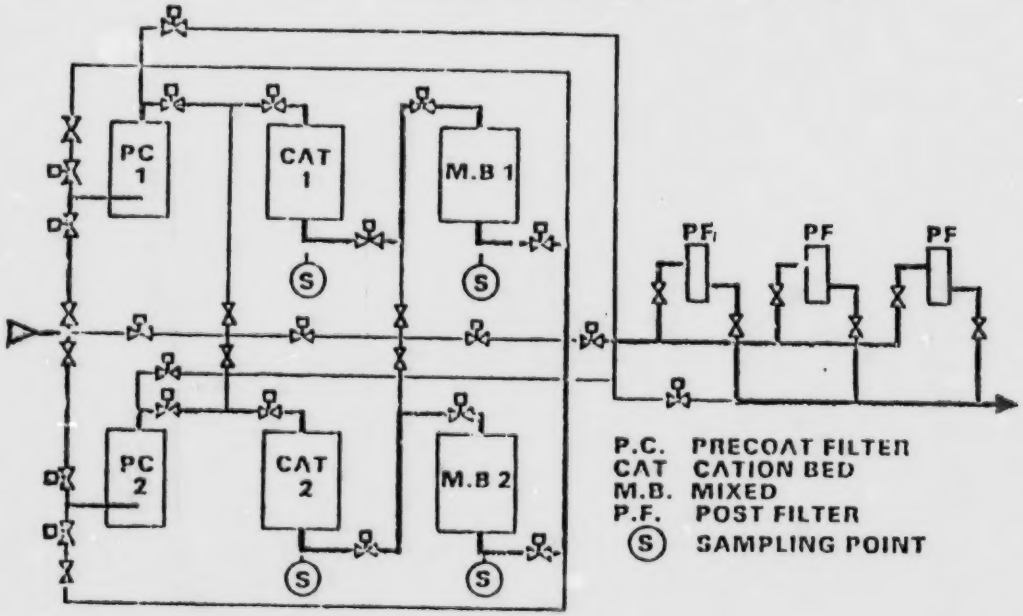
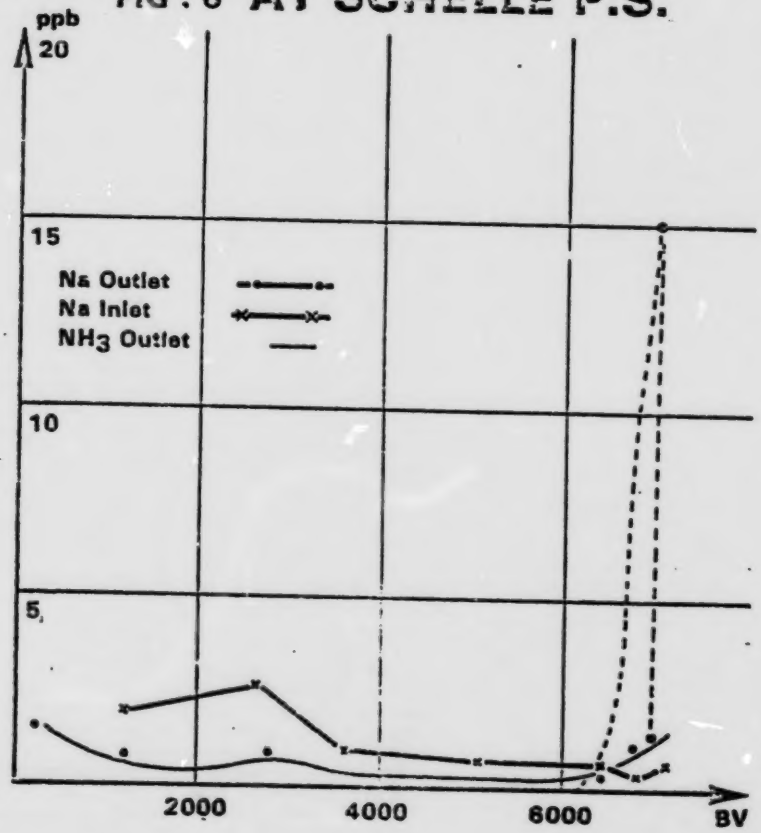


FIG : 6 Na LEAKAGE AT SCHELLE P.S.



Ion exchange resins in water treatment

Dr L. de Lange

The use of ion exchange resins have become accepted practice worldwide whenever water with a high degree of purity is needed or whenever the water has to be cleared of dissolved impurities. In South Africa large volumes of water are treated daily with ion exchange resins, either to purify the feed waters for industrial boilers, or to keep the level of dissolved pollutants in the effluent at acceptable levels.

Modern ion exchangers are synthetic resins with a bead of granular-like appearance 0,3 to 1,2 mm in diameter. Its macromolecular polymeric matrix is functionalised with sulphonic or carboxylic radicals in the case of cation exchangers or amines in the case of anion exchangers. Not only is each individual resin particle porous and permeable to liquids, but the total resin bed, which may consist of a number of cubic meters of resin, allows dissolved salts to come into contact with the functionalities of the resin, as it perculates through the resin bed. This enables the functional groups to fix the cations or anions in solution. The fixation process is reversable, for subsequently the H^+ ions from an acid or the OH^- ions from a base replace, in stoichiometric proportions, the ions which have been fixed by the resin. This operation is called regeneration and allows the resin to be re-used many times.

Ion exchange is the ideal process for selective removal of even low concentration of impurities in water which are ionised to a greater or lesser extent. The ion exchange plant will be placed after other processes which have made use of precipitation methods (employing lime, aluminium sulphate, ferric chloride, or other floculating agents) followed by filtration to remove the suspended solids.

Treatment of water with ion exchange resins concerns itself with:-

a) Softening of water: the replacement of the calcium and magnesium salts by non-scale forming sodium salts.

b) De-alkalization: the cations bonded to the carbonates and bicarbonates are fixed on a carboxylic exchanger and the freed CO_2 is deliminated in a degasifier.

c) Demineralization: various ionized minerals, cationic or anionic, and often of metallic origin, can be removed often on a fairly selective basis. Potentially hazardous ions such as flouirides, may also be removed wherever the level thereof is critical in the environment.

d) Removal of organic foulants: organics, such as phenols, are often part of the effluent of various industries. In the case of phenol, treatment of the water with chlorine for bacteriological reasons may give rise to the formation of cholorphenols, which worsen the pollution problem. Other organics, such as dyes from dye works, can also be removed, using ion exchange resins or specially developed adsorbent resins.

e) Removal of inorganic foulants: ion exchangers have proved to be extremely versatile to remove heavy metals from waste waters, systems have been developed, using highly specialised ion exchange resins to remove dangerous materials such as mercury from effluent.

Although ion exchange resins have been known and used for many decades in industry and processes such as demineralization and softening, there are demineralization and softening, there are continuously new developments in improving the efficiency of the process and the quality and potential of the resins.

a. The Sirotherm Process

The effluent from a conventional deionisation process, based on ion exchange resins, contains a larger quantity of mineral salts than is removed from the deionized water. Ion exchange resins have to be regularly regenerated by acids, or bases. Even the most modern processes (counter-current flow, stratified beds) allow at least 2,5 equivalents to pass into the effluent for everyone removed. It may thus be claimed that conventional ion exchangers result in considerable inorganic pollution, which is greater, the higher the salinity of the water to be treated. A new deionisation process, called the Sirotherm process, has been developed, using ion exchange resins which partially deionises the water without polluting it. This process uses very special ion exchange resins, which can be regenerated with hot water at 90 °C. The consumption of chemicals and hence the pollution released into the environment, is minimal because it is restricted to the amount required for pretreatment.

b. The Triobed Process

Certain modern industries such as nuclear power plants, require water of very high purity and some designers may specify 150 ppb chlorides and 100 ppb sodium entering the reactor with the water.

The standard method of obtaining very high quality water, is to pass it, possibly after a preliminary partial deionization treatment, through an ion exchange mixed bed consisting of a strong cation and strong anion resin. This mixed bed process presents a number of problems, which centres around the difficulties experienced with seperation of the resin as well as mixed regeneration during the regeneration cycle.

In the Triobed process one of the three components is an inert substance which posesses no ion exchange properties. The particle size distribution and bulk density of the inert matter are selected such that, once mixed with strong cation and strong anion resin beads of a given particle size and bulk density, the Triobed seperates clearly into three layers after a liquid flow has been passed through to expand it.

This new process has proved itself capable of considerably reducing the permanent leakage rates generally encountered with traditional mixed beds. It is therefore used whenever a conventional process produces permanent leakage or conductivity levels which are judged to be too high.

c. Absorbent Ion Exchange Resins

The mechanism of organic matter fixation comprises both ion exchange and adsorption, using Van der Waals-type bonds in the latter instance.

Often the resins do not possess any ionizable functionality through surface phenomena, much like activated carbon.

The resins must be used whenever water containing organic matter, is to be demineralised. An indication of whenever the system needs the protection of adsorbent resins, is when the organic matters concentration of the influent water to a strongly basic anion exchanger of type 1 reaches 4 mg/ℓ ($KMnO_2$), or 7 mg/ℓ in the case of a type 2 resin.

Kilpfontein Organic Products, P.O. Box 130, Kempton Park.

CONTINUOUS ION EXCHANGE SYSTEMS

NIMCIX

The NIMCIX continuous ion exchange process developed by the Council for Mineral Technology (MINTEK) in South Africa is based on the Cloete-Street patented bubblecap for multi-stage vertical fluid-bed ion exchange systems. Several NIMCIX installations have been installed in South Africa for uranium recovery but none so far in water or effluent treatment per se, except one at Welkom for incremental gold recovery from an effluent using carbon adsorption.

The basic components of a NIMCIX system are illustrated below along with a basic flow diagram for the successful ChemWes Ltd. installation at Stilfontein where two 4.85 m Ø adsorption columns with 12 stages have been installed for adsorption and two 3 m Ø elution columns with 8 stages each.

NIMCIX technology and experience is available through MINTEK or several licensed engineering contractors:

COUNCIL FOR MINERAL TECHNOLOGY
MINTEK
Private Bag X3015
Randburg 2125
South Africa
(011) 793-3511
Dave Boydell

BATEMAN URANIUM LTD.
Irongate, Building I
777 South Wadsworth Blvd.
Lakewood, CO 80226
(303) 989-4921
Peter Sutherland
President

DAVY McKEE CORPORATION
Ashmore House
Stockton-on-Tees
England TS18 3LT
(0642) 67-108
David Naden

PORTER CIX SYSTEM

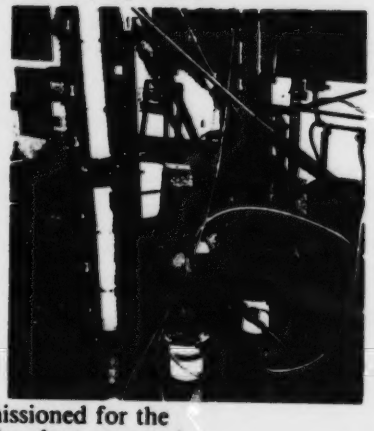
The Porter CIX system originally patented by Robert R. Porter of Salt Lake City, Utah, in 1975, has been installed at numerous uranium recovery plants including Rössing Uranium Ltd. and many of the in situ leaching operations in Texas. The Rössing plant employs two CIX trains to treat 80,000 m^3/day pregnant solution containing about 160

NIMCIX ION EXCHANGE CONTACTOR SYSTEM FROM MINTEK, SOUTH AFRICA

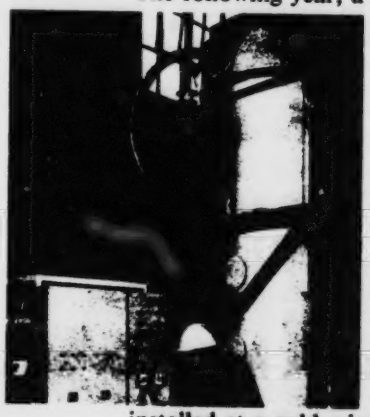
For three decades, the exciting possibilities of ion exchange as a continuous process have intrigued chemical engineers. Now, the National Institute for Metallurgy has a system that makes those possibilities a reality.

In its search for a continuous ion-exchange process (CIX) that could be applied to the hydrometallurgical extraction of metals from their minerals, NIM, as the Institute is known, took the work of Cloete and Streat at Imperial College as a starting point. An extensive research and development programme that involved NIM, the Extraction Metallurgy Division of the Atomic Energy Board, and the South African mineral industry has now resulted in the development of a commercially proved contactor.

The development of this NIMCIX contactor saw its first breakthrough in 1970, when a demonstration unit with a column diameter of 1,8 metres was constructed and successfully operated at NIM.



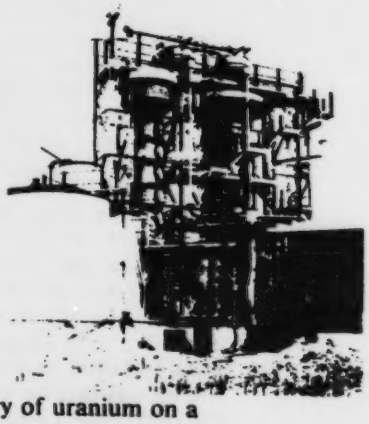
In 1972, a pilot plant that had a capacity of 100 litres per minute was commissioned at a South African gold mine for the recovery of uranium.



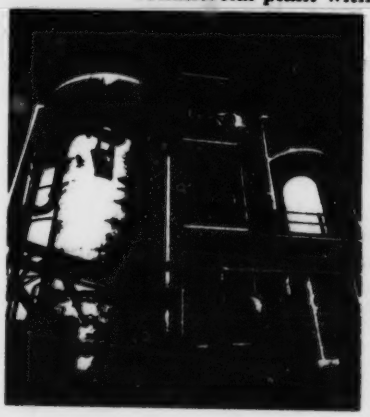
The following year, a commercial plant for the recovery of zinc from spent pickle liquors was put into operation. The plant had a capacity of 210 litres per minute.

In 1974 and 1975, a demonstration plant with a capacity of 1 500 litres per minute was designed and commissioned for the recovery of uranium. The plant operated very successfully under automatic control and full industrial conditions for many months.

In 1976, a 200-litre-per-minute plant was installed at a gold mine for the recovery of gold from waste solutions. The absorbent was activated carbon.



During the next two years, a large commercial plant with columns of 4,25 metres in diameter was designed and constructed for the recovery of uranium. The plant was commissioned successfully and is operating at designed capacity.



In 1978, a number of NIMCIX plants were designed for the recovery of uranium on a commercial scale.

The NIMCIX contactor is suitable for use with activated carbon and all commercially available ion-exchange resins.

hydrometallurgy

The unit operations of hydrometallurgical processes generally comprise four steps:

1 **leaching** in mechanically stirred or air-agitated vessels, or on dumps, or *in situ* underground,
2 **solid-liquid** separation by countercurrent decantation and/or filtration,
3 **concentration and purification** of the clarified leach liquor, and
4 **recovery** of the metal either as a metal or as a compound.

For example, the conventional hydrometallurgical recovery of uranium includes concentration of the filtered leach liquor by solvent extraction and precipitation of the uranium as ammonium diuranate. The extraction of copper involves leaching with sulphuric acid (mostly in dumps), and either cementation or solvent extraction followed finally by electrowinning.

The traditional processes have certain limitations.

a The feed solution to recovery plants must be well clarified. Where recovery by cementation is practised, final polishing filtration is required to eliminate colloidal constituents of the solution, which tend to coat the metal particles and thus inhibit the cementation reaction. In solvent extraction, suspended solids adsorb the solvent and entrain it into the raffinate. The higher the amount of solids, the bigger are the solvent losses. These losses, which represent a significant fraction of the operating costs of solvent-extraction plants, can amount to about one-third of the total operating costs for copper and uranium.

b The mixer – settler systems in solvent extraction are not satisfactory for the treatment of low-grade solutions; yet the long-term need for metallurgical development is in the processing of low-grade ores. One problem with the mixer – settler systems is that, because losses of the solvent are proportional to the volume of the solution, the cost of these losses is inversely proportional to the concentration of the solution. Moreover, the entrained solvent may represent a pollution problem. Also, the capacity of mixer – settler systems per unit volume of plant is low because of the difficulty in separating the organic phase from the aqueous phase. Large plants, large inventories, and thus high costs result.

c Very clear solutions can only be obtained if sophisticated and expensive solid – liquid separation plant is installed. The finer the grind required to liberate the metal values, the more expensive is the separation plant. In a conventional uranium plant, for example, the clarification and filtration steps account for a significant proportion of the overall operating costs.

nimcix development

NIM became aware of the inherent advantages of ion exchange over solvent extraction many years ago, and realized that the problems of ion exchange in hydrometallurgy were associated mainly with the fixed-bed equipment. NIM started developing improvements in the technology of ion-exchange engineering in 1968, and paid particular attention to the idea of continuous ion exchange.

Early work showed that the fluidized-bed system (as distinct from the fixed-bed system) offered the best prospects for the following reasons:

a its ability to treat solutions that contain suspended solids,
b potentially low losses of resin,
c simplicity of construction,
d potentially high efficiency in the recovery of metals.

NIM therefore undertook a major programme of research with the specific object of developing a practical commercial plant. This object was broken down into a number of distinct projects in two broad categories.

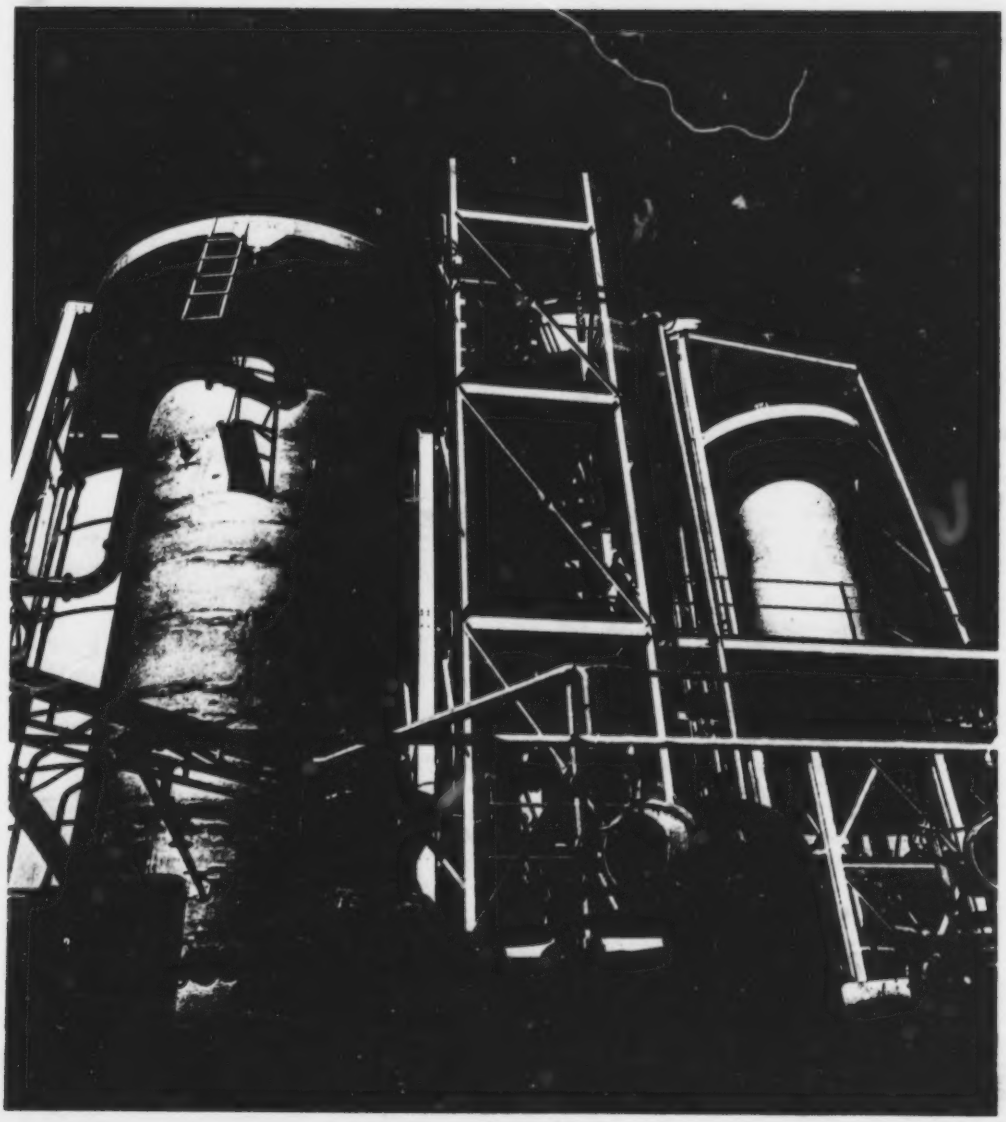
A Engineering

1 Design and development of inexpensive distribution trays that divide the ion-exchange column into stages.
2 Development of methods for the control of the resin inventory in those stages.
3 Perfection of a method for the control of the movement of the resin.
4 Development of methods for the achievement of a balanced resin inventory when the absorption and elution columns are linked.
5 Improvements to methods for washing the resin to prevent cross-contamination.

B Process Design

6 Development of standardized laboratory methods for the study of resin capacity, kinetics, and hydraulic properties.
7 Application of laboratory results to process design.
8 Analysis and optimization of plant-performance data by the use of computers.

▷ *A commercial NIMCIX plant for the recovery of uranium. The absorption columns are 4,25 metres in diameter.*



operating cycle

The NIMCIX contactor is operated, according to the Cloete and Streat principle of reverse flow, in such a way as to give an intermittent flow of resin countercurrent to the flow of solution. The operating cycle is completely automated and is divided into five basic periods.

1 **Forward flow**
During the period of forward flow (absorption), the pregnant solution flows up through the column and fluidizes the beds of resin contained in each stage.

2 **Settling**
During this short period, the flow of solution is shut off and the resin is allowed to settle, as can be seen in the diagram, onto the tray in each stage.

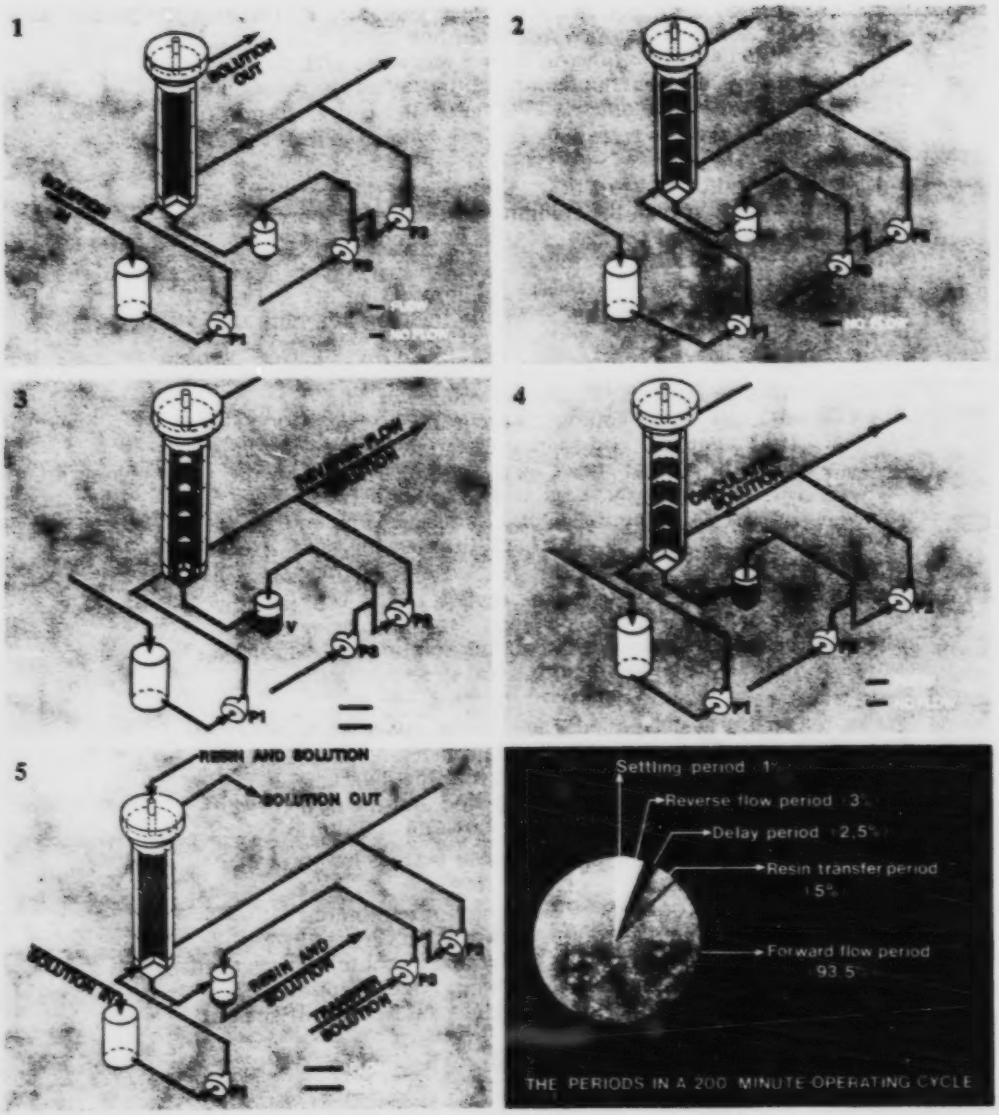
3 **Reverse flow**
During the reverse flow period, a fixed volume of solution is allowed to drain from the column to the transfer vessel (V). This causes a fixed volume of resin to be transferred between the stages and also out of the bottom stage. At the end of this period, the resin that has left the bottom stage is distributed between the conical section of the column, the pipe connecting the bottom of the column with the transfer vessel, and the transfer vessel itself.

4 **Delay**
A delay period is necessary to ensure that all the resin in the conical section of the column and the line from it to the transfer vessel is moved to the transfer vessel by circulating solution through the conical section of the column and the transfer vessel itself.

5 **Resin transfer**
During the resin-transfer period, the transfer vessel is isolated from the column, and the slug of resin in the transfer vessel is lifted to the top of the elution column (not shown in the diagrams) by hydraulic pressure. The resin-transfer period and the next forward-flow period start simultaneously, as is shown in diagram 6.

The relative time taken for each of the five periods is shown in diagram 6.

The NIMCIX contactor is equally suitable for continuous absorption and continuous elution. However, in certain circumstances, fixed-bed elution is preferable to continuous elution in combination with continuous absorption. An absorption cycle that is much longer than the elution cycle is an example of such a circumstance.

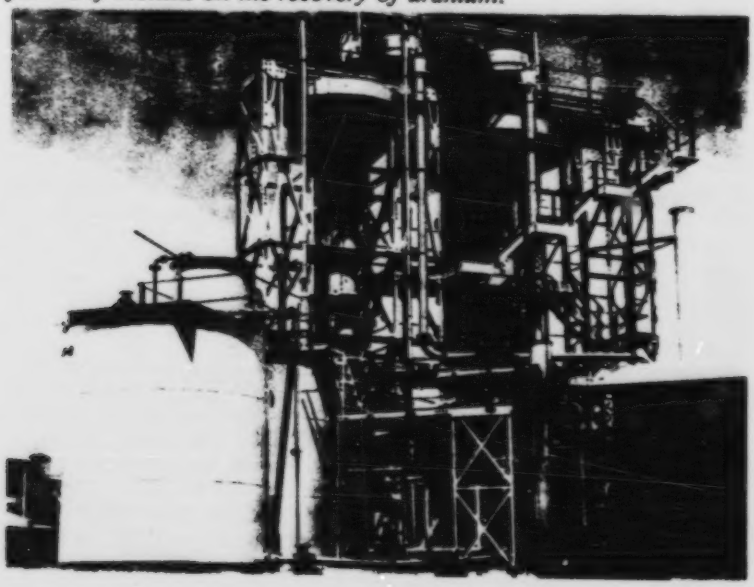

1
SOLUTION OUT
SOLUTION IN
P1
P2
P3
2
P1
P2
P3
3
REVERSE FLOW SOLUTION
V
P1
P2
P3
4
P1
P2
P3
5
RESIN AND SOLUTION
SOLUTION OUT
SOLUTION IN
RESIN AND SOLUTION
TRANSFER SOLUTION
P1
P2
P3
Settling period (1%)
Reverse flow period (3%)
Delay period (2.5%)
Resin transfer period (5%)
Forward flow period (93.5%)
THE PERIODS IN A 200 MINUTE OPERATING CYCLE

nimcix features

The NIMCIX contactor has many interesting features, the following being the most important.

1 It will treat solutions that contain suspended solids.
2 The residence times are equal for all the resin beads of standard column-grade ion-exchange resins.
3 The fluidized bed occupies the full volume of each stage despite changes in the density of the resin as it passes through the column.
4 The equipment and method of operation are simple.
5 The contactor can be successfully scaled up to large diameters.
6 Resin losses are low.
7 Capital costs are low.
8 Operating costs are low.
9 There are relatively few valves in the system.
10 Efficient and stable operation is achieved over a wide range of feed rates and concentrations.
11 The plant is highly automated.
12 Start-up and shut-down are effected with ease.
13 The efficiency of recovery is high.
14 The reliability of the plant is high.
15 The availability of the plant is high.

▽ *This large NIMCIX demonstration plant operated continuously for many months on the recovery of uranium.*



nimcix applications

Uranium

NIM staff have made a major contribution to the development programme of the Extraction Metallurgy Division of the Atomic Energy Board on the application of NIMCIX to the recovery of uranium. The following were key factors in this programme:

1 the willingness of the NUFCOR group of companies to finance the 2,5 m diameter NIMCIX demonstration plant erected and tested at the Blyvooruitzicht Gold Mine; and

2 the imaginative decision of Rand Mines Limited to incorporate countercurrent decantation (CCD) and NIMCIX in a plant for the treatment of reclaimed slimes-dam material at their Blyvooruitzicht uranium plant; the successful operation of this plant has shown that, for Witwatersrand acid-leach pulps, CCD is a viable alternative to filtration and that NIMCIX operating on unclarified solutions is a fully proved industrial process.

Gold

Activated carbon is a highly efficient scavenger of gold from cyanide solutions. The use of granular carbon in the NIMCIX contactor, as had been suggested by Anglo American Research Laboratories, and an elution technique that has been developed by them, has proved, on pilot-plant scale, to be a highly effective system for the recovery of gold from very dilute streams. These solutions include waste waters emanating from conventional cyanidation plants, liquors from dump leaching, and return waters from slimes dams. The pilot plant has been operating at a flow rate of 100 litres per minute.

Zinc

A successful process that incorporates the NIMCIX contactor has been developed for the recovery of zinc from spent pickle liquors. The conventional system of fixed-bed ion exchange was found to be economically unacceptable for this application for two reasons. Firstly, the high concentration of zinc in the feed demanded a large resin inventory, which is costly; and, secondly, difficulty was experienced in the removal of occluded iron from the resin. The NIMCIX contactor offered the solution to both problems.

Copper

Although selective organic reagents have proved successful for the recovery of copper from acid leach liquors, the limited capacity and high solvent losses of conventional solvent-extraction plants mean that the treatment of solutions containing less than about 1 gram of copper per litre is probably uneconomic. Resins are inherently better suited to the treatment of low-grade solutions, such as those obtained from dump leaching and *in situ* leaching than solvents are. The new copper-selective resins have tremendous potential for the recovery of copper by the NIMCIX contactor.

nimcix today process design licensing

NIMCIX today

The development of the NIMCIX contactor has reached a stage at which it is a completely viable engineering system. The laboratory techniques, pilot-plant design, and design models that have been developed enable NIM's engineers to proceed with complete confidence in applying the system to the commercial recovery of gold, uranium, copper, and zinc. Development work on the adaptation of the system to the treatment of dilute slimes (resin in pulp) continues. Further process development is aimed at the recovery of gold from cyanidation-plant streams and the improvement of selectivity in the recovery of copper.

Process design

Engineers at NIM and at the Extraction Metallurgy Division of the Atomic Energy Board can estimate what size of NIMCIX contactor is required for any application once the following information has been established:

1 the flow-rate and concentration of the feed solution,
2 the density and viscosity of the feed solution, and
3 the approximate concentration of any ions in the solution that might compete for absorption sites with the metal being recovered.

The detailed process design for a particular application is based on the results of a few simple laboratory tests on the feed solution. Given representative samples, NIM can conduct these tests, which are designed to provide the following information:

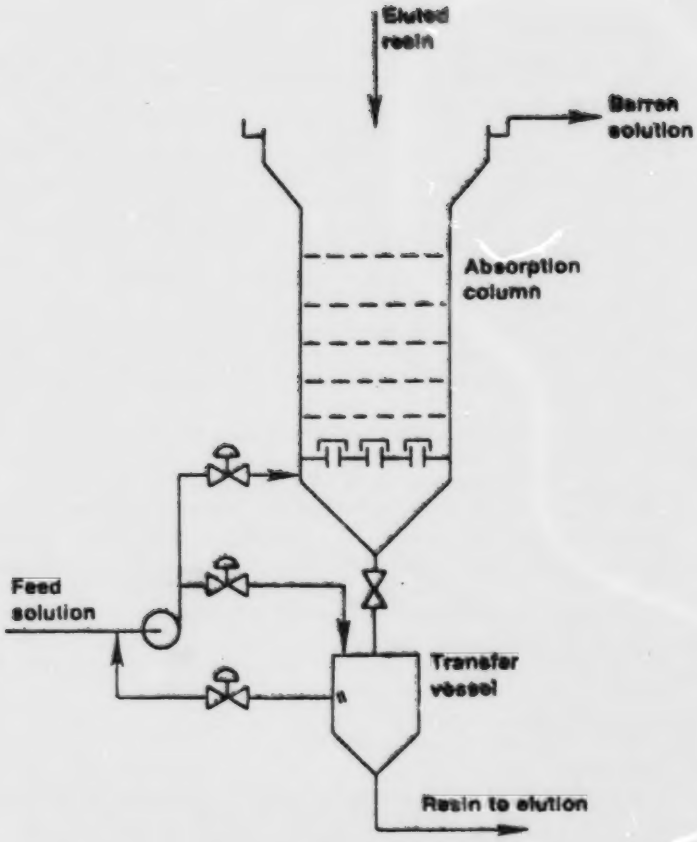
a the rate of absorption,
b the equilibrium isotherm between the concentration of metal ions in solution and their concentration on the absorbent,
c the rate of elution, and
d a full analysis of the feed solution.

Licensing

The NIMCIX system is patented in many countries. In the U.K. and U.S.A., the NIMCIX system falls under an umbrella patent (Cloete – Streat) the rights of which are held by the National Research and Development Council.

NIM is prepared to enter into licensed manufacturing agreements with design and construction companies or process-equipment manufacturers, and to assist licensees with design information and, if necessary, with commissioning of plants. Those requiring information about existing licensees or the terms of the licence agreements should write to

The National Institute for Metallurgy,
Private Bag X3015,
RANDBURG 2125,
SOUTH AFRICA.



. The NIMCIX contactor

Plate Perforations

Contrary to speculation that the perforations in the plates separating stages might be conical or some other nozzle shape, it was determined that the plate perforation holes are in fact parallel sided.

Plate Material

At Chemwes plates are made of 20mm PVC supported on large rectangular cross section hollow steel beams completely covered by fiberglass reinforced plastic.

At Blyvooruitsicht the original stage separaton plates were made from polypropylene sheet supported on steel pipes (3" ϕ schedule 80 pipe) encased in sealed PVC tubing.

At Blyvooruitsicht new elution columns have just been built and at Merriespruit the plate separators are made from redwood boards. Holes are drilled into each board using a special template. By installing the plates as boards they can be dismantled and changed if necessary as they can then be taken in and out of the columns through the manholes.

Equipment List *

WIM Contactor System

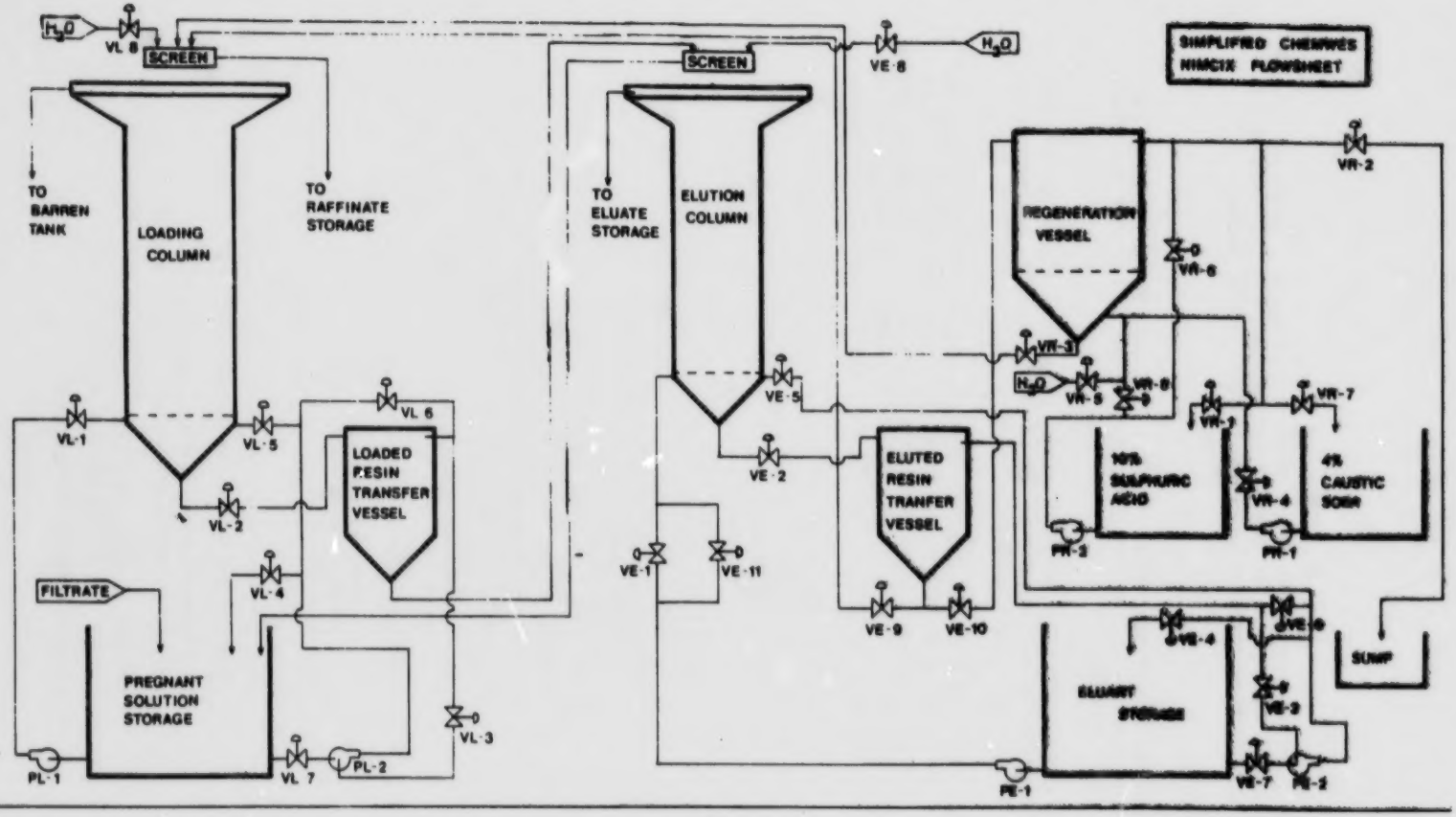
1	Pregnant Solution Head Tank 4m dia x 7 m high - open
2	Pregnant Solution Pumps 250mm disch. - RL & SS fitted (incl. Standby)
1	Contactor Column 9 stage, 4.8m dia x 13m high - open, with SS Separation Plates between stages, and resin screens
1	Barrens Resin Screen Assembly - SS 1.5mm open x 5 sqm W/RL Frame
1	Resin Transfer Pump SS wet end 100mm disch.
1	Transfer Vessel 3m dia x 3m high - 6 bar pressure with SS resin screens
1	Sump Pump Vertical SS Wet End - 100mm disch.

Connected hp=125/demand=60 hp /Resin Load 73 cu m

All Tanks and Vessels are spun fiberglass.

Source: Brian P. Canning, Davy McKee
AIME-SME Reprint 79-333

* Note: Loading Column only



VALVE SEQUENCING

LOADING COLUMN

FOWARD FLOW	VL 1	PL 1		
SETTLE PERIOD				
REVERSE FLOW	VL 2	VL 3	VL 4	PL 2
CONE FLUSH	VL 2	VL 3	VL 5	PL 2
RESIN TRANSFER	VL 6	VL 7	VE 8	PL 2

ELUTION COLUMN

FOWARD FLOW	VE-1	PE 1			
SETTLE PERIOD					
REVERSE FLOW	VE 2	VE 3	VE 4	PE 2	
CONE FLUSH	VE 2	VE 3	VE 5	PE 2	
RESIN TRANSFER	VE 6	VE 7	VL 8	VE 9	PL 2
RAPID REFILL	VE 11	PE 1			

REGENERATION

RESIN TRANSFER TO LOADING	VR-3	VR-8	VL-8	PR-1	
RESIN TRANSFER FROM ELUTION	VR-1	VR-8	VE-7	VE-10	PE-2
ACID DISPLACEMENT	VR 1	VR- 5	-	-	
CAUSTIC FEED	VR-2	VR- 4	PR 1	-	-
CAUSTIC CIRCULATION	VR-4	VR- 7	PR 1		
CAUSTIC DISPLACEMENT	VR 5	VR- 7	-	-	
RESIN WASH	VR 2	VR- 5			
SULPHATION	VR 1	VR 8	PR 2		

mg/l U_3O_8 to yield barrens of around 8-10 mg/l U_3O_8. The system is operated for optimum economics rather than optimum efficiency.

A major difference between NIMCIX and the Porter system is that the Porter CIX stages are constructed side by side whereas NIMCIX stages are stacked one on top of the other. The NIMCIX system is somewhat more elegant and space efficient which could be an advantage in cold climates where the system needs to be housed in a building, but the Porter system is probably more practical as individual stages can be isolated for maintenance. Also, the side-by-side Porter system presents a more complicated resin transfer challenge requiring pumps, eductors, and external piping which are avoided in the NIMCIX system. However, the Porter system allows more precise control of distribution of resin between stages.

The carbon columns employed for gold adsorption onto activated carbon are all variations of the original Porter ion exchange system. These use screens (internal) for solid-liquid separation to keep the resin in each CIX contactor as the solution flows down the CIX train by gravity. The Porter system employs an eductor system to advance resin (as a slurry) counter-current to the solution flow. In each stage, resin is fluidized by the upflow of solution through some form of distributor to prevent solution short circuiting.

Companies that have experience installing counter-current contacting systems of this sort (including carbon columns for gold recovery) include:

BECHTEL CIVIL AND MINERALS, INC.
Fifty Beale Street
San Francisco, CA 94119
(415) 768-3686
Laurence D. Hartzog
Anton R. Hendricksz

DAVY McKEE CORPORATION
2303 Camino Ramon
Post Office Box 5500
San Ramon, CA 94583

DR. MAURICE A. T. COCQUEREL
(415) 838-1166
Telex: 337635

DAVE McKEE (STOCKTON) LTD.
Ashmore House
Stockton-on-Tees
England Ts18 3LT
(0642) 602221
David Naden

A consultant engineer who is particularly interested in the further development of continuous ion exchange recovery systems is:

TEN OPERATING CIX PLANTS

		FBIX Hartebeestfontein	UTAH-TYPE El Mesquite	FAP RIP-GAS HILLS	ST. PIERRE PUK-RIP	USBM Fall City
SYSTEM		H_2SO_4	Alkaline	H_2SO_4	H_2SO_4	H_2SO_4
LOADING						
Feed rate per unit U.S.	gpm	160	400	390	165	385
Feed rate per unit m^3 per h		36	91	89	38	87
Solids in feed solution	ppm	20	low	10-15%	4%	
Compartment height	m	5.4	7.0 23 ft.	14 ft.	1.8m	
Compartment diameter	m	2.12	2.74m 9 ft.	14 ft.	1.5m	2.13
Specific flow rate	US gpm/ft.^{2}	4.2	6.3	2.5	8.6	10.0
No of compartments		2	3	7		8
U_3O_8 in feed	ppm	130	70	500	400	25-50
U_3O_8 in barren	ppm	2	2	1	2 ppm soluble	3-8
Recovery efficiency	%	98.5	97.0%	99.8%	99.5%	70-94
ELUTION						
Reagent concentration		60 g/l NO_3	58 g/l NaCl 15 g/l CO_2	150 g/l H_2SO_4	20 g/l H_2SO_4 80 g/l NaCl	1 M NaCl HCl pH 0.8
Reagent Temperature	°C	Ambient	Ambient		40°C	
U_3O_8 in eluate	g/l	8.0 g/l	20 g/l	7.0 g/l	3.5 g/l	1.0 g/l
Concentration Factor		62	286	14	9	25
RESIN						
Inventory	m^3	19m^3	37.2m^3	19.8m^3	12m^3	
Loss rate	% of inventory	less than 5%PA	not determined	25-50%	100%	
Type		IRA 400	Dowex 21K	Dowex 21K	Dowex 21K	Dowex 21K
Resin Size	USS mesh	30-40 mesh	16-20 mesh	14-30 mesh	800 u	

TEN OPERATING CIX PLANTS

	NIMCIX Chemwes Ltd. Transvaal	HIMSLEY Vaal Reefs O.F.S.	KERRMAC Kerr McGee New Mexico	PORTER Rossing Namibia	CHEM-SEPS Bingham Canyon Utah
SYSTEM	H_2SO_4	H_2SO_4	Neutral	H_2SO_4	H_2SO_4
LOADING					
Feed rate per unit U.S. gpm	1200	880	500	4000	2200
Feed rate per unit m^3 per h	270	200	113	900	500
Solids in feed solution	1000	150	50 max	2500 max	1000 max
Compartment height m	1	3.1	2.4	3.83	2.4
Compartment diameter m	4.85	4.0	2.4	6.2 x 6.2	3.4
Specific Flow Rate US gpm/ft^2	6.0	6.5	10.3	9.7	22.5
No of compartments	12	6	2	6	1
U_3O_8 in feed ppm	160	95	10	163	7
U_3O_8 in barren ppm	2	2	1 to 5	8	1.5
Recovery Efficiency %	99	98	80	95	78
ELUTION					
Reagent concentration	10% H_2SO_4	13% H_2SO_4	9% NaCl	10% H_2SO_4	15% H_2SO_4
Reagent temperature °C	25	25	20	25	50
U_3O_8 in eluate g/l	4.4	4.5	5-10	3.1	1.1
Concentration Factor	27	47	500-1000	19	170
RESIN					
Inventory m^3	150	72.6	8.5	176	21
Loss rate % of inventory	unknown	unknown	25	60-90	40-80
Type	A101DU	A101DU	DOWEX 21K IRA 430	Dowex 21K Dowex XFS 43116	Dowex MSA 1
Resin Size	420-840	420-840	840-1190	420-840	595-1190
USS mesh	20-40	20-40	16-20	20-40	16-30

DR. F. L. D. CLOETE
Dept. of Metallurgical Engineering
University of Stellenbosch
Stellenbosch C.P.
South Africa

RESIN SUPPLIERS AND EXPERTS

The following is a list of contacts among resin suppliers:

Bryan D. Freeman	Diaion Resins Chematron Products (Pty) Ltd. Post Office Box 13291 Witfield 1467 South Africa	(011) 892-3082
Jean-Jacques Wolff	Technical Manager Dia Prosim SA 107 Rue Edith Cavelle BP No. 8 94400 Vitry sur Seine France	(1) 680-2045
Paul Grammont	Dia Prosim S.A. Rue des Grands Navoirs Prologie BP No. 481 Chauny, France 02301	
Lief Syrstadt	Functional Polymers Division Diamond Shamrock Corp. 1100 Superior Avenue Cleveland, OH 44114	(216) 694-6080
	Functional Polymers and Systems Dow Chemicals U.S.A. 1691 North Swede Road Larkin Laboratory Midland, MI 48640	(517) 636-1484
Scott Josiff	Dow Chemical Company Post Office Box 5818 Denver, CO 80217	(303) 773-8800

Frank X. McGarvey Manager	Ion Exchange Tech Center Ionac Chemical Company Birmingham, NJ 08011	(609) 894-8211
John Unger International Manager	Ionac Chemical Company Birmingham Road Birmingham, NJ 08011	(609) 894-8211
Toshiro Yokoyama	Industrial and Fine Chemicals Div. Mitsubishi Chemical Industries Ltd. 5-2 Marunouchi 2 Chome Chiyoda-ku, Tokyo	(03) 283-6531
Gloria McDougall Manager	National Chemical Products Acix Division Post Office Box 284 Bedfordview 2008 South Africa	(011) 615-9100 Telex: 420116
Dr. Jim Clovis	Rohm & Haas Company Research Laboratories Spring House, PA 19477	(215) 643-0220
Barry Robin	Rohm & Haas Company Independence Mall West Philadelphia, PA 19105	(215) 592-3177
Dr. E. Zaginiaris	Rohm & Haas Company Sophia Antipolis 06560 Valbonne	(93) 33.24.45
Tony Strivens	Rohm & Haas SA (Pty) Ltd. Post Office Box 78 New Germany 3620 South Africa	(031) 72-0241
R. Kunin	Consultant 1318 Moon Drive Yardley, PA 19067	(215) 736-2420
J. Melling D. M. West	Warren Springs Laboratory Dept. of Industry Gunnels Wood Road Stevenage Herts SG1 2BX	(0438) 53964

SELECTIVE ION EXCHANGE RESINS FOR METAL RECOVERY

by F. X. McGARVEY AND J. UNGAR

Presented at the Symposium on Ion Exchange and
Solvent Extraction in Mineral Processing
Randburg, Tvl., Rep. of So. Africa February 7, 1980

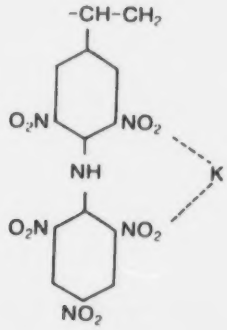
The development of ion exchange processes to assist in the recovery and refining of valuable metals is reviewed with particular attention to nickel, cobalt and copper. Several selective resins have been considered from the standpoint of their structure, including those useful for gold and silver recovery. Current practice with the resins will be dealt with and some of the economics discussed.

The occurrence of organic compounds with unusually high affinity for certain metals has been observed for many years. Certain shellfish have unusually high affinity for copper, mercury and other metals in the presence of large amounts of electrolyte. Classic examples also include hemin and chlorophyll which hold iron and magnesium very strongly. Some of these naturally occurring compounds hold metals so strongly that they are not easily regenerated from the structure without destruction of the chelating group. The ability to perform oxidation reduction reactions while in the complex structure permits these metals to be part of complex biological processes.

Early attempts to produce resins having such selective properties closely paralleled the structure and grouping of natural compounds. The development of a class of synthetic chelating compounds based on amino carboxylic structures resulted in the incorporation of several of these structures in conventional condensation and copolymer systems. These resins frequently have ion exchange properties as well as the capability to form chelation rings.

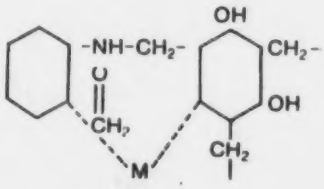
Some of these compounds which received early attention are summarized as follows (from Helffe-rich [1], and Samuelson [2]).

The following is a potassium selective resin based on the specific precipitation of potassium salts with dipicrylamine.



This compound shows the characteristic 8-member ring so common to chelating compounds.

Polycondensation compounds also form chelation units as shown for anthranilic acid condensed with phenols.



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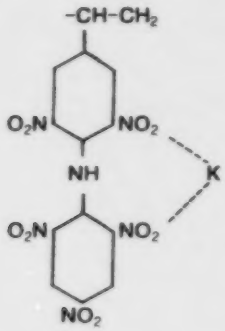

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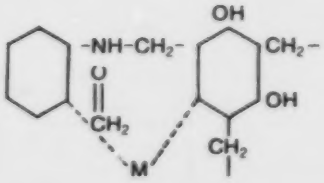
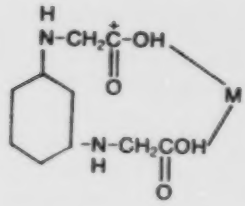
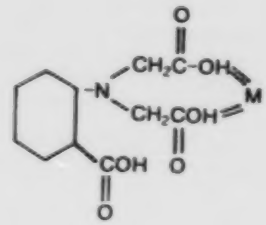
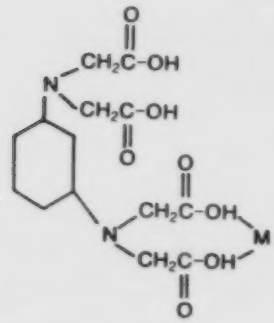


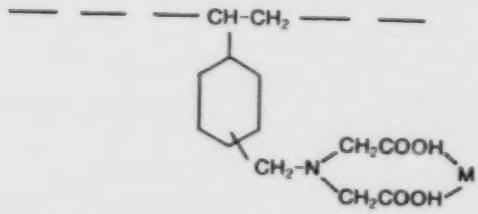
An important configuration includes those which contain amino acetic acid groups. These include anthranilic acid-diacetic acid, m-phenylene diglycine and m-phenylene diaminetetraacetic acid.







By far the most common of these resins has been based on styrene-divinylbenzene copolymers with iminodiacetic acid groups as the functional group. The structure is shown as follows:



This resin has properties similar to the ethylenediaminetetraacetic acid compound widely used in analytical work and for heat exchanger cleaning.

Selectivity series for this type of resin are summarized as follows:

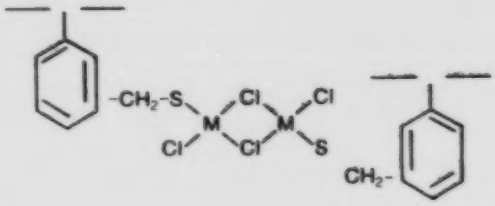
$Cu^{++} \text{-->>} Fe^{++} > Ni^{++} > Co^{++} > Pb^{++} > Mn >> Ca^{++} >> Mg^{++} >> Na^{+}$

also

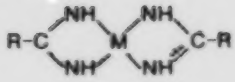
$Hg > Cu > Pb > Ni > Cd > Zn > Co > Mn > Ca > Mg > Ba > Sr >>> Na$

Small variations in structure can play a considerable role in the actual affinity of neighbors in the series. The possibility that a particular structure may have substantial influence on a particular cation should not be overlooked but the sharp geometrical relationship of some zeolites is not available for resinous structures. This is usually fortunate since very specific materials may not regenerate easily or in some cases may absorb irreversibly.

Noble metals have also been concentrated on a series of chelating resins prepared with sulfur groups as part of the complex[3]. The complex has a structure similar to the following:



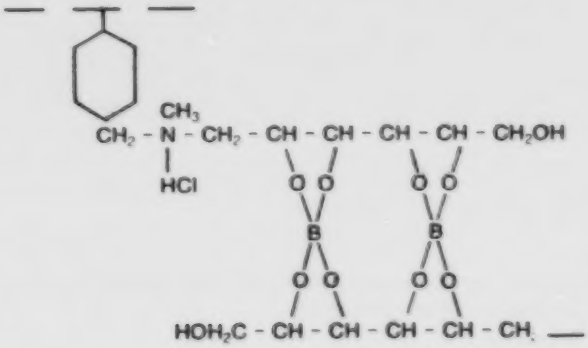
or



where M is a noble metal.

These resins bind gold and platinum metals very selectively from acid solutions. These resins can take part in redox reactions thru their double bonds so that substantial capacities for gold have been measured due to the formation of metallic gold. Similarly weak ester groups, $-CO_2R$, can be used in resinous structures to adsorb gold, probably thru hydrolysis of the group[4].

The various resins mentioned have differing degrees of selectivity but none can be classed as specific for a particular element. The only organic resin which can be called truly specific is one based on a styrene-divinylbenzene copolymer prepared with N-methylglucamine[5]. The structural formula is as follows:



Calmon[6] has prepared an interesting grouping of the various specific structures that might be considered for selective and specific ion exchange materials. He mentions thiourea and β-diketone structures among others for copper, cobalt and nickel as well as dimethylglyoxime for nickel. While it is doubtful that copolymer structures can be made sufficiently flexible to accept geometrical requirements of some of these compounds, there are many structures available for selective and specific ion exchangers.

Some modifications of these materials can also be considered where selectivity is required. First, the complexing agents may be bound on exchangers so that the functional groups are available at the exchange site. Rare earth separations are performed on such substrates with strongly held cations, as for example copper used to develop the trivalent cation separation[7].

It is possible to precipitate insoluble salts into resin pores so that the precipitate can act as a selective media for the removal of certain cations, including lithium, from brines. This method uses a macroporous anion exchanger to hold lithium aluminum silicate in the pores. When properly prepared the system can be used as a selective zeolite for lithium[8].

RECOVERY PROCESSES

The application of selective ion exchange materials must be compared to the performance of conventional ion exchange materials. The need for these materials arises from the lack of capability in conventional materials.

Selective (Chelating) Resins vs. Carboxylics for Base Metals

Conventional carboxylic cation exchangers have substantial selectivity at pH values above 4 or 5 for copper, nickel and cobalt in the presence of large concentrations of monovalent cations. Other divalent cations such as calcium and magnesium do not have the high degree of selectivity found in conventional carboxylics for copper.

However, to use the selective-adsorptive potential of a carboxylic resin, when working with acid solutions, it would be necessary to first neutralize the influent to the ion exchange column, not a very practical procedure in many hydrometallurgical applications associated with mining.

Consequently, carboxylic resins, such as Ionac CC or Ionac CNN, can be useful for heavy metal removed from industrial wastes, and from industrial (or potable water supplies), particularly where relatively low concentrations of heavy metals (still undesirable from the health or pollution standpoint) are present.

The selective resins, such as Ionac SR-1 or Ionac SR-11, on the other hand are much more effective for base metal removal at lower pH values (below pH 3 or 4), and their affinity for base metals (copper, nickel, cobalt, zinc) is such, that removal is essentially complete (residuals below the detection limits of analytical procedures), even for higher influent concentrations. This is contrary to the carboxylics, which would allow some leakage under such conditions. The selective (chelating) resins are therefore more suitable in hydrometallurgical applications (for economical considerations), and in pollution problems where absolute removal of the heavy metal ions is desired.

Some tests were also run on the sodium form resins, and a typical set of loading curves for nickel is shown in Figure 1, illustrating the advantage of Ionac SR-1 over Ionac CC at lower pH values. As however the total capacity of the carboxylic resin is higher, total loading to saturation is higher on it. The curves for copper and cobalt were almost identical.

A typical set of leakage and breakthrough curves is shown in Figure 2, illustrating the more complete removal of the base metal by Ionac SR-1.

Stripping of both types of resins was effected with 2N hydrochloric acid, and this is illustrated in Figure 3. It will be noted that somewhat longer tailing effects occur with the carboxylic resin than with the selective one, although because of its higher total loading, the stripping solution contained more copper chloride than found for IONAC SR-1.

Economic Considerations

Economics are only one of the factors in the choice of selective versus carboxylic resins in such process considerations.

The first and most important aspect is the tolerable heavy metal leakage in the effluent at the working pH. The selective (chelating) resins show much lower leakage, especially at low pH, so that their lower total capacity may well be offset by this factor. The breakthrough capacity difference will also be affected by the prevailing pH.

It is of course true that the selective (chelating) resins are generally more expensive per unit than the carboxylics, and this factor must be weighed against the others listed above.

Finally, the practicality as well as the operating expense of pH adjustment must be considered. The following two calculations for copper recovery will illustrate the points involved.

Case 1

Copper removal required - concentration: 100 ppm and pH must be retained at 2
Volume to be treated - 10 million liters per day
Capacity of Ionac CC - converted sodium initially-
5% (65 grams per liter)
= 3.25 grams per liter resin
Capacity of Ionac SR-1 - converted sodium initially -
36% (25 grams per liter)
= 9 grams per liter

Resin Requirement

Copper per day = 0.1 (10×10^6) grams per day =
1×10^6 grams

Ionac CC

$$\frac{1 \times 10^6}{3.25} = 0.308 \times 10^6 \text{ liters resin per day}$$

Ionac SR-1

$$\frac{1 \times 10^6}{9} = 0.11 \times 10^6 \text{ liters resin per day}$$

The chemical requirements and the conditioning of each resin would be in proportion to their capacity for copper so that these costs would tend to balance. The leakage of copper at this low pH would be quite high so that the chelation resin would have the best recovery and should be used.

Case 2

Copper removal required - concentration: 100 ppm and pH - adjustable to 4.5-5
Volume to be treated - 10 million liters per day
Capacity of Ionac CC
62% (65)
= 40 grams copper per liter
Capacity of Ionac SR-1
88% (25)
= 22 grams copper per liter

Resin Requirement

Copper per day = 1×10^6 grams
Ionac CC

$$\frac{1 \times 10^6}{40} = 0.025 \times 10^6 \text{ liters}$$

$$= 2.5 \times 10^4 \text{ liters}$$

Ionac SR-1

$$\frac{1 \times 10^6}{22} = 0.045 \times 10^6 \text{ liters}$$

$$= 4.5 \times 10^4 \text{ liters}$$

As in the previous calculation, the chemical consumption would be proportional to the capacity and would be equal per kilogram of copper recovered. Here the difference in resin cost would be crucial and the carboxylic should be selected if a small amount of leakage, roughly 0.1-0.2 parts per million, can be tolerated.

Polyamine and Amide (Weak Base Anion) Resins for Base Metals

The complexing of heavy metals by organic polyamine compounds is a well-known textbook reaction. The early polyamine-condensate type weak base resins, such as Ionac A-260 and Ionac A-305, are known to complex copper and other ions, and have occasionally been used in processes involving copper complexes.

Today's ion exchange technology provides us with a variety of other polyamines and amides, based on matrices such as styrene-DVB, styrene-acrylic, acrylic-DVB, pyridinium-DVB, etc., which may well offer suitable characteristics for hydrometallurgical separation or concentration processes. So far, little if any, work has been done in this direction, but it should be considered for some interesting possibilities.

NOBLE METALS AND MERCURY

The conventional process for recovering or concentrating noble metals by ion exchange usually accounts for the gold-cyanide anion complex, and sometimes the aurichloride or platinochloride complexes, being taken up by strong base anion exchange resins. While this is certainly a viable and economical process widely used, there is no selectivity involved, and substantial interference is experienced from anionic complexes of base metals, such as copper, nickel, cobalt, etc.

A macroporous chelating resin, Ionac SR-3, has been developed, which is highly selective for precious metals such as gold and others of the platinum group from acid solutions, as well as for mercury and methyl-mercury compounds.

Base metals such as iron, copper, lead, etc. do not react at all with this resin and do not interfere with the selective process. The noble metals are very strongly attached to the resin, yet their recovery presents no difficulty.

For example, one microgram of gold dissolved in one liter of slightly acidified water was completely recovered with the aid of Ionac SR-3. Furthermore, even after adding hundreds of milligrams of nickel and copper to the solution, precious metal recovery was complete to the exclusion of the other metals

Ionac SR-3 also quantitatively collects methyl mercury and inorganic mercury compounds. Both forms are collected from solutions of pH 1-9.

Table I shows the typical full loading potential of this resin for the various metals:

Table I
Capacities of Ionac SR-3

Gold	150 g/l
Platinum	65 g/l
Palladium	58 g/l
Iridium	25 g/l
Mercury	150 g/l

This resin is currently being used on the commerical scale in recovering gold from waste effluents and rinse waters of acid goldplating solutions. It is also suggested for noble metal extraction from ores and wastes, the separation of noble from base metals, the recovery of spent catalysts, the concentration of very dilute solutions containing noble metals and the refining of noble metals.

In addition, Ionac SR-3 is applicable to the removal of mercury (and methyl-mercury) compounds in pollution control.

Suggested Use Procedures

For the start of laboratory and/or pilot plant tests, the following use procedures should be considered, and would then lead to optimizing the process for scale-up:

1. The pH of the solution coming into contact with the resin should preferably be adjusted to between 0.5 and 2.5.

2. Adsorption of noble metals or of mercury is carried out at room temperature using conventional ion exchange column techniques. Minimum bed depth should be 750 mm and the flow rate about 10-20 bed volumes per hour.

3. The recovery of the noble metals from the resin is possible in two ways:

3.1 Ignition — Slowly roasting the exhausted resin in air at 900-1000°C leaves the metal in a very pure metallic form.

3.2 Elution — Eluting immediately after adsorption with a 5% aqueous solution of thiourea to which 5 ml/liter of HCl has been added yields a solution from which the metal can be recovered by reduction. When elution is applied, the resin can be reused for many cycles.

4. The elution of the mercury can be also accomplished by treating the resin with 4% sodium sulfide at a level of 200 g Na_2S per liter of resin.

Following the elution, it is necessary to regenerate the resin by treatment with 10% hydrochloric acid at a level of 100 g HCl per liter of resin.

SUMMARY

Selective and chelating ion exchange materials represent a significant advance in technology to meet the substantial demands for environmental control and material conservation so important in our modern day. These materials also have properties extremely valuable for nuclear decontamination where the trace leakage frequently found with conventional materials can be reduced.

Much applications development remains to be done on the various potential uses, but it is obvious that the probability that selective resins can be used to recover valuable materials in mining operations has a bright future indeed.

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I&EC Product Research and Development 3, #4, 304 (1964)

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(7) Spaulding, F. and Powell, J.
Ion Exchange Technology (editors Nachod and Schubert), Academic Press, New York (1956)

(8) Bauman, W. and Lee, John
U. S. Patent 4,116,858, September 26, 1978

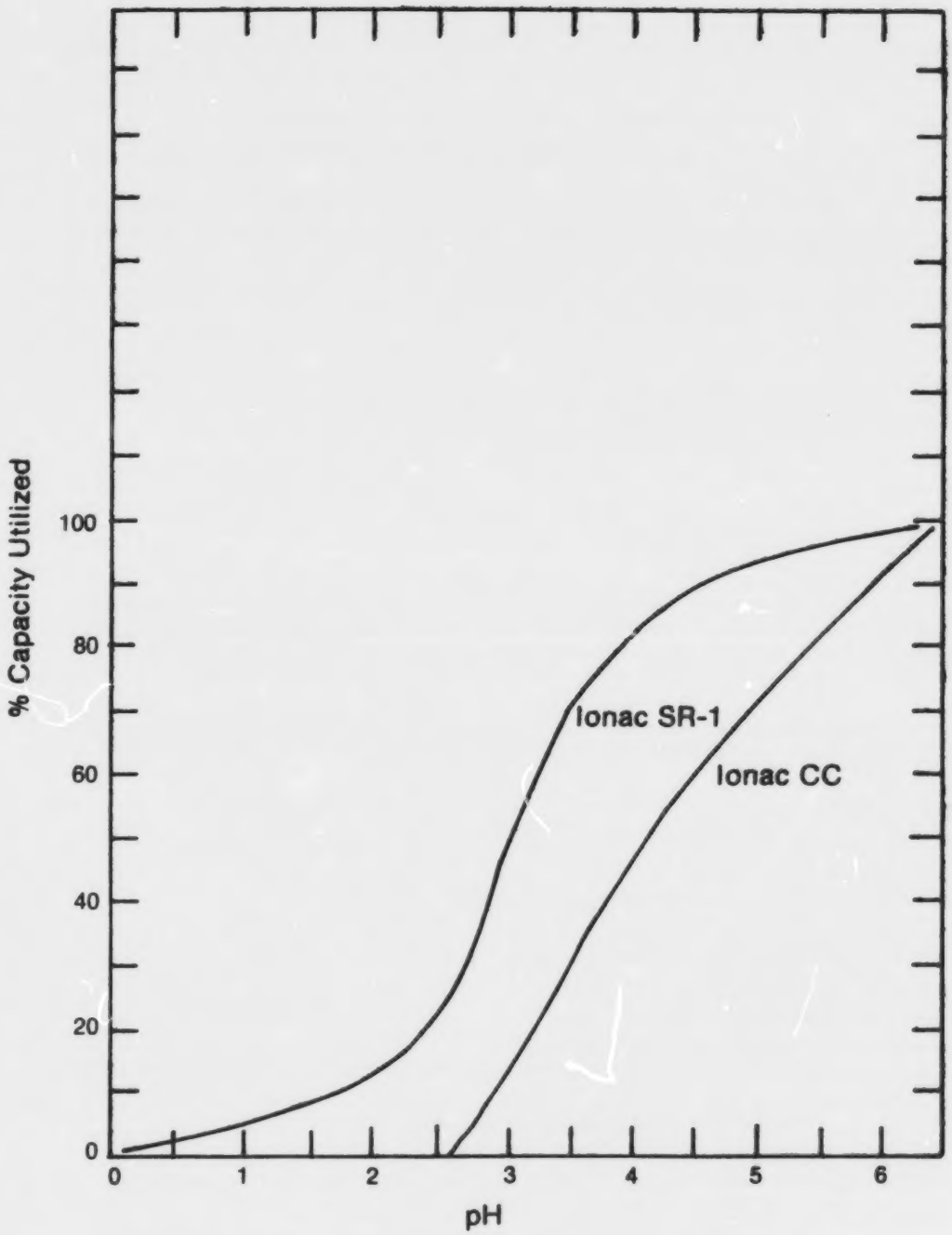

Figure 1: Comparison of Chelating Resin with Carboxylic: Nickel-NaCl-HCl

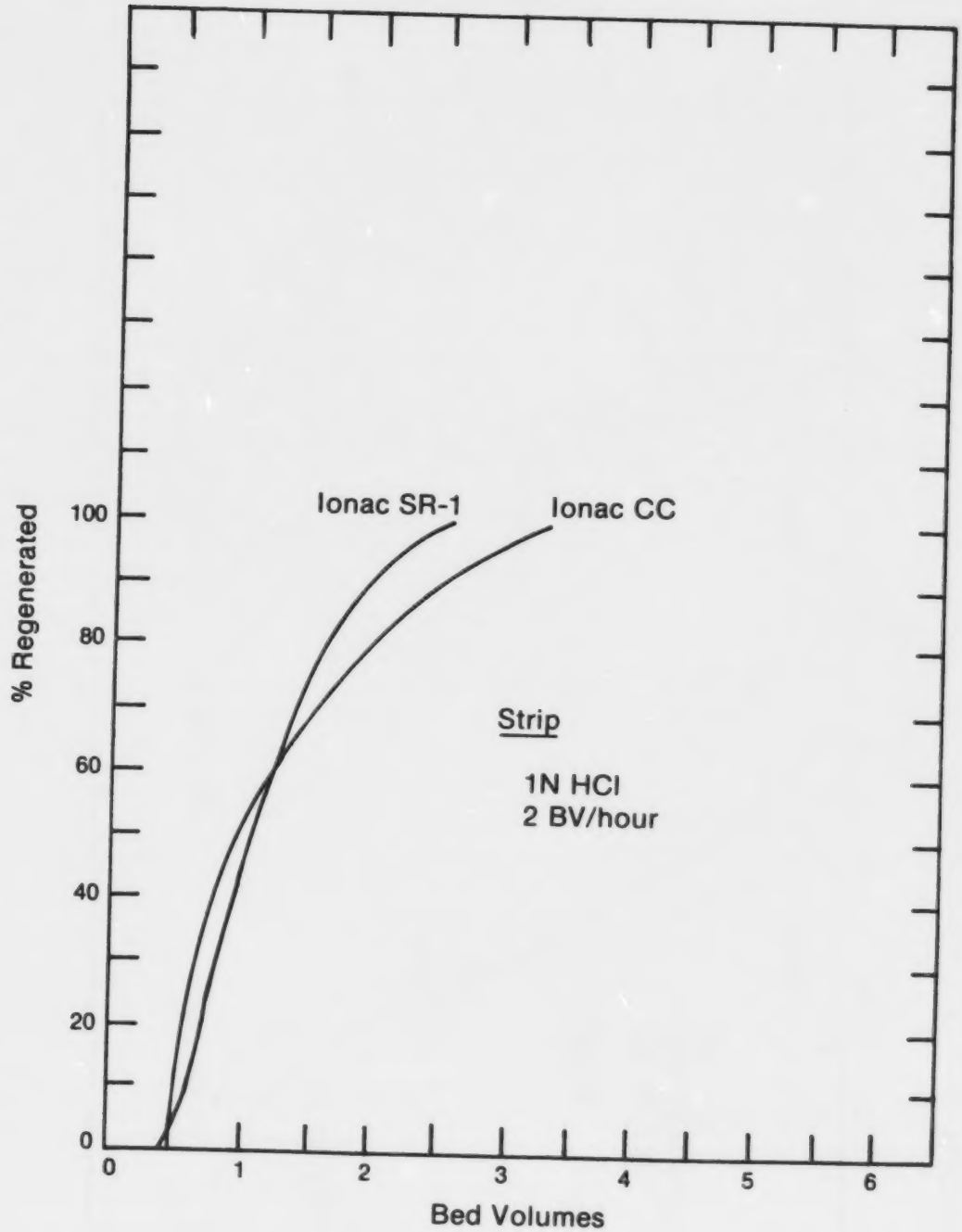

Figure 3: Regeneration of the Base Metal from Chelating and Carboxylic Resins.

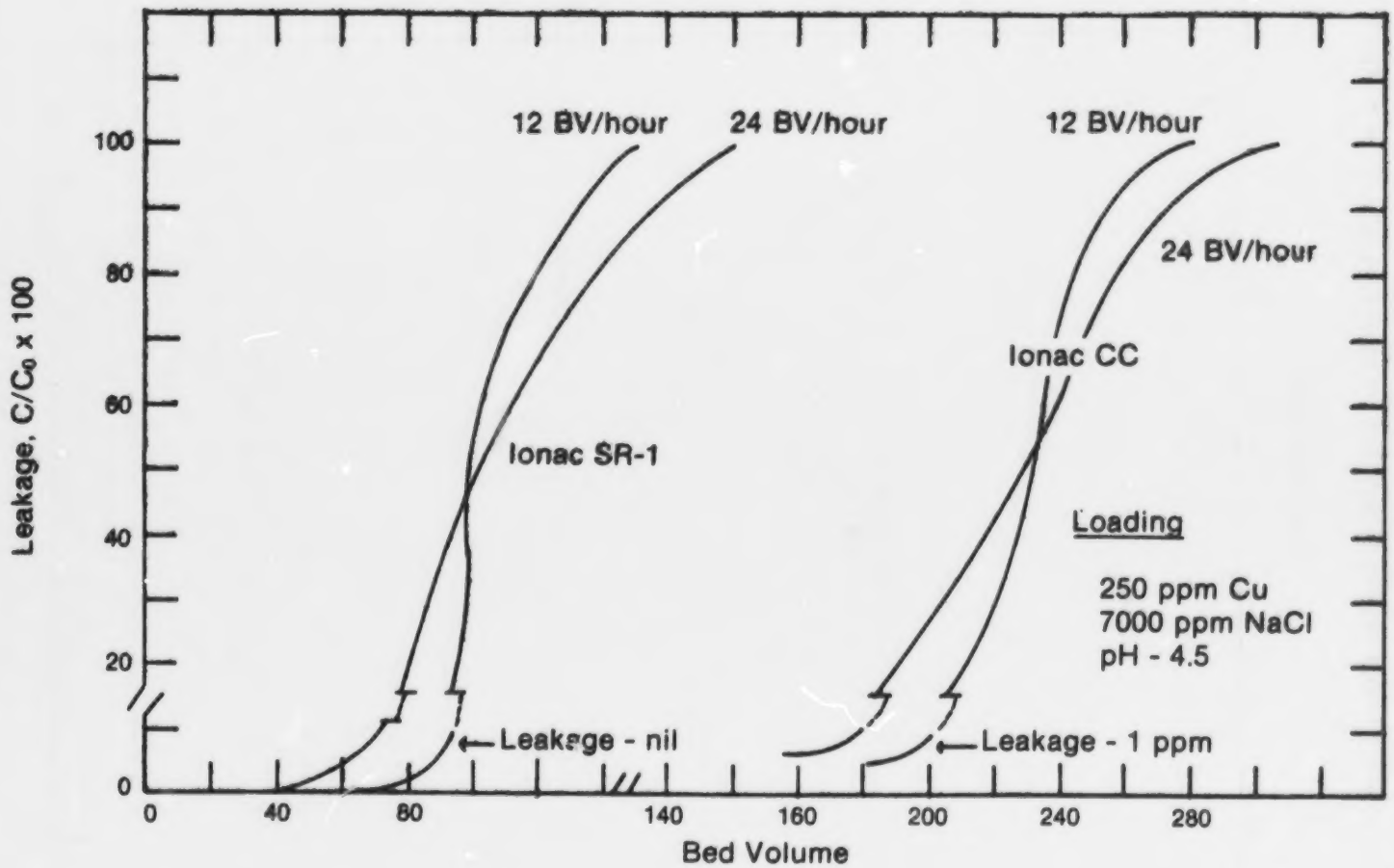

Figure 2: Loading Curves on Chelating and Carboxylic Exchangers. Copper-NaCl Feed

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ION EXCHANGE - LIQUID-FILLED MEMBRANES

Liquid-filled membrane technologies offer potential improvements in selectivity and efficiency of metal recovery from solutions. There are two main thrusts of these investigations:

1) Development of organic ion exchange reagents with greater selectivity.

2) Development of contacting devices allowing simultaneous adsorption of metals from solutions on one side of a membrane and elution into a concentrated eluate at the other.

SELECTIVE ION EXCHANGERS

Significant progress has been made, albeit still at the pure research level, at developing highly specific ion exchange compounds. One of the leaders in this research is:

DR. ABRAHAM WARSHAWSKY
Dept. of Organic Chemistry
The Weizman Institute of Science
76100 Rehovot, Israel
(08) 48-2242
Telex: 361900

WARSHAWSKY (1982) reviewed current trends in the synthesis of selective ion exchange polymers incorporating oxygen, nitrogen, phosphorus, and sulfur ligands. Chelating ion exchange polymers incorporating hydroximes, amino phenols, polyethyleneimines, selective anion exchange resins incorporating pseudocrown ethers, or isothiourea groups and polymeric crown ethers are discussed in detail. WARSHAWSKY discussed synthesis of forty-one different types of ion exchange active groups for improved selectivity. Some of these are illustrated below just to show the variety of compound types under development.

WARSHAWSKY (1984) described hydrometallurgical processes for the separation of platinum group metals in chloride media in which these metals form ion complexes of the form $[MCl_x\ (OH)_y\ (H_2O_2)_z]^{n-x-y}$ which demonstrates the powerful nature of these processes.

WARSHAWSKY, et al. (1984) described thermally regenerable polymeric crown ethers with emphasis on their synthesis and application in electrodialysis. His paper is inserted below, again to illustrate the nature of these cyclic compounds which have selective metal extraction properties. Clearly, synthesis of these compounds is well beyond the scope of this study, but it is the nature of the compounds from which will emerge much more powerful ion exchange processes that is important here.

Thermally regenerable polymeric crown ethers. II Synthesis and application in electrodialysis

A. WARSHAWSKY, Department of Organic Chemistry, I. RUBINSTEIN, Department of Applied Mathematics, and O. KEDEM, Department of Membrane Research, The Weizmann Institute of Science, Rehovot, Israel

Polymeric crown ethers are synthesised from chloromethylated styrene divinylbenzene copolymers (I), which are converted to polycatechol (II) or polybenzylamine (IV). Cyclisation with α, ω-dihaloethylglycols, leads to polymeric benzocrown series (III) or polymeric diazapseudo crown series (V). These polymers can bind alkali metal salts, and the complexation process is temperature-dependent. Through complexation of alkali salts, the polymeric crown ethers behave as anion exchangers, and thus fill the function of anion exchangers in the electrodialysis system, without causing water-splitting.

1. INTRODUCTION

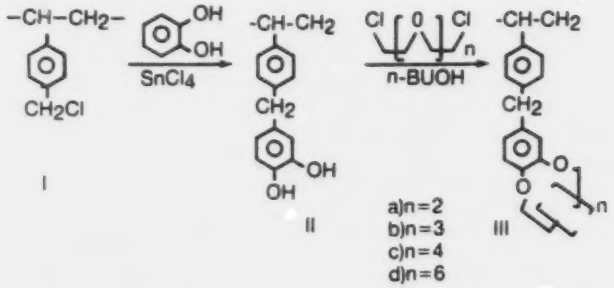
Recently, we described the synthesis of thermally regenerable polymeric crown ethers, starting from chloromethylated styrene divinyl benzene copolymers by two alternative routes.

(1) Friedel Crafts alkylation on I by catechol to give II, followed by Williamson condensation with α, ω-glycol dihalide in *n*-butanol to yield III [3, 4] (see scheme 1).

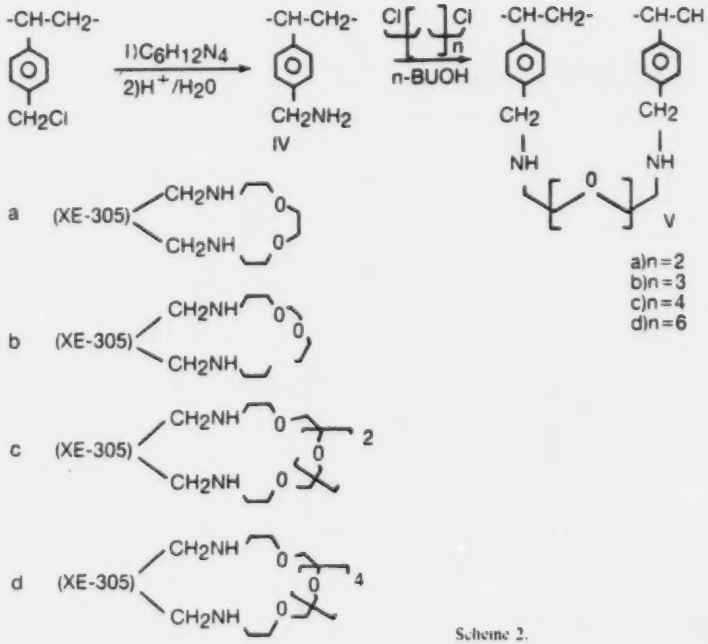
(2) Conversion of I to poly(benzylamine) IV, by reaction with hexamethylenetetraamine, and acidic hydrolysis, followed by a disubstitution reaction on a α, ω-glycoldihalide to yield V [1] (see scheme 2).

Another approach to the synthesis of polymeric crown ethers involves the sulphonylation of polybenzylamine [5] by 4-chlorosulphonylbenzocrown ethers [6], yielding polymers VI as described in scheme 3.

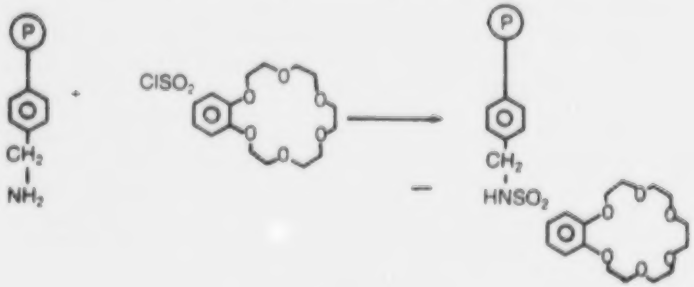
The polymeric crown ethers described bound alkali metal salts in a fashion similar to parent crown ether macrocycles, based primarily on the matching of cycle and cation radii. The main advantage of the polymeric crown ethers is the thermal decomplexation process, which occurs within a narrow temperature range and which allows the regeneration of the polymer and the alkali metal salt.



Scheme 1.



Scheme 2.



Scheme 3.

The thermoregulated decomplexation of polymeric crown ether complexes is determined by the properties of the ligand: the polymer serves as a 'separation medium' allowing the partition between the ligand and the metal salt.

In this paper, we describe a rather unusual application of polymeric crown ethers, in which the crown ether serves as an anchoring group for the cation, and the resulting positively charged entity acts as an anion exchanger. As such, it can replace conventional anion exchange membranes (AX) in electrodialysis. Since AX membranes are responsible for water dissociation, which occurs in a thin layer of the AX membrane — a phenomenon known as water-splitting.

2. RESULTS

For the preliminary study reported here a benzo-crown ether bound to a hydrophobic chain [6] was incorporated into dense cellulose acetate (CA) membranes. When the mixture of CA and complex (ligand + CsBr) was solvent cast and evaporated to dryness, clear films were obtained. These proved to be non-ideal anion-exchange membranes, as expected.

Transport and polarisation tests were carried out in a four-compartment cell (Fig. 1), with the tested membrane in the middle. Carbon suspension electrodes (7) were used to avoid pH changes by the electrode reactions. The area of the membranes confining the electrode compartments (C-membrane at the cathode and normally, except where stated otherwise, A-membrane at the anode) was 28.3 cm^2, while the area of the tested membrane varied between 0.8 and 3.1 cm^2. No stirring was applied in compartments I and II, so that polarisation was limited by natural convection only, and due to the different membrane areas was much more pronounced at the examined membrane.

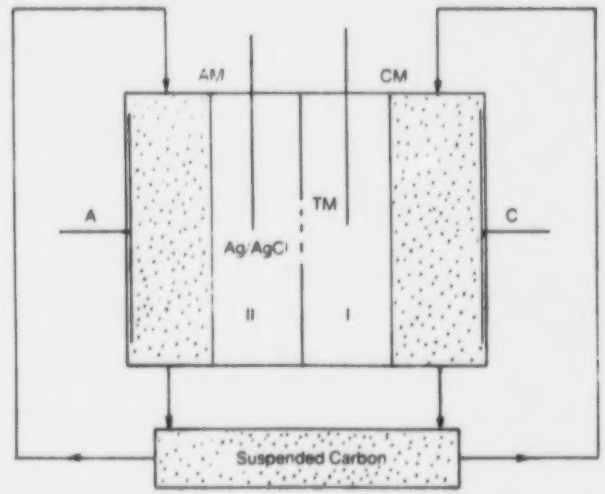


Fig. 1. Scheme of the cell: A - anode; C - cathode; AM and CM-membranes confining respectively the anode and cathode compartments; TM - tested membrane.

Current was determined as a function of the potential across the tested membrane, measured between a pair of Ag/AgCl electrodes inserted on both sides at a distance of 3.5 cm. The potential thus contains some of the IR drop in the solutions. The plot of I versus V shows a linear region at low voltage, a plateau of varying breadth, and then a further rise of current at higher voltage, reaching a slope similar to the initial one. The current in the flat region is the limiting current.

Following this characterisation, current was passed through the membrane for 1–2 hours, at two current densities: one in the low linear region, and the other above the limiting value. Salt concentrations and pH were measured at the start and end of this period. The coulombic efficiency, η, refers to desalting of compartment I for the tested A-membranes, and to desalting in II for the C-membrane which was checked in comparison. τ is the transport number of the counterion, calculated from the membrane potential measured between 0.01 and 0.1 solution. pH_0 is the initial value and $pH_f^{I,II}$ the final ones.

Table 1 shows the corresponding results with the cellulose acetate–crown ether complex (CAC) membranes.

Table 1.

Water-splitting and coulombic efficiency in CAC membranes.

Tested membrane	τ	I(mA)	i(mA/cm^2)	i^{lim}(mA/cm^2)	Δt(min)	pH_0	pH_f^{II}	pH_f^{I}	η(%)	Protective A
I	0.89	2.00	2.55	1.5	125	5.67	6.25	5.30	83	Heterogeneous
		0.70	0.89		180	5.95	5.67	6.06	89	A
II	0.83	2.00	2.55	2.2	120	6.40	6.22	6.10	90	Heterogeneous
		0.60	0.76		121	6.45	6.20	6.31	98	A
III	0.89	8.00	2.55	1.5	120	6.50	6.15	6.45	64	Heterogeneous
		1.50	0.48		120	7.25	6.10	6.20	68	A
IV	0.92	8.00	2.55	1.5	60	6.50	6.35	6.20	77	Heterogeneous
		1.50	0.48		180	6.50	6.30	6.88	98	A
V	0.89	8.00	2.55	1.6	60	6.62	6.10	6.22	90	Heterogeneous
		2.00	0.63		150	6.62	6.25	6.65	92	A

Electrolyte solution was 0.01N CsCl (initial concentration). The coulombic efficiency, η, refers to desalting of compartment I for the tested A-membranes and to that of compartment II for C-membranes. I stands for the total electric current in the cell τ, for the counterion transport number of the tested membrane, calculated from the membrane potential i-current density at the tested membrane. i^{lim}-limiting current density, determined from the 'plateau' of the voltage/current curve: pH_0 refers to the initial state of solution, $pH_f^{I,II}$ to the final state in the appropriate compartments after time Δt of passage of current. Protective A refers to the type of membrane confining the anode compartment.

These results show clearly that water-splitting is indeed determined by the character of the charged groups in the anion-exchange membrane. pH-changes obtained at strong polarisation near the complexing membranes were very small. The decrease in coulombic efficiency for removal of Cl^- ion is small, but still evident, and is not necessarily accounted for by OH^- transfer. It should be remembered that we are dealing with fixed charges which are not covalently bound, and it is possible that permselectivity decreases at high current density.

3. CONCLUSIONS

Crown ether membranes can act as anion exchange membranes by incorporation of an alkali salt. The inertness of such membranes in an electrodialysis system has been demonstrated. Polymeric crown ether membranes have the potential of eliminating the problem of water-splitting, commonly associated with conventional anion exchange membrane of the weak and strong base types.

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[7] Kedem, O., Cohen, J., Warshawsky, A. and Kahana, N., *Desalination*, **46**, 291–299 (1983).

Other, not quite so complex, compounds have also been tested, e.g., EDTA (a chelating compound) and Triane, an organic sulfur-containing compound, and conventional solvent extraction reagents have been tested, and their ion exchange selectivity and efficiency documented.

Many researchers at universities, chemical companies, and research institutions are working at developing these types of extraction reagents. These researchers include:

UNIVERSITY OF PADERBORN
Paderborn, West Germany
M. Grote
A. Kettrup

UNIVERSITY OF READING
Reading, England
M. Hudson

IMPERIAL COLLEGE
London, England
S. Gonzales-Luque

TOKYO INSTITUTE OF TECHNOLOGY
Tokyo, Japan
M. Abe
M. Tsuji
K. Hayashi

BRITISH NUCLEAR FUELS LTD.
England
H. Eccles

INSTITUTE FOR POLYMER SCIENCE
University of Stellenbosch
Stellenbosch, South Africa

IX CONTACTING SYSTEMS - LIQUID-FILLED MEMBRANES

There are two reasons that liquid-filled membrane extraction is of interest to the water treatment industry:

1) Highly selective ion exchange reagents are being developed, but many of these will be expensive. By impregnating an organic matrix with these reagents, it is hoped that losses will be minimized to make their use affordable.

2) If a liquid-filled membrane can be designed such that as the metal ions of interest are adsorbed on the side in contact with the feed solution and simultaneous elution of the adsorbed metals to an eluting solution on the other side of the membrane, then the equilibrium of the transfer process could be shifted to be highly favorable.

LIQUID MEMBRANES

CAHN, et al. (1981) described the application of liquid membranes to copper recovery, specifically summarizing the results of development work carried out by DAVY McKEE R&D in Stockton-on-Tees on behalf of the EXXON MINERALS COMPANY. In this innovative form of liquid membrane (LM), an emulsion of eluant solution within the organic phase is dispersed into the aqueous feed so that loading and elution (stripping) occurs simultaneously.

Whereas SX requires multi-stage countercurrent mixing and settling followed by a similar stripping plant, also multi-stage, LM requires only multi-stage mixing followed by one settler to achieve the combined loading and elution. The result is a saving in equipment cost and cost of the organic inventory. Additional emulsion making and breaking equipment is required in LM.

The LM emulsion globules, typically 0.5 mm in diameter, are dispersed in the feed solution. There are many thousands of droplets of the strip solution within organic phase globules and the, of course, are very much smaller than the emulsion globules.

Copper transfers across the organic phase into the internal phase, and the organic phase thereby behaves like a membrane. The efficiency of extraction is similar to that of SX, and the resulting internal phase is suitable for feeding to a copper electrolytic tankhouse following emulsion breaking.

The organic membrane (that part of the globule separating feed liquor and microglobules of eluant) consists of three comonents:

- A chelating agent for copper extraction as in SX.
- A diluent or carrier solvent as in SX.
- A surface active agent to stabilize the emulsion which is not found in SX.

The diluent is often a mixture of solvents with a specific viscosity to assist in emulsion stabilization.

In addition to copper transfer, osmosis also occurs, and water transfers across the liquid membrane. This leads to internal phase dilution or emulsion swell. Some emulsion breaking occurs, and the internal phase leakage results in a net acid loss from the electrolyte (eluant). Both the emulsion composition and contacting equipment must, therefore, be designed to minimize swell and leakage.

In continuous test runs using real leach liquors, the emulsion was made up continuously. In full-scale operation, the emulsion would be made in conventional high shear emulsion making equipment which has demonstrated by both Davy McKee and Exxon. Contact

between organic and feed solution was in four mixer boxes in series, each with a residence time of 2½ minutes. A conventional gravity settler was used and provided the correct method of dispersed phase entry to the settler is used, no problems occurred. A novel new settler design of Davy McKee would likely be used for full-scale operations.

Emulsions are easily broken in an electrostatic coalescer, and this technique was used to continuously break emulsions in the test.

Steady state performance of the equipment and the membrane system was experienced over nine days of continuous operation. The same batch of membrane phase was used throughout. Extractions of 92-94% were achieved readily and to achieve 95% recovery, a slight increase in mixer box size or the addition of a mixer box would be implemented.

Osmotic swell was about 10%, which increased the volume of electrolyte and diluted its acid content. The increased volume must be compensated for by a bleed of spent electrolyte. Losses of the "internal phase" was between 1-2% and in this case, was calculated to add 0.5¢/lb. of copper for each 1% leakage.

The test program indicated where crud would accumulate and how much would have to be catered for.

The liquid membrane system operated successfully on an aqueous feed containing 200 ppm solids is typical of CCD overflow without feed clarification or filtration, thereby eliminating a capital cost item.

Conditions of the continuous test were:

Feed: 2.5 g Cu/l
Internal: 30 g/l Cu, 150 g/l Acid
Throughput: 300 ml/min. aqueous; 150 ml/min. of Emulsion
Retention Time: 10 min. (4 Boxes)
Duration: 9 Days

Results of the continuous tests:

Osmotic Swell: 10% by Volume of Internal Phase
Breakage: About 1%
Selectivity Cu/Fe: 130 to 1

A capital cost savings of 30-40% over conventional SX was indicated by the test results.

Within the objectives of this investigation, the two main areas of interest are:

1) The test demonstrates an interesting and potentially useful effluent treatment process which may potentially be refined to work more economically selectively than resin IX for metal removal.

2) The organic loss of 1-2% is still too large for consideration in applying the super-selective but expensive new ion exchange reagents being developed--however, if combined with super-efficient organics collecting techniques to recover them from treated effluent, this process may be developed for this purpose.

Further inquiries may be directed to:

DAVY McKEE LTD.
Research and Development Dept.
Bowesfield Lane
Stockton-on-Tees
Cleveland TS18 3HA
(0642) 67-108
David Naden

EXXON MINERALS COMPANY
Post Office Box 4508
Houston, TX 77210-4508
K. N. Subramanian

KENNECOTT MINERALS COMPANY
Process Technology
1515 mineral square
Post Office Box 11248
Salt Lake City, UT 84147
(801) 534-8345
Raph W. M. Lai

LIQUID-FILLED CARBON

D. Bhattacharyya has investigated the recovery/removal of metals in organic chelating agents adsorbed in carbon particles with a macroporous surface. EDTA, a chelating compound, and TRIANE, an organic sulfur-containing compund, were impregnated into carbon particules with 300 Å macropores. The carbon particles were then contacted with the feed solution. Once loaded, the carbon was recovered physically, and the metal values eluted by mixing them into an aqueous eluant at lower pH.

Although this mechanism is expected to result in a lower loss of organic phase due to its protection in the carbon macroporous housing, this process does not offer the advantage of simultaneous loading and elution (stripping).

It is not known how far the above development has advanced, but burther inquiries may be directed to:

PROF. D. BHATTACHARYYA
Dept. of Chemical Engineering
University of Kentucky
773 Anderson Hall
Lexington, KY 40506-0046
(606) 257-2794

LIQUID-FILLED MEMBRANES

New membrane materials have been developed which can be impregnated or coated with extremely thin films of the expensive but selective compounds. The concept is to use hollow filaments or film-type membranes which allow transport of the feed solution on one side and a continuous flow of eluant (stripping solution) on the other.

There has been some progress in this direction, but the companies and researchers involved are, for the most part, not yet prepared to discuss their results.

BEND RESEARCH

Bend Research has spent several years testing and developing liquid-filled plastic membranes.

BEND RESEARCH
64550 Research Road
Bend, OR 97701
(503) 382-4100
Dave Kamperman
Manager of Metal Separation
Harold K. Lonsdale
President

Bend Research is associated with a new company called Concept, Inc. that will fabricate products as needed. Bend Research undertakes R&D only. They have undertaken test programs to extract uranium and copper from acid solutions using membrane films and filaments. The conclusion drawn from work carried out on government contract was that the kinetics of film diffusion (the controlling factor for dilute solutions) made this type of recovery system too slow to be practical using the types of membrane configurations tested.

Bend Research, however, successfully demonstrated a practical recovery process for the recovery of metal ions from more concentrated solutions; for example, hexavalent chromium from metal finishing plant effluents. They developed a patented hollow filament 0.025 inch of i/d applying their liquid membrane technology. The walls of the membrane are filled with IX reagent. The Cr^{VI}-bearing effluent solution is transported through the inside of the tube, and Cr^{VI} migrates to the outside and is eluted continuously to the eluant in the surrounding space. This configuration was found to eliminate concentration

polarization problems. High flow rates are achieved through the length of the tube, and a high Cr^{VI} flux is achieved through the walls of the membrane. The modules are similar in appearance to R.O. module shell and tube design measuring 4"-6" Φ by 3' long. The concept is to recover Cr from more concentrated metal finishing rinse solutions before it is diluted while there is a smaller volume at several hundred mg/l Cr^{VI}. The process reduces the Cr^{VI} level to below 30 mg/l Cr^{VI}.

According to Bend Research, crown ether-type extractants may be very selective, but so far they result in low flux rates, especially for low-concentration feed solutions.

The comments of a company with several years of experience in trying to develop liquid-filled membrane systems appear to be relevent in alerting sponsors to what appears to be the big challenge in treating low-level solutions--namely, how to increase the surface area or the kinetics of film diffusion transfer.

WEIZMAN INSTITUTE, ISRAEL

Working closely with the reagent development experts mentioned above (Dr. A. Warshawsky's group), the Dept. of Membrane Research is developing membranes for application of powerful new reagents to metal recovery processes. This work is supervised by Dr. Ora Kedem who is certainly one of the most experienced and talented in this field.

DR. ORA KEDEM
Department of Membrane Research
Weizman Institute of Science
P.O. Rehovot, Israel 76100
Telex: 361900

UNIVERSITY RESEARCH IN SOUTH AFRICA

The Chemical Engineering Department of the University of Potchefstroom, located about 60 miles west of Johannesburg, is conducting research into liquid-filled membrane systems using various thin-membrane configureations.

The work is being carried out by Professor Johan Smit who claims several early successes but because the work has been sponsored by a mining house, they are reluctant to discuss any aspects of it at all.

DEPT. OF CHEMICAL ENGINEERING
P.V. Vir CHC
University of Potchefstroom
Potchefstroom 2520
(01481) 22112

The Stein Hall Company, a supplier to the mining industry in South Africa and affiliate of the Celanese Company, is also interested in supplying membranes for use in this type of technology.

STEIN HALL SA (PTY) LTD.
Post Office Box 5200
Meyerton 1960
South Africa
(01612) 22340
Telex: 8-3167
Martin Hattingh

It was also established that Dr. Don Hebden of the Chamber of Mines Research Laboratories is conceptually interested in this type of technology and its possible application in water treatment. His thesis is that not all the salt species in effluents need to be removed, yet if they are removed into a concentrate by processes such as evaporation and R.O., then they enhance the brine disposal problem. He sees the advantages of selective metal removal processes.

DR. DONALD HEBDEN
Chamber of Mines Research Laboratories
Post Office Box 91230
Auckland Park
(011) 726-3020

The University of Stellenbosch is also undertaking work on membrane materials and systems and on the synthesis of selective ion exchange compounds including crown ethers. The principle contacts there are:

INSTITUTE OF POLYMER SCIENCE
University of Stellenbosch
Stellenbosch 7600
(02231) 71054
Telex: 52720783
Professor Ron Sanderson
Michael Whelan
Ed Jacob

It is concluded that liquid-filled membrane technology is an important R&D frontier, but that it <u>currently</u> offers no products or processes that are sufficiently developed for commercial application.

LIQUID MEMBRANE PROCESSES FOR COPPER EXTRACTION

Ralph W. M. Lai

Kennecott Minerals Company

Norman N. Li and R. P. Cahn

Exxon Research and Engineering Company

David Naden

Davy McKee Company
Stockton-on-Tees, U.K.

82-98

Introduction

The liquid membrane separation process was first patented in 1968 for separating hydrocarbons.[1-4] This stimulated many researchers to join in the area of separating organic compounds.[5-11] Since then, its applications have been extended to the removal of contaminants from waste water,[12-33] encapsulation of enzymes and/or microorganisms for reaction and/or separation,[24-28] oxygenation of blood (artificial lung),[19] removal of toxins from blood (artificial kidney)[26,20] and metal extraction.[31-63]

This paper discusses the possible process schemes for using liquid membranes to separate and concentrate copper ion from its acidic leaching solution.

Analogy to a Conventional Liquid Ion Exchange Process

In a conventional liquid ion exchange process, there exists three distinct phases: an aqueous phase as the source of metal ion; an organic phase consisting of an ion exchanger dispersed in an organic solvent; and an aqueous phase as the sink for recovering metal ion from the organic phase. The process of recovering metal ion is accomplished in two consecutive steps. In the first extraction step, the metal ion in the source aqueous phase reacts with the ion exchanger in the organic phase to form a metal complex. The metal complex is soluble in the solvent but not in the aqueous phase. The organic phase, which now contains the metal complex, is referred to as the loaded organic. In the subsequent stripping step, the metal ion is stripped from the metal complex in the loaded organic and recovered as an ion in the sink aqueous phase.

In the liquid membrane metal extraction (LMME) process, the sink aqueous phase is emulsified into the organic (membrane) phase which contains the ion exchanger, and the transfer of metal ion is accomplished in a single simultaneous extraction-stripping process. As in the copper extraction case, the extraction step from the source aqueous phase involves the chemical reaction:

$$Cu^{++}_{(aq)} + 2HR_{(org)} \rightarrow CuR_{2(org)} + 2H^{+}_{(aq)} \qquad (1)$$

where $HR_{(org)}$ is the ion exchanger dissolved in the organic phase and $CuR_{(org)}$ is the copper complex in the organic phase.

The intermediate step consists of the diffusion of $CuR_{2(org)}$ within the membrane phase from one side of the membrane to the other side of the membrane.

The stripping step involves transferring copper into the sink aqueous phase by the inverse of reaction (1)

$$CuR_{2(org)} + 2H^{+}_{(aq)} \rightarrow Cu^{++}_{(aq)} + 2HR_{(org)} \qquad (2)$$

The overall transport of Cu is illustrated in Figure 1.

Equations (1) and (2), and Figure 1 explicitly indicate that the transfer of copper from a source aqueous phase through a liquid membrane into a sink aqueous phase depends on the copper concentration gradient in the membrane phase. This gradient is a function of the square of the hydrogen ion concentration in the two aqueous phases, the copper concentrations in the aqueous phases and the equilibrium constant of the ion exchanger in the particular solvent at a given temperature.

Potential Advantages of a LMME Process Over a Conventional Liquid Ion Exchange Process

The potential advantages of a liquid membrane metal extraction process are that 1) the extraction and stripping of metal ion can be accomplished in a single-stage operation and 2) the ion exchange molecule can be repeatedly used in a multicycle transfer of metal ion between two sides of the membrane during the single-stage extraction. The working capacity of the ion exchange molecule is thus increased accordingly, resulting in the use of lower concentration and consequently, lower inventory and losses of this expensive material.

Application of LMME Process to Copper Extraction

In the application of the LMME process to copper recovery, the first step is to extract the copper ion from the external aqueous phase (in this case, mine water or leaching solution) and then store it in the internal aqueous phase (in this case, sulfuric acid). The ion selectivity is controlled by the use of an ion exchange reagent such as Henkel's LIX 64N® dispersed in the membrane phase.

There are two basic ways of subsequently recovering the copper from the dispersed internal aqueous phase as illustrated in Figure 2. In one, the extracted copper is recovered directly from the internal aqueous by breaking the emulsion into an organic phase and a copper-rich aqueous phase. The breaking of the emulsion can be accomplished by a mechanical means,[65] by electrical coalescence, or by the addition of an emulsion breaker,[68] which can be separated from the organic and aqueous phases, usually by distillation and can be reused. The aqueous phase, loaded with copper, goes to electrowinning; afterward, the lean electrolyte is re-emulsified with the organic and recycled to the extraction unit.

The second recovery process, which has the same sequence of events as conventional solvent extraction, does not involve breaking the emulsion. Instead, the copper is recovered in a separate reverse liquid membrane extraction step to transfer copper from the internal aqueous to a new external aqueous, namely lean electrolyte, which thus becomes loaded electrolyte. This step is referred to as re-extraction.

For presentation at the SME-AIME Annual Meeting
Dallas, Texas - February 14-18, 1982

The schemes involving the mechanical breaking of the used emulsion and re-extraction were the subjects of a joint study between Exxon and Kennecott, while the scheme involving coalescing the emulsion was studied jointly by Exxon and Davy-McKee. The latter is currently recommended over the other two for copper extraction. All the above-mentioned schemes, however, will be discussed in this paper.

Experimental

Materials Used in Experiments

The membrane oil used was a mixture of surfactant and solvent. The surfactant used was a polyamine with an average molecular weight of 1500. The solvents used were S100N, Isopar M, and LOPS, either singly or a mixture of S100N with either Isopar M or LOPS. All these solvents are basically isoparaffin hydrocarbons manufactured by Exxon Chemical Company. However, S100N is much heavier than the other two -- the specific gravity for S100N is 0.836, whereas that for Isopar M and LOPS is 0.791. The "carrier" or complexing agent for copper can be any of the commercially available ones as long as it is completely soluble in the membrane oil. LIX 64N was one of several used in this work. The feeds used were synthetic mine water, synthetic leaching solution, and real leaching solution. The copper concentrations in these feeds ranged from 0.2 to 2 g/liter with pH varied from 0.5 to 3.5. The internal and external stripping aqueous solutions were prepared with reagent-grade cooper sulfate and sulfuric acid.

Emulsion Preparation in Laboratory

Emulsions were made either by extensive mixing of oil with internal aqueous in a glass vessel or Waring blender, or by mixing oil with internal aqueous in a colloid mill.

To prepare emulsions in a colloid mill, the mixture of oil and internal aqueous was charged into a mill made by Grifford-Wood, Inc. A milling time of six minutes was used in all cases.

Results and Discussion

Maximum Copper Loading Capacity of an Emulsion

One of the major differences between conventional copper extraction and a liquid membrane process is that of the function of copper storage in the intermediate extractant. In the former process, the copper is stored in the organic phase as a complex of the ion exchange reagent. For example, in selective extraction of copper with LIX 64N, the LIX will react with copper to form a hydrophobic copper complex which will preferentially remain in the oil phase. The maximum copper extraction depends on the total LIX available and the equilibrium conditions established between the aqueous solution and the organic. In the LMME process, on the other hand, the membrane phase is merely a transfer vehicle, and the copper is stored mainly in the internal aqueous phase as an ion, with only a small portion of copper stored in the membrane phase as a copper complex. The amount of copper stored in the membrane phase depends on the equilibrium between the membrane and the internal aqueous. The loading capacity of the emulsion depends mainly on the acid content of the internal aqueous and on the volume of internal aqueous (or the internal aqueous to oil ratio of the emulsion).

For a direct comparison of the loading capacities of the two processes, three sets of experiments were run to compare the loading capacity of copper in kerosene containing 7.5% active LIX 64N vs loading capacity of copper in an emulsion containing 7.5% LIX 64N in the membrane oil.

In the tests, a given amount of organic consisting of LIX 64N in kerosene or emulsion was repeatedly contacted with an equal volume of fresh mine water. In each step, the raffinate was drained and fresh mine water was added. The experimental results are given in Figure 3, showing the trend in the stepwise decay of extraction for three cases.

In the case of LIX in the kerosene, the extraction efficiency decreases drastically after just two steps. The percent copper extracted decreases from 92.1% in the second step down to 56.78% in the third step. In six steps the loading is completed, and no further extraction takes place. The total loading capacity of copper per gram of active LIX 64N was found to be 0.068 g/g of LIX.

In the case of an emulsion containing low acid internal aqueous (20 g/l H_2SO_4), the total loading capacity for copper was 0.147 g/g of LIX. This is more than twice the loading achieved with LIX in kerosene.

In the third case, where an emulsion containing high acid in the internal aqueous (151 g/l H_2SO_4) was used, the copper extraction was much better. Figure 3 gives the results of 17 repeated cumulative loading tests using a high acid internal aqueous. The percent copper extracted in each of the first 13 steps is more than 90%. The extraction efficiency of copper from mine water decreases gradually as the H_2SO_4 in the internal aqueous phase decreases and the copper increases. In 17 steps, the total copper extracted per gram of active LIX is about 0.35 g, a value about five times as high as the run for LIX in kerosene. It is expected that extraction can be continued for many more steps beyond 17 steps. Thus, the total loading capacity would be much higher than 0.35 g.

The above results indicate that in terms of LIX utilization per unit weight of LIX, the loading capacity of an emulsion is much higher than that of kerosene solvent. The advantage of using emulsion over conventional solvent extraction can be illustrated as follows: refer to Figure 3. Suppose a cross flow scheme is used to extract copper from parallel streams of mine water with the assumption that the extraction efficiency must be better than 90% in each step. In

conventional solvent extraction, the same solvent stream can be employed for only two cross flow stages, while an emulsion achieves target recovery for as many as 13 cross flow stages.

In the emulsion process, the loading capacity for copper can be increased by increasing the volume fraction of internal aqueous and by increasing its acid content. However, LMME with the maximum acid content has its limitations. For example, where subsequent stripping is used to recover the copper out of the emulsion, the acid content in the internal aqueous has to meet the constraint of allowing reasonable stripping of copper. Usually a high acid content will inhibit the re-extraction of copper into an external acid phase. Also, there may be problems with unfavorable water transfer where very high acid concentrations are used, and the emulsion/leach liquor density differential may be jeopardized.

Internal Phase Acid Concentration

The effect of increasing internal phase stripping acid concentration on copper extraction is illustrated in Figure 4. The greater driving force of the higher acid content is seen to lead to an increase in the rate of extraction. Emulsion swell due to osmotic transfer of water into the highly acidic internal phase has, however, increased by approximately 30%. Very high acid concentrations are not, therefore, recommended unless the membrane formulation is modified to reduce the transfer rate of water.

Bench-Scale Evaluation of Flow Sheet for Copper Recovery from Mine Water

The emulsion has the advantage of a high loading capacity per unit weight of extractant used. To make use of this loading capacity in the extraction stage, a cross flow scheme was designed where the emulsion is contacted repeatedly with fresh mine water.

The following describes the evaluation of an integrated flow sheet which incorporates a cross flow extraction section, a stripping stage, and electrowinning. The basic assumptions in the flow sheet are that the mine water contains 0.5 g/l Cu, the spent electrolyte composition is 170 g/l H_2SO_4, and 30 g/l Cu, and the internal aqueous cycles between 30 and 50 g/l Cu, an optimal range needed to meet the extraction efficiency target and a reasonable copper recovery in stripping.

A detailed cross flow extraction stage utilizing the emulsion of the above internal aqueous was evaluated by using a series of response surface experiments.

The extraction experiments were carried out in a jacketed separatory funnel at 35°C. The emulsion-to-mine water ratio was kept at 1:4, while the ratio of oil to internal aqueous in the emulsion was kept at 2.

In each experiment, 40 g of emulsion and 160 g of mine water were charged into the separatory funnel. After the equilibrium temperature was established, the mixture was tumbled for three minutes at the rate of one turn per second. After the tumble mixing, the dispersion was allowed to settle and separate into two layers. Small aliquots of raffinate were collected for copper analysis. From the analysis of the spent mine water, the change in copper content of the internal aqueous, the total copper concentration after the extraction, and the percent copper extracted were calculated. It was assumed that the copper retained in the membrane phase is negligible compared with the total copper extracted.

The design and the results of the regression experiments are given in Tables 1 and 2. The data in Tables 1 and 2 were used for regression analysis, and the results of this analysis are summarized in Figures 5, 6, and 7.

Figure 5 gives the contour of copper content in the internal aqueous after the mine water is extracted with a specified emulsion. Figure 6 gives the contour of percent coper extraction from the mine water when the mine water is extracted with a given emulsion. Figure 7 gives the contour of copper content remaining in the raffinate after the mine water is extracted with a given emulsion.

The construction of a flow sheet for the extraction of copper from mine water containing 0.5 g/l Cu can be resolved graphically as follows:

Suppose the mine water to be treated cross-flow with an emulsion containing 35 g/l Cu and 43.1 g/l H_2SO_4 in the internal aqueous at a ratio of emulsion to mine water of 0.25 in each contacting stage, and suppose the criterion of the extraction is to be that either more than 85% extraction is necessary or less than 100 ppm Cu (0.1 g/l) should remain in the raffinate so that it can be recycled after one contact. If the extraction is less than 85%, or if the spent mine water contains more than 100 ppm Cu, then the mine water requires a second extraction stage. The stepwise construction of the extraction flow sheet will be as follows: in the first step, an emulsion containing 35 g/l Cu is used to extract a mine water of 0.5 g/l Cu (point A1 in Figure 5); the copper content of the internal aqueous will rise to 40 g/l after the extraction (reading from contour in Figure 5). The extraction efficiency is better than 85% (point A1 in Figure 6). The copper remaining in raffinate is less than 100 ppm (point A1 in Figure 7). Thus, the raffinate can be recycled. In the next cross flow extraction stage, the above emulsion which now contains 41 g/l Cu is to be contacted with fresh mine water containing 0.5 g/l Cu (point A2 in Figure 5). After the extraction, the copper content will rise to 46.6 g/l Cu. The extraction efficiency is better than 85% (point A2 in Figure 6) and the copper remaining is less than 100 ppm (point A2 in Figure 7). This raffinate thus can also be recycled. In the next cross flow extraction stage, the above emulsion which contains 46.6 g/l Cu is again contacted with fresh mine water of 0.5 g/l Cu (point A3 in Figure 5). After the extraction, the copper

content will rise to 52.4 g/l. The extraction efficiency is better than 85% and the copper remaining in the raffinate is less than 100 ppm, still suitable for recycle.

Since batch experiments in the laboratory showed that 88 to 96% extraction can be achieved in three minutes, a residence time of five to eight minutes will be required in the plant under continuous extraction conditions, if we assume that each cross flow contacting stage is provided with several mixing compartments in series.

The re-extraction experiments were carried out under the following assumptions: 1) the aqueous phase in the emulsion contains about 50 g/l Cu, 2) the loaded electrolyte (external aqueous from stripping) to electrowinning contains 40 g/l Cu, and the spent electrolyte (external aqueous fed to stripping) contains 30 g/l Cu.

Four experiments were conducted at 60°C to recover copper from an emulsion (2 oil/l internal aqueous) containing 50 g/l Cu and 20 g/l H_2SO_4. The two external aqueous phases fed to stripping had the following compositions: 30 g/l Cu, 170 g/l H_2SO_4, and 32.5 g/l Cu, 166.2 g/l H_2SO_4. The ratio of emulsion to external aqueous was 0.5. The results were as follows: the increases of copper content in the external aqueous were, respectively, 3 g/l, 2.4 g/l, 3.1 g/l, and 1.7 g/l (average 2.5 g/l).

The stripping experiments indicated that the arithmetic average of copper increment during the stripping was 2.5 g/l Cu per step.

Assuming that each step of stripping recovers the same amount of 2.5 g/l, then a complete flow sheet of cross flow can be constructed for the stripping section.

Effects of Copper Concentration Gradient in Re-Extraction of Copper from Loaded Emulsion

A series of experiments was conducted to evaluate the importance of a copper concentration gradient in stripping copper from a loaded emulsion. In the experiments, the sulfuric acid concentrations for internal aqueous and for external aqueous (i.e., electrolyte) were 20 g/l and 170 g/l, respectively. The levels of copper in the internal aqueous were between 30 g/l to 50 g/l with H_2SO_4 levels as shown in the extraction experiments (see Table 2). The stripping was carried out in a jacketed separatory funnel at 55°C. the emulsions were made with an oil to internal aqueous ratio of 2. the results of the tests are given in the following table:

Initial Copper Concentration Gradient Cu (Internal-External), g/l	Net Increase in Copper Cu External g/l
45	8.95
35	6.4
20	4.8

From the above results, one could conclude that the copper re-extraction, or stripping, rate appears to be highly dependent on the copper concentration gradient. The bigger the concentration difference, the faster the stripping. However, internal acid concentration, which varies inversely with the internal copper concentration, has an even greater effect on the copper concentration gradient in the membrane, and it is this gradient which sets the stripping rate. This is further illustrated in the following section.

Stripping Experiments without Positive Copper Concentration Gradients

A number of re-extraction or stripping runs were made to show that stripping occurs even when there is little or no apparent copper concentration driving force in the outward direction. However, there was a sufficient difference in acid concentration between the internal and external phases to establish a copper concentration gradient in the membrane in the right direction to bring about the desired stripping action.

These experiments were batch with a 10-min. contact time, a 2:1 ratio of stripping liquor to emulsion, and a 1:1 aqueous/oil emulsion. All the experiments were conducted at 55°C.

Initial Internal Aqueous		Initial Stripping Liquor		% of Cu Stripped from Emulsion
Cu g/l	H_2SO_4 g/l	Cu g/l	H_2SO_4 g/l	
60	24	60	120	29
60	24	50	155	38
30	70	30	163	23
30	70	20	200	34

Note that in all cases the final copper concentration in the stripping liquor will be higher than the copper concentration of the aqueous phase in the emulsion.

Another observation is that stripping is a relatively slow phenomenon, as is to be expected because of the low copper concentration levels in the membrane phase when contacting both of these highly acidic aqueous solutions.

Continuous Stripping Experiments

A batch extraction time of 10 min. to remove about 30% of the contained copper from the emulsion translates to about 15 min. in a multi-compartment continuously-fed mixer. Continuous bench-scale stripping runs were carried out showing that 25 to 30% of the contained copper could be stripped out of an emulsion in 15 min. in a three-stage device. However, water balance becomes a problem since during this long contacting, the high acidic stripping liquor draws water out of a less acidic internal solution.

Conceptual Flow Sheet for the Re-Extraction Process

A conceptual flow sheet utilizing emulsion stripping rather than emulsion breaking can now be put together, based on mine water containing 0.5 g/l Cu. It is shown in Figure 8 with three cross-flow extraction stages operating at 35°C and four cross-flow stripping stages at 60°C. The emulsion circulating between these two sections swings between 35 and 50 g/l Cu. Stripping is done with the spent electrolyte containing 30 g/l of Cu, returning to the cell house with 40 g/l Cu.

Not shown, but certainly required, will be a small emulsion breaking facility to allow internal solution purge and adjustment and oil phase cleanup.

Equipment Design Studies

The equipment design variables examined are:

- Number and Size of Mixer Boxes
- Impeller Design and Speed
- Settler Design
- Method of Entry of the Dispersion into the Settler

Various types of impellers are being tested for use in the continuous equipment. The conclusions will prove valuable for impeller selection in larger scale plants. The interaction of impeller speed and emulsion type is also important. The effect of impeller speed on extraction efficiency in a continuously-fed four-compartment mixer is illustrated in Figure 9.

It may be seen that in this case there is no increase in extraction efficiency after 400 rpm has been reached and above this level, emulsion breaking and internal phase leakage increases rapidly (Figure 10). No effect on emulsion swell was observed. Selection of impeller type and speed is, therefore, as important here as in solvent extraction.

Emulsions were prepared successfully both with an impeller and with commercial equipment, such as a 10 gpm Tekmar Dispax DR 3-6/6. Depending on the membrane formulation and viscosity, emulsions sometimes needed to be recirculated through the emulsifier in order to reach uniform small droplets, such as $<1\ \mu m$.

The emulsions can be broken by several methods -- as noted previously, namely, by the commonly known electrostatic coalescence, or chemical methods, or a physical method which involves the use of centrifugation followed by high shear. The last method was tested with large-scale equipment. The centrifuges used were Sharples 6 in. bowl diameter Westfalia disc centrifuge. The high-shear device used was the Tekmar Dispax emulsifier. The centrifuges had no difficulty in handling the removal of the heavy emulsion which resulted when about 80% of the oil was separated. The heavy emulsion was then mixed with previously broken IR at 1 to 10 ratio (1 part of emulsion) in the Tekmar emulifier for inversion and thereby breaking. The results of demulsification sometimes could be improved by recycling the feed through the Tekmar emulsifier. The highest percent of IR recovery was 84%. Current design favors the use of an electrostatic coalescer because of its lower cost. A specially-designed coalescer gives excellent results of demulsification.[70]

Another equipment variable which requires special attention is the settler and the method of introducing the dispersed phase into the settler. The most important feature is that flow in the settler should be upflow so that the emulsion is carried to the under side of the settled emulsion phase. Complete and clean separation is then achieved and contact time between raffinate and emulsion in the settler which might lead to emulsion swell is minimized. The number and size of mixer boxes used in a continuous run will be discussed later.

Continuous Run using Freshly Prepared Pag. Leach Liquors

A continuous run was made at the laboratory of Davy-McKee to determine the long term effects of the constituents of real leach liquor on the LM system with membrane and internal phase recycle.

Fresh pregnant solution was prepared daily over a period of nine days. Freshly milled oxide ore was leached using sulfuric acid to an end pH of 2 under conditions previously determined in small scale tests. The suspended solids content of the feed was 200 ppm. At no time was the solution used more than 24 hr old.

The flow sheet used is shown in Figure 11. It has the following features:

a) Feed solution continuously fed to the extraction unit and raffinate recycled to ore washing.

b) Emulsion continuously broken and membrane phase recycled to emulsion making.

c) Electrowinning was simulated by adding acid and water to the recovered internal phase to simulate an electrowinning section spent electrolyte. A portion of this solution was then recycled to the emulsion making section.

d) Emulsion was continuously made.

Conditions of continuous operation are as follows:

Feed:	2.5 g/l Cu
Internal:	30 g/l Cu, 150 g/l Acid
Throughput:	300 ml/min. of Aqueous 150 ml/min. of Emulsion
Retention Time:	10 min. total (four boxes)
Duration:	9 days

Four mixer boxes in series each with a residence time of 2½ min. were used. A conventional gravity settler was used in the test. When the correct method of dispersed phase entry to the settler was adopted, as discussed previously, no problems occurred. The loaded emulsion was easily broken in an electrostatic coalescer.

Performance of the Membrane System in the Davy Continuous Run

Steady performance of the equipment and the membrane system was experienced over the nine days of continuous operation in Davy-McKee's laboratory. The same batch of membrane phase was used repeatedly, the only membrane added being the very small amount required to make up losses.

The extraction was between 92 and 94% throughout indicating that slightly longer contact time is probably required if over 95% recovery is to be attained. This may be achieved by increasing the size of each mixer box or by adding one more mixer box.

Osmotic swell of the emulsion internal is approximately 10%. Swell has the effect of increasing electrolyte volume and reducing the acid content of the electrolyte. The increased volume must, therefore, be removed in a bleed of spent electrolyte. The copper content of the bleed must be recovered, and this may be achieved using an electrolytic cell. Alternatively, the whole bleed may be passed to the leach section. In both cases, the acid content of the bleed will provide a part of the leach acid. When copper is not removed before recycling, however, the effect is to increase the quantity of copper circulating in the flow sheet, and it is therefore very important to achieve a high extraction efficiency if losses in the leaching operation are to be avoided.

Internal phase loss, or leakage, was between 1 and 2%. The significance of internal phase loss lies in loss of acid and consumption of tails neutralizing agent. Extraction efficiency is not greatly affected as the copper is rapidly reabsorbed. It has been estimated that internal phase losses add approximately 0.05¢/lb of copper for each 1% leakage.

In the continuous run, the ability of LM to operate successfully on an aqueous feed containing 200 ppm solids has been demonstrated. This level of solids is equivalent to that in the leaching section effluent and feed clarification may therefore be eliminated, reducing the capital cost.

Process Economics

The re-extraction LM process was compared with solvent extraction and cementation for recovery of copper from mine water. The investment for the LMME re-extraction process turned out to be intermediate between the low cost cementation and solvent extraction, a high investment process. Operating costs for the LMME process were somewhat lower than for the existing technology.

Subsequent comparison of the LM re-extraction process with LMME process alternates in which the emulsion is broken indicated a decided advantage for the latter. The whole stripping section with its four large mixer-settlers could be deleted, leading to a reduction in plant investment and solvent inventory. On the other hand, emulsion breaking facilities had to be increased to handle the full emulsion circulation, rather than just a purge stream. As the following table shows, the operating cost of the LMME process involving breaking the emulsion by centrifugation and high shear is about 20% cheaper than the solvent extraction process. A comparison of solvent extraction with the latest LMME process costs incorporating the emulsion breaking scheme is given in another publication[34] which shows a 40% reduction in investment for the liquid membrane process.

OPERATING COST INCLUDING 15% DCF RETURN

Solvent Entrainment in Raffinate ppm	Operating Cost: Conventional SX	Operating Cost: LMME ¢/lb Cu	Cementation: Scrap Cost $/ton	Cementation: Operating Cost ¢/lb Cu
0	25.7	20.5	—	—
30	27.1	21.8	—	—
90	28.2	22.7	—	—
190	33.2	27.0	—	—
—	—	—	80	26.7
—	—	—	100	29.7
—	—	—	100	31.2
—	—	—	120	32.7

Summary

The liquid membrane separation process is applicable in extracting and concentrating copper from its leaching solutions. Several process schemes were examined in this paper. The extraction part of all these process schemes is similar. The difference lies in how to treat the copper-loaded emulsion after the extraction step.

The emulsion can be broken to recover the internal copper-loaded phase by two effective physical methods — electrostatic coalescence and centrifugation followed by intensive shearing. In another scheme, the copper ion in the internal phase of the emulsion can be re-extracted out into an acid phase. In this method, the emulsion is regenerated without going through the demulsification and re-emulsification steps in a process.

In general, the re-extraction scheme should be used if the process requires a particularly stable emulsion, which is very difficult and costly to break; or where separation selectivity is insufficient with a simple permeation and re-extraction is needed to increase the enrichment. In the latter case, the re-extraction step

ought to be followed by demulsification in which a portion of the emulsion is broken to purge the accumulated impurities.

In comparison with solvent extraction, the liquid membrane process, in general, is cheaper. It requires less contacting stages, and the capacity of the liquid membrane emulsion for the material being extracted can be much higher than the capacity of the simple organic solution in a solvent extraction process. This is due to the presence of the encapsulated aqueous phase which acts as a storage reservoir. In addition, the concentration of the "carrier" or ion exchanger in the organic phase can be reduced, leading to lower inventory cost and potentially to lower organic losses.

For copper extraction, the liquid membrane process that utilizes electrostatic coalescing to break the emulsion is the presently recommended process over the other liquid membrane process schemes discussed.

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Table 2. Results of Extraction Experiments (30 g/l Cu to 50 g/l Cu in Internal Aqueous)

Run No.	Mine Water Added, ml	Cu, g/l		Total Cu, g/l		% Cu Extracted	Internal Aqueous (calculated)				
		Before Extraction	After Extraction	Before Extraction	After Extraction		Before Extraction		After Extraction		
							H_2SO_4 g/l	Cu g/l	Cu g/l	Total Cu g/l	H_2SO_4 g/l
1	149.5	0.615	0.0130	0.0919	0.0019	97.9	50.8	30	7.36	37.36	39.46
2	149.5	0.205	0.0039	0.0306	0.0006	98.3	50.8	30	2.47	32.47	46.99
3	149.5	0.204	0.0076	0.0306	0.0011	96.3	35.4	40	2.48	42.48	31.58
4	149.5	0.205	0.0177	0.0306	0.0026	91.4	20.0	50	3.20	52.30	16.46
5	149.5	0.615	0.111	0.0919	0.0166	82.0	20.0	50	6.27	56.27	10.34
6	149.5	0.615	0.0546	0.0919	0.0082	91.1	35.4	40	6.84	46.84	24.87
7	149.5	0.409	0.0102	0.0611	0.0015	97.6	43.1	35	4.96	39.96	35.46
8	149.5	0.409	0.0280	0.0611	0.0043	93.0	27.7	45	4.64	49.64	20.55
9	149.5	0.409	0.0154	0.0611	0.0023	96.2	43.1	35	4.85	39.85	35.63
10	149.5	0.409	0.0353	0.0611	0.0053	91.4	27.7	45	4.69	49.69	20.48

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68. Martin, T. P., and Davies, G. A., Hydrometallurgy 2, 315 (1976).

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Table 1. Rectangular Experiments Factor Levels and Responses (30 g/l Cu to 50 g/l Cu in Internal Aqueous)

Factor Levels		Design Levels		Yields			
Cu g/l in IA	Cu g/l in Mine Water	X_1	X_2	Y_1	Y_2	Y_3	Y_4
30	0.6	-1	1	7.36	37.36	97.9	0.013
30	0.2	-1	-1	2.47	32.47	98.3	0.0035
40	0.2	0	-1	2.48	42.48	96.3	0.0076
50	0.2	1	-1	2.30	52.30	91.4	0.0177
50	0.6	1	1	6.27	56.27	82.0	0.111
40	0.6	0	1	6.84	46.84	91.1	0.0546
35	0.4	-0.5	0	4.96	39.96	97.6	0.0102
45	0.4	0.5	0	4.64	49.64	93.0	0.0288
35	0.4	-0.5	0	4.85	39.85	96.2	0.0154
45	0.4	0.5	0	4.69	49.69	91.4	0.0353

Y_1 = Cu in g/l in internal aqueous

Y_2 = Total Cu in g/l in internal aqueous

Y_3 = % Cu Extracted from mine water

Y_4 = gpl Cu left in mine water

$$Y_1 = 4.8 - 0.3\,X_1 + 2.2033\,X_2 - 0.06\,X_1^2 - 0.14\,X_2^2 - 0.23\,X_1X_2$$

Multiple correlation R^2 = 99.96%

$$Y_2 = 44.8 + 9.7\,X_1 - 2.2033\,X_2 - 0.06\,X_1^2 - 0.14\,X_2^2 - 0.23\,X_1X_2$$

Multiple correlation R^2 = 100.0%

$$Y_3 = 94.87501 - 5.5\,X_1 - 2.5\,X_2 - 1.3\,X_1^2 - 1.175\,X_2^2 - 2.25\,X_1X_2$$

Multiple correlation R^2 = 98.6%

$$Y_4 = 0.02112 + 0.0263\,X_1 + 0.025\,X_2 + 0.0052\,X_1^2 + 0.01\,X_2^2 + 0.0209\,X_1X_2$$

Multiple correlation R^2 = 98.91%

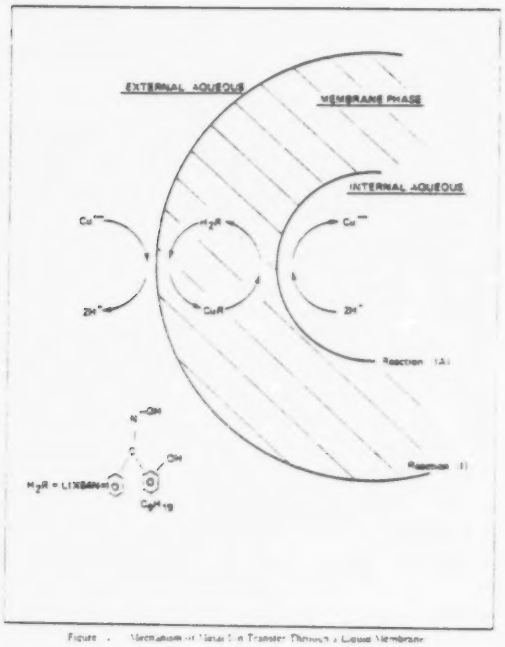


Figure . Mechanism of Metal Ion Transfer Through a Liquid Membrane

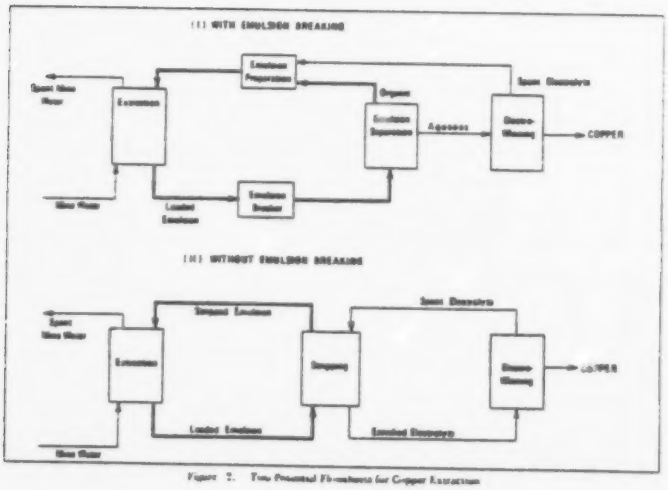


Figure 2. Two Potential Flowsheets for Copper Extraction

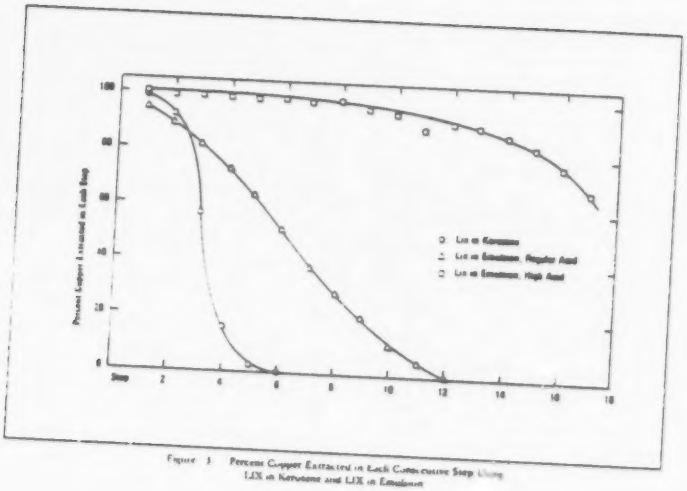


Figure 3 Percent Copper Extracted in Each Consecutive Step Using LIX in Kerosene and LIX in Emulsion

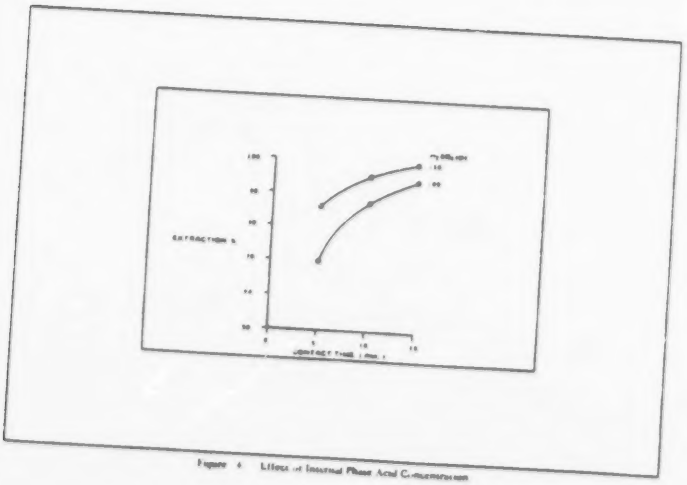


Figure 4 Effect of Internal Phase Acid Concentration

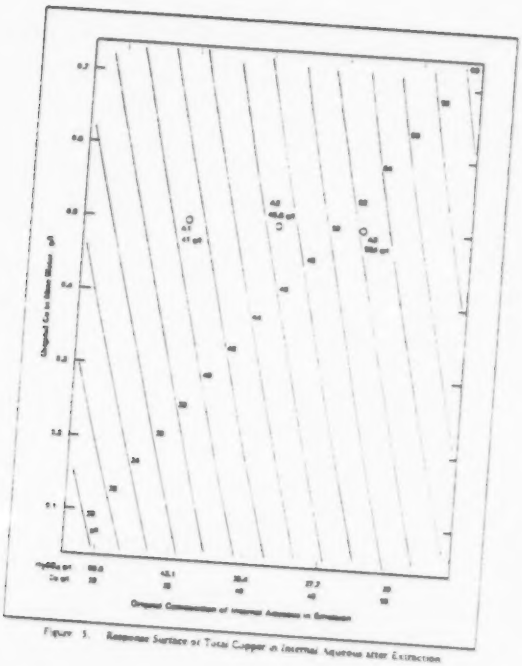


Figure 3. Response Surface of Total Copper in Internal Aqueous after Extraction

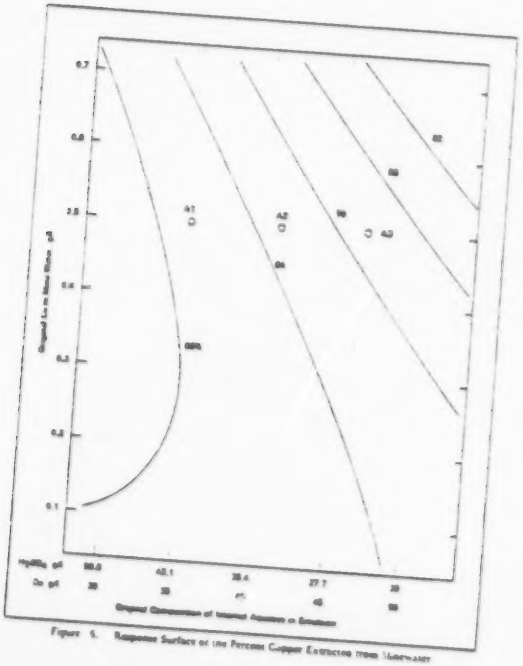


Figure 5. Response Surface of the Percent Copper Extraction from Sludge

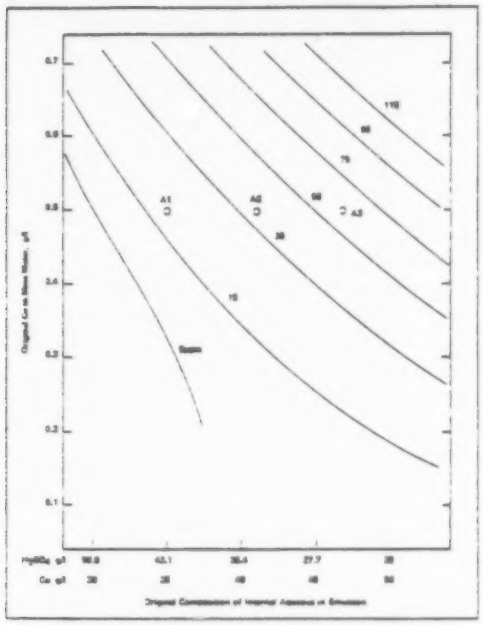


Figure 7. Response Surface of the Content of Copper Remaining in Raffinate

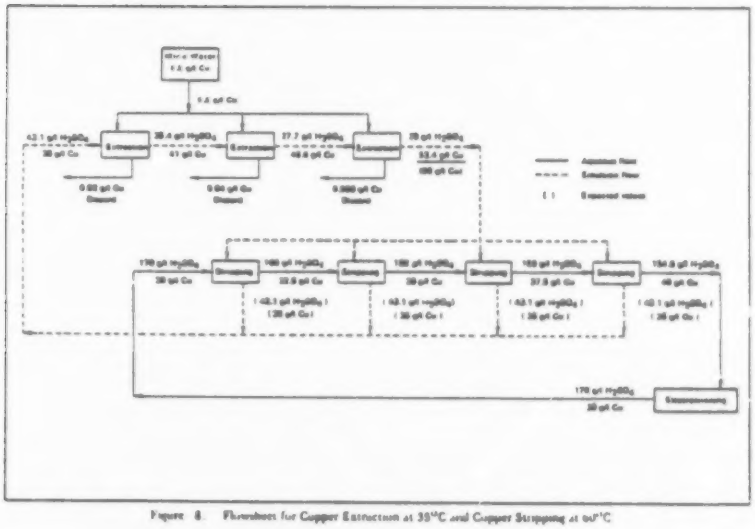


Figure 8. Flowsheet for Copper Extraction at 35°C and Copper Stripping at 60°C

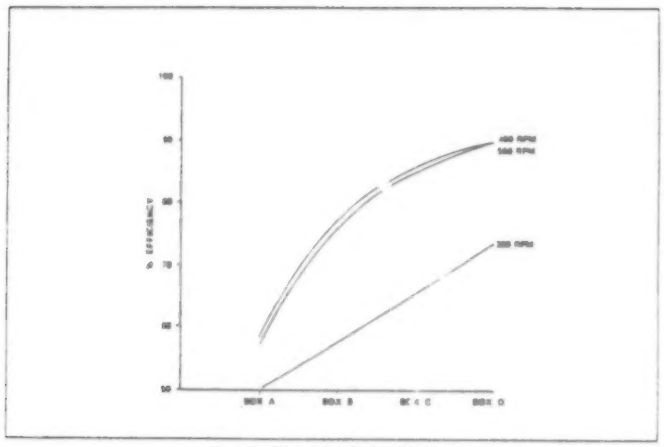


Figure 9. Effect of Starter Speed on % Efficiency

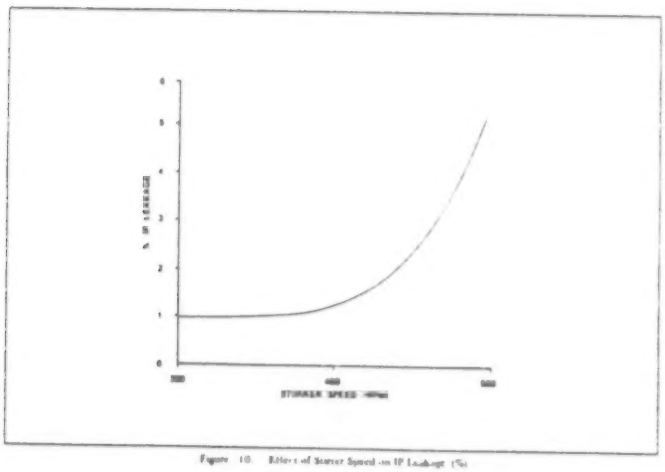


Figure 10. Effect of Starter Speed on IP Leakage (%)

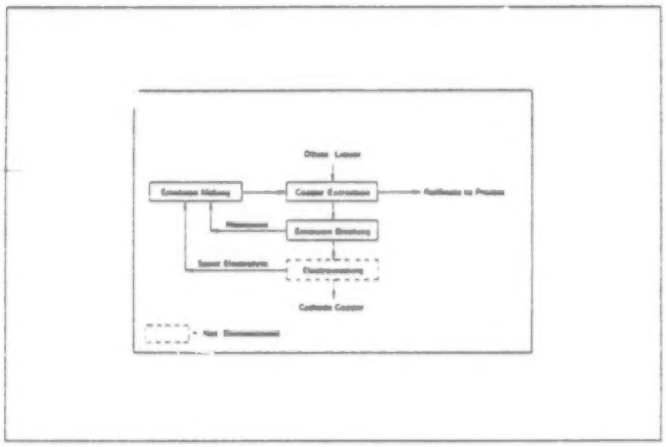
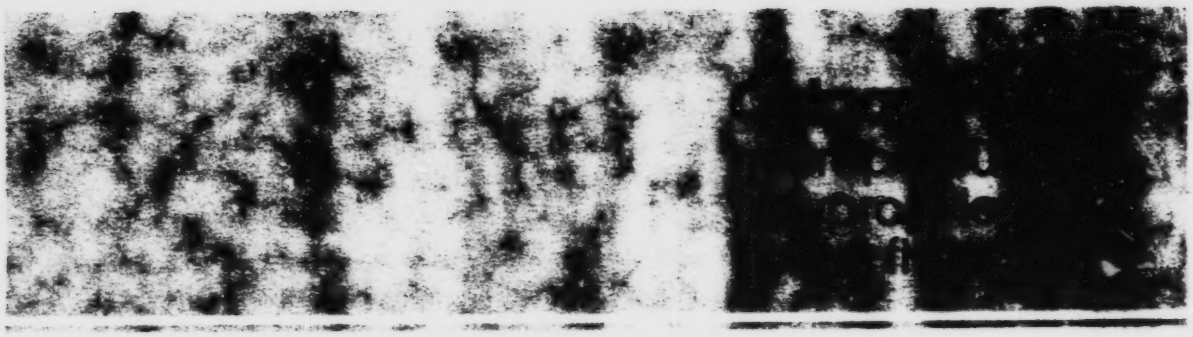


Figure 11 Continuous Demonstration

ION FLOTATION

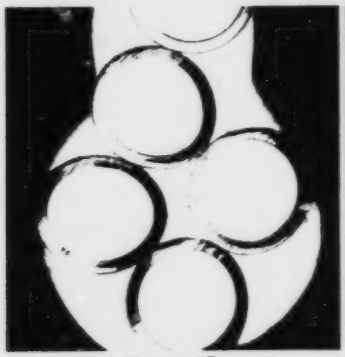
The Japanese in particular have conducted research into ion flotation. IZUMI, et al. (1976), for example, developed a process for foamy complex formation for removing and recovering heavy metal ions in dilute solutions with N-monodecanol diethylenetriamine. Heavy metals, i.e., Cu, Zn, Pb, Ni, Cd, Co, and Mn were removed and recovered from real and simulated waste waters by a foam-separating method using the organic reagent to extract the metals as foamy complexes that can be readily floated. The results are reported in a Japanese Journal in English.

MIYAMATSU, et al. (1983) studied the recovery of uranium from dilute uranium mine water solutions by fibrous anion exchangers. He found that the fibrous exchangers showed adsorptive capacities adequate for the recovery of U from solutions such as H_2SO_4 leach liquor, alkaline leach liquor, and mine water. Compared with conventional ion exchange resins, the fibrous anion exchanger demonstrated faster adsorption kinetics and better dispersion properties in solution. The adsorbent was stirred into the solution for best results. In an adsorption test using a two-stage counter-current system to recover U_3O_8 from an H_2SO_4 leach liquor containing 34.6 ppm U_3O_8, a repeatable 98% recovery of uranium and 60 fold concentration factor were obtained. Flotation was used to collect the fibrous adsorbent from the treated solution.



Celgard™ microporous polypropylene is now offered as hollow fibers as well as film. The fiber wall has properties similar to Celgard 2500 film. This hollow configuration may offer an advantage of higher surface area per unit volume in a separation device. Inside diameters are available in a range from 100-400 μ.

For further information, orders, or samples, please contact a Celgard representative at the address given below.



Cross-Section of Filaments (58X)

Diagonal Filament Cross-Section (90X)

Fiber Surface (8,000X)

Following are properties typical for 250-μ I.D. Celgard fibers. Most of these properties can be engineered to meet the requirements of specific end uses.

Properties of Celgard™ Microporous Hollow Fibers

Property	System	
Wall Thickness	0.98-1.18 mil	25-30 μ
Tensile Strength	7.8 oz/fil	220 g/fil
Elongation at Break	55%	55%
Hot-Water Shrinkage (90°C, 1 hr)	<6%	<6%
Bursting Pressure	100 psig	689 kPa
Oxygen Permeability	1.5 $in^3 \cdot in^{-2} \cdot min^{-1} \cdot in^{-1} Hg$	1.125 $cm^3 \cdot cm^{-2} \cdot min^{-1} \cdot kPa^{-1}$

CELANESE

Celanese Fibers Marketing Company, Box 32414, Charlotte, N.C. 28232 Tel. (704) 554-2289

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March 1981

CELANESE

Celgard microporous polypropylene film

Product Description

2000 Series	**CELGARD 2400.** Air-breathable and water-repellant, 1 mil thick, 38% porosity with 0.02-micron effective pore size.
	CELGARD 2402. Two-ply form of CELGARD 2400.
	CELGARD 2500. Air-breathable and water-repellant, 1 mil thick, 45% porosity with 0.04-micron effective pore size.
	CELGARD 2502. Two-ply form of CELGARD 2500.
3000 Series Wettable Films	**CELGARD 3400 & 3401.** Air-breathable and water-wettable grades of CELGARD 2400.
	CELGARD 3500 & 3501. Air-breathable and water-wettable grades of CELGARD 2500.
4000 Series Plain Laminates	**CELGARD 4410.** Water-repellant, embossed laminate of CELGARD 2400 to a polypropylene nonwoven. No adhesives are used.
	CELGARD 4510. Water-repellant, embossed laminate of CELGARD 2500 to a polypropylene nonwoven. No adhesives are used.
	CELGARD K-442.* Water-repellant, embossed laminate of CELGARD 2400 between layers of polypropylene nonwoven.
	CELGARD K-443.* CELGARD 2400 laminated to a polypropylene screen.
5000 Series Wettable Laminates	**CELGARD 5410 & 5411.** Air-breathable and water-wettable embossed laminates of CELGARD 2400 to a polypropylene nonwoven.
	CELGARD 5510 & 5511. Air-breathable and water-wettable embossed laminates of CELGARD 2500 to a polypropylene nonwoven.

*Developmental products illustrating product line capabilities. Other treated and laminated variations are available for specific applications.

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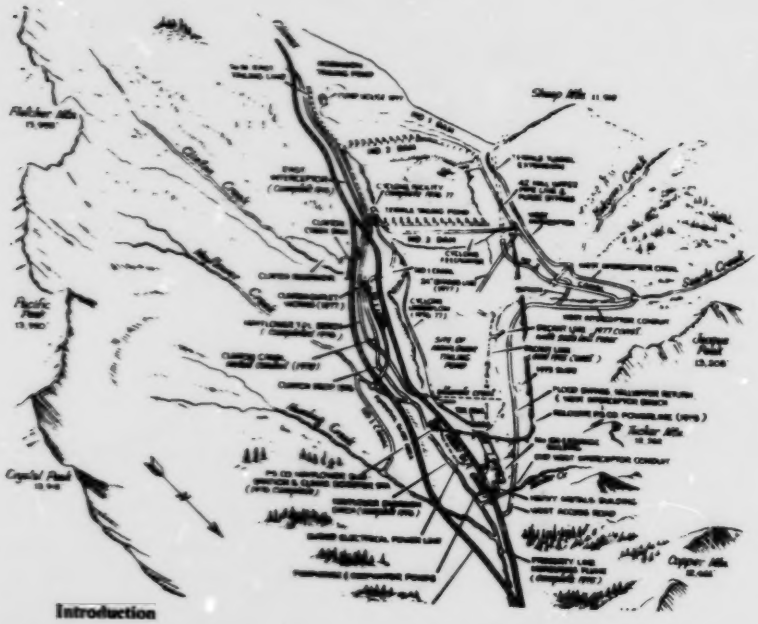
November 1980

Development of Waste Water Treatment at the Climax Mine

by Richard D. Gott and John M. Laferty, Jr.

Prepared for the
1977 American Mining Congress
San Francisco, California



Introduction

Since the 1930's Climax Molybdenum Company has operated a water recycle system utilizing active tailing dams and water storage facilities to collect mill water and return that water for reuse in the plant. This system allowed total containment of waste water, except during the annual spring snow melt period. The rapidly increasing runoff into the tailing system made it necessary to discharge some industrial water to keep the total system in balance. Annual discharge, occuring historically between April and June, averaged 2,400 acre feet per year and was bled into Ten Mile Stream at a controlled and monitored rate to maintain stream quality.

In addition to the recycle system, seep water pump facilities have long term been incorporated below each tailing dam at individual drainage areas to pick up all seep water for return into the tailing system.

Climax, desiring to go to a continuous discharge mode of operation, has been involved for the last four years in the development of technology to effectively treat plant waste water prior to any discharge from the Climax property. To implement this program, it was essential to define the drainage system surrounding the tailing impoundment area and effectively reduce this area with a series of interceptor canals to bypass as much runoff waters around the tailing system and into the natural streams. This series of interceptors then allowed for projections of the amount of runoff waters which could not be excluded from the tailing system and would amount to an inflow quantity of water which would have to be handled on an average annual basis to maintain total system integrity. Figure 1 graphically details the Climax tailing system with interceptors.

Climax outfall water contains small concentrations of heavy metals such as molybdenum, copper, and zinc in levels of a few parts per million. These metal constituents are the result of minor metal solubilization during the molybdenite flotation process. The mill water also contains combined cyanide in concentrations of less than one part per million. This is introduced into the mill circuit in the Regrind Plant as sodium cyanide where it is used as a copper depressant.

Laboratory work on removing impurities from Climax mill outfall water was started in 1973 with the removal of molybdenum from the mill water. This work led to the operation in 1975 of the Chem-Seps continuous Counter current ion exchange (CCIX) Pilot Unit. Through 1976, an intensive effort including pilot plant tests with the Swift Lectra Clear process has been underway to develop a system to remove the remaining heavy metals and cyanide. This paper discusses the process route selected to remove molybdenum, heavy metals, and cyanide.

Table I	Effluent and Feed Analysis						
	Fe	*Mn*	*Cu*	*Zn*	*Mo*	*Cd*	*CN*
Effluent Target-mg/l	2.0	1.0	0.05	0.2	2.0	0.015	0.025
Feed Ranges-mg/l	3.0-7.0	5.0-7.0	0.025-0.16	0.20-0.40	2.0-20.0	0.015	0.2-0.5

Laboratory and Pilot Plant Development

Laboratory and pilot plant programs directed at developing Climax waste water treatment technology were divided into two major efforts. Our first objective was to remove molybdenum to levels of 2.0 parts per million Our second effort focused on removal of heavy metals and cyanide. Target effluent concentrations for the heavy metals of interest and cyanide are listed in Table I along with typical influent concentration ranges of these same contaminants.

Development of a Molybdenum Ion Exchange Recovery System

The development of ion exchange technology for the removal of molybdenum to the low concentrations of 1-2 parts per million was started in mid-1973. The test work was restricted exclusively to the weak-base amine type anion exchange resin for two reasons: 1) the molybdenum absorption capacities were greater, and 2) the resin's high affinity for the hydroxyl ion allows for effective molybdenum elution with smaller alkaline requirements. Earlier column loading tests indicated that the amine type resins had a low capacity to absorb molybdenum when the resin was in the hydroxyl form but had a much greater capacity in the bisulfate or chloride form. Sulfuric acid was selected as the regenerant not only because of its lower cost, but also to avoid contamination of the effluent water with chloride ions.

Column Upflow Loading-Acidified Feed

Because of previous work done by AMAX[1] and others,[2] it was recognized that Mo sorption is most efficient at a pH between 3.0 and 4.0. Accordingly, the feed was acidified to pH 3.5 to 4.0 before entering the column. Amberlite XE-299 was selected after comparing loading capacity of the weak-base type resins available. With Amberlite XE-299, laboratory loadings of up to 12 pounds of Mo per cubic foot of resin at a cumulative percent recovery of 90.8 were obtained.

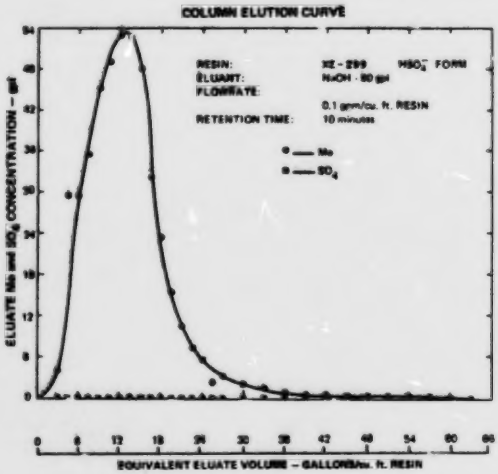
Resin Elution

Resin molybdenum elution efficiencies in excess of 98% were obtained. A typical elution curve is shown in Figure 2.

[1] Zundel, W.P., August 1965, Metal Extraction by Ion Exchange: French Patent 1,458,378.

[2] MacInnis, M.B., Kim, T.K., and Laferty, J.M., 1973, The use of Solvent Extraction for the Production and Recovery of High-purity Ammonium Paramolybdate from Normal Alkali Molybdate Solution. Paper presented at a Symposium jointly sponsored by the University of Reading and the Climax Molybdenum Company.

Figure 2



Ion Exchange Pilot Plant Operation

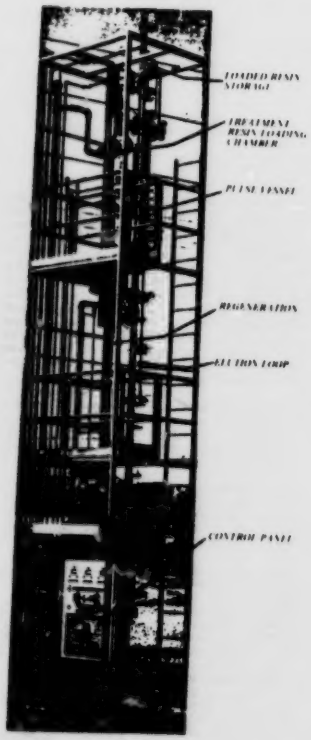
Chem-Seps Counter Current Ion Exchange Unit (CCIX)

The final phase in the molybdenum recovery program was to decide on an operating system to translate the laboratory procedure developed to a commercial plant. The CCIX unit was selected for piloting because, when compared to a fixed bed system, it requires considerably less resin inventory, it offers operating advantages at the high flow rates to be treated, and it occupies much less space.

The water processed in the CCIX unit was primarily Robinson Pond Tailing water. The Mo level in this water at the beginning of the test period was 11 parts per million. By the end of the period due to the dilution during the spring runoff the Mo concentration had dropped to 1 part per million. It was therefore decided to "spike" the feed with sodium molybdate to the level of 20 to 25 parts per million to facilitate the collection of the data required to design a full scale plant (resin loading, cycle time, elution efficiency, and resin degradation in operation).

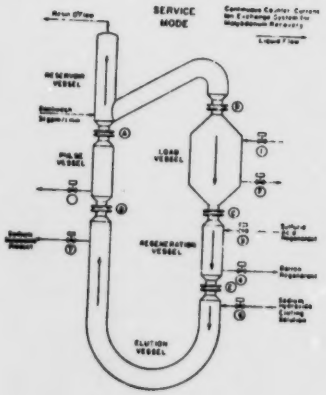
The resin used was Rohm and Haas XE-299, a macroreticular weakly basic anion exchange resin, with tertiary amine functional groups. Sodium hydroxide and sulfuric acid were used exclusively for resin elution and regeneration at a concentration level of approximately 50 grams per liter. A photograph of the pilot CCIX unit is shown in Figure 3. Figures 4 and 5 describe the operation of the column in the service and pulse modes respectively.

Figure 3
CCIX PILOT PLANT UNIT
Tested at Climax, Colorado



The CCIX Unit is installed within a frame of structural steel tubing 5' x 5'6" x 27' high. The column is 31'6" total height. The pulse and load chambers are made of 304 stainless while the regenerate and elution sections are of tempered glass (later many were changed to PVC). The load chamber is 12" diameter. All others are 3" diameter.

Figure 4



Service Mode

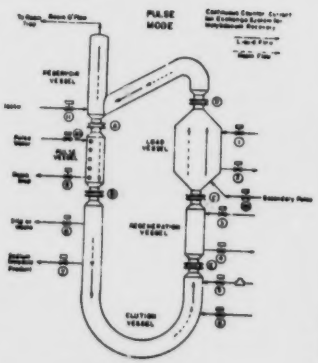
The fully automated system operates by continuously cycling between a "service mode" and a "pulse mode." During a service mode, the loop valves A, B, C, D, and E are closed, effectively dividing the loop into five sections: loading, regeneration, elution, pulse, and resin storage. In the resin loading chamber feed water is pumped (Valve 1) downflow through the resin bed and treated effluent is delivered (Valve 2) from the bottom of the resin loading chamber.

Sulfuric acid regenerate at 50 grams per liter is pumped (Valve 3) through eluted resin in the regenerate section between loop Valves C and E and exits (Valve 4) as a barren regenerate after sorption by the resin of the bisulfate ion. Simultaneously, sodium hydroxide eluting solution at 50 grams per liter is pumped (Valve 6) through loaded resin in the elution section between loop Valves F and B and exits (Valve 7) as a sodium molybdate solution after desorption of the molybdenum on the resin by the hydroxyl ion.

Backwash water, which enters at the base of the reservoir vessel, fluidizes the loaded resin bed and carries foreign materials and resin fines out the resin overflow line.

Following backwashing, loaded resin from the resin storage area is gravity fed through loop Valve A into the pulse section. Sonic pulse control sensors close Valve A when the pulsing section is properly filled.

Figure 5



Pulse Mode

During the pulse mode, loop Valve A is closed and loop Valve B, C, D, and E are open. Valves 1, 2, 3, 4, 5, 6, 7, 8, 9, and 11 are closed. A hydraulic pulse of water (Valve 10) and a hydraulic secondary pulse of water (Valve 2a) transfer the resin around the loop for a preselected distance. This movement puts loaded resin from the pulse vessel into the elution section, moving stripped and rinsed resin from the elution section into the regenerate section into the loading chamber, and finally moving the loaded resin from the loading chamber aroun to the storage area. The pulse mode takes about 30 to 45 seconds. The unit then returns to the "service mode."

Evaluation of Pilot Plant Test Run

The test series demonstrated that an average Mo concentration of 2.0 parts per million could be obtained from feed concentration ranging from 2 to 24 parts per million. Average resin loadings were 3.66 pounds Mo per cubic foot of resin.

Molybdenum resin elution efficiencies in excess of 98% were obtained. Average eluate Mo concentrations ranged between 16 and 19 grams per liter.

At a downflow rate of 41 gallons per minute per square foot the pressure drop through the resin bed was 40 pounds per square inch. This was within the allowable maximum of 50 pounds per square inch as recommended by the resin manufacturer to avoid excessive physical resin degradation. No evidence of physical resin degradation was found during the pilot plant test period. A 20% resin loss per year has been established in laboratory test work.

Tabulated pilot plant test results are presented in Tables II, III, and IV.

Table II

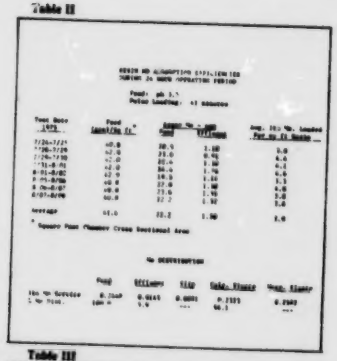


Table III

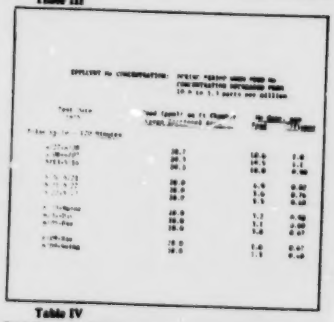
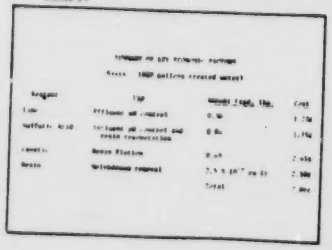


Table IV



Heavy Metals Removal

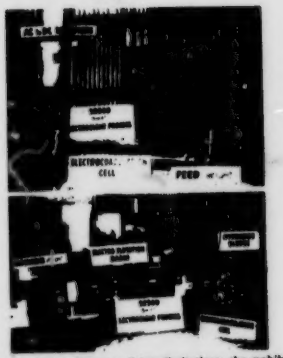
As shown in Table I, the total amount of contaminant is quite small, however the difficulty of developing a viable process to remove that small quantity of contaminant is significant. After reviewing potentially applicable technologies, it was decided that five possible routes might yield workable processes for heavy metal removal. After running bench tests on all five options, it was clear that the only viable process was Swift's Lectro Clear system. The five technologies evaluated are reviewed below.

1. *Lime Precipitation:* Lime precipitation by itself was not successful as a potential solution due to the poor settling rates of the precipitated heavy metal hydroxides. Low water temperatures (0-4°C) and very low solids concentrations were responsible for the observed precipitate settling characteristics.
2. *Cation Exchange* — Column Loading Tests: Column loading tests showed that manganese, cadmium, and cyanide were not sorbed in any appreciable quantities.
3. *Sorption of Heavy Metals — MnO_2:* Column loading tests using a commercial grade pyrolusite (-6 +20M) as the absorbent was not effective because of early breakthrough of the heavy metals (250 gallons per cubic foot of sorbent).
4. *Ferric Hydroxide Sorption:* Increasing the amount of ferric-hydroxide via the addition of ferric sulfate prior to the lime precipitation step at a 8.6 pH showed no contribution to heavy metals or cyanide removal through physical sorption by the hydroxides, nor did it aid in solids settling.
5. *Swift Lectro Clear Process:* Positive bench scale tests and tests with a mobile trailer-mounted demonstration pilot unit at Climax during July, 1976 showed that the *Swift Lectro Clear* process held the most potential for meeting effluent requirements and thus should be tested further.

The Swift Lectro Clear process is a primary waste water treatment technique, designed to remove suspended material and/or hydroxide precipitates. After lime precipitate is conditioned in an electrocoagulation cell via contact with hydrogen and oxygen gases that are generated by electrolysis. The slurry is then mixed with a polymer flocculant and is floated in the electroflotation basin by "micro bubbles" of electrolytically generated oxygen and hydrogen and is subsequently skimmed off for disposal. The pilot unit was designed for an average flow of 10 gallons per minute and at this flow rate, residence times in the mobile unit were ten minutes in the neutralization tank, one minute in the electrocoagulation cell and 25 minutes in the electroflotation basin. Because of time limitations, the mobile pilot plant run used reagents in amounts necessary to produce a stable skim produce without attempting any optimization. Encouraging results of the preliminary trailer run led to a follow-up laboratory program to optimize reagent type and usage. During the laboratory testing program, a 10 gallon per minute pilot plant, Figure 6, was purchased from Swift and assembled in the No. 3 Mill Building at Climax. Laboratory findings were incorporated into a three month pilot plant program that culminated in an around-the-clock verification run. Table V presents performance results on the Lectro Clear system operation.

Table VI gives operating costs based on results from the continuous verification run.

Figure 6



Removal of Cyanide

There are currently many processes available for the detoxification of water cyanides. From a fundamental basis most of the commercially available methods utilize an oxidative approach to accomplish removal of both free cyanide and transition metal coordination cyanide complexes. A number of these processes have been evaluated in the context of Climax's needs and the results are summarized below.

Table V

PERFORMANCE OF LECTRO CLEAR PILOT PLANT PROCESS

Sample	Heavy Metals - mg/l						pH	CN	Turbidity
Analysis	Pb	Mn	Zn	Cu	Cd	Mo		mg/l	Ntu
EPA Permit Max. July 1977	1.0	1.0	0.2	0.05	0.025	2.0	6.0-8.5	0.025	n/a
Feed	5.0	5.4	0.10	0.10	0.01	3.1	7.4	0.25	15
Effluent	1.0	1.0	0.05	0.05	0.01	2.7	10.5	0.13	9.5
Filtered*	<1	0.16	0.05	0.050	0.01	2.7	10.5	0.05	0.2

*Filtered Effluent is effluent filtered through No. 5 Whatman Paper

Table VI

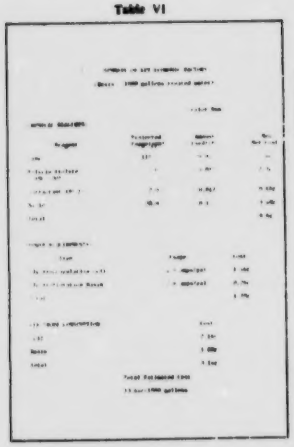


Table VII

Laboratory Test
Alkaline Chlorination of No. 3 Mill Water

CN CONCENTRATION				
pH	9.5		10.5	
Residence Time	15 min	30 min	15 min	30 min
20 ppm Cl_2	0.07	0.05	0.06	--
30 ppm Cl_2	0.13	0.05	0.05	-
50 ppm Cl_2	0.04	---	0.02	-
Feed	0.18	0.18	0.18	0.18

Alkaline Chlorination

The alkaline chlorination process oxidizes cyanide by the addition of chlorine gas. The cyanide solution is first rendered alkaline (pH 10.5-11) and chlorine gas is injected into the process water stream. Laboratory test results, studying the effect of residence time, pH, and chlorine concentration are summarized in Table VII. Temperature was maintained at less than 10°C throughout all testing.

A confirmation test was carried out in our 10 gallons per minute Lectro Clear pilot plant at Climax. Chlorine gas was introduced directly after the lime precipitation step. Cyanide concentration was reduced from 0.14 parts per million to 0.07 parts per million with chlorine additions ranging from 5 to 50 parts per million. The low levels of 0.02 to 0.04 parts per million obtained in the lab were not reproducible in the pilot operation.

Table VIII

Laboratory Testing
Effect of Resident Time, pH, and NaOCl Concentration on CN Degradations

pH	8.8		10.6		11.6	
NaOCl Conc	10 ppm	20 ppm	10 ppm	20 ppm	10 ppm	20 ppm
30 minutes	0.08	0.04	0.03	0.03	0.01	
60 minutes	0.05	0.03	0.02	0.03	0.02	
90 minutes	0.07	0.04	0.02	0.03	0.02	

Feed cyanide concentration was 0.19 parts per million.

Table IX

Lectro Clear Pilot Plant Test
Effect of Residence Time, pH, and NaOCl Concentration on Cyanide Degradation

			Residence Time			
Date	pH	NaOCl (ppm)	(33 Min)	48 Min)	(78 Min)	
5 and 11 Nov.	8.8	10	.06	.04	.05	
11 Nov.		20	.07	.08	.07	
5 and 11 Nov.	10.6	5	.03			CN
11 Nov.		20	.04	.03	.03	(ppm)
5 and 11 Nov.		10	.02	.03	.01	
11 Nov.	11.0	20	.04	.04	.04	
17 Nov.		40	.05	.03	.04	

Table X

Lectro Clear Pilot Plant Test
Continuous Verification Run

Date	Effluent pH	NaOCl	Residence Time	Feed CN	Shift Number	(ppm)
4-17	10.6	20.9 ppm	33 minutes	0.2	1	.09
Nov.				Average	3	.05
					4	.04
					5	.06

Hypochlorite Treatment

Essentially the same reactions as in alkaline chlorination result from the addition of aqueous solutions of sodium or calcium hypochlorite. The use of sodium hypochlorite has been extensively studied in the lab as well as in the pilot plant at Climax. The use of calcium hypochlorite was evaluated in the lab and performed as well as sodium hypochlorite, however, economics dictate the use of the sodium form as it can be electrolytically generated from sodium chloride solutions.

Table VIII summarizes the laboratory tests utilizing NaOCl. Feed solution was fresh No. 3 Mill water and all tests were carried out at less than 10°C.

Based on the results of these tests, a continuous verification run, utilizing the most appropriate operating conditions and reagent addition levels, was executed. In

Table XI

PILOT PLANT RUN TO VERIFY FINAL PROCESS PERFORMANCE

Analysis	Heavy Metals milligrams per liter						pH	CN	Turbidity
Sample	Fe	Mn	Zn	Cu	Cd	Mo		mg/l	N/A
EPA permit Max. July 1977	2.0	1.0	0.2	0.05	0.015	2.0	6.0-8.5	0.025	N/A
Feed	4.3	6.4	0.29	0.19	0.01	5.9	6.5	0.29	19-30
IX Effluent	---	6.2	0.28	0.17	0.01	1.1	3.5	0.08	---
Effluent[1]	0.65	1.0	0.05	0.05	0.01	0.6	10.5	0.035	7-9
Filtered Effluent[2]	0.10	0.10	0.022	0.013	0.01	0.6	10.5	0.01	---
Lectro Clear Skim	8.9	1.7%	0.5%	0.22%	10 ppm	0.35%	10.5	10 ppm	---

Specific flow through filter: 5.0 gallons per minute per foot squared

[1]Effluent after Lectro Clear treatment for heavy metals removal

[2]Lectro Clear effluent after filtration

the pilot plant effort, the effect of pH, residence time, and NaOCl concentrations were studied. As is shown in Tables IX and X, the laboratory results were not reproduced in the Lectro Clear unit. The initial pilot plant cyanide test results were erratic with CN^- levels in the effluent varying between 0.04 and 0.08 parts per million. The average cyanide concentration in the effluent during the 66 hour run was 0.052 milligrams per liter. Also noted was that increasing the amount of hypochlorite addition did not materially affect cyanide degradation. Concentrations as high as 40 parts per million NaOCl resulted in no significant decrease in effluent cyanide levels as compared with 5 parts per million.

Although the laboratory results for cyanide degradation were not fully realized in the pilot plant circuit, the combined effects of cyanide removal in the ion exchange process and in the hypochlorite addition allowed the effluent to meet the cyanide limits.

Concurrent with the cyanide removal pilot plant testing it became evident that the heavy metal removal goals were not fully met with the Lectro Clear process. The problem centered on the requirement for a more complete elimination of precipitate. A decision was made to incorporate a high rate sand filter into the process scheme to "polish" or insure the quality of the effluent.

Tables XI and XII present a total circuit analysis including ion exchange, Lectro Clear process, oxidation, and sand filtering.

Table XII

PILOT PLANT RUN - OVERALL MATERIAL BALANCE*

Description	Fe	Mn	Zn	Cu	Mo	CN
Mass into System-grams	641	959	43	28	886	43
Removal by IX Column	---	3.1%	3.7%	11.6%	81%	71%
Removal in Lectro Clear	85%	81%	80%	63%	9.5%	16.1%
Removal by Filtration	15.1%	15.6%	10.7%	18.4%	-0-	0.9%
Leaving Filter to Pond	-0-	-0-	7.4%	6.8%	9.7%	5.6%
Removal by Total System	100%	100%	93.4%	93.7%	90.3%	96.4%

*Basis: 66 hours, 2.66% solids in skim, effluent pH = 10.5, feed pH to IX column 3.5.

Conclusion

Process definition for waste water treatment at Climax incorporates counter current ion exchange for molybdenum removal, followed by Swift electrocoagulation-electroflotation for heavy metals removal with a polishing filter for final effluent clarification. Sodium hypochlorite is added prior to the electroflotation basin as an oxidant for cyanide destruction. Pilot scale operations indicate essentially all the iron and manganese and in excess of 90% of the zinc, copper, molybdenum and cyanide are removed. The molybdenum removed by the ion exchange unit will be processed by solvent extraction-crystallization producing a marketable sodium molybdate. Skim electroflotation products will be chem fixed and returned to the tailing area for impoundment. The above processes are now being incorporated into a dual 2,000 gallon per minute plant with all pilot processes included in the production facilities. Full scale operation is planned in early 1978, to treat process water prior to that year's annual snowmelt.

The success of this process development is attributable to the cooperative effort between the Climax Mill, AMAX Extractive Research Group in Golden, and the AMAX Environmental Services Group, all providing specific expertise in outlining specific goals and objectives to this complex problem. The inclusion and adaptation of the Swift Lectro Clear process to treatment of process water at Climax is, we think, a first for the mineral industry and provides a novel and exciting approach to waste water treatment in the minerals industry for the future.

Mr. Richard D. Gott holds a BS in Mining and Metallurgical Engineering from the University of Idaho, School of Mines. He became Mill Superintendent at the Climax Colorado Mill in January, 1976. He chaired the AIME Intermountain Minerals Conference at Vail, Colorado.

Mr. John M. Laferty, Jr., is Manager, Extractive Metallurgy for AMAX Extractive Research & Development, Inc., at Golden, Colorado. Prior to 1974, he was with G.T.E. Sylvania as Manager, Chemical Research and Development in Towanda, Pennsylvania. He holds a B.S. Degree in Chemical Engineering from Villanova University.

In the development of this process, special thanks are due to Paul Zundel and Gary Van Riper of the Golden Lab and, also, to John Richards, Climax, Chief Metallurgist.

CHEMICAL SEPARATIONS CORPORATION
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WYOMING MINERALS CORPORATION
BINGHAM CANYON

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CONTACTS	J. C. Compton, Executive Vice President Fred Hohne, Vice President Carmine Mancuso Dr. Eric Tiepel Frank Ludeman
TELEPHONE	(303) 988-8530
RESEARCH	Westinghouse Research & Development Center Pittsburgh, PA
CONTACT	Mike Skriva
TELEPHONE	(412) 256-5035
CAPACITY	Three CHEM-SEPS units treat 6,600 US gpm solution (1500 m^3/h) i.e. 2,200 US gpm each or 500 m^3/h. This is average flow rate. Loading section ϕ is 8 ft. Since the units pulse 45 seconds every six minutes, the flow rate during the 'Run' mode must be 8/7 x 2,200 US gpm = 2500 US gpm (545m^3/h). This is considerably less than was originally designed based on pilot plant work.
SPECIFIC FLOW RATE	Originally the units were designed for 55 US gpm/ft^2 2200 US gpm average flow rate corresponds to 44 US gpm/ft^2 specific flow rate. 2500 US gpm flow rate during 'RUN' mode corresponds to 50 US gpm/ft^2.
NOTE	Wyoming Minerals Corp is sensitive about information on the HIGGINS LOOP operation. The information provided here should be regarded as confidential even when talking to Wyoming Minerals' staff.

URANIUM GRADE	6-7 ppm U_3O_8 Grade may fluctuate to 5 ppm depending on the weather due to run-off dilution or depending on which tailings piles Kennecott Copper leaches that day. This corresponds with 6,600 US gpm flow rate for 365 days/year at 6.5 ppm head grade and 1.5 ppm barrens, i.e. 0.005 g/l extracted.
URANIUM PRODUCTION	140,000 lbs. U_3O_8/year
BARRENS	Used to be 1.7 ppm U_3O_8, now barrens of 0.9-1.2 ppm are experienced. The 1.7 ppm U_3O_8 average includes the third HIGGINS LOOP unit which doesn't run as well and gives higher barrens.
UNIT SIZE	8 ft.ϕ at loading section, the units are 55 ft. high. The three HIGGINS LOOPS fit into a remarkably small building.
LOADING STAGE	Originally the loading stages were 8 ft. high. Now loading stages have been reduced to 5 ft. height to reduce the pressure drop across the resin bed which was causing damage to the resin beads.
RESIN INVENTORY	750 ft.^{3} resin per unit (21.2m^3 each) Originally resin inventory was 1000 ft.^{3} (28.3m^3) prior to modification of the units.
RESIN TYPE	Macroreticular resin. Porous beads. DOWEX MSA 1 16-30 mesh (U.S. Std. Sieve)
RESIN COST	About \$125/ft.^{3} resin delivered \$4400/m^3 R 3500/m^3
RESIN SELECTION	DOWEX MSA1 was selected because it is both mechanically strong and resistant to osmotic shock. Ron Platzke claims losses are now such that the operation is economically viable. Gel type resins resulted in impossible resin losses to the extent that stable operation could not be achieved. DOWEX MSA1 has been used for the last 1½ years and has given a stable operation.
RESIN LOADING	1 to 2 g/l

RESIN LOSS

Resin loss in the CHEM-SEPS unit is high and is caused by:

-Osmotic Shock
-Mechanical Movement of the Resin
-Valves Closing on Resin
-High Pressure Drop Across the Resin Bed

Ron Platzke claims that resin loss is a result of valves closing on beads is low.

In the two years of their program with HIGGINS LOOPS to date Wyoming Minerals Corp. have used up about 12,000 ft.^{3} (340M^3) of resin in the three HIGGINS LOOPS WITH 750 ft.^{3} (21.2m^3) resin inventory each. This is roughly 270% per annum of resin inventory lost per year. A disastrous situation.

When Wyoming Minerals Corporation installed their first unit, the 1000 ft.^{3} resin inventory was destroyed within 6 hours. The unit had been started up under Chem-Seps supervision.

The resin inventory was replaced and it too broke in a day or so.

Then after performing some osmotic shock tests, the unit was filled with DOWEX MSA1 resin. This resin load lasted a week.

Each 1000 ft.^{3} resin load was worth $100,000, so in less than two weeks of running the unit, $300,000 worth of resin was destroyed. As a result, Wyoming Mineral's Corporation undertook a major resin test program, and modified the HIGGINS LOOP to downgrade its capacity thereby reducing the affects on resin loss.

Wyoming Minerals found that the resin breakage due to high osmotic shock and high mechanical shock applied t resin simultaneously was greater than the sum of the resin loss due to the two influences separately. In fact it was greater than the product of the resin losses from the two causes because the resin simply 'explodes'.

Mike Skriba of Westinghouse Research & Development has developed an RST (resin strength test) procedure and apparatus to measure resin losses on samples.

Resin losses now are believed to be around 100% PA of inventory or 54 PPM of flow rate of feed which is not bad at all.

Wyoming Minerals Corp. is actively searching for better resins and have developed a set of specifications which will enable resin to be manufactured for the HIGGINS LOOP that will last much better.

When comparing resin loss data for different CIX systems it is very misleading to compare on the basis of percent of resin inventory lost per year.

The HIGGINS LOOP treating 2200 US gpm has a resin inventory of only 750 ft.^{3} (21.2m^3).

NIMCIX at 1200 gpm requires a resin inventory of 5300 ft.^{3}. (150m^3).

Hence a 100% per year loss of resin inventory on a Chem-Seps unit at 2200 US gpm flow is equivalent to 5.3 PPM of flow.

5.3 PPM resin loss on a NIMCIX unit at 1200 gpm flow with 5300 ft.^{3} resin (150m^3) inventory would work out to 12.6m^3/year resin loss or 8.4% of the resin inventory.

It is therefore more appropriate to compare resin losses in terms of ppm of solution treated or volume of resin lost per unit of uranium produced.

Cost of resin loss per m^3 feed treated and per pound of U_3O_8 produced is compared below for 30%, 50% and 100% per year resin inventory losses on a Chem-Seps unit.

COST OF RESIN LOSS

21.2m^3 (750 ft.^{3}) Resin Inventory @ \$100/ft.^{3} per unit. Each unit produces 4.38mm m^3 x 5ppm x 2204.6 tbs = 48,280 lbs U_3O_8

At 30% Resin Loss Per Year

4.38 million m^3 solution treated per year per unit
= 6.36m^3 (225 ft.^{3}/yr) resin loss per year
= \$28,000 per year
= \$0.58 per lb U_3O_8 produced

At 50% Resin Loss Per Year

4.38 million m^3 solution treated per year per unit
10.6m^3 (375 ft.^{3}) resin loss per year per unit
= \$46,900 per year (\$125/ft^3)
= 0.97 per lb U_3O_8 produced

At 100% Resin Loss Per Year

4.38 million m^3 solution treated per year per unit
21.2m^3 (750 ft.^{3}) resin loss per year per unit

$94,000 per year cost of resin per unit ($125/ft^3)
$1.95 per lb U_3O_8 produced

RESIN DENSITY

The DOWEX MSA1 resin has an SG of 1.08 compared with SG = 1.1-1.2 for gel types. Resin density is not as important a feature for this type of contactor as for upflow systems.

FEED SOLUTION

Product of heap leached tailings dump rich in copper and high in particulates.
pH = 2.8 - 3.0 as received.

No resin poisons.

Very low SiO_2 content in feed.

ELUTION

Elute with three bed volumes of 150 g/l (3N)H_2SO_4
No copper gets carried over in the eluate.

ELUATE

300-500 PPM U_3O_8

TEMPERATURE

80°F or higher.

RUN/PULSE CYCLE

Resin is moved every 6 minutes. Each pulse lasts 10 to 15 seconds but the whole sequence including opening and closing valves takes 45 seconds.

SILICA

Very low SiO_2 buildup experienced--Less than 1% per year SiO_2 on the resin. pH is kept high enough to reduce the SiO_2 problem. At low pH's Ron Platzke believes that SiO_2 polymerises and "glues up."

RESIN REGENERATION

Not required at Bingham Canyon.

PARTICULATES

Suspended solids content of the feed solution at Bingham Canyon are high and vary considerably. Suspended solids of 1000 ppm are not uncommon. Variation depends on rainfall or snow melt runoff.

The particulates consist of flakelike particles of organics from the tincans used for precipitating copper cement.

In addition there are varying amounts of silt in the feed.

Particulates have a big impact on the HIGGNS LOOP operation. As particulates in the feed increase the pressure drop across the resin bed in the loading stages increases significantly.

Particulates also cause severe abrasion of pump.

PARTICULATE REMOVAL

Particulates are controlled as much as possible through three factors:

1. Installation of a one stage wooden settling tank ahead of the CIX unit.
2. Overflow solution is then filtered through sixty four ZURN strainers.
3. One section of the HIGGINS LOOP is used to backwash solids accummulated during the loading phase. The packed resin bed acts as a very good filter and will accumulate any solids present in the feed.

The HIGGINS LOOP is operated on a very short cycle of 6 minutes. The shorter the cycle, the less solids have a chance to build up in the loading stage between backwashes.

MAIN LOOP VALVES

21SSB Crane Monarch valves with squeegy disc wiper to reduce resin damage.

MAIN COST FACTORS

- Operators & Maintenance
- Resin Loss
- H_2SO_4 for Elution
- Na_2CO_3
- SX Chemicals
- Utilities e.g. Pumping Costs

MANPOWER REQUIRED

A total of 16 people plus three maintenance engineers are required to operate the plant.

5 foremen
6 process technicians
1 metallurgist
2 laboratory chemists
1 manager
1 clerk
16 Total

3 Maintenance Engineers

After Jacobs Constructors, who built the plant, left the site one of their crew left to go into business for himself and set up a small company that maintains the CIX units under contract.

OPERATIONAL AVAILABILITY

Now improved to 97-98%. Expected to drop to 90-98% as the new units get older and require more maintenance.

OPERATING SENSITIVITIES

All concerned emphasized that the HIGGINS LOOP is a very sensitive unit to operate.

When resin is pulse transported around the column in plug flow fashion it moves in what has been described as a "stick-slip" method. This leads to tremendous water hammer possibilities and enormous pressures seem to build up in the loop. Strain guage tests showed incredible forces in the column that could only be explained by resin bridging effects.

At times when resin blinds the collector screens drawing barrens from the loading stage of the loop, tremendous forces build up which bend the collectors which are very robustly constructed. Forces up to 1000 PSI on the collectors are experienced at times.

WMC SATISFACTION WITH HIGGINS LOOP

Mike Skrba at Westinghouse Research & Development Center, Pittsburgh indicated that the HIGGINS LOOP could be developed into the best system for continuous ion exchange in the world for cases where:

(1) Feed rate is very high
(2) Recoverable grade is very low
(3) Value of recovered material is high
(4) Sophisticated operators with prior experience running a HIGGINS LOOP are available.
(5) There is a space constraint for the plant.

RESIN REGENERATION

If resin regeneration is required then a means would have to be built into the system to do so.

The resin regeneration cycle would be different to other CIX systems.

The whole hoop might be taken off line temporarily and the whole resin inventory regenerated simultaneously.

MODIFICATIONS

Numerous modifications were made to the units at Bingham Canyon.

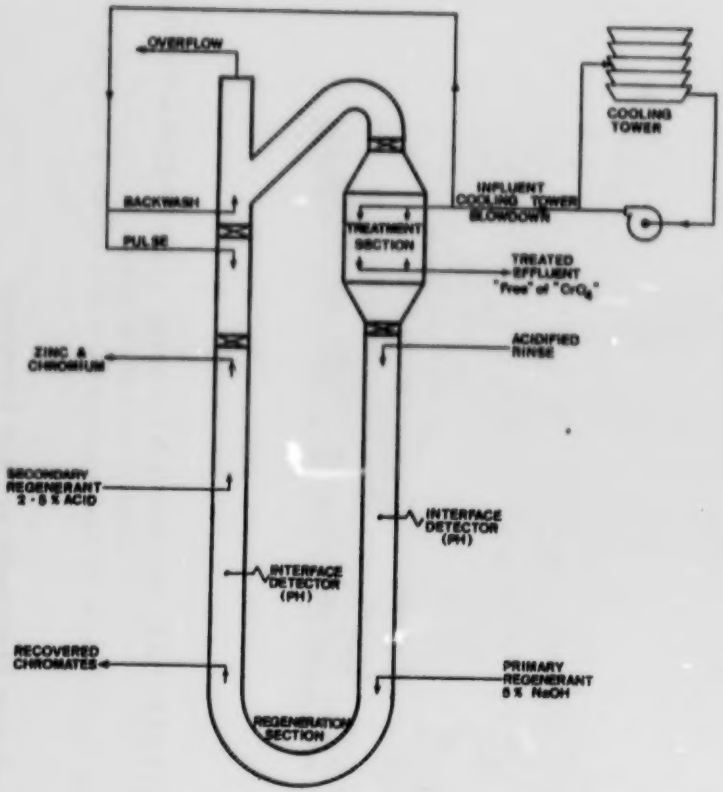
1. The LOAD section has been reduced in size from 8' to 5' to reduce pressure drop across the resin bed.

2. The ferric strip stage was removed. Ferric is now stripped from the resin in a different manner.

3. Flow rates to the units were cut back to 2200 US gpm average.

4. Several piping modifications have been made by Wyoming Minerals Corp on the units.

5. Wyoming Minerals Corp have modified the solution tenor control system.



CHEM SEPS CHROMIX SYSTEM

CHEM-SEPS CHROMIX PROCESS

Chem-Seps Chromix process provides a unique system for recovery of Chrome VI, Chrome III, and Zinc from cooling tower blowdown.

The use of the recovery system allows the preferred corrosion inhibitor chromates to be used and eliminates the pollution problems. The destruct system which is another alternative does not necessarily eliminate pollution. Chrome VI is reduced to Chrome III and precipitated. But today's EPA and other regulatory agencies requirement of 0.05 ppm total chrome are not achievable with the destruct system. Further the destruct systems are expensive to operate. A comparison of chemical consumptions between recovery and destruct is shown below.

	Recovery System	Destruct System
Sulfur Dioxide	None	2 lbs SO_2 /lb Cr^{+6} or 1 lb SO_2 /lb CrO_4
Sodium Hydroxide	0.75 lbs/lb CrO_4	2.5 lbs/lb Cr^{+6}
Sulfuric Acid	1.00 lbs/lb CrO_4	24.5 lb/lb Cro_4*

*This consumption is based on 20 ppm of CrO_4 and reduction of pH from 6.0 – 8.5 to 2. The reaction of reduction is best carried out at pH 2.

Typical System

A Chromix system to treat one million gallons per day (700 GPM) of blowdown with a Chromate concentration of 20 ppm would require one Chem-Seps Continuous Unit Model No. 5412 as shown in the flowsheet.

The cooling tower blowdown is pumped to the treatment section of the chromix system where the Chrome VI, Chrome III and Zinc are picked up on Chem-Seps special blend of ion exchange resins. The water leaving this section is essentially chromate-free and may be discharged. After the resin is loaded with the valuable corrosion inhibitors it is moved to the regeneration section. In the regeneration section Sulfuric Acid and Sodium Hydroxide are used to remove the Chrome VI, Chrome III, and Zinc from the resins. The sodium Chromate dichromate and Zinc Sulfate leaving this section may then be recycled to the cooling tower instead of going to sludge as in the destruct system.

OPERATING COST ECONOMIC ANALYSIS

Basis – Chromix System to treat one million gallons per day of cooling tower blowdown containing 20 ppm chromate. Unit model No. 5412 recovers 166 pounds of CrO_4 per day or 4,950 pounds per month. Capital Cost $200,000.

	Cost Per Month
Resin Replacement at $80 per Cu.Ft.	$ 350
Replacement Parts 3 percent of equipment cost	500
Chromate Make Up Cost 1 percent (50 pounds) at $1.75 per pound CrO_4	90
Chemicals and Utilities	
Sulfuric Acid	110
Caustic	180
Power	153
Estimated Labor Cost	
Operation at 1500 per month	1,000
Maintenance at 500 per month	500
TOTAL MONTHLY OPERATING COST	$2,883

Summary

Estimated value of chromate recycled equals $8,662.50 per month.

Payback on capital cost is estimated to be 2.9 years, plus installation cost.

Standard Continuous Units Fully Assembled

A full line of standardized continuous countercurrent ion exchange units have been designed to recycle chromates from 100 gpm up to 2000 gpm in a single unit. Each of these units are shipped fully assembled. A unit arrives on your site ready for feed and service piping connections plus power tie-in to the control panel. Installation and Start-Up cost are low.

Equipment Specifications Available

If you now operate a cooling tower and treat with chromates as corrosion inhibitors or if you do not presently use chromates but would prefer to use them, please contact Chem-Seps. Let us know blowdown rate and chromate level. You will receive a prompt reply including equipment specifications, operating data and an economic analysis that fits your specific cooling tower operation. It could be the start of improved, more economical, pollution-free cooling tower operation for you.

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NITRATE REMOVAL FROM MUNICIPAL WELL WATER

JOHN C. GREGG, P.E.
SIDNEY B. BOWNE, JR., P.E.
PARTNERS
SIDNEY B. BOWNE & SON
MINEOLA, N.Y.

The Garden City Park Water District is located on Long Island in Nassau County, New York. Nassau is a Suburban County containing about 1,450,000 people in its 274 square miles and has fourty-four separate water purveyers within its bounderies. Long Island could most simply be described as a large sandbar separated from the mainland by salt water and the various water bearing formations underlying the Island and not geologically connected with the continental land mass. The result is that the only recharge available to these aquifers is that which comes from above in the form of precipitation, leaching from cesspools in unsewered areas, and storm water recharge basins.

Ground water quality has been closely watched for many years and after the rapid development of the area in the forties and fifties an increase was noted in the nitrate content. Not too much concern was paid to this increase except as a possible indicator of increasing pollution from cesspools, in fact at the time we were all concentrating on how to recharge the aquifers using effluent from sewage plants containing high concentrations of nitrates.

In the mid sixties references began appearing in literature indicating a probable correlation between the ingestion of water containing over 45 mg/l of nitrates by pregnant women in the last few months of their term, infants during their first few months, and the "blue baby syndrome". "Blue Babies" are actually suffering from methemoglobinemia, a serious and sometimes fatal disease caused by the nitrates interfering with the ability of the blood to carry oxygen to the tissues. Drinking water standards which limited nitrate as nitrogen to 10 mg/l were adopted by the U.S. Public Health Service and Nassau County.

In December of 1967, fully aware of the developing nitrate problem, the Garden City Park Water District received bids on No. 9 Well which was to be developed at the bottom of the deepest available aquifer at a depth of about 400 feet (122 m.). The double cased well was drilled by the reverse rotary method and the area between the outer casing and the soil wall was pressure grouted with a cement grout. After the customary one hundred hours of development and test pumping a complete chemical analysis was run which indicated a nitrate count of 1.8 mg/l. As all other items were also well below the prescribed limits we undertook the general construction, mechanical, electrical and site work and were ready for the final acceptance test in April of 1969.

After pumping the well to clear it, the final eight hour acceptance test was run at 1,200 gpm. (0.075 m^3/s). Samples for complete physical and chemical analysis were taken thirty minutes after the start of the test. Results of the chemical test indicated a nitrate level of 14 mg/l which later increased to as high as 22 mg/l. We had not then, and have not now, any satisfactory explanation for this increase. In any event, we ended up with a $300,000 installation which could not be used.

About this time in 1969 the Nassau County Department of Health analyzed 333 public supply wells for nitrate content and upon comparing the results with previous analyses determined that 24% of these wells showed rapidly accelerating rates of increase in nitrate content. In the case of Garden City Park, within a six month period, five of the older wells experienced rapid increases in nitrate content and three of them had to be removed from service. The District was faced with a 60% reduction of its 8,900 gpm (0.562 m^3/s).

Having no idea how to remove the nitrates, our first attempt at a solution was to backwash the well with system water which, by this time, contained about 6 mg/l nitrates. Our hope was to wash away or dilute any possible unknown concentration of nitrates in the area of the well screen or at least to dilute the groundwater in the screen area so that when withdrawn the nitrate concentration would be less than 10 mg/l. Over a period of several months we tried all kinds of combinations and permutations, but the results were consistently and conclusively negative. We were able to withdraw just about what we put into the ground for a net yield of zero. During this period we contacted and held discussions with various agencies and groups regarding purification processes used in other fields which might be adapted to solving our problem.

Investigation of various U. S. Department of the Interior programs for the removal of sulfuric acid and other wastes from various ordnance plant effluents disclosed interesting results from the use of an ion exchange process involving the use of "Continuous Countercurrent Ion Exchange" equipment which had been developed by Chemical Separations Corporation of Oak Ridge, Tennessee. In this process, Dowex synthetic ion exchange resins are used for the adsorption of contaminants. An installation which utilized tandem units to remove mineral impurities from strip mining water runoff was evaluated and we decided to process some Garden City Park water through a Chem-Seps pilot plant at Oak Ridge. Approximately ten thousand gallons (37.85 m^3) of water from Garden City Park and the Bethpage Water District, which was having similar problems, were trucked to Oak Ridge and processed through the Chem-Seps prototype plant. Analysis of the effluent by Chem-Seps, The Nassau County Department of Health and several independent laboratories confirmed that the process could reduce the nitrate content to well below the level required by the U.S.P.H.S. On the basis of these results, it was decided to design a plant for Garden City Park incorporating this ion exchange process.

The closed loop prototype unit consisted of 20 foot (6.1 meter) high loop of 3 inch (7.62 cm) diameter tubing and was operated in a batch mode at nominal pressure. Adapting this process to a continuous flow process at a rate of 1,200 gpm (0.075 m^3/s) at system pressures of approximately 80 psi (550 kPa) resulted in a loop approximately 32 feet (9.7 m) high containing a 24 inch (61 cm) diameter loop section for regenerating and rinsing of resin and a 72 inch (1.8 m) diameter section for treatment of the 1,200 gpm (0.075 m^3/s) flow.

The closed loop exchanger (Fig. 1) incorporates ion exchange "treatment", regeneration, rinse, and storage sections. A typical operation cycle consists of an initial pumping of a fresh charge of resin from the regenerant section to the ion exchange or "treatment" section. After adsorption of the nitrate ions, spent resin is pulsed into a resin regeneration section where it is regenerated by means of a brine solution. While the resin is being regenerated at one portion of the loop, high nitrate "raw water" is simultaneously flowing into the "treatment" or ion exchange section, being denitrated as it contacts the ion exchange resin, and flowing out. Resin is moved or "pulsed" around the loop about every ten minutes. The pulsing operation takes approximately thirty seconds during which time flow through the unit is momentarily diverted.

The ion exchange system cycles between a run mode and a pulse mode. During a 10 min. run mode, main valves at A, B, C are closed to make it a 3-section loop. Raw water is pumped into the contacting section through pipe 1 and flows down through the ion exchange resin bed; denitrated water flows out through pipe 2. Simultaneously, brine fed through pipe 4 into the regeneration section containing resin holding nitrate waste strips nitrate from the resin, and exits through valve 5 to the municipal sewage system. At the same time loaded resin drops through open valve D into the pulse section. Clear rinse water enters through valve 3 and washes brine traces from resin about to re-enter the "contacting" section of loop. The conductivity-sensitive controller regulates rinse until traces of brine are removed. This properly positions the interface for the next pulse.

During the 30-second pulse mode, main valve D is closed and valves A, B and C are opened. A timed pulse of raw water through valve 7 transfers loaded resin from the pulse section to the regeneration section, regenerated rinsed resin back into the contacting section, and loaded resin into the storage sections. Backwash water from valve 6 cleans resin fines and foreign particles from the loaded resin. Upon return to the run cycle, valves A, B and C close and valve D opens allowing resin to drop into the pulse section.

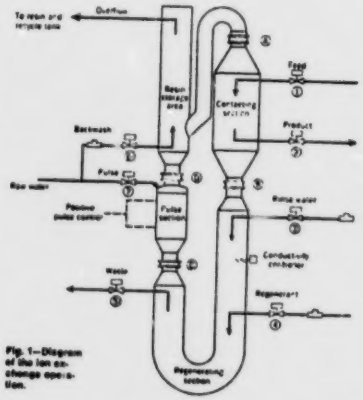

Fig. 1—Diagram of the ion exchange operation.

In other applications, untreated water is drawn from an unpressurized tank as needed, and the treated water pumped into an open receiving tank. The pulsing characteristic or stop-and-go operating cycle therefore does not pose problems.

Such start-and-stop operation could not be tolerated in the Garden City Park water system. Elevated storage tanks are about one mile distant, too far to allow economic, direct pumping of treated water. Water must be pumped directly into the system's mains which operate at 80 psi (550 kPa). Stop-and-go pumping would pose serious wear and short-life problems on the well pump, valves, and electrical equipment and cause additional problems from sonic and hydraulic harmonics, comparable to "water hammer".

The interrupted flow problem was solved by introducing a bypass system which would allow the well pump to operate continuously, maintaining proper water volume and pressure in the mains and distribution system.

The final system devised utilizes a bypass system of piping, automatic valving and a hydropneumatic tank. Start up of the plant is initiated by a drop in water level in elevated storage tanks, which signals the well pump to start. When the well goes on stream, it signals the ion exchanger to operate. After a preset period of pumping, solenoid valves shut down delivery of the raw, nitrate laden water from the well to the chamber, and divert it

automatically into a bypass water circuit which includes a 5,000 gal., (18.9 m^3) capacity hydropneumatic tank. Well water is diverted for 30 seconds directly to the hydropneumatic tank, mixing with the denitrated water pumped there earlier from the ion exchange chamber. The system is designed to operate continuously at 80 psi. (550 kPa). If pressure exceeds 100 psi (690 kPa) the entire system shuts itself off.

Automatic Nitrate Analysis – The Nassau County Health Department requires that the nitrate content be monitored. This is done by a Delta Scientific automatic nitrate analyzer which is set to shut the well pump and ion exchange system off should the nitrate content of the processed water rise to 5 ppm. It also shuts the system down on a zero reading caused by reagent or analyzer failure.

The on-line instrument originally had a sample-to-readout lag of 23 minutes as compared with a laboratory chemical analysis time of at least an hour. The 23 minutes lag between sample drawing readout would amount to 27,600 gallons (104.6m^3) of water at 1,200 gpm (0.075 m^3/s.) This time lag has since been reduced to 15 minutes at the recommendation of the Nassau County Department of Health.

The 33 ft. (9.5 m) tall exchange loop and associated equipment are hidden from view within a specially designed "ranch house", compatible with the residential community. The ranch house, of contemporary design, is 28 ft. (8.5 m) by 54 ft. (16.2 m). Its basement is large enough to permit equipment to be installed 18 ft. (5.4 m) below grade. The new plant is the latest in automatic, failsafe operation, with a remote alarm in the community's firehouse. Total cost of the housed system is about $425,000.00.

Nitrate Removal Study
Pilot Plant Run at Oak Ridge, Tenn.
Garden City Park Water District – Well No. 9

Constituent	Raw Water at Source Aug. 7, 1970	Raw Water at Feed to Pilot Plant Aug. 12, 1970	Treated Water Aug. 12, 1970	Waste Water Aug. 12, 1970
Color Units	5	5	5	5
Turbidity Units	1	1	1	144
Odor Cold	1A	1A	1A	1A
Odor Hot	1A	1A	1A	1A
Iron	0.02	<0.02	0.02	0.18
Manganese	0.03	0.03	0.03	
CO	38	5	15	192
NH_3-N	0.002	0.002	0.002	0.283
Albuminoid-N	0.007	0.002	0.006	
NO_2-N	0.001	0.001	0.001	0.425
NO_3-N	14.25	14.00	0.05	2800
Oxy. Cons.	0.5	0.7	0.7	200
Chlorides	16.8	18.0	87.0	54000
Tot. Hard. as $CaCO_3$	182	190	88	820
Tot. Alk.	22	13	29	2650
pH	6.1	6.7	6.6	7.0
Tot. Solids	259	302	322	96350
MBAS	0.02	0.02	0.02	0.02
Cr + 6	0.01	0.01	0.01	0.01
Ca. Hard as $CaCO_3$	58	58	50	400
Temp. Rab.) °C	20	24.5	24.0	24.0
Tot. Phos.	0.02	0.02	0.02	0.13
Orthr. Phos.	0.01	0.02	<0.02	0.13
SO_4		34.9	1.9	4100

All results given in mg/l unless noted otherwise.
Sampling and analysis by Nassau County Department of Health

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P 192.1

CHEM-SEPS CONTINUOUS ION-EXCHANGE CONTACTOR AND ITS APPLICATIONS TO DE-MINERALISATION PROCESSES

By I. R. HIGGINS and R. C. CHOPRA

(Chemical Separations Corporation, Oak Ridge, Tennessee 37830, U.S.A.)

The Chem-Seps continuous counter-current ion exchange contactor is described and its applications in both the water treatment and chemical process industries are given.

The principal application for the Chem-Seps single loop continuous system is in the de-mineralisation of water for boiler feed and other uses. Chemical efficiencies and therefore lower operating costs have been the principal reasons for installing Chem-Seps systems.

The 'down flow' system used by Chem-Seps overcomes many of the handicaps of continuous 'up flow' systems. There is no minimum flux requirement. Untreated water is used for pulsing. The process water requirements for complete de-mineralisation of water with a high content of solids (1800 ppm) are less than 10% of throughput. The 'down flow' configuration also keeps heavier liquids in the lower regions of the equipment allowing more efficient interface control and preventing channelling.

The resin inventory in Chem-Seps continuous counter-current ion exchange can be as low as 15% but rarely over 30% of the volumes required for conventional fixed-bed systems.

The Chem-Seps system can handle slurries effectively. The capability to handle slurries makes the regeneration of resin with low-cost lime practical. In Sul-biSul, the acid produced in regeneration step if neutralised with lime slurry reduced waste volume and higher utilisation of resin capacity. The increased efficiency of the system makes it worthy of consideration for de-mineralisation.

The waste volume in continuous counter-current ion exchange is normally 2·5–5% of throughput for waters with 400–1000 ppm total dissolved solids.

Addition of the 'down flow' design to the 'Higgins' on single loop system has enhanced its versatility as a process tool in both water and chemical process de-mineralisation applications.

Introduction

There are over 70 continuous counter-current ion-exchange units designed by Chem-Seps installed around the world de-mineralising, de-alkalising, and softening water and working on various other chemical process flowsheets. Predominantly, the larger installations are involved in the de-mineralisation of water for boiler feed and process water requirements. Partial de-mineralisation of brackish waters for potable uses is becoming increasingly important. De-alkalisation for process water for such applications as textile bleaching and softening for low-pressure boiler water would rank next in importance. There are a number of units used in the softening of potable water for municipal or private water districts. Examples of some of the other chemical process flowsheets are: magnesium removal from phosphoric acid to prevent after-precipitation in the production of 'super acid'; recovery and treatment of certain plating wastes for cost reduction and pollution control; extraction of uranium from ore pulp; de-mineralisation of thin sugar juice to increase yield and reduce scaling of heat exchanger; and many other special types of chemical process flowsheets.

The use of continuous ion exchange for de-mineralisation of water accounts for about 70% of the total use and will be emphasised in this paper. There are many variations possible in devising a de-mineralisation flowsheet. The final choice of flowsheet and the equipment to be used is dependent upon the characteristics of the untreated water, the quality requirements of the effluent, cost and the availability of regenerant. Most of the engineers and operators who have decided to install Chem-Seps continuous counter-current ion-exchange (CCIX) systems most frequently have based their decision on the savings in operating costs that are possible because of the characteristic counter-current flows in the Chem-Seps system, compared with conventional fixed-bed systems.

Chem-Seps system

Chem-Seps continuous counter-current ion-exchange is a loop in which various sections are separated by valves to separate the sections performing different functions simultaneously (see Fig. 1). The resin is moved in small increments by the hydraulic ram action. All solution flows are counter-current to the flow of resin. The contaminants are removed in the process cycle and the resin is moved in the pulse cycle. A controller in the effluent stream from the loading section senses the upper limit permissible in the effluent. In the process cycle, the influent enters through a set of distributors, moves downward and leaves through another set of distributors. Simultaneously the regenerant enters through valve K and leaves through valve E. The rinse enters through valve I and its duration is controlled by an interface controller.

In the process cycle valves B, C, and D are closed, isolating all the sections.

The duration of the process cycle is 4–10 min, depending on the contaminants to be removed, and is controlled either by a timer if the contaminants are fixed or a controller in the effluent stream, if the contaminants vary considerably over short intervals.

Valve A opens and resin drops in the pulse section simultaneously with the removal of contaminants in the loading section, regeneration of loaded resin in the strip

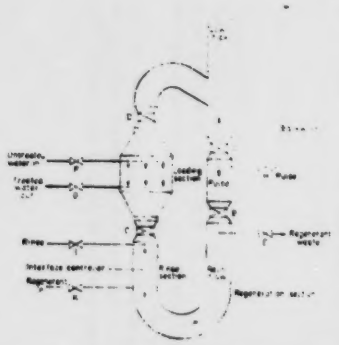

Fig. 1. *Schematic diagram of Chem-Seps continuous counter-current ion exchange contactor*

Valve positions during cycles:
(a) Run cycle. Valves A, E, F, G, I, K open; valves B, C, D, H closed
(b) Pulse cycle. Valves B, C, D, H open; valves A, E, F, G, I, K closed

section, and rinsing of regenerated resin in the rinse section. As the resin drops through the valve A, it is backwashed to remove the suspended solids or resin fines. Removal of these fine particles is important to avoid the unnecessary pressure drop in the bed and plugging of the distributors.

At the end of process cycle, all flows going into and out of the unit are automatically shut off. The valve A closes and valves B, C, and D open in proper sequence. A slug of water enters through valve H, a predetermined incremental volume of resin moves into the regeneration section, an equal volume of regenerated and rinsed resin enters the bottom of the loading section, and an equal volume of the loaded resin leaves the top of the loading section and goes into the overflow section. (The resin movement is plug flow with the Reynold's number being in the laminar region of the curve, and no fluidisation occurs during the pulse cycle.) The total time required for proper sequencing of valves and the movement of resin is 20–30 sec. At the end of this period, the valves B, C, and D close and valve A opens. The solution valves open and normal steady state operation begins. All valves are interlocked and properly sequenced.

Special features

Down flow

The feed moves downward and the resin moves upward in the loading section. The down flow of feed overcomes the handicap encountered in up flow systems. The up flow of feed requires a certain minimum flux during the process cycle to lift the bed and keep it in suspension. If a certain flux is not maintained, resin begins to 'churn' in the loading section. In the down flow system, resin drops in the loading section by gravity, and flow of feed in the downward direction further keeps the resin settled. The maximum flux in down flow is 60 gal/min/ft^2 and there are no limitations on the minimum flux, compared with a minimum flux of 20–30 gal/min/ft^2 in up flow systems.

Another advantage of down flow is the use of untreated water during pulse and backwash. The water which is used for pulse goes out in the waste. The resin in the pulse section is fully loaded, whereas in an up flow system the resin in the pulse section is fully regenerated and rinsed, thus use of treated water is mandatory.

The only treated water requirement is the rinse water which equals the volume of resin moved.

One other advantage of down flow is that the liquids with higher specific gravity are always at the bottom part of the loop; thus it is easy to control the interfaces and obtain concentrated wastes.

The performance of a down flow system using low-density resins is superior to up flow performance with similar resins. A weakly basic resin such as Amberlite IRA-93 in hydroxide form when transferred after regeneration and rinsing in an up flow system is an example of such a situation. The settling of the resin in the pulse section requires a considerable time, and slows down the production rate in an up flow system. However, in a down flow system the resin when transferred to the pulse section is in sulphate or chloride form, which is of greater density, and settling presents no problems.

Use of slurries

Slurries can be used for regeneration in Chem-Seps continuous counter-current ion exchange because of the inherent advantages of the moving-bed and counter-current flows. Suspended solids will plug up the conventional ion-exchange system and it is impossible to use lime as regenerant for weakly basic resins, whereas slurries do not present any particular problems in the Chem-Seps single-loop system and are easily handled by using special distributors.

Reduction of waste volume

The resin is thoroughly rinsed in a Chem-Seps single loop system with an equal volume of water owing to the inherent efficiencies gained by counter-current flows in a single loop. The liquid interfaces are precisely controlled by using various interface controllers and excess water is eliminated from the waste. The volume of waste in a standard de-mineralisation process is reduced to one-tenth of the volume by using Chem-Seps CCIX instead of a conventional de-mineraliser.

Reduction of operating costs

The regenerant chemicals required in Chem-Seps CCIX are 20–100% over stoichiometric amounts; compared with 2- to 10-fold excess over stoichiometric amounts required in conventional systems.

Applications

De-mineralisation of boiler feed and process water

Usually the largest single cost in operating an ion-exchange de-mineraliser is the cost of chemicals used for

regeneration. A conventional fixed-bed ion-exchange de-mineraliser will be found to use a 100% or more excess of regenerant chemicals over the stoicheiometric amounts. The counter-current flow efficiency of continuous ion exchange has given a reduction of regenerant consumption to within 10–25% excess over stoicheiometric amounts. An example of a continuous de-mineralisation plant installed in a fertiliser complex in Canada includes a strongly acidic cation unit followed by an atmospheric decarbonator with a weakly basic anion unit and a strongly basic silica polisher (see Fig. 2). The untreated feed water to this system contains from 1200 ppm total dissolved solids (*TDS*) to as high as 1800 ppm *TDS*, depending on the season. Approximately 65% of the *TDS* is sodium. The effluent requirement is 5 ppm *TDS*. The real aim for the system is to maintain the chloride content in the effluent to ~3 ppm. Sodium tailings in this system are critical. The cation unit is regenerated with 10–12% nitric acid. This acid was selected because it is an 'in-plant' product with a relatively low cost. It is of interest that the excess nitric acid may be piped to the blending plant so that the nitrate values are actually calculated as part of the product of this fertiliser complex. The regenerant for the weakly basic anion unit is 3–5% NH_3 as ammonium hydroxide solution. Ammonia is a product of this plant, and thus available at low cost. This unit (see Fig. 3) serves as an example of water treatment that was considered to be impractical by conventional fixed beds. Sodium tailing is a common problem in de-mineralisation and is the key factor in control of conductivity and pH of water in the cation unit and the final water. The equipment for continuous detection of sodium is sensitive to very low levels. Sodium removal is over 99·4% and is reduced from 500 ppm to less than 3 ppm.

Since a weakly basic resin is used in this installation the down flow system is the 'key' to the production rate. As already mentioned, the resin transferred to the pulse section is in sulphate and chloride form, and settling of the good resin is achieved in 2–3 min which helps maintain the fast production rate.

The operating and capital cost comparisons between a conventional and Chem-Seps continuous counter-current ion exchanger are given in Table I.

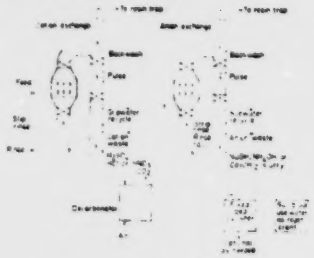

Fig. 2. *Typical layout for de-mineralisation*

The savings in chemical cost alone amount to $48,500 per year.

The resin inventory in continuous counter-current ion exchange is 20% of conventional fixed-bed systems.

Conventional fixed-bed equipment designed for regeneration every 8 h will require 'on stream' two cation units of 9 ft dia. × 4 ft bed depth, and two 'off stream' on regeneration and the same number of anion units with 8 ft dia. × 3 ft bed depth.

The Chem-Seps continuous counter-current ion-exchange units are 10 ft × 10 ft base and 27 ft high, one train occupying 200 ft^2 or 5400 ft^3. The fixed beds will require 550 ft^2 and 8000 ft^3. The piping of so many fixed-bed units is an extensive operation.

For a high degree of removal of sodium (to less than 3 ppm) 100% excess over stoicheiometric amounts of nitric acid is used. A conventional system would use 350% excess over stoicheiometric amounts at 10 lb/ft^3 of H_2SO_4 or 38·6 lb HNO_3/1000 gal using 6 lb/ft^3 at 250% excess over stoicheiometric amounts. Recently, at this particular installation, the cation resin has been mixed with a weakly acidic resin Amberlite IRC-84. The percentage of weakly acidic resin is being gradually increased to 30%. In the next few months the weakly acidic percentage will be increased, and it is hoped that nitric acid consumption can be reduced to less than 50% when the optimum ratio of the two resins has been reached in the operation. This will result in savings worth $10,000 per year using the normal 'in-plant' cost of nitric acid.

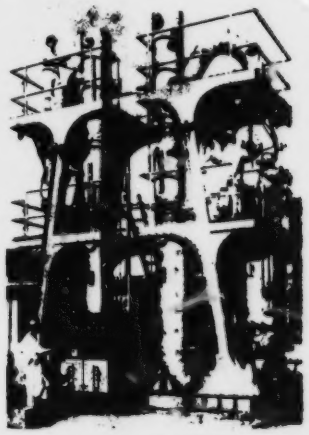

Fig. 3. *Continuous de-mineralisation plant of fertiliser complex in Canada*

TABLE 1

Capital and operating costs comparisons of a conventional and a Chem-Seps continuous counter-current ion exchanger

Basis *TDS* 1500 ppm
Flow 880,000 U.S. gal/day

	Conventional fixed beds	Chem-Seps CCIX
Capital cost:		
Equipment cost (actual bid) delivered uninstalled	$130,000	$120,000
Installation and start-up	$ 26,000	$ 12,000
Total investment	$156,000	$132,000
Major equipment:		
Total resin inventory		
Strong acid cation		
Weak base anion	950 ft³ 550 ft³	190 ft³ 190 ft³
Operating cost		
Chemical:		
NH_3		
HNO_3	2·92 lb/1000 gal	0·575 lb/1000 gal
NH_3 at 3c/lb	38·2 lb/1000 gal	22·1 lb/1000 gal
HNO_3 at 1·75c/lb	50·07	50·02
Cost of chemicals/1000 gal	50·67 50·76	50·59 50·41
Resin attrition:	Assume equal for both case	
Savings/day		$11·13/day
Savings/year at 365 days/year operation		$48,500/year

Weak resins and mixed beds

The use of mixed resin beds or weak- and strong-type cation resins in order to lower acid regenerant costs is becoming a widely used practice. This practice already used in fixed-bed design also fits well with continuous counter-current cation design. The mixture usually contains a higher fraction of the weak-type resin. This fraction is greater than the fractional amount of bicarbonate in the water to be treated. The additional amount of weak-type resin provides for the migration of alkaline earth elements from the strongly acidic resin that use some of the exchange capacity of the weak-type resin. A treatment of waters containing high quantities of bicarbonates, in the region of two-thirds of the total anion content, allows use of stoicheiometric amounts of sulphuric acid regenerant. The second hydrogen atom on the sulphuric acid molecule is poorly ionised and is lost in regenerating strongly acidic resins but is effective in regenerating the weak-type resin. An example of an installation of weak- and strong-acid types of resin is indicated in Fig. 4. This water is about 80% bicarbonate and most of the cation is sodium. The resin mixture is 75% Amberlite IRC-84 and 25% Dowex 50W-X8. Stoicheiometric use of sulphuric acid was demonstrated in pilot tests and 25% excess was guaranteed for this installation. Samples taken within the strip section show complete utilisation of free acid.

Pilot tests were also run for a water that contained anions made up of 85% SO_4^{2-} and Cl^- and 15% bicarbonate. Sulphuric acid consumption was between 25 and 50% over the stoicheiometric amount. It was noted that a disproportionate amount of hardness ions

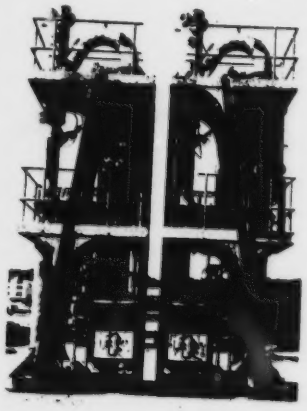

Fig. 4. *Typical installation of weak- and strong-type resin plants*

were associated with the weakly acidic resin relative to the amount of bicarbonate present. This is one reason for using a preponderant amount of the weakly acidic resin. It is an effect not realised in a 'layered' fixed bed.

Another reason for using a bulk amount of weakly acidic resin is the lower utilisation capacity at high production rates, since the exchange rate is lower if the utilisation capacity is increased. The typical span of capacity loading planned is 0·0–0·5 equiv/l., whereas the strong-type resin might be loaded to 80–90% of its total capacity.

The typical high degree of expansion and contraction of this resin is of no concern in a Chem-Seps single loop continuous counter-current contactor.

Another factor in favour of Chem-Seps continuous counter-current ion exchange was low resin capacity utilisation, since there is over 95% sodium in the cations. The theoretical capacity for Amberlite IRC-84 for this application using conventional system and manufacturers data is 7·5 kg/ft³. If the units are designed to normal requirements of regeneration once every 8 h, it would require a total resin inventory of 1100 ft³ to treat 750 gal/min. The total resin inventory in two Chem-Seps continuous counter-current ion-exchange units to treat 375 gal/min each is 150 ft³.

The cost of resin alone, if fixed bed units were used was $55,000.

In this application the system provided by Chem-Seps has more reliability than the conventional fixed-bed system, since there are two continuous units each performing the full task, compared with only one fixed-bed unit in operation with one constantly in regeneration.

Slurry regenerant

Lime slurry is a low-cost regenerant. If lime slurry could be used effectively without causing plugging of the equipment by the very high content of solids in the regenerant feed stream, it was reasoned that this would reduce the cost of anion regenerant. In earlier work on the extraction of uranium, a slurry of about the same solids content as would be found in a lime slurry regenerant feed stream was used. Some work was done in the past with lime slurry in the exploration of a flowsheet to produce caustic soda by ion exchange. The use of lime slurry as an anion regenerant is hazardous since precipitation of calcium carbonate and calcium sulphate within the resin bed would mean a prolonged shutdown. In the treatment of water with a high bicarbonate content, the hazard of calcium carbonate is eliminated by the use of an effective decarbonator in front of the anion unit. The fear of precipitation of calcium sulphate has been groundless in the Chem-Seps single loop design. It has been demonstrated that anion resin in the sulphate form may be effectively regenerated with lime slurry without precipitation of calcium sulphate within the moving bed.

Regeneration of weakly basic anion resins with lime slurry is effective. An excess of 10% over the stoicheiometric amount is standard practice.

The Sul-biSul process is an example of an effective demineralisation system with low operating cost; in it, lime slurry is used for neutralisation of free acid formed in the regeneration step. The introduction of lime slurry keeps the volume of waste down. Chem-Seps is one of the licensees of the process.

The maximum capacity is only half the theoretical capacity of anion resin. The anion resin inventory for a half million gallon per day plant, by Chem-Seps continuous counter-current ion exchange, would be 250 ft³ for a water containing 1500 ppm of sulphates, but for conventional system, the resin inventory would be 1200 ft³ if the units are regenerated every 8 h.

For an application using Sul-biSul, the Chem-Seps continuous system is highly efficient and reduces the capital cost.

DISCUSSION

Resin attrition

In a system where valves are closed on pipelines full with resins, is not resin attrition a considerable problem?

It is 'assumed' that valves closing in a bed of packed resin will cause considerable attrition. Resin life up to ten years has been measured in a unit with four valves opening and closing every five minutes.

Uranium Plant

As Mr. Chopra mentioned, my company has been carrying out experiments in the Western Uranium Fields of the U.S.A. with a Higgins Ion Exchange Contactor. Uranium is extracted from a sulphuric acid-process leach pulp containing 7–8% suspended solids. The pulp is desanded and contains a considerable amount of wood pulp in addition to the clay fraction of the uranium ore. The wood pulp is a common problem associated with underground mining of the ore as anyone in the uranium mining can testify. More problems may be expected from the wood fibres which do not separate too well in either hydrocyclones or screens. The contactor was operating successfully for up to 98 hours, tests being terminated by reasons not connected with the contactor.

Author's reply. This is not the first time slurries have been handled in Chem-Seps equipment. See AEC Report, ORNL-2308.

Uranium (William Ruby & Co.)—Of the speakers this morning only M. Bouchard's paper mentioned the use of continuous ion-exchange plants for mixed bed applications. In view of the extremely low leakage possible from mixed bed plants at very high regenerant efficiencies could the three authors mentioned above,

explain whether their processes are applicable to mixed bed operation and if so, in what way their basic process would be changed?

Author's reply. We have done a considerable amount of test work related to mixed bed continuous ion exchange. We very definitely are expecting to offer a system after we finish pilot plant testing. Our main goal has not been to make a high degree polisher, but a bulk demineraliser using weak type resins and stoicheiometric regeneration.

Mr. R. C. Clayton. There is no reason why the system described in my paper cannot be adapted for mixed bed applications provided a satisfactory resin separation stage is introduced.

Dr. D. G. Stevenson. Fluidised bed systems cannot of course be used for mixed bed operation in the normally accepted sense. Normal grades of anion and cation resin will segregate in the bed. Alternatively, if the size ranges are chosen so that a true mixture of the resins is obtained, it will not be possible to segregate them for regeneration. However, it is expected that a useful system will prove possible whereby a layer of cation/anion resin is present above each distributor plate. It would not be difficult to have for example four double beds in this manner. Performance should be very much better than that of a single cation/anion combination. The particular resin transfer system developed for this work is capable of transferring both components in any such dual bed.

Dr. R. Hönigschmid-Grossich (c/o Dynamit Metal A.G.).—Question to all who presented papers on countercurrent systems: what happens when valves, pumps etc. break down; can this fact not minimise the advantage of this system in relation to normal 'old-fashioned' ion exchange equipment?

Author's reply.—In this day and age, what is the problem in choosing reliable pumps, valves, and other component parts? I have 172,000 miles on my automobile. Any well built and well cared for piece of machinery can do as well.

Mr. R. C. Clayton.—It is cheaper to produce plant in a series of standard sizes or modules, and any water requirement will frequently be supplied by two or more continuous plants. Any outage time can thus be catered for by temporarily increasing the flow through the other modules. In fact, valve failure in ion-exchange plant is a rarity, and there is no reason why it should be more common on C.I. plant provided correct maintenance procedures are followed.

Presented at the
Conference of Ion Exchange in the Process Industries
held at
Imperial College of Science and Technology
London
July 16–18, 1969

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Principle Suppliers of Evaporation Equipment

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- The Aquaport Brine Concentrator 962
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INTRODUCTION

Evaporation as a desalination tool is applicable for feed solutions with higher concentrations of dissolved solids. The concentration of dissolved solids at which evaporation becomes competitive with reverse osmosis or EDR will vary from case to case depending on:

- Size of Installation
- Cost of Electricity
- Salt Composition in Solution
- Recovery of Water Required
- Cost of Disposing of Brine Concentrate
- Credits for Useable By-Products

According to a LURGI brochure inserted below, the crossover between economics favoring R.O. and evaporation occurs at around 10,000 mg/l TDS. There are, however, several R.O. plants that were selected for seawater (35,000 mg/l TDS) desalination at much higher TDS levels than this, so clearly other factors play a role.

One way to get the "best of both worlds" is to use R.O. for primary concentration and evaporation for final water recovery from the R.O. brine and for final volume reduction of the concentrate for less expensive or more convenient disposal. At a metallurgical plant (platinum and base metal refinery) at Rustenburg, an acid metallurgical solution is neutralized and evaporated to yield a salable Na_2SO_4 product avoiding the need for any brine disposal method.

The problem with installing two processes in tandem for water recovery is that then there are two plants with two types of technology to maintain and operate instead of one which adds complications, but in some circumstances, it has proven to be the most economical way to achieve zero discharge. Where tandem systems using R.O. for primary concentration followed by a smaller capacity evaporator system are to be installed, it would also be attractive to have the option of using one contractor/engineering company to be responsible for the total water recovery and salt disposal package. There are not many companies that have experience in more than one type of desalination technology, particularly not in a mineral processing environment. The following companies are known to have that experience, however:

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Russell Vandenberg
Thomas Wolfe
Reams Goodloe

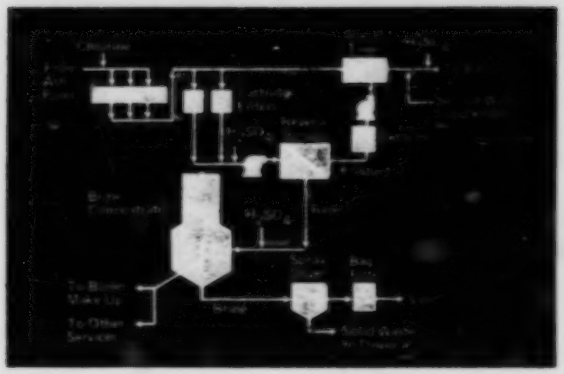
RESOURCES CONSERVATION COMPANY
INTERNATIONAL
Post Office Box 784561
Sandton 2146
(011) 783-7121
Pat di Benedetto

PROCESS SYSTEMS (PTY) LTD.
Box 10142
Johannesburg 2000
(011) 82-4230
Ralph A. Jones
Managing Director
(Licensee for Ionics, Inc. and
Signal Swenson Evaporators)

BATEMAN ENGINEERING LTD.
Post Office Box 565
Boksburg 1460
South Africa
(011) 899-9111
Telex: 8-7880
P. J. Woollam
(Licensee for: Israeli Desalination
Engineering Ltd.)

The basic principles of evaporative desalination are outlined below in an excerpt from SCHUTTE (1983). There are several innovative approaches to evaporation and condensing as illustrated in excerpts from various company brochures that follow. For each case, a potential user is well advised to "shop around" to obtain several quotes, bearing in mind too that he may also be comparing "Mercedes Benzes with Fords" and that, in some cases, a price differential may be justified.

Because desalination is a specialized field, it would always pay to retain a consultant to review the quotations tendered for a given job, particularly a consulting firm with a wide breadth of experience. One such consulting firm is the Resources Conservation Company listed above who has installed a wide variety of desalination plants around the world for several different industries, and who has developed several highly innovative technologies such as, for example, slurry seeded evaporation. This company is also an experienced water resource management firm who may be able to devise a water management plan to minimize or avoid the need for desalination altogether. The following excerpt from their brochure shows one example where improved water management and a three-step desalination processing train (R.O. and evaporation) achieved zero discharge for a client.



Wastewater inventory reduced by 50%

A significant and unexpected growth of wastewater was about to cause major problems at a southeastern utility's 1,900-MW coal-fired station. RCC moved onsite, analyzed all major streams, and produced a near-term solution to intercept and divert rainwater and reroute some existing wastewater. Simultaneously, we developed long-term alternatives to better manage the internal streams. Now operating, our water management system has not only reduced accumulated wastewater but has also allowed zero liquid discharge.

Finally, at the end of this chapter, inserted is a pamphlet and a publication by GORE (?) describing a highly innovative new approach to evaporative desalination processes that employ a membrane. The Gore-Tex membrane disttillation is not yet working commercially but offers exciting potential in the future of desalination technology.

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DESALINATION: A SOUTH AFRICAN PERSPECTIVE

C.F. SCHUTTE

Senior Adviser:
Water Research Commission

CHAPTER 5

DISTILLATION

5.1 Introduction

Desalination can be effected by different processes including distillation, reverse osmosis, electrodialysis, ion exchange and freezing. Although the large scale application of these processes for water production is relatively new, distillation was employed more than a hundred years ago on board ship for the production of potable water from sea water. However, distillation only became commercially viable on large scale with the introduction of the multi stage flash process in 1958.

In this chapter a brief description is given of the different distillation processes, advantages and disadvantages are given together with process requirements, practical experience and economic considerations. In the following chapters the other desalination processes are discussed.

5.2 Process description

There are three essential steps involved in desalination by distillation, i.e. production of vapour from the feedwater, removal and transportation of the vapour to the condensor and condensation of the vapour. These processes are incorporated in a number of different distillation processes configurations i.e. multistage flash, multiple effect and vapour compression.

5.2.1 Multistage flash (MSF)

A conceptual design for a MSF distillation plant is shown in figure 5.1 (USAID 1980). The basic principle is that pre-heated seawater enters the evaporation chamber under reduced pressure, resulting in flash boiling of part of the seawater. The vapour produced by flashing is then condensed on the outside of tubes conveying cooler seawater to the hot end of the plant.

The incoming seawater passes first through a heat rejection stage and is then heated in the heat recovery sections of each subsequent stage. Before entering the first stage the seawater is heated to its maximum temperature by external steam. The feedwater then passes through the various stages where flashing takes place. The vapour passes through demisters and is condensed on the outside of tubes conveying seawater to the hot end of the plant. The fresh water formed by condensation is collected in each stage and is passed to subsequent stages where it is also flashed to recover heat for preheating of the feed.

The number of stages employed in a MSF plant largely determines its efficiency. The normal range is from 20 to 50 for commercial plants. The more stages the higher the fuel efficiency but the higher the capital costs also.

MSF plants are used exclusively for seawater desalination and have captured by far the largest part of this market. The installed capacity of MSF plants in 1980 was $4,8 \times 10^6 m^3/d$ which accounted for 67% of the world's total installed desalination capacity (Techno-Economic Services 1981). The main reason why MSF has done so well is that these plants can be constructed with large capacities - 25 000 m^3/d not being uncommon and the technology and expertise is available to construct much larger size plants. Another main advantage is that boiling does not take place on the heating surface but the seawater flash boils instead. These plants require well skilled operators and great care during start up.

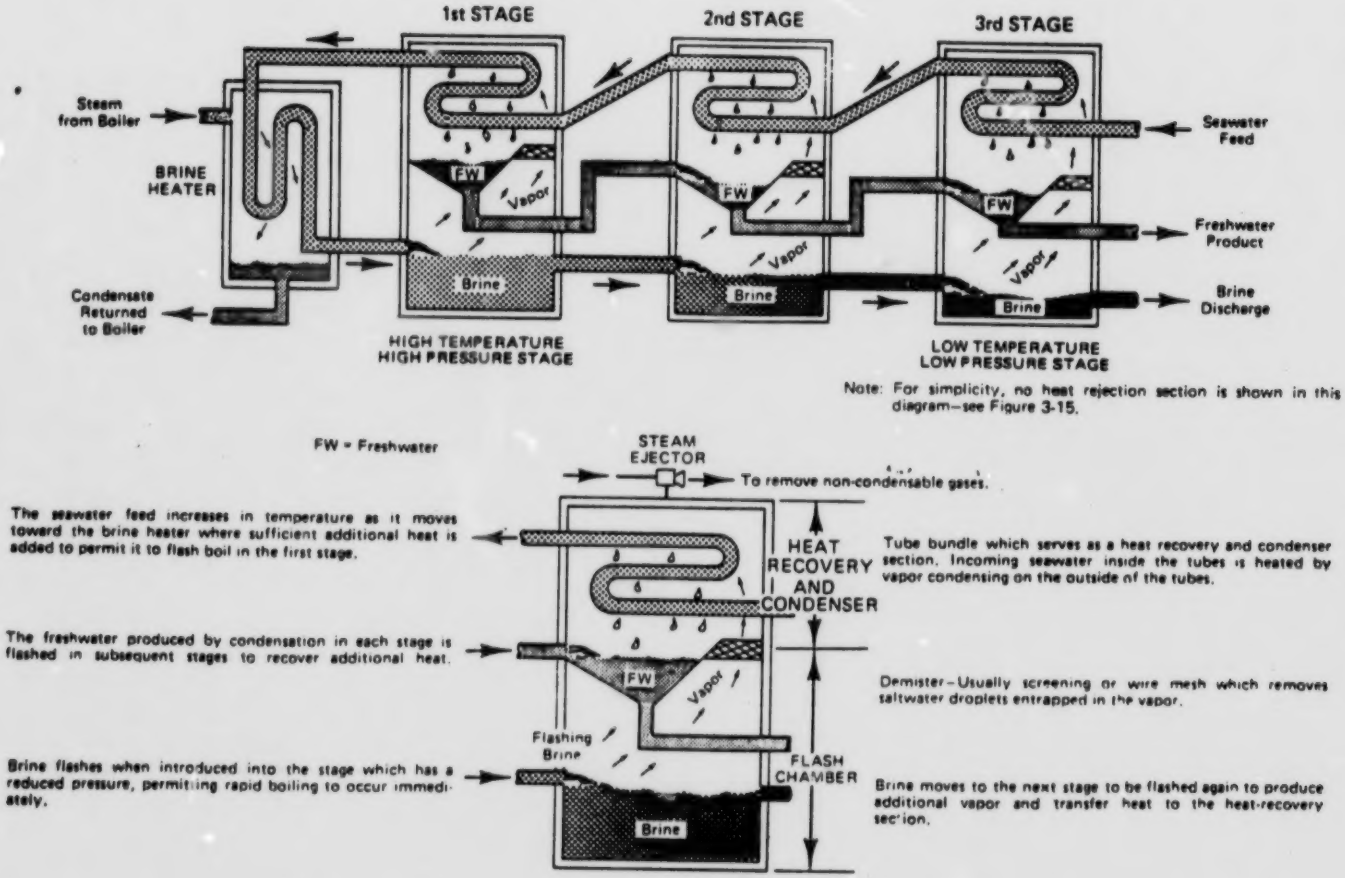


FIGURE 5.1 Conceptual diagram of the multistage flash (MSF) process. (USAID 1980)

5.2.2 Multiple-effect evaporators

A conceptual design for a multiple-effect vertical tube evaporator (VTE) is shown in figure 5.2 (USAID 1980). In each effect steam is condensed on one side of a tube and the heat of condensation is utilized to evaporate water on the other side of the tube wall. The cascading use and reuse of the heats of vapourization and condensation is made possible by progressively reducing the pressure in each subsequent effect. This allows the brine to boil at progressively lower temperatures as it flows through the plant.

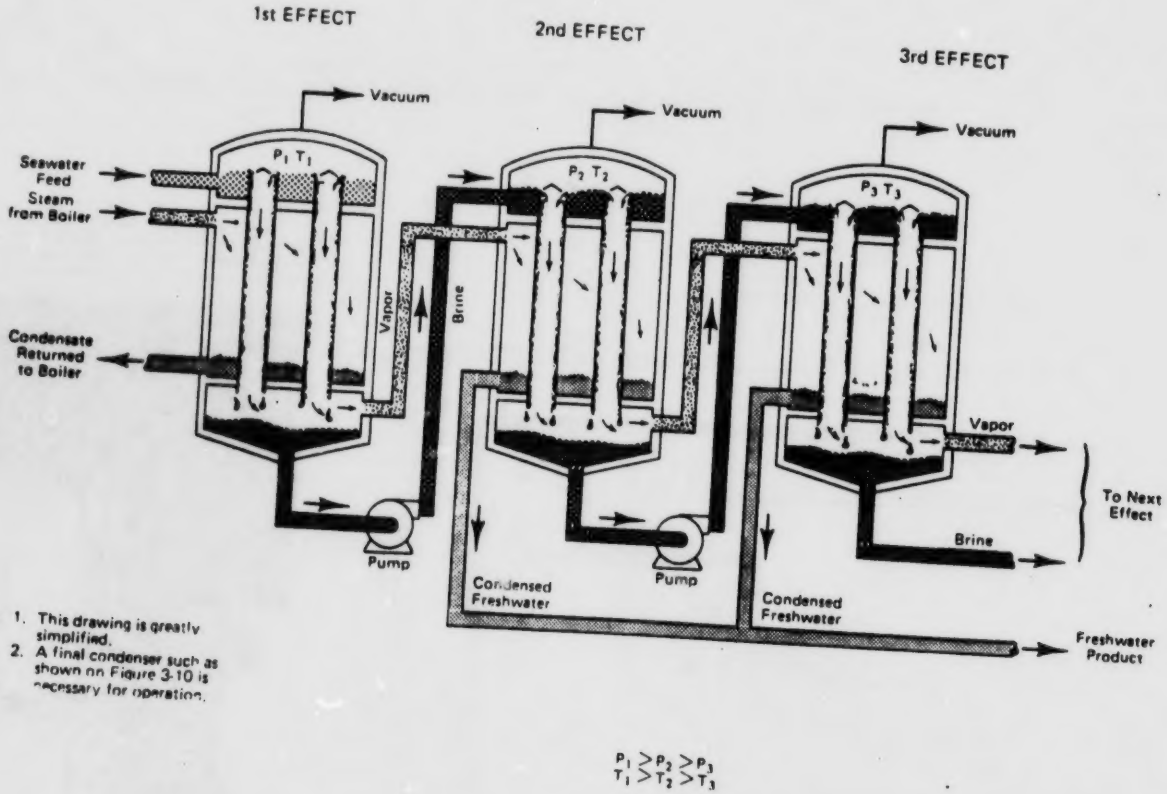
The same principle is also used in horizontal tube multiple effect configurations. Only limited experience with horizontal tube units is available compared to the vertical tube configuration.

The first multiple effect units utilized submerged tube heaters but due to problems with scaling on the submerged tube surfaces and the lower evaporation efficiencies this configuration is not used any more for large scale applications.

Low temperature multiple-effect distillation offers a number of advantages such as reduced scale forming and corrosion but in spite of all these potential advantages it has not found large scale application.

5.2.3 Vapour compression

Figure 5.3 (USAID 1980) shows a conceptual design for a vertical tube vapour-compression process. This process differs from other distillation processes in that it does not use an external heat source as primary energy source, but utilizes instead mechanical energy to drive a compressor to increase the vapour pressure of the water and thus its condensing temperature (a steam ejector may also be used). Condensation takes place on one side of a tube which acts as heat transfer surface while feed is evaporated by the heat of condensation on the other side of the tube.



Notes: 1. This drawing is greatly simplified.
2. A final condenser such as shown on Figure 3-10 is necessary for operation.

FIGURE 5.2 Conceptual diagram of a vertical-tube evaporator (VTE). (USAID 1980)

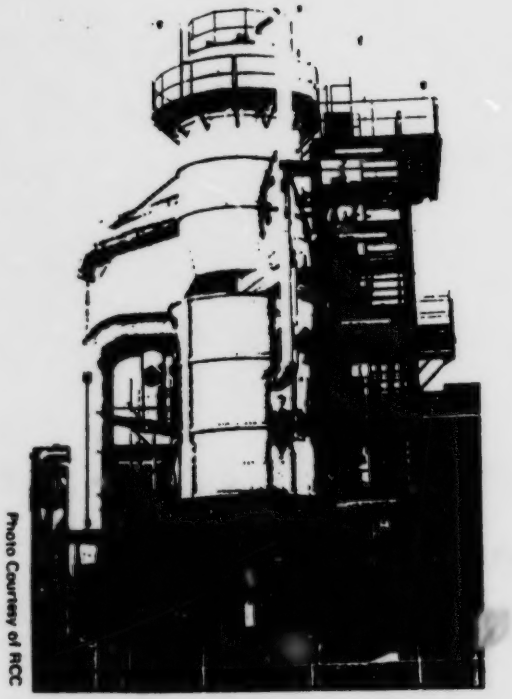


Photo Courtesy of RCC

A vertical-tube vapor compression unit to concentrate brine from a coal-fired generating station in southwestern USA. This unit processes about 0.225 mgd [852 m^3/d] of brine with a freshwater recovery of up to 98%.

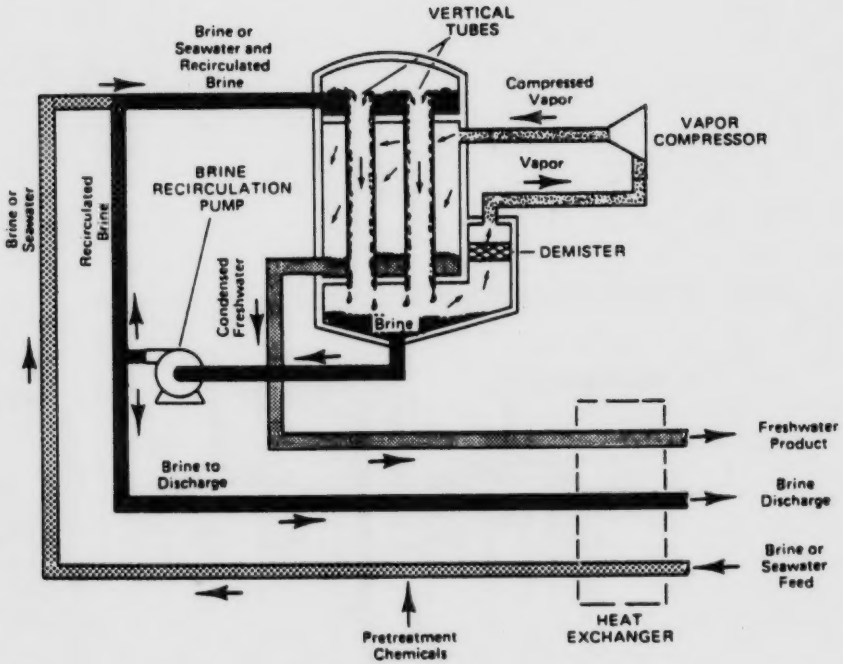


FIGURE 5.3 Simplified flow diagram for a vertical-tube vapor-compression process. (USAID 1980)

The compressor compresses the vapour, raising its condensation temperature and at the same time lowers the pressure on the feedwater thus reducing its boiling temperature. The only major energy input during operation is that required to drive the compressor, since the heats of condensation and vapourization are being recycled across the heat transfer surface. Feed heaters are normally only required during start-up and once the unit is running only mechanical energy is required.

The two configurations used in vapour compression units are vertical tube falling film and horizontal tube spray film types.

A specialized type of vertical tube vapour compression plant is the brine concentrator. It employs vertical titanium tubes through which the brine or wastewater is recirculated in a slurry containing calcium sulphate or other crystals. In this way scale formation on the heat transfer surfaces is minimied since precipitation preferentially takes place on the crystal surfaces. Very high concentrations of dissolved solids can be handled in this way and water recoveries of up to 98% can be achieved. A similar process but using horizontal tubes is also available.

Low temperature vapour compression distillation for the desalination of seawater is highly energy efficient. It has a specific energy consumption of about 10 kWh/m^3 which is of the same order as for reverse osmosis without energy recovery (Hoffman and Ophir 1982). These plants operate within the temperature range of 30-70°C which results in low scaling and low corrosion rates and therefore require only fairly simple feed pretreatment.

These units utilize a special aluminium alloy suited for seawater use. They have been operating successfully as low temperature multi effect vapour compression plants.

The performance factor (kg product/M J energy input) of vapour compression plants is high (8,5) compared to multiple-effects (7) or multi-stage flash (5). However, they are limited in size to about 1000 m^3/d per unit by the size of commercially available compressors and therefore they do not have the economy of scale with respect to capital cost for large size plants.

Vapour compression units are available as skidmounted packaged units with capacities ranging from small to about 1000 m^3/d. For larger capacities a number of units have to be used.

5.3 Distillation process characteristics

5.3.1 Efficiency

The efficiency of a distillation plant is measured by the mass of water produced per unit of heat energy and can be expressed in terms of performance factor or economy ratio.

(i) Performance factor is expressed as kg water per MJ energy input.

(ii) Economy ratio (or gained output ratio GOR) is the ratio of kg water produced to kg of heating steam supplied. For vapour compression units using mechanical power a steam equivalent based on the energy input per kilowatt hour is used to calculate the performance factor.

The performance factor of multi-stage flash plants is restricted to about 5kg/MJ due to the limited number of stages that can be installed between the hot and cold ends of the plant. Calcium sulphate scale formation restricts the upper temperature to about 121°C.

Multiple effect plants may be built with performance factors as high as 8 kg/MJ but construction of large MED plants is impeded by a lack of prototype units.

The efficiency of vapour compression units vary from 25-50 kWh/m^3 product but recent developments in low temperature vapour compression could bring this figure down to 10 kWh/m^3 (Hoffman and Ophir 1982).

5.3.2 Scaling in distillation plants

One of the most serious problems limiting the efficiency of distillation plant is scale formation due to precipitation of calcium carbonate, magnesium hydroxide and calcium sulphate. All of these have inverted solubility characteristics and become less soluble as the temperature is raised.

The control of scale formation is essential in any desalination unit if it is to be operated for long periods at or near optimum efficiency. Two methods are being used for scale control i.e. acid treatment and chemical addition to prevent formation of hard scale. Acid addition is used to remove the alkaline scale forming potential by removing bicarbonate ions.

$$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$$

Although effective in preventing alkaline scale formation, acid addition results in increase corrosion rates. Corrosion can be reduced by removing dissolved oxygen in the feedwater to the plant to very low levels (0,05 mg/l) by vacuum deaeration and/or the addition of reducing agents such as sodium sulphite.

The addition of chemicals such as polyphosphate based products and more recently certain polymers retards the formation of alkaline scale and is used extensively in distillation plants. These "threshold" additives distort the crystal structure and prevent the formation of hard scales. The advantage of using inhibitors rather than acid treatment in distillation plants is that the rate of corrosion is reduced markedly.

None of these methods is effetive in the control of calcium sulphate scale formation in distillation plants. These plants are therefore operated within the calcium sulphate solubility limits although higher efficiencies may be obtained at higher temperatures.

Materials of construction is the one item which most significantly influences the capital cost and life of distillation plants. Distillation plants are exposed to high temperatures, concentrated brine solutions and often corrosive chemicals and great care must therefore be taken in selecting materials of construction.

5.3.4 Reliability

Distillation plants can be built to be extremely reliable in operation. However, reliability can also be poor as a result of poor design, selection of construction materials or poor operation.

5.3.5 Product water quality

Product water from a distillation plant is extremeley high, usually less than 25 mg/l dissolved solids. It is therefore usually aggressive to water distribution systems and must either be blended with brackish water if available or otherwise chemically conditioned if the product is used for water supply.

5.4 Dual purpose desalination-power generation plants

At thermal power plants steam is generated and expanded to drive turbines which in turn drive power generators. The exhaust steam from the turbine is condensed in a condensor and reused as boiler feed. The waste heat in the exhaust steam may, however, be used to evaporate water in a distillation plant. Plants of this nature where steam is extracted from an extraction turbine or obtained from a back pressure turbine (without the last low pressure stages) are referred to as dual-purpose or co-generation plants. The advantage of this type of plant is that the energy required to produce electricity and desalinated water is drastically reduced as compared to two separate plants. The main disadvantage is that power generation and water production becomes interdependent and if either does not operate the other has to shut down. Operation becomes more complicated and stand-by equipment has to be installed.

There are practical limits to the lowest pressure at which the steam can be extracted from the turbine. At low pressures the specific volume of steam can be prohibitively large. Systems such as the waste heat distillation concept in which it is proposed to use waste steam from the turbine house for desalination of effluents suffer from this constraint.

5.5 Application of distillation processes

The main application of distillation processes is for the desalination of sea water for municipal and industrial water supplies. Multi-stage flash had the major share in installed desalination capacity in June 1980 viz 67% compared to 4% for thin film vertical tube, 1,1% for thin film horizontal tube and 1,6% for vapour compression, 20% for reverse osmosis and 3,8% for electrodialysis. (Total installed capacity $7274 \times 10^6 m^3/d$) (Techno-Economic Services 1981). Because the energy consumption in distillation is independent of water quality there is very little cost difference between the production of fresh water from seawater or from brackish water. There is, however, a marked difference in production cost for membrane processes and since membrane processes have been commercialized for large scale applications distillation processes have been limited almost exclusively to seawater desalination and a small number of specialized applications.

Multistage flash is almost exclusively (98%) used to desalinate seawater while multiple effect processes are used for both sea and brackish waters with new plants almost exclusively for sea water.

A specialized application of vapour compression is the vertical tube seeded slurry application for the desalination of wastewaters. A total of thirteen plants are in operation in the USA with a combined installed capacity of 28250 m^3/d. A vapour compression plant of this type is at present being installed at SASOL and should be operational during the second half of 1983.

A plant operating on the same principle but employing horizontal tubes have been commissioned recently in South Africa in New Castle. It is the first of its kind to be installed and no previous operating experience is available.

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Falling-film evaporators recover chemicals efficiently

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Falling-film evaporators provide stable operation at low heat-transfer values with high heat-transfer rates. These features permit more energy-efficient pulp liquor evaporation than can be achieved with other types of evaporators. With falling-film evaporation, it is possible to select either a vapor compression system or a system having eight or more effects (or a combination of the two), depending on capital and energy cost trades and the mill's energy balance. A vapor-compression, vertical-tube, falling-film evaporator that concentrates both kraft and sweetened semichemical liquors to 50% has been providing significant energy savings and operational benefits to a containerboard mill since this evaporator began operating in Feb. 1981.

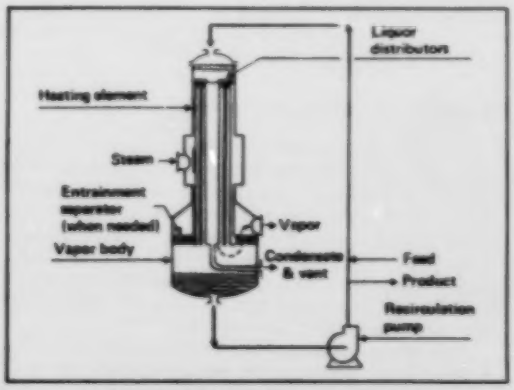
KEYWORDS: Energy • Recovery • Evaporators

Falling-film evaporation permits energy-efficient evaporator configurations because it is able to operate stably at low heat-transfer temperature differentials (ΔT) between the condensing vapor and liquor temperatures and with high heat-transfer coefficients. These features make possible the design of multiple-effect systems capable of many more effects than are possible with other evaporator types. For example, up to 14 falling-film effects are feasible for kraft liquor evaporation to 50%, whereas with rising-film evaporators, unstable operation results at the lower ΔT values associated with more than six effects.

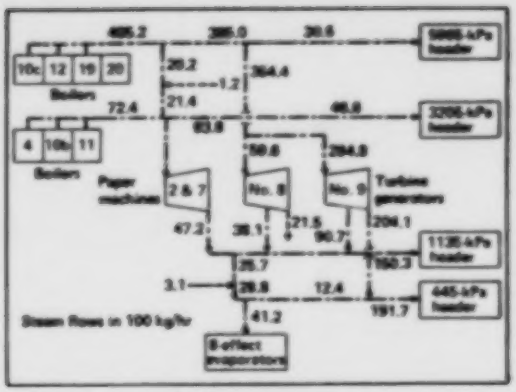
Low-ΔT capability also permits energy-efficient vapor compression systems, even for concentrated liquors having high boiling-point rises (BPR), such as kraft liquor. The high heat-transfer coefficients keep falling-film evaporators economically sized at the low ΔT values. Effective mechanical recirculation of the liquor over heat-transfer surfaces, now possible with a new patented distributor, is the feature that permits vertical-tube, falling-film evaporators to operate stably at low ΔT values.

How falling-film evaporation works

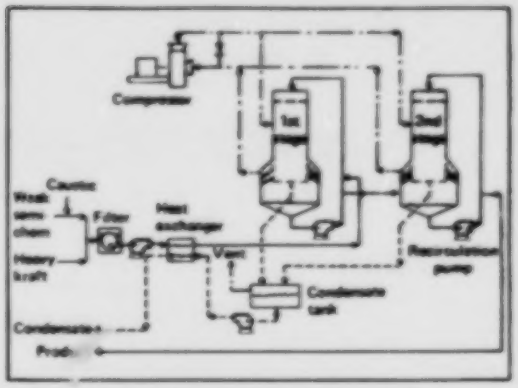
The principal parts of a falling-film evaporator are the heating element, vapor body, a pump to circulate liquor through the heating element, and an effective distribution system that uniformly films the liquor onto the heating surface. A typical, vertical-tube, falling-film evaporator body is shown in Fig. 1



1. Vertical-tube, falling-film evaporator body.



2. Mill steam balance.



3. Semichemical, falling-film, vapor-compression evaporator.

Liquor is continuously recirculated within the evaporator from the lower vapor body to the upper liquor box. Flow is maintained with a high-capacity recirculation pump. Complete wetting of the heat transfer surfaces is a key requirement, met by liquid distributors installed in each heat-transfer tube of the heating element. These distributors are inserted in the upper tube sheet and are held in the tube by friction. Liquid flow is directed through holes in the top of each distributor, forming a uniform thin film that completely wets the inside surfaces of the heat-transfer tube. A head of recirculating liquid several inches high is maintained above the distributors to provide the desired flow through each tube. The high liquor-recirculation rate minimizes fouling by eliminating dry spots and limiting concentration increases across the heat-transfer surfaces to only 2% or 3%.

Liquor evaporating in the heat-transfer tubes produces vapor that flows to the vapor body along with the recirculating liquor. As it flows through the vapor body and out of the evaporator, the vapor is subjected to scrubbing and centrifugal and gravitational forces to remove entrained droplets. Each vapor body can be fitted with entrainment separators to achieve a higher condensate quality if needed. Shell-side venting removes noncondensibles and, when required, reduces biological oxygen demand (BOD) and total reduced sulfur (TRS) levels in the condensate.

Evaporator selection—a case study

The falling-film, vapor-compression evaporator was an integral part of a multimillion dollar modernization that makes a containerboard mill 70% self-sufficient in energy by using renewable sources. This modernization also reduced labor requirements by 35%. Two new Kamyr digesters produce pulp for five paper machines rated at 1,034 machine-dry metric tons/day of linerboard and 417 machine-dry metric tons/day of corrugating medium.

Pine wood is pulped in a continuous two-vessel Kamyr kraft digester. Its design capacity is 1,179 air-dry metric tons/day at a yield of 54.5%. A single-vessel semichemical Kamyr digester is used to process mixed hardwoods. The design calls for use of kraft mill green liquor to pulp to a yield of 76% at an anticipated chemical charge of 8% total alkali, both based on oven-dry wood. Blow-line refining is required at this high yield. Conventional washing is incorporated into the semichemical pulping line. Spent liquor is designed to be about 7% solids. Use of green liquor combined with wood acids from the hardwoods results in a spent semichemical liquor with reduced pH and a high carbonate content when compared with kraft.

In addition to the new evaporators, spent liquor is concentrated in 4 sets of conventional rising-film, multiple-effect evaporators which use 445 kPa steam at an economy ranging from 4 to 5. This provides a use for turbine extraction and other lower pressure steam. While kraft liquors are normally handled by these evaporators, a high-carbonate, low-pH spent green liquor would quickly foul and corrode the existing rising-film evaporators, so the latter are restricted to use on kraft liquors. They produce a liquor containing 48–50% solids by weight. This liquor is fed directly to oxidation or is used to sweeten the semichemical liquor.

Steam generation is provided by 7 boilers burning waste liquor, heavy oil, natural gas, and/or wood waste. Generation pressures are 5,965 and 3,205 kPa. Two turbine generators contribute to the mill's electrical power. Both turbines use steam at 5,965 kPa and extract at 1,135 kPa. One turbine is noncondensing and exhausts to the 445-kPa header; the other acts as a condensing turbine when the mill's low-pressure steam requirements are below the production indicated by power demands on the turbines. Two of the paper machines are driven by 3,205-kPa turbines exhausting to the 1,135-kPa header.

In applying the requirements of the vapor compression evaporator to the mill's energy balance, it was determined that adequate minimum-cost, shaft-turning power would be available for the compressor. The mill was found to have a low-pressure steam consumption which made electrical generation possible with little condensing turbine operation. This was important since steam turbines operating in the condensing mode would use far more energy than when operating in the noncondensing mode.

Future plans include installation of a new steam-saving, eight-effect, falling-film evaporator for kraft liquor to replace the older evaporators, so extraction steam consumption was checked on that basis. The steam balance for this condition is given in Fig. 2. The turbines are expected to operate on minimum condensing load while taking full advantage of the vapor compression evaporator.

Semichemical evaporator design

The mill required an evaporator system to concentrate 7% semichemical liquor to 50% solids at an evaporative capacity of 80,740 kg/hr (178,000 lb/hr). The two-stage, vertical-tube, falling-film, vapor compression evaporator system, shown schematically in Fig. 3, meets these requirements.

The weak semichemical liquor is first sweetened with caustic and heavy kraft liquor as required to minimize both the fouling and the release of noncondensible gases. The blended liquor is filtered through a 100-mesh, rotary gravity filter to remove fiber, which is returned to the mill. The feed is then heated in a plate-type heat exchanger using evaporator condensate prior to entering the first evaporator stage. The blended semichemical and kraft liquor is concentrated to about 38% in the first stage. Concentrated liquor from the first stage is fed to the second-stage evaporator body where the final product concentration of 50% is attained. Each evaporator body contains 5.1-cm-diameter heat transfer tubes 10.5 m long. Liquor recirculation in each body is accomplished with 150-kW centrifugal pumps.

The vapor formed in each body flows out through mesh pad entrainment separators and then to a single-stage, centrifugal compressor where it is compressed from near-atmospheric pressure to about 150 kPa. The mesh pad entrainment separators were selected to protect the compressor from carryover. A small amount of vapor is bypassed around the compressor to obtain about 5°C of superheat at the compressor inlet. The compressor is driven with a 3000-kW electric motor.

The compressed vapor is condensed on the shell side of the tubes in the heating element, where the full heat of vaporization of 625 kW·hr/1000 kg is recovered for an electrical energy input equivalent to only about 39 kW·hr/1000 kg evaporated. Condensate flows to a tank and then is pumped out of the system through the feed heat exchanger. Noncondensible gases are collected in a vent tube extending the full length of each heating element at the centerline, and flow with the condensate to the condensate tank. The vent vapors are condensed and the noncondensible gases disposed of in the recovery furnace.

The input to the evaporator system is fed at 93°C. Discharges consist of product at 107°C, condensate at 95°C, and vent gases at 111°C.

Provisions are made for boilout of the evaporator system with warm mill water as required. The entrainment separators are washed on the inlet side on a 6-hr cycle during operation. Continuous washing of the entrainment separators on both the inlet and outlet sides occurs during evaporator boilout. The heat exchanger is kept clean by switching the feed and condensate flows.

Controls are provided for automatic system operation. Feed flow to each evaporator body is controlled by liquid level in the vapor bodies. Product concentration is maintained at a preset point by a density controller on the discharge line. Condensate flow is regulated by level control on the condensate tank. Operating pressure is maintained in the evaporator bodies by controlling the vent rate. The desired evaporative capacity is established by manual adjustment of the compressor inlet guide vanes.

Materials in contact with liquor streams are principally 304 stainless steel. Vapor ducts and the shell of the heating element external to the vapor bodies are carbon steel. The compressor casing and inlet nozzle are cast iron with the rotating assembly 17-4/15-5 PH stainless steel.

Operating results

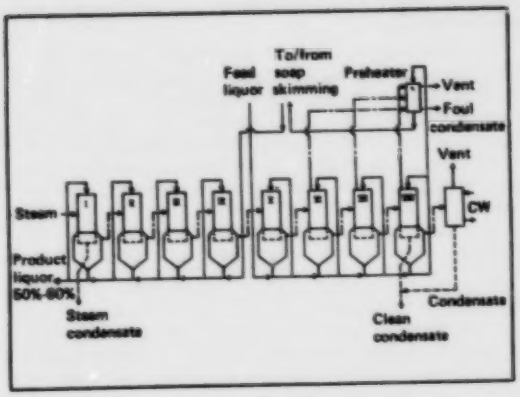
The system is operated with electrical energy. No makeup steam is required at design feed temperatures. Energy input is through the electric motor drives on the vapor compressor, recirculation pumps, feed pump, and condensate pump. The energy requirement is about 39 kW·hr/1000 kg evaporated. Based on \$0.04/kW·hr power, \$11/1000 kg steam, and 64,600 kg/hr average evaporation, the vapor compression evaporator provides a yearly energy savings to the mill of about \$700,000 over what would have been provided by a five-effect alternative operating at a steam economy of four.

The semichemical, vapor compression, falling-film evaporator provides the mill with operating flexibility. The evaporator system can be brought on line or returned to a hot standby condition in a matter of minutes. Once on line, capacity can be changed quickly, depending upon mill requirements, from full load to as much as 50% turndown. This ease of operation has led the mill to use the semichemical evaporator for as much as 3MW of electrical load trimming. Flexibility is seen in the demonstrated ability to handle a semichemical feed, a straight kraft feed or as a blend as the need arises. The ability to produce a product at a constant, predetermined concentration has been of distinct advantage to the mill. The system normally produces a 50% product but has operated in excess of 60% without any problem.

Foaming has occurred when feed and evaporator concentrations were low. Complete control has been achieved by filling the evaporators with heavy kraft liquor on startup and then keeping the semichemical feed sweetened to design levels.

The evaporator shows no evidence of fouling during operation, making a regular boilout cycle unnecessary. Rather, the system is boiled out on an infrequent basis, usually only when it is scheduled down during periods of low liquor supply. This is compared with the existing rising-film units which must be boiled out on a regular basis.

The condensate produced by the evaporator is of high quality, containing less than 1 ppm sodium measured as Na_2O. This condensate is returned to the



4. Multiple-effect, falling-film evaporator.

mill at approximately 95°C for use in the brown-stock washers.

Multiple-effect, falling-film evaporators

Exceptional steam economy can be obtained from falling-film evaporators with eight or more effects. In some cases, it may be practical to replace inefficient evaporators with a new falling-film, multiple-effect system and pay for the installation out of energy savings. The number of effects are selected to match the mill's specific energy balance requirements. Falling-film, multiple-effects have been proven in commercial seawater desalination applications where up to 17 effects are in use.

A typical falling-film, multiple-effect evaporator system is shown in Fig. 4. This schematic is for an energy-efficient, eight-effect system designed to concentrate weak kraft (13–16% solids) to 50–65% solids. Provisions are shown for soap skimming and segregation of foul condensate. Operating advantages include control of product concentration to a preset point by a density controller and turndown to 25% of full load. Steam economies between 7 and 8 are possible with a system of this type.

Conclusion

Falling-film technology permits the use of both multiple-effect and vapor-compression energy-saving evaporator systems. The semichemical, falling-film vapor-compression evaporator at the Crown Zellerbach Bogalusa mill provides significant energy savings. Additional advantages include the ability to handle a variety of liquors, low fouling, ease of operation, positive control of product concentration, and production of a high-quality condensate. Because of the unique energy-saving features, falling-film evaporation is expected to be the principal type of evaporator used at modern pulp mills.

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Plant Energy Conservation:

Energy Conservation By Vapor Compression Evaporation

Vapor compression provides lower energy consumption and operating costs than comparable multi-effect evaporators.

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Vapor compression is a proven means to significantly reduce energy required for evaporation. Vapor compression evaporation has seen rapid growth in North America in the past two decades, especially for pulping liquors, dairy products, and sweeteners, but many engineers are not familiar with its application.

The first vapor compression evaporators using mechanical compressors were built in Europe about one hundred years ago. Since that time, thousands of mechanical vapor compression evaporators have been put into service around the world for desalting seawater and brackish water; several hundred evaporators have been installed in the chemical process industries to concentrate solutions ranging from inorganic chemicals to temperature-sensitive food products. The primary advantage of mechanical vapor compression evaporation over conventional single- or multi-effect arrangements is far lower energy consumption. The rapidly rising prices of oil and other energy sources in the past six years have been an increasing incentive to investigate vapor compression evaporation as a means of reducing energy usage and energy's contribution to product costs.

Operating principles

In a single-effect evaporator, Figure 1, heat released by condensing steam is transferred across a heat exchange surface to an aqueous solution which is boiling at a lower temperature than the condensing steam. The solution absorbs heat and part of the water in the solution vaporizes causing the remaining solution to become richer in solute. The water vapor flows to a barometric or surface condenser where it condenses by releasing its latent heat to cooling water at a lower temperature. The finite temperature differences between the steam, the boiling liquid, and the condenser are the driving forces required so that heat transfer surface areas can be less than infinite. Practically all of the heat removed from the condensing steam (which had been generated initially by burning fuel) is rejected to cooling water and often is dissipated to the environment without being of further use.

The water vapor which flows to the condenser in a single-effect evaporator is at a lower temperature and pressure than the heating steam, but has almost as much enthalpy. Instead of releasing its latent heat to cooling water, the water vapor may be used as heating steam in another evaporator effect operating at a lower temperature and pressure than the first effect.

In a similar manner, additional effects may be added, Figure 2, each effect generating additional vapor which may be used to heat a lower temperature effect. The vapor generated in the lowest temperature effect finally is condensed by releasing its latent heat to cooling water in a condenser. The economy of a single- or multi-effect evaporator may be expressed as the ratio of kilograms of total evaporation to kilograms of heating steam.

The number of effects, and thus the economy, is limited by the total temperature difference (ΔT) between the saturation temperature of the heating steam (or other heat source) and the temperature of the cooling water (or other heat sink). The available temperature difference may also be constrained by temperature sensitivity of the solution to be evaporated. The total temperature difference, less any losses, becomes allocated between effects in proportion to their resistance to heat transfer, the effects being thermal resistances in series.

Heat transfer surface area for each effect is inversely proportional to the net temperature difference available for that effect. Increasing the number of effects reduces the ΔT and evaporation duty per effect which increases the total area of the evaporator in rough proportion to the number of effects.

The temperature difference available to each effect is reduced by boiling point evaluation and by the loss in vapor saturation temperature due to pressure drop. The boiling point elevation (BPE) of a solution is the increase in boiling point of the solution compared to the boiling point of pure water at the same pressure. The boiling point elevation

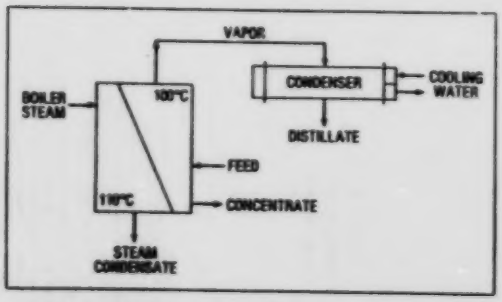

Figure 1. Single-effect evaporator.

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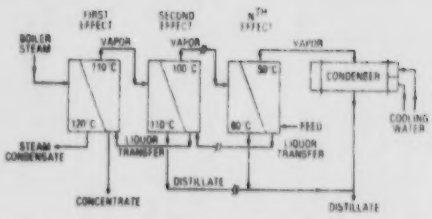


Figure 2. Multi-effect evaporator.

depends on the nature of the solute and increases with increasing solute concentration. In a multi-effect evaporator, the boiling point elevation and vapor pressure drop losses for all the effects must be summed and subtracted from the overall temperature difference between heat source and sink to determine the net driving force available for heat transfer.

A vapor compression evaporator system, Figure 3, is similar to a conventional single-effect evaporator, except the vapor released from the boiling solution is compressed in a mechanical compressor. Compression raises the pressure and saturation temperature of the vapor so that it may be returned to the evaporator steam chest to be used as heating steam. The latent heat of the vapor is used to evaporate more water instead of being rejected to cooling water.

The compressor adds energy to the vapor to raise the saturation temperature of the vapor above the boiling temperature of the solution by whatever net temperature difference is desired. The compressor is not completely efficient, having small losses due to mechanical friction, and larger losses due to nonisentropic compression. The additional energy required because of nonisentropic compression is not lost from the evaporator system, however, and serves to superheat the compressed vapor. The compression energy added to the vapor is of the same magnitude as energy required to raise feed to the boiling point and make up for radiation and venting losses. By exchanging heat between the condensed vapors (distillate) and the product with the feed, it is usually possible to operate with little or no make-up heat in addition to the energy necessary to drive the compressor.

Compressor power is proportional to the increase in saturation temperature (ΔT) produced by the compressor. The evaporator designer must trade off compressor power consumption vs. heat transfer surface area.

Selecting the most economical method

Selecting the lowest cost method of evaporation requires knowledge of the costs of energy, capital, operating labor, and spare parts and maintenance over the life of the evaporator. Energy and capital costs dominate and show the greatest variance among types of evaporators, and can be traded off to optimize the type of evaporator selected.

It is often difficult to assign true costs to energy sources. For example, a single- or multi-effect evaporator may be designed to use a source of low-grade heat which would have no other use, such as hot water, flash steam, or turbine exhaust steam. A vapor compressor might be driven by a steam turbine which acts as a reducing valve to provide low pressure steam already needed elsewhere in a plant. Sometimes a costly piece of equipment such as a boiler or electrical substation has to be installed to provide energy for a new evaporation installation. Each case must be considered individually and most equipment suppliers are willing to help investigate the various options.

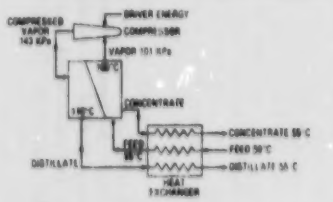


Figure 3. Vapor compression evaporator.

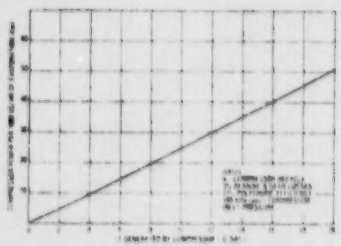


Figure 4. Energy consumption of vapor compression evaporation.

With those considerations in mind, information is provided to compare energy usage and costs of typical vapor compression and multi-effect evaporators. Figure 4 shows compressor power consumption vs. compressor ΔT. Compressor ΔT is the sum of boiling point elevation, vapor saturation temperature losses due to pressure drop, and net ΔT across the evaporator. If the solution boiling point elevation is too high, compressor power consumption will be prohibitively expensive.

Since boiling point elevation increases with solution concentration, it is often economical to use a vapor compression evaporator to remove part of the water from a solution and reach an intermediate concentration which has a moderate boiling point elevation. Final concentration can then be reached in a single- or multi-effect evaporator. Figure 4 does not include driver efficiency, and is based on a 105-kPa (absolute) evaporator shell pressure. Power requirements change slightly at different pressures.

Factors affecting costs

Vapor compression evaporators in process plants are usually powered by electric motors or steam turbines. Figure 5 shows energy costs for evaporation of 1000 kg of water by a motor-driven vapor compression evaporator. Energy consumption of a multi-effect evaporator may be estimated by using an economy of 0.85 per effect. For example, a three-effect evaporator will evaporate $3 \times 0.85 = 2.55$ kg of water for every kg of steam used. Figure 5 shows that in many cases energy costs for a vapor compression evaporator will be far lower than for a multi-effect evaporator.

Capital costs for vapor compression systems are usually higher than for multi-effect systems, because they are usually designed for a lower ΔT across the evaporator than a multi-effect. Thus, the heat transfer surface area must be greater. In addition, the compressor and driver must be purchased. In some cases a multi-effect evaporator system with more than five or six effects is more expensive than a vapor compression system of the same capacity. Equipment costs are affected by such variables as feed properties, materials of construction, available energy supply, and required scope of supply. It is recommended that manufacturers be consulted for cost information for specific cases.

To understand in what cases vapor compression evaporation may be used successfully and economically, it is necessary to examine some of the factors and limitations that influence the design of vapor compression systems.

Equipment selection

Two types of compressors have been used most often in recent years, positive displacement and single-stage centrifugal machines; each has advantages for certain applications.

Positive displacement compressors, such as rotary lobe or screw type, pump a relatively constant volume of vapor against whatever back pressure (resistance to heat transfer) is developed by the evaporator. Rotary lobe compressors are used for compression ratios (the ratio of discharge pressure to inlet pressure) up to about 2.0, the compression ratio being limited by mechanical and thermal distortion of small clearances inside the machine. Sometimes water must be injected into the compressor casing to reduce the superheat of the discharge vapor to limit thermal distortion. The efficiency of positive displacement compressors will be between 60 and 75%.

The maximum inlet capacity of a single-stage rotary lobe compressor is about 11.6 m^3/s, which is equivalent to 35,400 kg/hr of vapor at atmospheric pressure. Since a positive displacement compressor pumps against whatever resistance is developed by the evaporator, discharge pressure

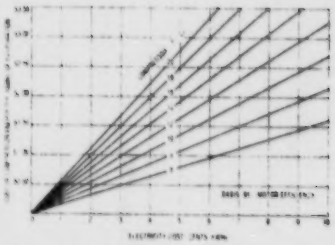


Figure 5. Energy cost for motor-driven vapor compression evaporator.

will increase and evaporation rate will remain relatively constant as the evaporator becomes fouled. Evaporator capacity may be varied when using positive displacement compressors by: 1) using a variable speed driver, 2) using multiple compressors in parallel, or 3) varying evaporator shell pressure to change vapor specific volume.

Centrifugal compressors are commonly used to compress larger volumes of vapor at lower compression ratios than can be handled by positive displacement machines. Centrifugal compressors have inlet capacities ranging from about 0.07 m^3/s to 94 m^3/s, equivalent to 303,000 kg/hr of vapor at atmospheric pressure. The maximum compression ratio of a single-stage centrifugal compressor is about 1.7 for inlet volumes to 94 m^3/s. The compression ratio is limited by rotor dynamics, gearing, and impeller strength considerations.

One manufacturer (Turbonetics) operates successfully at higher speeds by using high-strength impeller materials, integral gearing, and operation above first critical speed to achieve compression ratios up to 2.0 with a maximum inlet capacity of 29 m^3/s. Higher compression ratios may be obtained either by operating two single-stage machines in series or by using a multi-stage compressor. However, using two single-stage compressors in series is much less expen-

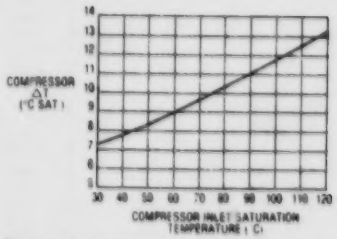


Figure 6. Compressor T vs. inlet saturation temperature for 1.5 compression ratio.

Photo courtesy Allis-Chalmers

Figure 7. Inlet guide vanes.

sive than using a multi-stage compressor. Efficiency of centrifugal compressors is approximately 75 to 80%.

Factors influencing design

Selection of compression ratio is a major design decision, since it requires a trade-off of capital cost and energy consumption. Making the proper decision requires knowledge of energy costs and desired payback period. The decision will also be influenced by feed characteristics, materials of construction, type of evaporator, and hours of operation per year.

Evaporator shell pressure also has a strong influence on capital and operating costs. The most desirable shell pressure is slightly above atmospheric. Vacuum operation is used when it is necessary to keep the solution at a low temperature. Vacuum operation has the following disadvantages:

1) The vapor specific volume is greater, requiring larger compressors and vapor piping.

2) Air leaks into the process, increasing noncondensable loading.

3) A vacuum system with its steam, power and cooling water requirements is necessary to remove noncondensables.

4) Vessels must be constructed for vacuum.

5) Lower solution temperature increases viscosity and reduces heat transfer coefficients.

6) The compressor saturation ΔT decreases with decreasing pressure for a given compression ratio, Figure 6.

7) Many of the disadvantages of operating under vacuum may also be present in single- and multi-effect evaporators, and vapor compression operation under vacuum may be the only means of achieving better than single-effect economy for heat sensitive solutions. Operation at pressures well above atmospheric increases the cost of pressure vessels and the higher solution temperature may increase the rates of fouling and corrosion.

Solution boiling point elevation is a major consideration in selecting compression ratio and heat transfer surface area. If too high, it may make vapor compression evaporation uneconomical due to high compressor power consumption or the need for compressors in series. As mentioned earlier, vapor compression evaporation can often be used for the bulk of evaporation duty on a solution with high boiling point elevation by use as a preconcentrator followed by a single- or multi-effect concentrator. For example, if a vapor compression preconcentrator concentrates kraft pulping liquor from 11 to 40% solids followed by a multi-effect concentrator which does the remaining evaporation to 65% solids, the vapor compression preconcentrator does 87% of the total evaporation duty using far less energy than would a multi-effect evaporator doing the entire job.

System control

The choice of electric motor or steam turbine centrifical compressor driver is determined by the type of energy available in a plant and its cost. Turbine steam rate depends on inlet steam pressure and temperature, exhaust pressure, number of turbine stages, and turbine efficiency. With a turbine driver, evaporation rate may be controlled by varying compressor speed, making sure that turbine and compressor critical speeds do not fall in the evaporation range of interest.

Electric motor and gear drives are less expensive than steam turbines but are not suited for compressor speed control. Instead, evaporator capacity may be controlled by use of inlet guide vanes or a butterfly valve in the inlet to the compressor. The butterfly valve creates a pressure drop and lowers inlet pressure to the compressor. The compressor maintains a constant compression ratio so discharge pressure is also lower. The net ΔT to the evaporator is then lower and evaporation rate decreases.

Inlet guide vanes, which are more expensive than an inlet butterfly valve, operate by causing a prerotation to the vapor entering the impeller. This varies the compressor flow/pressure rise characteristic and provides a compressor power-saving compared to butterfly valve control. Inlet guide vanes are shown in Figure 7.

Compressor speed control and inlet guide vane control have different abilities to accommodate evaporator fouling and part load capacity. This can be seen by examining plots of ΔT vs. flow for the compressor and evaporator together, Figures 8 and 9.

Figure 8 shows use of inlet guide vanes for capacity

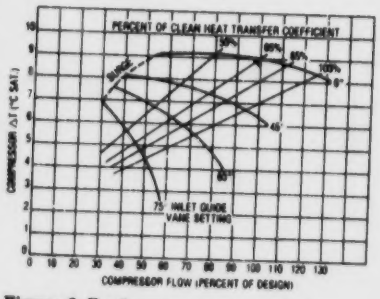


Figure 8. Performance curve of vapor compression evaporator with inlet guide vane control.

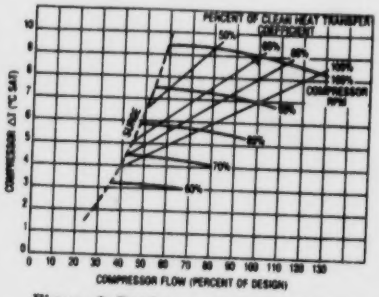


Figure 9. Performance curve of vapor compression evaporator with speed control.

control. The evaporator curves are a series of straight lines showing that capacity varies linearly with ΔT. The lines have different slopes corresponding to different amounts of fouling (percentage of clean heat transfer coefficient). The compressor curves, each for a different inlet guide vane setting, show that compressor ΔT decreases with increasing flow rate. The intersection of the proper evaporator line with the proper compressor curve is the system operating point. The dashed line marking the left end of the compressor curves is the surge line. Compressor operation to the left of the surge line is unstable, with oscillation of inlet flow. If surging becomes violent or prolonged, the compressor will be damaged.

Figure 9 shows use of speed control. Compressor curves are shown at various speeds. It can be seen that inlet guide vane control allows greater capacity turndown and allowance for evaporator fouling before the surge condition is reached.

Reliability and protection

Large centrifugal compressors have proven to be highly reliable in chemical process evaporator installations. Excessive carry-over from the evaporator and improper matching of compressor and evaporator have been the cause of most operational problems.

It is strongly recommended that a single party take system responsibility for engineering the interfaces between the evaporator, compressor, and driver. Failure to do so has caused some expensive problems. The evaporator manufacturer should be provided with samples of representative feed, because of the influence of feed characteristics on heat transfer coefficient. If the solution is one that foals or foams, pilot testing should be undertaken before the evaporator is designed.

Several actions are recommended to maximize compressor reliability:

1. Minimize entrainment in the vapor by using suitable entrainment separators.

2. Recycle a portion of the superheated compressor discharge vapor to the inlet to dry any remaining entrainment. Water droplets can erode the compressor impeller.

3. Monitor solids content in the distillate. Solids in the vapor may build up on the impeller and break off in pieces to cause imbalance.

4. Examine the impeller periodically through a sight glass in the inlet pipe. Check for evidence of deposits or erosion. The impeller can be checked while running by using a strobe light.

5. Install vibration and temperature monitors on compressor, driver, and gear bearings to warn of imbalance or excessive wear. Automatic shutdown alarms will avoid catastrophic failures. Do not allow operators to override alarms without determining the cause of abnormal vibration or temperature.

6. Open compressor casing drains during shutdowns and use a forced air dryer to keep the compressor dry to avoid corrosion.

Good operator training is of great importance as is a program of regular inspection and operating data collection and review.

In conclusion

The main advantage of vapor compression evaporation is significantly lower energy consumption than single- or multi-effect evaporation in most applications. The vapor compressor may be driven by an electric motor, so evaporation can be used (to reduce the volume of a waste stream, for example) in plants or locations having little or no steam supply. Vapor compression is a means of achieving better than multi-effect economy when evaporating solutions which do not permit use of multi-effects because of sensitivity to high temperatures.

Vapor compression evaporators have no final condenser. Thus, they require little or no cooling water. A vapor compression evaporator may require less space than a multi-effect evaporator of the same capacity; in smaller sizes can be packaged and skid-mounted to reduce installation expenses. In some cases, a vapor compression evaporator can have a lower capital cost than a multi-effect evaporator with many effects.

Vapor compression evaporators are being used in new facilities and to provide added capacity or improved efficiency in existing facilities, they are frequently being used with an existing multi-effect evaporator. To determine the lowest cost method of evaporation, each application must be considered separately based on evaluation of feed characteristics, cost and type of energy sources, possible use of existing evaporators, overall plant energy balance, and return on investment criteria. It is recommended that one party take responsibility for engineering the interfaces between evaporator, compressor and driver.

Vapor compression has proven to be a very reliable method of achieving low energy evaporation when properly engineered and operated. ■

A. H. Beesley, application engineer Aqua-Chem, Inc., earned his B.S. degree in mechanical engineering and biomedical engineering and a M. Eng. degree in biomedical engineering at Rensselaer Polytechnic Institute. A registered professional engineer in Wisconsin, his responsibilities with the Process Systems group include design of evaporators, distillation, and stripping systems.

R. D. Blakesmith, who is product manager of process systems at the Water Technologies Div. of Aqua Chem, Inc., earned his undergraduate degree in petroleum refining engineering at the Colorado School of Mines. In his current position, he directs Aqua-Chem's activities in sales and marketing of its evaporator products to the chemical process industry.

Signal Swenson Division

15700 Lathrop Avenue • Harvey, Illinois 60426
Telephone 312 • 331-5500 Telex 25-3274

December 11, 1984

Randol International Ltd.
21578 Mountsfield Drive
Golden, Colorado 80401

Attention: Hans von Michaelis

Reference: Details of Swenson Evaporator Desalination

Gentlemen:

Thank you for your letter of November 19.

Signal Swenson licensee Process Plant (Pty.) Ltd. has supplied to Rustenburg Refiners a metallurgical brine evaporator, which is a mechanical vapor recompression unit on sulfate brine. Swenson expertise lies in the custom design of evaporators, crystallizers and dryers, and we would welcome the opportunity of working on any specific project you may have in mind.

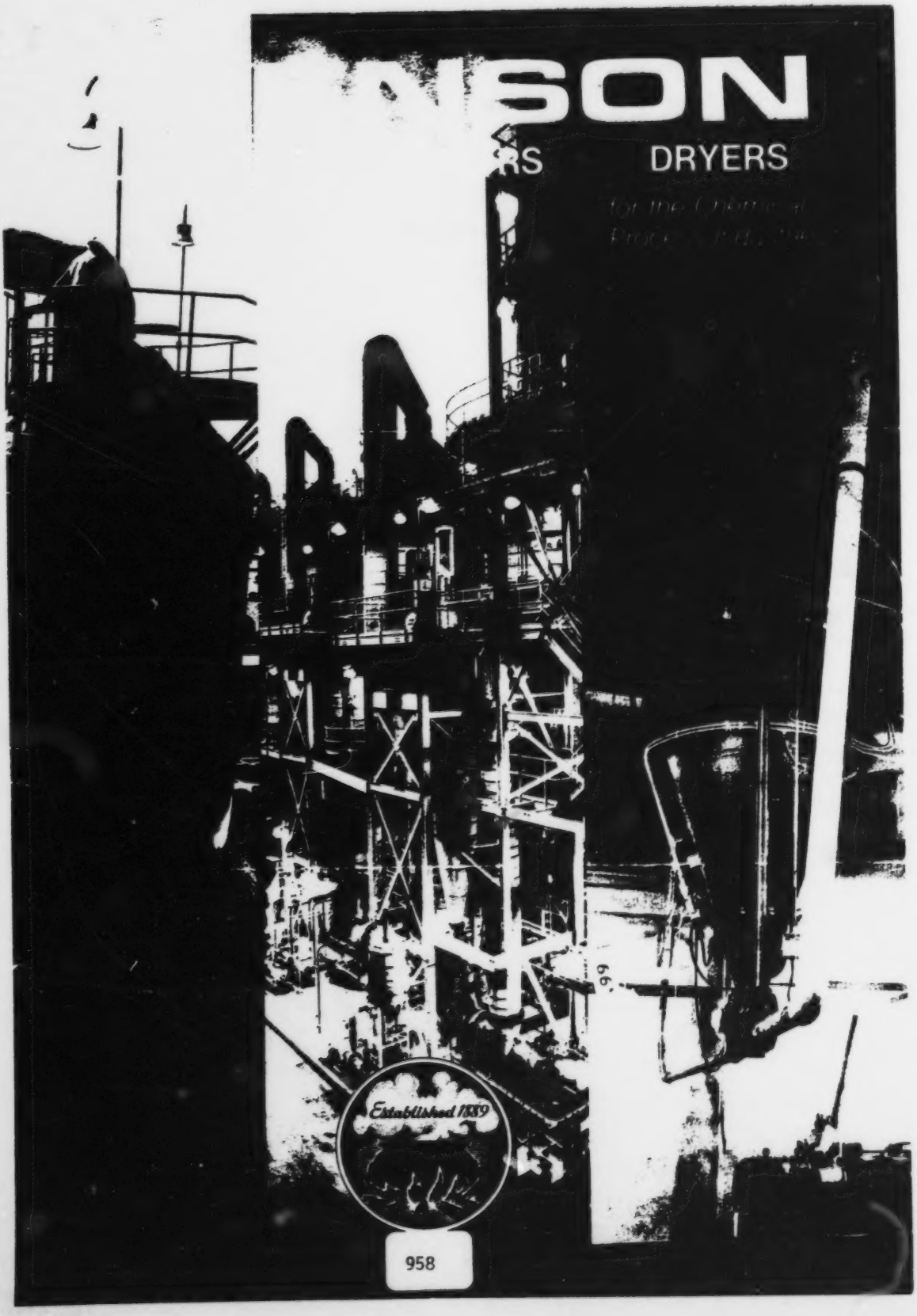
Yours very truly,

SIGNAL SWENSON DIVISION

Joseph V. Rozycki

Joseph V. Rozycki
Director of Marketing

JVR:nd



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SWENSON EXPERTISE

— from testing to completion

Swenson engineering expertise is known throughout the world in the areas of evaporation, crystallization and drying. This reputation began in the 1880's when Magnus Swenson built his first evaporator. And it has grown ever since, as Swenson equipment has performed as specified for the worldwide chemical process industries.

To these process industries, Swenson provides a single, responsible source for testing, engineering, fabricating and installing the complete system.

Analysis of individual customer requirements is made in the Swenson Test Center where products are thoroughly tested to determine the feasibility of concentrating, crystallizing and drying. With the Swenson expertise in these areas and the extensive testing equipment in the research center, the results of these analyses indicate which process is best suited for each individual application.

Once the process has been determined, Swenson engineers the equipment and carries the job through to the completed, operating installation.

Swenson Test Center at Harvey, Illinois

Parallel-flow spray dryer in Test Center

Laboratory technician preparing for crystallization research

Draft tube baffle crystallizer performing tests

SWENSON CRYSTALLIZERS

— for a wide variety of applications

A wide range of general and special purpose crystallizers are designed and manufactured by Swenson for the specific needs of the chemical process industries.

Among the most popular of these are the following types:

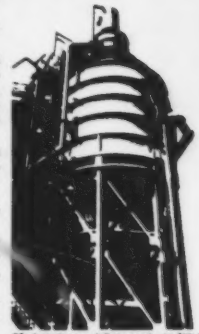
Forced-circulation crystallizers are well suited for applications where high rates of evaporation are required, where there are scaling compounds, where crystallization is achieved in inverted solubility solutions, or where the solution has a relatively high viscosity.

Draft tube baffle crystallizers are preferred where excess nucleation makes it difficult to achieve a crystal size in the range of 10 to 30 mesh. This growth-type crystallizer is noted for long operating cycles and stable crystal size, regardless of change in capacity.

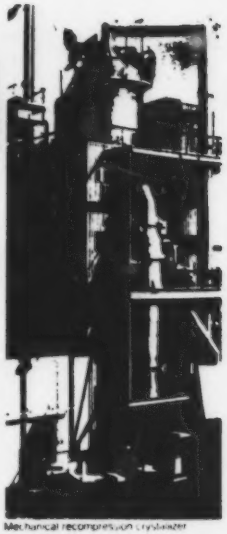
Surface-cooled crystallizers are utilized at temperatures below which it is not economically feasible to use vacuum equipment or with solutions having very high boiling point elevations.

More detailed descriptions of these and other types of crystallizers are included in current Swenson crystallizer literature.

DTB crystallizer used for the production of ammonium sulfate



22' diameter crystallizer produces 600 tons of $(NH_4)_2SO_4$ per day



Mechanical recompression crystallizer

SWENSON EVAPORATORS

— a choice of four types

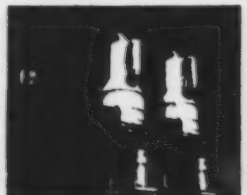
Swenson designs and manufactures four basic types of evaporators. The first two are used for concentrating solutions where no precipitates are formed. The other two are used for salting and scaling applications.

Long-tube vertical (LTV) rising-film evaporators are commonly used for concentrating many non-salting liquors. **Long-tube vertical (LTV) falling-film evaporators** are preferred for liquors requiring evaporation at extremely low ΔT's and for critically heat-sensitive liquors. Both types provide maximum evaporative performance for the least capital investment.

Forced-circulation evaporators, usually with submerged inlets, are the most desirable choice for applications where precipitates are formed during evaporation.

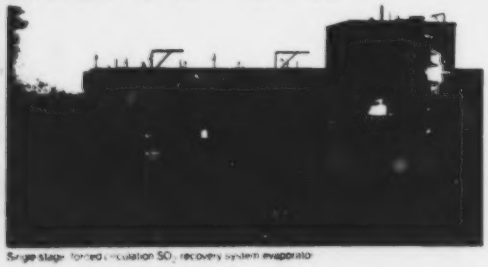
Calandria, or short tube, evaporators can handle both salting and scaling applications as well as those where no precipitates are formed.

For more specific information, send for current Swenson evaporator literature.



Two-stage forced circulation evaporator used to concentrate wet process phosphoric acid

Super phosphoric acid evaporator at Bartow, Florida



Single-stage forced circulation SO_2 recovery system evaporator

SWENSON DRYERS

— designs for every drying need

Several types of dryers are produced by Swenson to meet virtually any drying requirement.

Spray dryers suitable for either parallel, reverse or mixed-flow operation, dry liquids or slurry.

Flash dryers handle a variety of materials, drying the product in a hot gas stream which pneumatically conveys the material through the body of the dryer.

Fluid bed dryers are available for both open and closed cycle operation.

Steam tube dryers are designed to transfer heat indirectly through the tube wall to the material being dried.

Rotary dryers are designed with parallel current or counter-current operation to suit the specific requirement of the material being processed.

A Swenson bulletin, SW-300, describes each of these dryer types in greater detail.

Fluid bed dryer for the production of sodium chlorate

4' x 25' dryer for the production of sodium sulfate

Ammonium sulfate system with 9' x 40' long rotary dryer

SWENSON® EQUIPMENT FOR THE PROCESS INDUSTRIES

CONDENSERS
- Direct Contact Type
- Digester Blow
- Surface Type

COOLERS
- Flash
- Fluidized Bed
- Rotary
- Spray

CRYSTALLIZERS
- Batch
- Decomposition
- Direct Contact Refrigeration
- Draft Tube
- Draft Tube Baffle
- Forced-Circulation
- Multistage Horizontal
- Reaction
- Recompression
- Surface-Cooled
- Teflon Tube

DRYERS: FLUIDIZED BED
- Closed Cycle
- Direct Fired
- Indirect Heated

DRYERS: ROTARY
- Counter-current
- Direct Fired
- Indirect Heated
- Parallel-Flow
- Steam Tube

DRYERS: SPRAY
- Closed Cycle
- Counter-current
- Mixed-Flow
- Parallel-Flow
- Research
- Reverse-Flow

DRYERS: FLASH
- Direct Fired
- Indirect Heated

LABORATORY FACILITIES
- Crystallization
- Evaporation
- Flash Dryers
- Fluidized Bed Dryers—Cooler
- Rotary Dryers
- Spray Dryers
- Bench Scale Tests

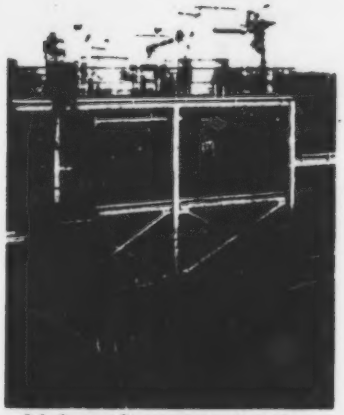
EVAPORATORS
- Calandria
- Elbow Separator
- Forced-Circulation
- Long-Tube Vertical Falling Film
- Long-Tube Vertical Rising Film
- Natural Circulation
- Recompression

FILTERS
- Top Feed Drying-Type Filter

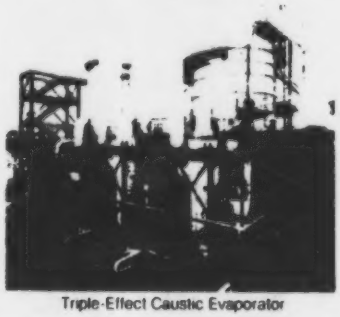
HEAT EXCHANGERS
- Direct Contact
- Shell and Tube

PROCESSES AND PROJECT ENGINEERING
- Ammonium Sulfate Crystallization & Drying
- Caustic Soda Systems
- Continuous Sugar Crystallization
- Fluorine Recovery
- MgO Removal from Phosphoric Acid
- Potash Crystallization & Drying
- Salt Crystallization & Drying
- Soda Ash Calcining, Crystallization & Drying
- Sodium Sulfate Recovery & Drying
- Wet Process Phosphoric Acid
- Others

Rotary Dryer



D.E. Thermal Recompression Crystallizer



Triple-Effect Caustic Evaporator

SWENSON LICENSEES

JORD PROCESS PLANT PTY., LTD.
Crows Nest, N.S.W. Australia

ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES CO., LTD.
Tokyo, Japan

JARAGUA S/A INDUSTRIAS MECANICAS
Sao Paulo, Brazil

LARSEN & TOUBRO, LTD.
Bombay, India

PROCESS PLANT (PTY), LTD.
Sandton, South Africa

SAMSUNG SHIPBUILDING & HEAVY INDUSTRIES CO., LTD.
Seoul, Korea

ROBT. STONE & CO., LTD.
Auckland, New Zealand

SWECOMEX, S.A.
Guadalajara, Jal., Mexico

WELLMAN MECHANICAL ENGINEERING, LTD.
Warley, West Midlands, England

SWENSON S.A.
Paris, France

SWENSON ITALIANA S.R.L.
Milan, Italy

WHITING EQUIPMENT CANADA, INC.
Welland, Ontario, Canada

Signal Swenson Division

15700 Lathrop Avenue, Harvey, IL 60426
Phone: 312 • 331-5500 • Telex 25-3274
UOP Inc.

BATEMAN ENGINEERING LIMITED
P.O. BOX 565, BOKSBURG 1460 • TELEX 8-7880 • TELEPHONE (011) 899-9111

X0668/PJW/CX/cg/84

17th April 1984

Mr Hans von Michaelis
Randol International Ltd
21573 Mountsfield Drive
Golden
COLORADO
80401

Dear Hans

Thank you for your letter of 28 March. We have noted your new address. The IDE process and equipment is handled by one of IDE's own staff - Daniel Hoffman - Israel Desalination Engineering Ltd, P.O. Box 450488, Miami, Florida 33145.

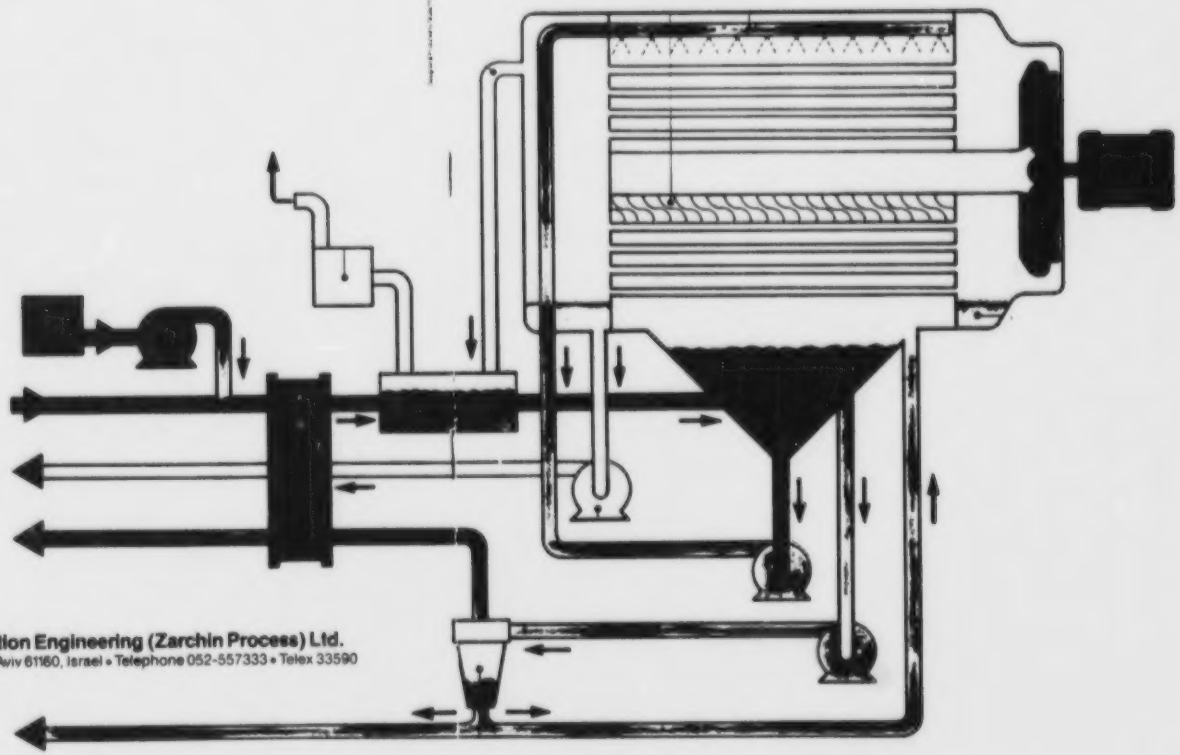
I also enclose a black and white photograph of the Aiprene units which photograph is currently in IDE's new brochure - also enclosed. I hope you find them useful.

Sincerely

P.J. WOOLLAM

c.c. Joe Weinberg

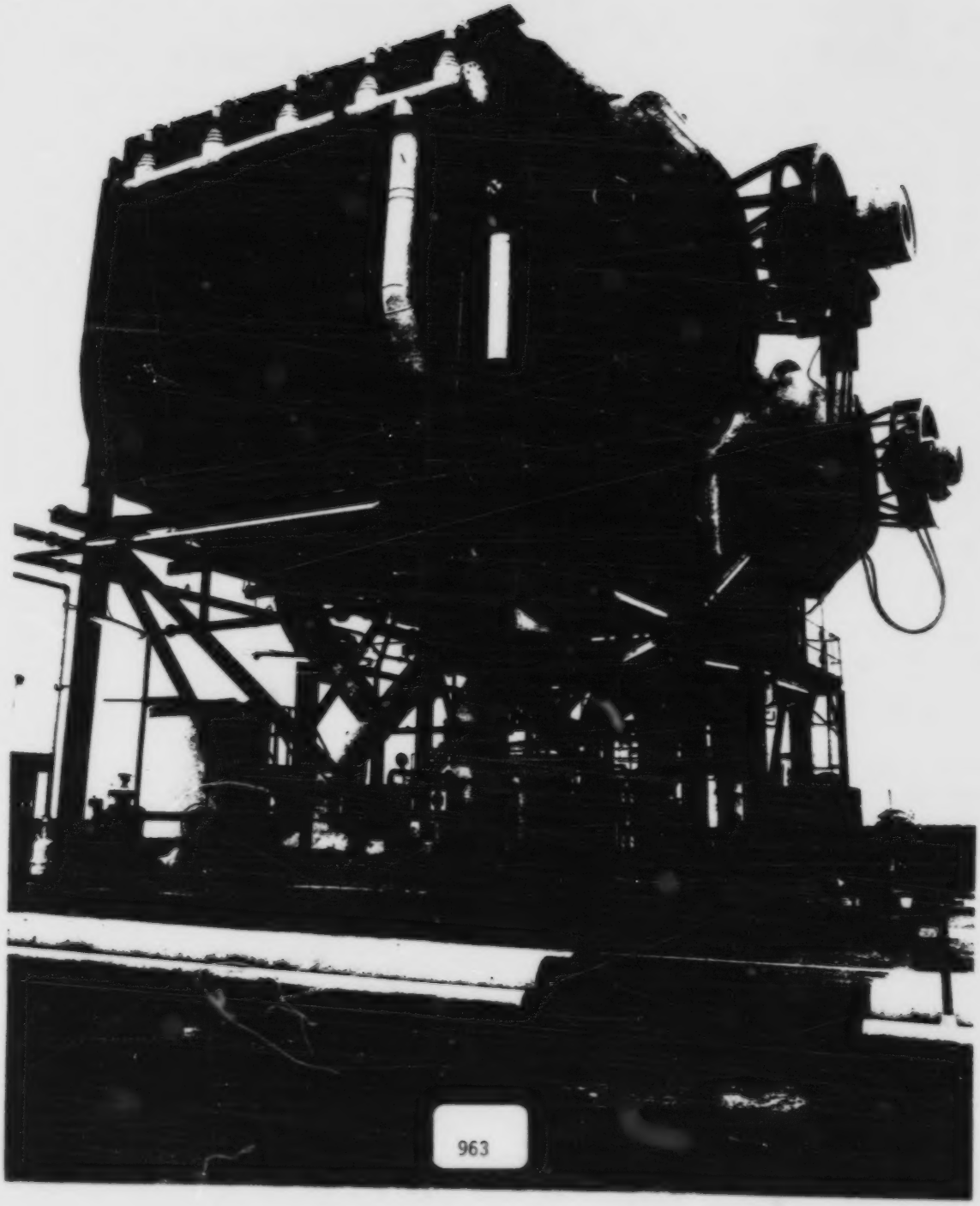
aquaport



Israel Desalination Engineering (Zarchin Process) Ltd.
P.O. Box 18041, Tel-Aviv 61160, Israel • Telephone 052-557333 • Telex 33590

Member of IDE Group

Brine Concentrator



The Aquaport Brine Concentrator

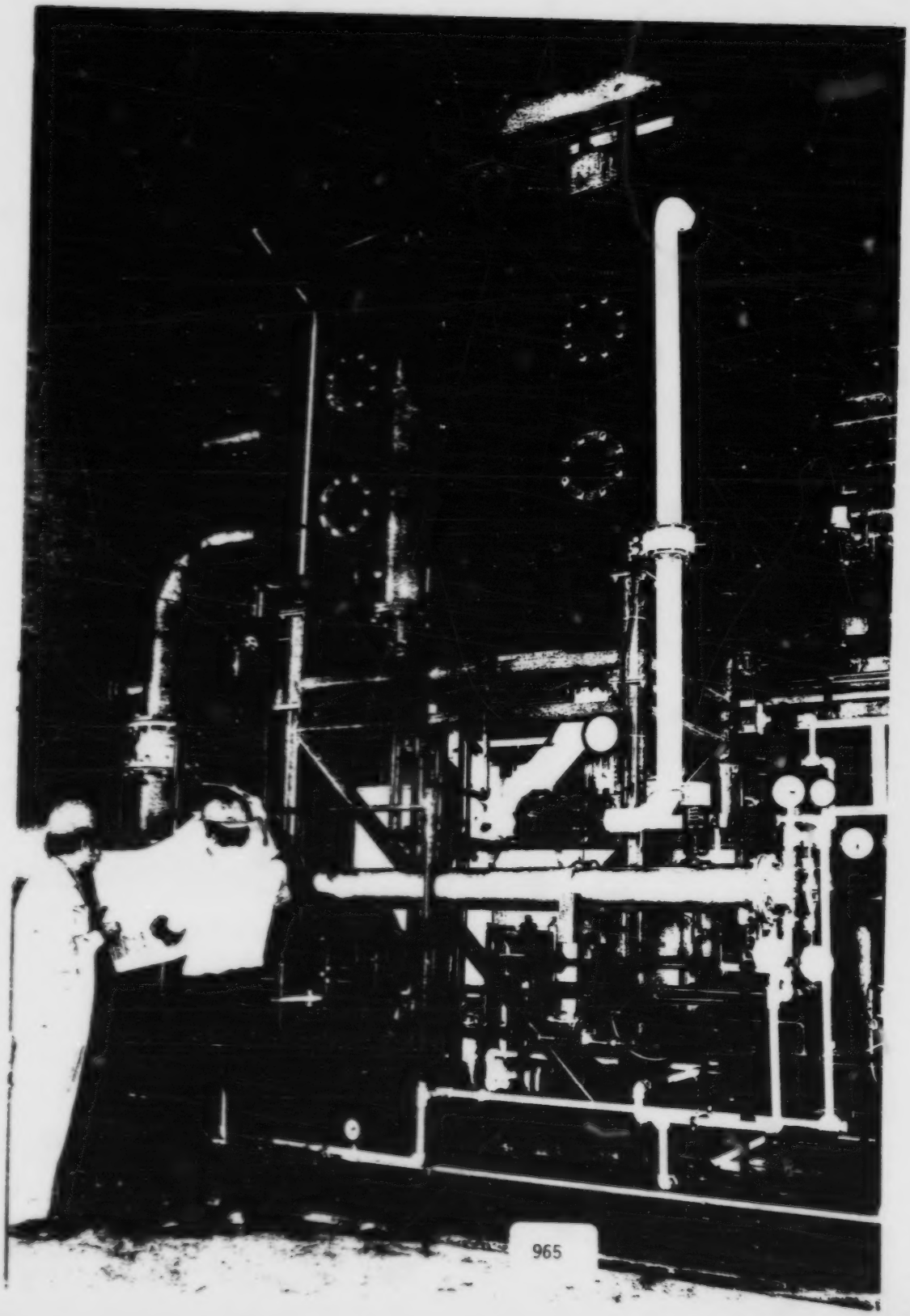
For Separation of Pure Water and Soluble Materials

The Aquaport Brine Concentrator (A.B.C.) is an advanced type of evaporator, designed to remove most of the water from aqueous solutions, by concentrating them well above their saturation limits. Custom-engineered for specific applications, or package-designed for a multitude of others, the performance and efficiency of the A.B.C. are far ahead of conventional evaporators.

Less than two decades ago, the unique **I.D.E.** low-temperature evaporator systems became commercially available. Since then, more than 150 of these exceptionally cost effective systems, ranging in unit capacity from 20 to 20.000 cu.m. per day, have been installed all over the world.

During all these years, Research & Development teams at IDE have been expanding, modifying and testing the Aquaport designs for a variety of industrial applications requiring the concentration of effluents by evaporation. The result of their efforts is the **Aquaport Brine Concentrator** for recovery of high quality water and concentration of solubles for disposal or recuperation.

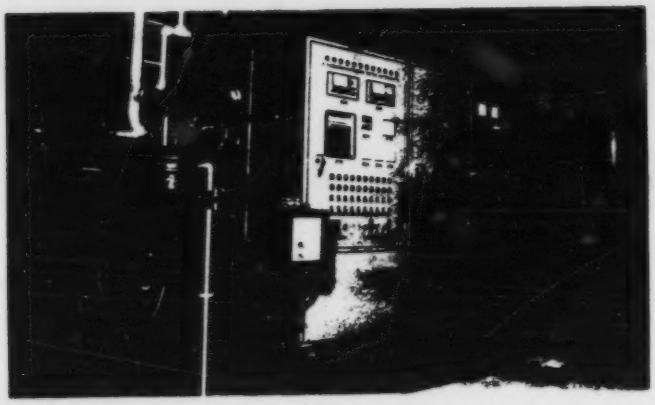
The Aquaport Brine Concentrator provides economical solutions to a variety of material recovery and waste disposal problems, ranging from the treatment and concentration of power plant blow-down to zero discharge of chemical plant effluents, and the retrieval of expensive chemicals from noxious industrial residues.



Suspension is the Solution

Threshold and Seeding Pre-Treatment

The seeding technique developed for the A.B.C. prevents scale formation on heat transfer surfaces. It provides nuclei upon which low-solubility compounds such as calcium carbonate and sulfate, and silica will crystallize or precipitate and remain in suspension rather than adhere to metal surfaces. By encouraging the formation of suspensions, seeding actually raises brine concentration levels far above those prevailing in solutions, even at high temperatures. Moreover, since undissolved solids in suspension do not elevate the boiling point of the liquid in which they are suspended, there is a saving in energy requirements. Additional advantages include elimination of the need for water softeners and acids. This reduces the danger of corrosion and minimizes environmental pollution.



Low Temperature Operation

As demonstrated by many years of trouble free operation, the Aquaport low-temperature evaporation process ensures:

- reduced scale formation
- prevention of hard scale
- virtually no corrosion
- many years of trouble-free service
- high availability (ratio of on-line time to total time)
- widest choice of suitable construction materials for specific applications
- no need for make-up heat
- stable operation
- easy regulation of capacity within a wide range.

High Efficiency, Lower Maintenance Costs

The falling film-horizontal tube arrangement of the A.B.C. is probably the most efficient and cost-effective design available today. It only requires low grade heat sources. Therefore, industrial waste heat can generally provide the system's total energy requirement.

Because of the non-erosive film flow and minimal scale buildup on the tubes, the system is virtually maintenance-free. The relative absence of scale results in unrestricted water flow and the effective scavenging of non-condensible gases (NCG) averts the formation of diffusion barriers.

Another important advantage is that the distillate is never contaminated by brine leakage, since the higher pressure of the vapor on the distilled water side is an effective impediment to brine infiltration.

Low-Cost Energy Source Options

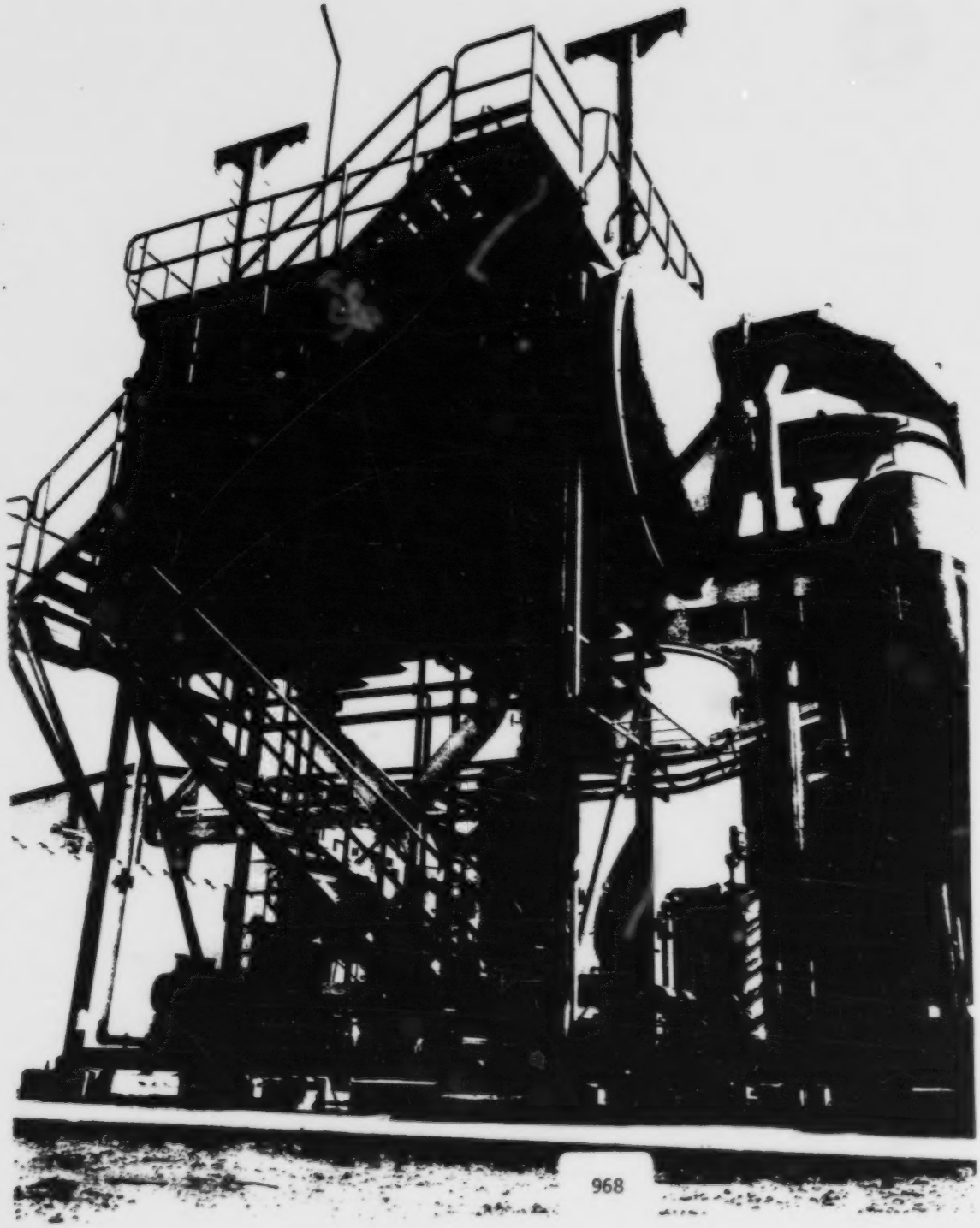
Motive power for the Aquaport Brine Concentrator can be provided by either of two efficient methods:

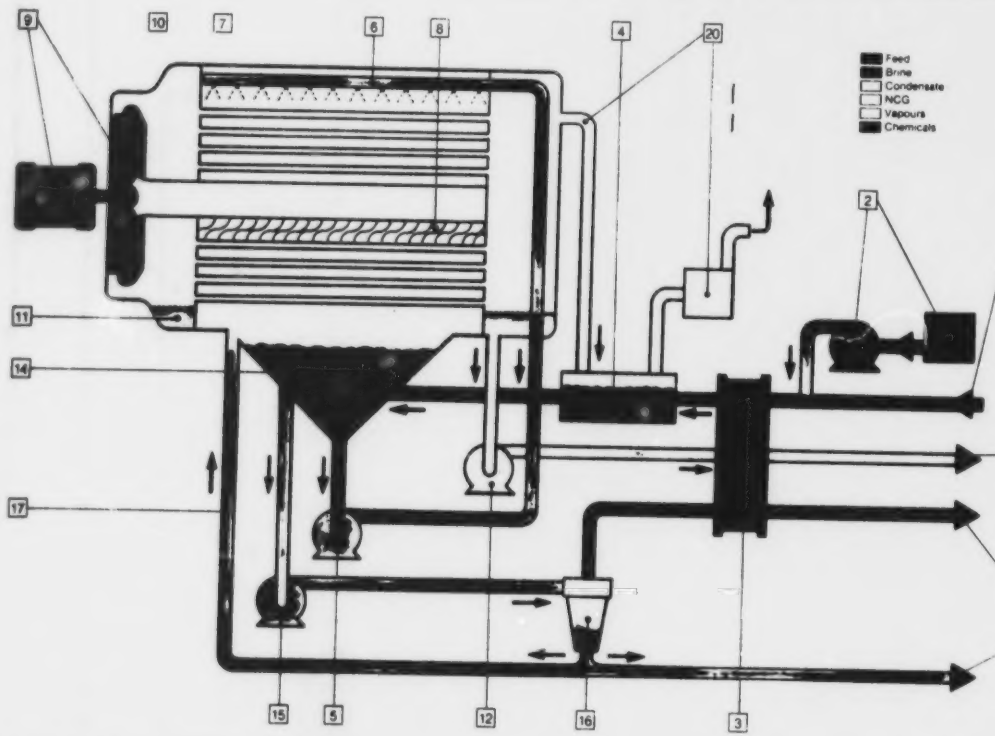
- electrically-driven Vapor Compression utilizing the heat-pump principle
- low-grade heat, especially waste heat, in Multi-Effect Distillation with or without vapor recompression.

Aquaport systems have the industry's highest economy ratios, i.e., the ratio of end product to energy consumption.

Sound Engineering Principles

Sound engineering principles, reliable manufacturing practices and reputable ancillary equipment enhance the quality and reliability of every A.B.C. The many features incorporated in the A.B.C. are illustrated in the following flow diagram (page 8-9).





Horizontal Tubes, Falling Film, Evaporator Condenser

1. Feed from boilers and cooling towers blow downs, dilute process solutions and industrial effluents
2. Chemical Dosing System: chemical additives harmlessly precipitate scale-forming chemicals and keep them suspended in the brine, virtually eliminating scale deposits on heat transfer surfaces
3. Feed Heat Exchanger
4. Air removal auxiliary condenser
5. Recirculation pump
6. Brine spraying system
7. Low cost high durability heat transfer surfaces
8. Droplet separator minimizes brine carrying over into water vapor
9. Vapor compression system
10. Compressed vapor condenses inside the horizontal heat transfer tubes
11. Distillate Chamber
12. Distillate Pump
13. High quality water outlet
14. Saturated brine containing suspended solids collects in chamber for recycle or discharge
15. Brine pump
16. Hydrocyclone separates brine into clear stream and slurry
17. Part of the slurry is returned to the unit to ensure solid concentration
18. Out going clear brine stream
19. Out going concentrated slurry stream
20. NCG removal vacuum system

Solving Problems of Economy and Ecology

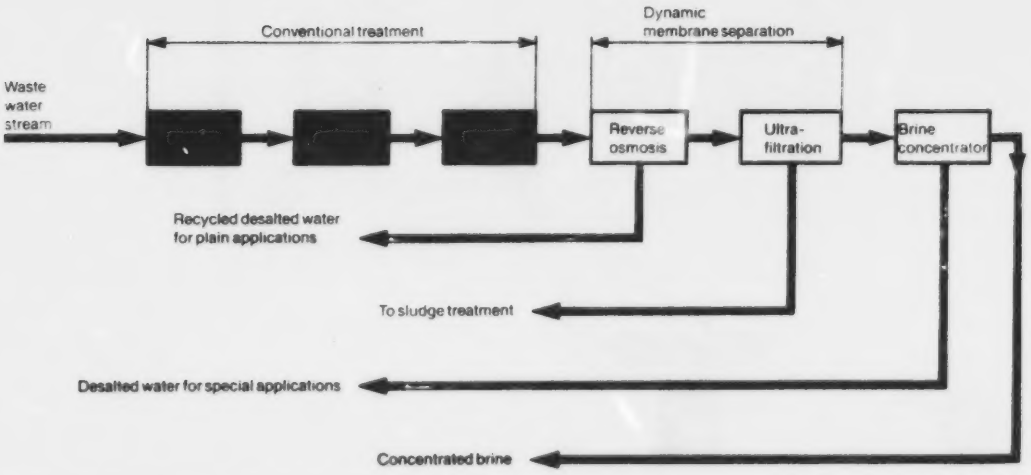
The growing awareness, worldwide, of the damage caused by industrial pollution to the environment has prompted many countries to pass legislation designed to conserve natural resources and reduce air and water pollution. The Aquaport Brine Concentrator offers industry a sound solution to many pollution problems, and an economic way to comply with such legislation.
The following are typical examples of the Aquaport solution to pollution problems.

The Pulp and Paper Industry

Since pulp and paper mills are almost always located alongside streams, their untreated effluents can harm vegetation and wildlife along the watercourse. The Aquaport Brine Concentrator helps this essential industry to achieve zero discharge.
The figure below illustrates typical Aquaport treatment of waste from kraft mills.

Suspended, dissolved and biodegradable matter are removed by conventional primary, secondary and tertiary treatment. After the brine has been concentrated in the A.B.C., it is solidified in a crystallizer. The crystallized waste is disposed of harmlessly.

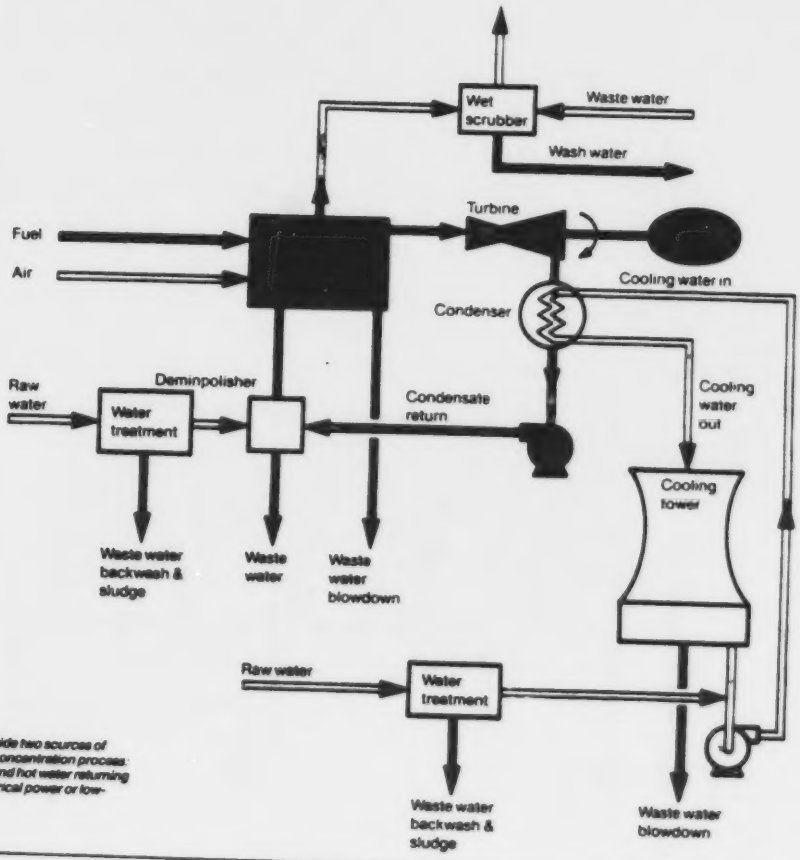
Pulp Mill Effluent Treatment



Electrical Generating Installations

The Aquaport Brine Concentrator can be effectively used for continuous treatment of;

- cooling tower blow-down
- boiler blow-down
- wet scrubber effluents
- ion exchange regeneration wastes



Typical effluents from electric utilities.
As shown above, most power stations provide two sources of waste heat which can be exploited for the concentration process: exhaust heat from turbine back pressure, and hot water returning from the cooling tower. Alternatively, electrical power or low-pressure steam can be used.

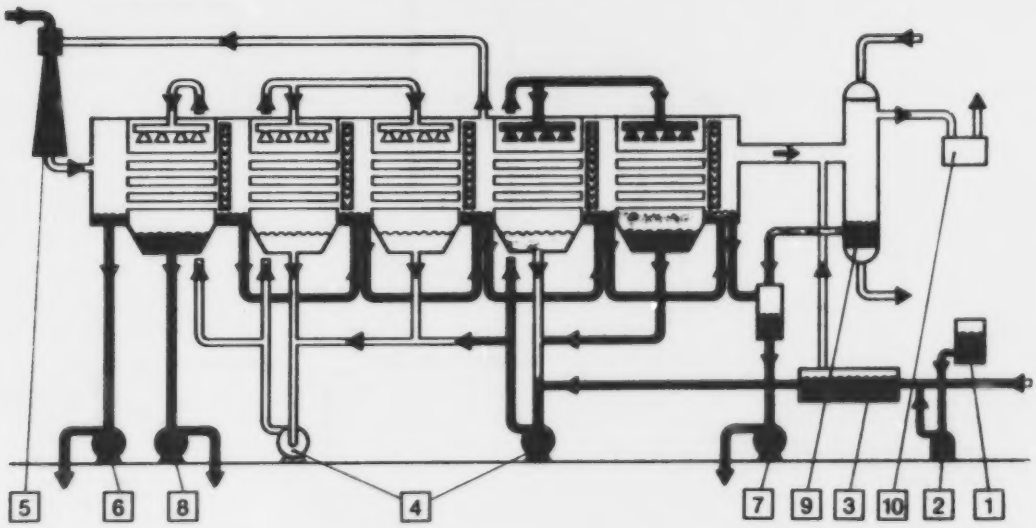
The Water Supply Industry

Many countries in dry sub-tropical and equatorial regions have the possibility of utilizing paleo-aquifers and other underground water sources for domestic and agricultural use. In some areas, geothermal water is a potential source of low-cost energy. Both these types of water sources are characterized by excessive hardness salinity, sulfurous smells and other noxious odors, finely suspended insoluble solids, and other factors which render them unusable in their natural condition.

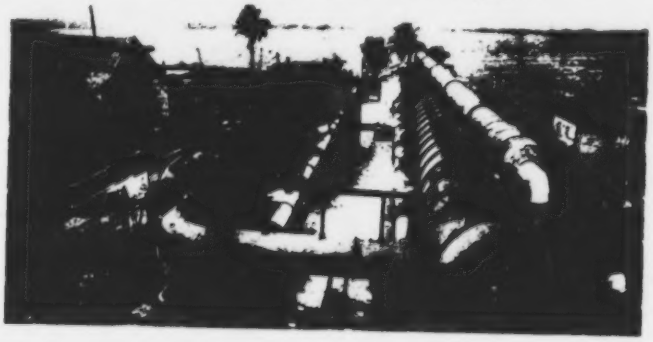
M.E.C. Multi Effect Concentrator Schematic Flow Diagram

- Feed
- Brine
- Vapours
- Distillate
- Air
- Chemicals
- Steam
- Cooling water

1. Pre-treatment tank
2. Dosing pump
3. Deaerator
4. Recirculation pumps
5. Thermocompressor
6. Condensate pump
7. Distilled water pump
8. Concentrate pump
9. Condenser
10. Vacuum system



The Aquaport Brine Concentrator, in either the VC or MED models, provides a greater yield of a product with higher purity than can be obtained with any other treatment system.



Typical Duties:

Example		A Blow-down from Public Utility	B Blow-down from Public Utility	C Mineral Effluent Chemical Complex	D Well Water
Flow	cu.m./day	5,000	5,000	1,000	2,000
pH		7.7	8	5.5-85	8.1
T.D.S.	ppm	1,000	3,000	20,000	36,000
Ca^{++}	ppm	100	500	2,000	700
Mg^{++}	ppm	40	100	200	375
Na^{+}	ppm	190	350	1,500	11,000
K^{+}	ppm	—	—	3,000	—
$NH4^{+}$	ppm	—	—	1,000	—
Total P	ppm as $PO4^{-3}$	10	10	100	—
Silica	ppm as SiO2	20	25	50	55
$HCO3^{-}$	ppm	320	350	300	1,650
$SO4^{--}$	ppm	260	800	10,000	11,850
$Cl1^{-}$	ppm	200	1,000	3,000	9,900
Solution		R.O. + Brine Concentrator	Brine Concentrator	Brine Two stages Concentrator Crystallizer Centrifuge	Brine Concentrator
Output:					
Distilled Water cu.m./day		4,985	4,950	980	1,770
Clear Brine		14	49	—	230
Crystallized Solids		1	1	20	—
Energy Requirements:					
Steam Tons/hr		8.5	16.5	—	—
Power, KWh/cu.m. distillate		3.5	2.5	22	23

Selecting The Right Concentrator

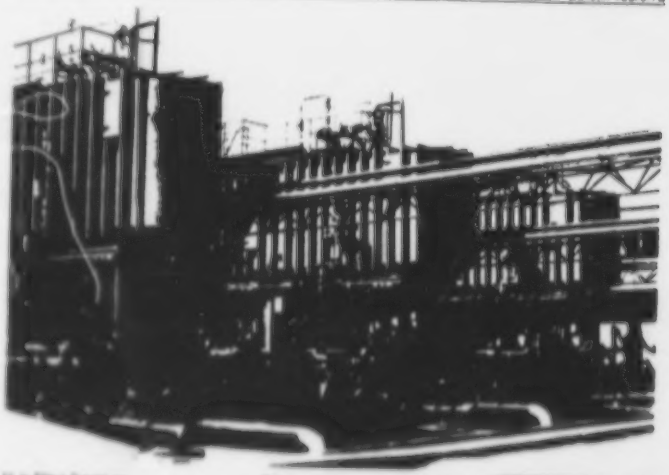
Concentrators can be driven either by a vapour compressor or steam (live or waste). Compressor size limits the vapour compression concentrator to about 3000 ton vapour/day above which multi-effect units must be used. However, when steam is available even small units can use multi-effect configurations. A wide range of concentrators is available to meet specific requirements of any project. The following table is an example for cooling tower blowdown applications.

Capacity Tons of Vapours/	Brine Concentration T.S.	Driving System	Number of Effects	Specific Consumption KW hr. per ton vapours	Specific Consumption Kg. Fuel No. 6 per ton vapours
100-300	10%	Compressor	1	10-18	—
	20%	Compressor	2	16-24	—
	30%	Compressor	2	18-26	—
300-3000	10%	Compressor	1-3	10-16	—
	20%	Compressor	2-4	14-24	—
	30%	Compressor	2-4	16-24	—
1000-6000	10%	Steam	8-14	4	6-7
	20%	Steam	6-12	3.5	7-8
	30%	Steam	4-10	3	8-9

The I.D.E. Approach From F.O.B. to Turnkey

- to solve your effluent disposal problems
- to recover valuable chemicals from aqueous solutions
- to optimize your process economics
- to produce pure distilled water for any need I.D.E. will offer you a broad range of services.

I.D.E. can help you identify your problem, suggest the optimal solution and implement it, undertaking total project responsibility for performance and reliability. From laboratory testing to power source optimization, from F.O.B. supply of components to complete turnkey project implementation (including long-term operation and service insurance if desired) – I.D.E. will solve your problem efficiently, flexibly and economically.



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Bulletin 108-9.78
Press Release - September 15 1978

High performance, low temperature IDE Multi-Effect Distillation Plants win in Virgin Islands 3.75 MGD competition

After intense competition with the world's desalination giants, Israel Desalination Engineering Ltd. has been selected to provide three 1.25 million gallon per day sea water desalination plants to the U.S. Virgin Island Water and Power Authority (VIWAPA). Cost effectiveness combined with proven plant performance and reliability gave IDE the edge over others for the plants to be installed next to existing power and desalination stations, two on St. Thomas and one on St. Croix Islands.

The plants are based on IDE's unique Low Temperature, Horizontal-Tube, Falling Film, Aluminum Alloy, Multi-Effect Distillation process which is ideally suited for dual purpose applications requiring steam at only 6 psia, i.e. low grade back pressure steam that has been almost completely expanded in the turbine. For VIWAPA's project, however, 40 psia steam has been made available from existing turbine extraction points. The plants will utilize this steam in a thermo compression cycle to achieve an Economy Ratio in excess of 10:1.

In the future, VIWAPA will consider the feasibility of converting its 35 MW turbine (St. Thomas) to low back pressure operation, thereby making available sufficient steam to produce 6 million GPD of desalinated water with an overall loss of less than 6 MW in power output. In this manner, the energy cost chargeable to the water would be equivalent to only 24 kwh/1000 U.S. gallons.

The IDE supplied plants will operate with a top brine temperature of only 165°F. Harmless polyphosphate scale inhibitors will be used for feed pretreatment in contrast to corrosive sulfuric acid required in older type (MSF) plants.

The IDE multi-effect desalination aluminum alloy design is embodied in the 1 million gallon per day plant in operation in Eilat, Israel since February 1974. The plant, operated by the Mekorot Water Company as a primary water supply to the city of Eilat, has had an on-line demand availability of over 90% since start of commercial operation in May 1974. This single purpose plant has a demonstrated Economy Ratio of over 11:1 with a top brine temperature of only 160°F and simple polyphosphate feed pretreatment.

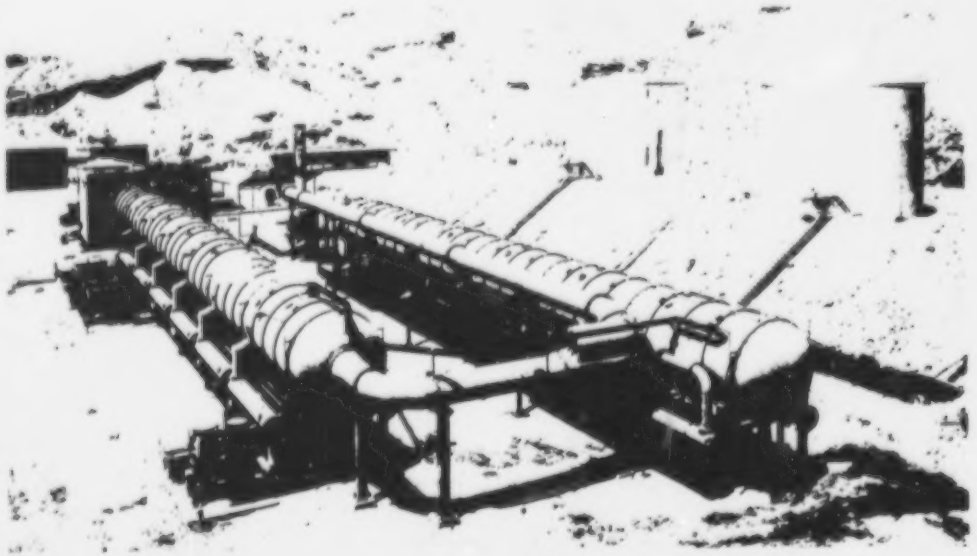
Additionally, IDE commissioned in January 1977 five similar 500,000 gpd plants on Kish Island in the Persian Gulf. As a result of performance of these plants exceeding specifications, IDE has recently received an order for a sixth unit and a contract to supply five more similar plants for another Persian Gulf installation.

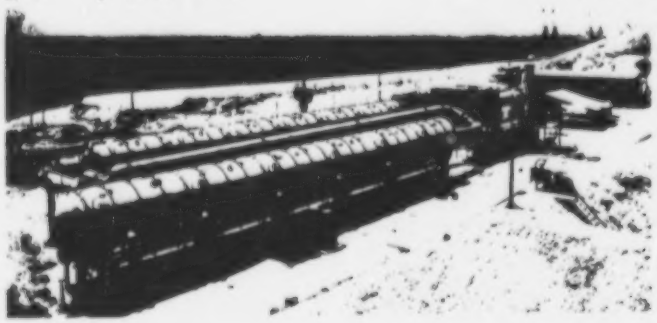
IDE's First In Caribbean, But No Newcomer to Desalination

Althought the Virgin Island contract represents its first project in the Caribbean, IDE is no newcomer to the field of sea water desalination. As a fully owned government company, Israel Desalination Engineering was commissioned in 1961 to find solutions to the long term national water problem. Initial development of freezing processes gave way to development of vapour compression and multi-effect distillation processes operating at low temperatures. Product commercialization on the international market was undertaken in 1967 with the installation of the first of over 100 AQUAPORT vapour compression distillation plants sold to date.

Simultaneously, a succession of MED pilot plants were built leading to the sale and commissioning in 1974 of the first commercial 1 million GPD plant in Eilat and more recently to eleven 500,000 GPD plants in the Persian Gulf area.

Now, IDE is designing and will soon initiate construction of a 10 million GPD dual purpose desalination plant in Ashdod as part of the joint US-Israel governments' program for developing economic, large scale desalination technology. The plant will operate on 5.5 psia back pressure steam from an existing 50 MW power plant and will be the prototype module for the next generation of MED plants up to 100 million GPD to be coupled to conventional and nuclear power plants.





Multi-Effect Distillation
Sea Water Desalination Plant
(1 MGD), Eilat, Israel

the

aquaport®

vapor compression distillation at ambient temperatures

Israel Desalination Engineering (Zarchin Process) Ltd., IDE, is recognized internationally as a leader in the development, engineering and production of advanced desalination systems.

Relying on a nucleus of highly skilled scientists, engineers and technicians, most of whom have been with the company since its establishment in 1958, IDE has maintained steadily one of the highest sales growth rates in the industry.

Behind this remarkable growth lies the fact that all IDE products are unique, based on original, self-developed processes and designs, with distinct advantages and features.

To the cost conscious operator or the profit minded businessman involved in the production of desalinated water these features mean a substantial and real saving of money, lower annual costs, larger profit margins.

The professional engineer will recognize and appreciate the beauty of a simple yet sophisticated design which assures long term trouble-free operation and superior performance.

The Aquaport Ambient Temperature Vapor Compression distillation plants described in this brochure represent IDE's successful solution for small and medium capacity desalination applications.

They are clearly in a class by themselves.

® registered trade name

BATEMAN ENGINEERING LTD.

Bringing Water Cost Down

The success of the Aquaports is due to two basic features which distinguish them from other distillation plants.

Ambient temperature operation = dependability

The Aquaports operate at unparalleled low temperatures, 30 to 55°C (85 to 130°F), reducing scaling and corrosion to a minimum. Scaling and corrosion are behind 90 percent of all problems plaguing conventional high temperature distillation plants, which operate at 90 to 120°C (200 to 250°F).

The Aquaports' low temperature operation is the key to long term trouble-free service and to reduction of maintenance and labor costs to negligible proportions. This is particularly critical in small and moderate sized plants where such costs must be charged to relatively low outputs.

Low energy consumption = economy

Energy contributes today 60 to 80 percent of desalinated water cost.

The standard Aquaports' specific energy consumption is only 18.5 kwh/ton (70 kwh/1000 US gal.). This is equivalent to 4 kg fuel per ton (33 lbs/1000 gal) product, where power is derived from an adjoining diesel generator set, or to an Economy Ratio (ER) of 18:1 in steam operated distillation plants. These plants, however are manufactured with ERs of only 4:1 to 8:1 in the capacity range covered by the Aquaports, requiring as much as 10 to 20 kg of fuel per ton product.

With the Low Energy LE series of Aquaports, which require only 12 to 14 kwh/ton (45 to 53 kwh/1000 gal.), this wide margin of economy is increased even further. The LE units' energy consumptions are equivalent to ERs of 30 to 35:1 and to a specific fuel consumption of 2.5 kg fuel/ton product (21 lbs/1000 gal), namely a water to fuel ratio of 400:1.

Other Features

High Quality Water. Normal product purity is better than 10 ppm TDS. Less than 2 ppm TDS possible if required.

Simplicity. Easy to operate and control. Fully automatic, requiring minimum attention. Safety shutdown and alarm system protects unit during unattended operation. Easy personnel training. Reduced labor costs.

Flexibility. Quick startup. Little time lost for heating up. Immediate production. Convenient for intermittent operation. Capacity regulated by simple controller adjustment to meet varying demand rates. Relaxes storage requirements. Allows supply of power to other consumers during peak load hours.

Reliability. Experienced engineering, rugged construction, quality fabrication and proven standard equipment. Each unit is factory assembled and tested to satisfaction before shipment.

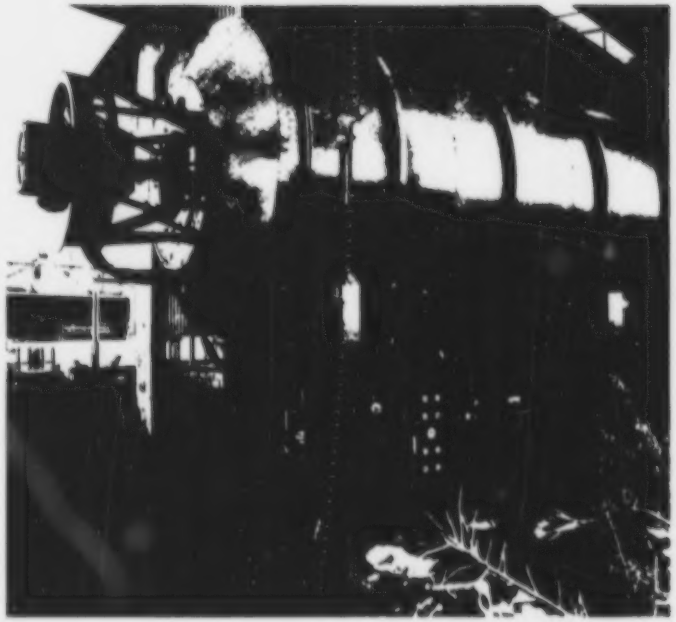
Safety. Safe to operate and maintain. No acids, caustics, fire hazardous fuels, hot surfaces or high pressures.

Environmentally Clean. Neat, functional and colorful design. Requires electrical or mechanical power only. No steam plant. No smoke stack. No fumes. No pollution.

Easy Installation. Great savings in erection time and costs. Units are compact and skid mounted. Minimal site preparation and civil works. Few and simple connections. Small sea-water intake system.

Guarantee. Full one year guarantee for all parts and components.

Service. World-wide sales and service organizations.



Typical operating cost breakdown

	Standard AQ-590 Model	Low Energy LE-590 Model
Energy @ 2.5 US¢/kwh	46 US¢/ton	32 US¢/ton
Labor @ 3 US$/man-hr	3	3
Consumables (spare parts and chemicals)	6	6
Total operating costs	55 US¢/ton (2.00 US$/1000 gal)	41 US¢/ton (1.55 US$/1000 gal)

The Ambient Temperature Vapor Compression Distillation Process

Inherently simple and efficient

Vapor Compression Distillation is inherently the most efficient distillation process. It achieves its high efficiency in a simple, single-effect fashion, without the need for a complex design based on a large number of stages or effects, by application of the "heat pump" principle to continuously recycle and keep within the system the latent heat exchanged in the evaporation-condensation process. In this scheme the heat required to evaporate part of the processed feed, which flows on one side of a heat transfer surface, is supplied through the simultaneous condensation of the distillate-producing vapor on the other side of the surface.

The driving force for this heat transfer, plus the energy required to separate the solution and overcome dynamic pressure drop losses and other irreversibilities are provided through the work of a compressor, which acts as the "heat pump", pumping the vapor generated from the solution to the higher pressure-enthalpy level required on the condensing side.

This work, plus a fraction required for liquid pumping, is the only energy consumed by the process. No additional heat is required.

In the Aqueports even this low energy requirement has been reduced to a minimum by adopting a highly efficient falling film, horizontal tube evaporator, which incorporates large heat transfer areas and reduces parasitic pressure drop losses by integrating the compressor within the evaporator. Due to this evaporator design the pumping head of the compressor is equivalent to a total ΔT of only 4°C (7°F) in the standard models and as low as 2.5°C (5°F) in the special LE (Low Energy) models.

The Aqueports are unique also in that the distillation step is carried out at close to ambient temperatures. The ability to operate at such low temperatures is due to the exclusive development by IDE of a novel lightweight, high volumetric flow compressor which is capable of handling the large rarefied volumes typical of low-temperature, low-pressure steam.

Features Due to the Vapor Compression Process

- Low energy requirements, due to "heat pump" principle.
- Simplicity. Plant is a single effect distiller, requiring only a tube heat, a compressor, a feed heat exchanger and pumps.
- Easy operation. Few controllers required to achieve complete automation, allowing long term unattended operation.
- Easy regulation of capacity through one controller adjustment. Power consumption directly proportional to production rate.
- Small saline water supply system, since no cooling water is required. Feed rate is only 2 to 2.5 times product rate. Simple shallow well by sea is sufficient, eliminating expensive civil engineering for jetties, trash racks and filters. Saving in feed pumping power consumption.

Features due to Low Temperature Operation

- Minimum scaling rates. Long term operation (up to 2 years) between scale cleanings. Low consumption of scale removing chemicals.
- Allows use of low cost non-corrosive polyphosphate for feed pretreatment. No acid feed pretreatment required.
- Scale is mostly soft acid-soluble carbonate scale. Operating conditions far removed from saturation curves of problematic calcium sulphate and magnesium hydroxide scales. Descaling is a simple procedure of mild acid recirculation using the plant's own recirculation pump.
- Minimal corrosion rates. Extends lifetimes of all plant materials. Allows use of non exotic materials and epoxy coatings.
- Small feed heat exchangers, since feed must be preheated by only 10 to 30°C (18 to 54°F) rather than by 80 to 100°C (145 to 180°F), as in high temperature vapor compression plants.
- Allows use of corrosion proof, smooth PVC pipes, valves and accessories which would lose rigidity at temperatures above 80°C (180°F).
- Eliminates need for cumbersome and costly plant insulation.
- Eliminates the need for makeup heat to maintain thermal balance.
- Allows quick startups. Little time need be wasted for heating to process temperature.

Features due to Falling Film, Horizontal Tube, Evaporator-Condenser

- Single effect distillation. Simultaneous transfer of latent heat on both sides of heat transfer surface at a constant temperature difference. No loss of effective thermal driving force due to sensible heating of liquid.
- Thin film flow avoids static head suppression of the driving force for evaporation.
- Dominant liquid to liquid heat transfer resistance reduced through film thickness control rather than through turbulent high velocity flow as in forced circulation systems.
- Low liquid flow rates. Small pumping energy requirement.
- Gentle non-erosive film type flow increases material lifetime.
- Non-pressurized brine flow. Vapor and product side pressures always higher than brine side pressures. No contamination of product through brine leakage possible even in case of tube perforation.
- Efficient scavenging of NCG reduces its partial pressure and avoids creation of diffusion barriers.
- Integral compressor design shortens vapor flow path and eliminates cross-section restrictions and unnecessary pressure drops through external piping and valves.
- Large vapor release surfaces. No violent flashing. Reduces brine carryover and demister requirements. Assures high quality product. Lower susceptibility to foaming. No need for anti-foaming additives.

Principles of Operation

The incoming saline feed is pretreated with a minute dose of scale inhibiting additive and passed through a heat exchanger, where the heat in the discharged brine and product streams is recuperated.

This heat is generated in the unit itself, and is a converted form of the mechanical energy supplied to compress and circulate the fluids. Consequently, no separate makeup heat source is needed.

By simple preset of an automatic controller, which regulates heat-exchanger flows, the unit's operating temperature, and hence production rate, may be easily adjusted. These temperatures are always below 55°C (130°F) to minimize scaling and corrosion.

The feed is mixed with recirculated brine and sprayed on the outside of a bundle of horizontal heat transfer tubes, at a rate just sufficient to create thin, continuous liquid films.

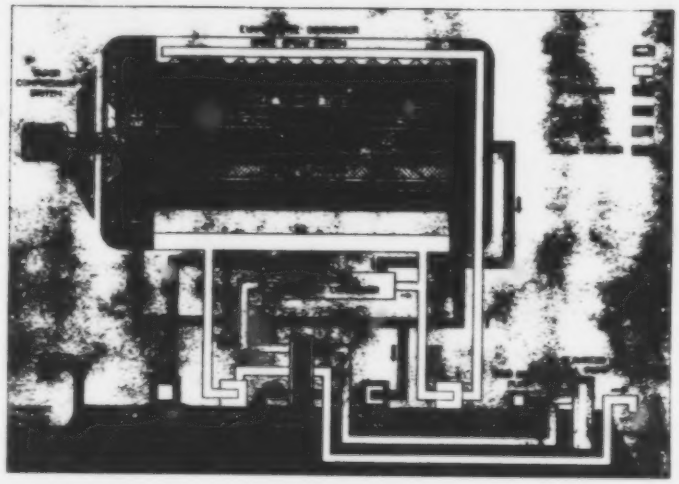
A unique centrifugal compressor provides, through its suction, a pressure lower than the equilibrium pressure of the brine. As a result, part of the brine flashes into vapor.

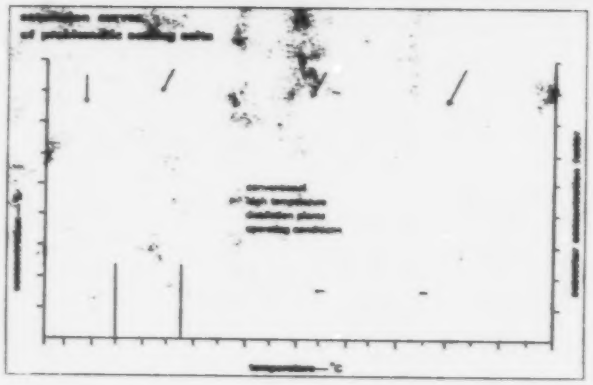
After passing through a demister, to remove droplet carryover, the vapor is compressed and discharged to the inside of the tubes. There it condenses, supplying the latent heat required for the flashing process.

The condensate, which is the salt-free product, and the rejected brine are pumped out, after exchanging heat with the feed.

Non-condensible gases are first concentrated in an auxiliary condenser and then exhausted by means of a rotary vacuum pump, which also serves to create the initial vacuum.

Flow diagram





Falling film evaporative condenser consisting of:

Main vessel: Welded pressure vessel, designed to British and A S M E Standards. Mild steel, coated with six layers of epoxy-resin, with pinhole detection quality control to ensure effective corrosion resistance

Heat transfer tubes: Of special corrosion resistant aluminum alloy suitable for sea water applications

Droplet separator: Stainless-steel wiremesh type demister for efficient elimination of brine carryover, ensuring high product purity with a negligible vapor pressure drop

Brino spray system: Efficient non-clogging, corrosion-proof ebonite spray nozzles

Pumps: Centrifugal low suction head back pulled type to A S M E standards for easy maintenance. Double mechanical seals. Materials and characteristics specified to ensure trouble-free high-efficiency service. Stainless steel casings, impellers and shafts for brine and sea water service

Valves: Diaphragm type to ensure max tightness. Mouth PVC with neoprene diaphragms, totally immune to corrosion

Piping: Mouth PVC clean and smooth, totally immune to corrosion

Feed heat exchangers: Double-pass plate type for efficiency at low cost. Compact and easy to service. Titanium plates. Nitrile rubber gaskets

Air removal condenser: Direct contact type for efficient air extraction of non-condensable gases and concentrate feed deaeration

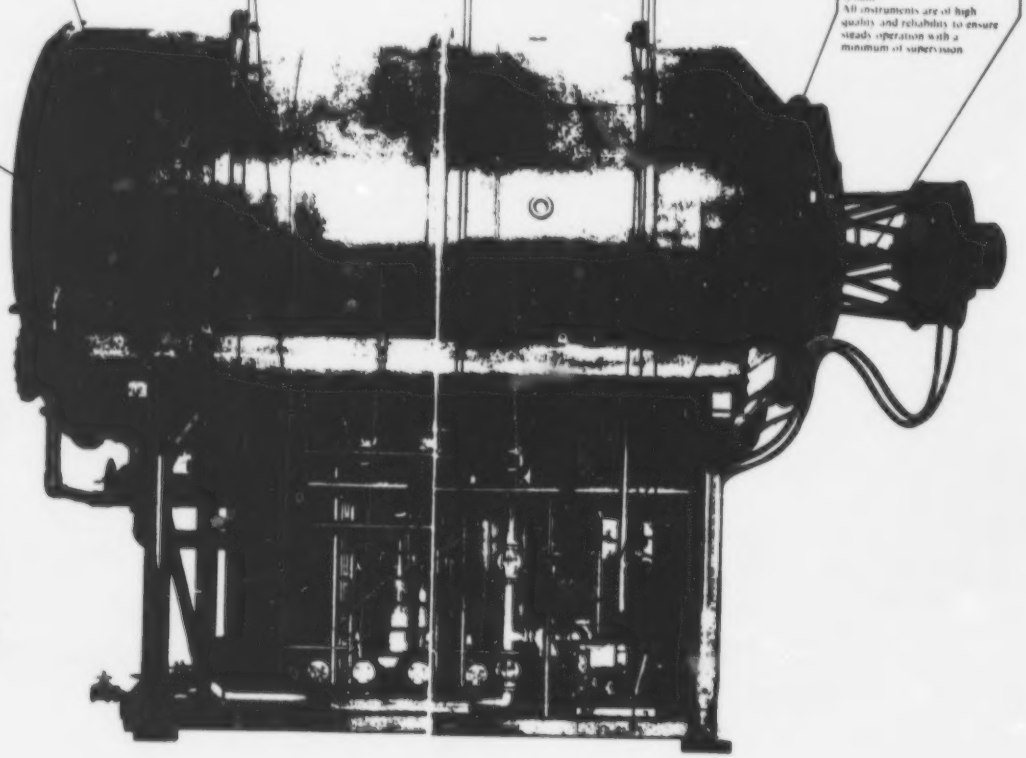
Pump motors: Totally enclosed fan cooled, to ensure trouble-free outdoor operation

Skid base: A steel frame uniting the main vessel support structure, all pumps, motors, piping and the central instrumentation controls and electricals cabinet

Vacuum pump: High performance rotary piston type

Central controls, instrumentation and electricals panel: Drip-proof cabinet. Easily accessible. Containing complete electrical system, push-button motor starters and controls. A central display of all instruments and controls allows easy supervision of plant operation. Instrumentation and controls connected to an integrated sequence sensitive, safety alarm and shutdown system. All instruments are of high quality and reliability to ensure steady operation with a minimum of supervision

Compression system: Patented lightweight, radial blade centrifugal compressor. Rotor of special low density and fatigue-resistant materials. Stainless-steel shaft. Force-lubricated top quality bearings. Mechanical seal. Simple direct-drive power transmission



The Plant - A Compact and Elegant Design

proven in over 10 years of field operation refined through experience with over 100 units

The Mobile Series up to 100 tons/day

Instant water on a temporary basis

The Mobile Series answers the need for portable desalination plants capable of rapid deployment and immediate production.

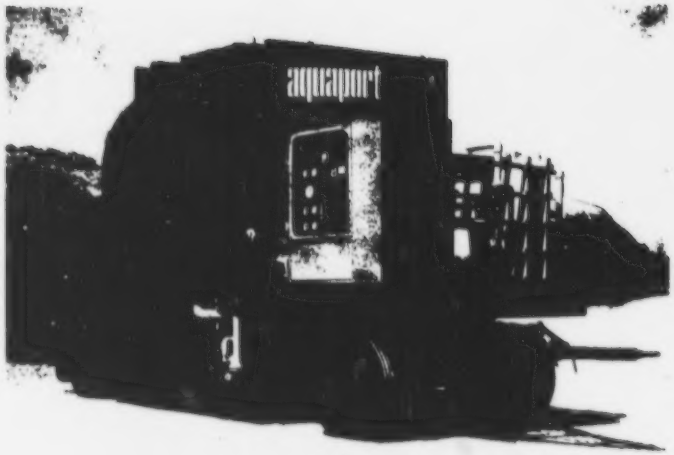
The plants are supplied with an auxiliary feed intake system, complete with feed pump, the filter end of which can be inserted into any brackish or polluted water hole or submerged in the sea. Standard flexible feed line length is 15m., but longer lines may be supplied upon request.

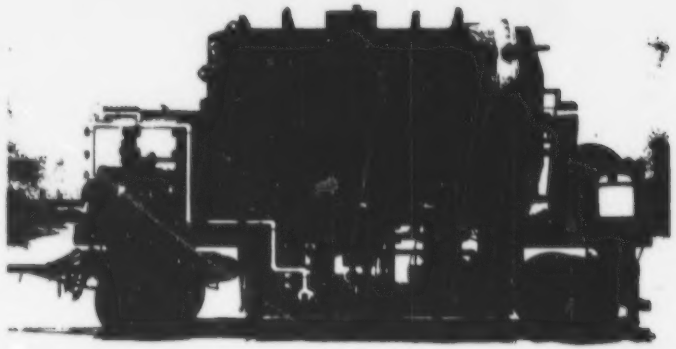
Power can be provided from any portable diesel generator set stationed alongside the plant. A 10m long power cable connection is provided as standard equipment.

Typical applications are military logistic support, civil emergency sets for disaster areas, oil drilling and other temporary work camps, nomadic sheep or cattle raising herds, which shift from one water hole and grazing ground to the next.

Where storage capacity is available, one mobile unit can be rotated and operated periodically, serving several small communities spread out over a large area whose small water requirements do not justify installation of a fixed plant with fixed personnel.

Model No.	AQ2500	AQ5000	AQ7500	AQ10000
nominal capacity (tons/day)	25	50	75	100
saline feed rate (tons/hr)	2.5	5	7.5	10
specific energy consumption (kwh/ton)	21	21.5	20.5	20
nominal power consumption (kw)	22	45	65	84
minimum power supply rating (kva)	60	110	150	170
dimensions (m) L	4.5	6.5	6.5	7.5
W	2.0	2.5	2.5	2.5
H	2.0	4.0	4.0	4.0
A	3.5	5.3	5.3	6.3
B	1.0	1.4	1.4	1.4
transport weight-dry (tons)	7	20	30	35
maximum weight-flooded (tons)	12	35	35	45
shipping volume (m^3)	30	65	65	90





The Mid-Range Series 100 to 500 tons/day

the classic models

The Mid-Range Aquaports are ideal for serving hotels, tourist development centers, real estate developments, military bases, power stations and moderate size municipalities.

Over the past ten years more Aquaports have been sold in this capacity range than any other distillation plant of comparable size.

Model No.	AQ100	AQ150	AQ200	AQ250	AQ300	AQ350	AQ400	AQ450	AQ500
nominal capacity (tons/day)	100	150	200	250	300	350	400	450	500
saline feed rate (tons/hr)	15	20	25	30	35	40	45	50	
specific energy consumption (kwh/ton)	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	
nominal power consumption (kw)	115	155	193	232	270	308	347	386	
minimum power supply rating (kva)	245	330	440	550	660	675	750	785	
dimensions (m) L	7.7	7.7	8.8	8.8	8.8	8.8	9.0	9.0	
W	3.8	3.8	3.8	3.8	3.8	3.8	4.3	4.3	
H	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	
shipping weight (tons)	25	27	28	29	30	30	32	32	
shipping volume (m^3)	160	160	200	200	200	200	240	240	

The Low Energy (LE) Series

lowest energy consumption of any distillation plant

The fourfold increase in fuel price since 1973 has magnified the energy cost component in desalinated water costs and provided an incentive to design plants in which the trade-off point between capital and energy costs is shifted in favor of lower energy consumption.

The LE Series of Aquaports has been developed along this line, incorporating larger heat transfer surfaces and more efficient vapor compressors. They require only 12 to 14 kwh/ton product (45 to 53 kwh/1000 gallons). To gain greater economy, the LE plants are designed to utilize waste heat from the power supply diesel or from any other low grade heat source.

The LE Series is ideal for high fuel cost areas and where continuous operation, i.e. a high annual utilization factor, is foreseen.

Model No.	LE 150	LE 200	LE 250	LE 300	LE 400	LE 500
nominal capacity (tons/day)	150	200	250	300	400	500
saline feed rate (tons/hr)	15	20	25	30	40	50
specific energy consumption (kwh/ton)	14	13	13.5	14	12.5	13
nominal power consumption (kw)	90	110	145	175	210	270
minimum power supply rating (kva)	210	250	300	365	450	560

The Top Range Series 500 to 1000 tons/day

bigger building blocks for larger capacities

The Top Range Aquaport Series has been developed to meet the demand for larger Aquaport units to supply new large-scale regional projects and to replace existing inefficient single purpose MSF distillation plants.

The Top Range Aquaports offer economies of scale and enable meeting multi-thousand tons per day requirements with a battery containing a reasonable number of units.

Scale-up has been achieved without losing the easy handling and installation features of the smaller sized Aquaports. The Top Range Aquaports are, similarly, skid based, packaged units. Dimensions and weights have been kept within internationally accepted limits required to allow ready transport over main thoroughfares.

Model No.	AQ500	AQ600	AQ1000
nominal capacity (tons/day)	500	600	1000
saline feed rate (tons/hr)	60	80	100
specific energy consumption (kwh/ton)	15.5	17	18.5
nominal power consumption (kw)	387	587	770
minimum power supply rating (kva)	600	1190	1560
dimensions (m) L	9.0	9.0	9.0
W	4.5	4.5	5.0
H	7.0	7.0	7.5
shipping weight (tons)	40	45	50
shipping volume (m^3)	280	280	320

Israel Desalination Engineering has been leading the desalting industry in technological innovations for over 10 years, with its novel, highly reliable, efficient and simple evaporator-condenser. Now, after years of development and testing IDE announces its unique new

BRINE CONCENTRATOR

to recycle or extract valuable chemicals from aqueous solutions, to meet environmental requirements for effluent disposal or to retrieve suspended or dissolved constituents IDE Brine Concentrator is your dependable partner.

DEMONSTRATION OF THE CONCENTRATOR PERFORMANCE

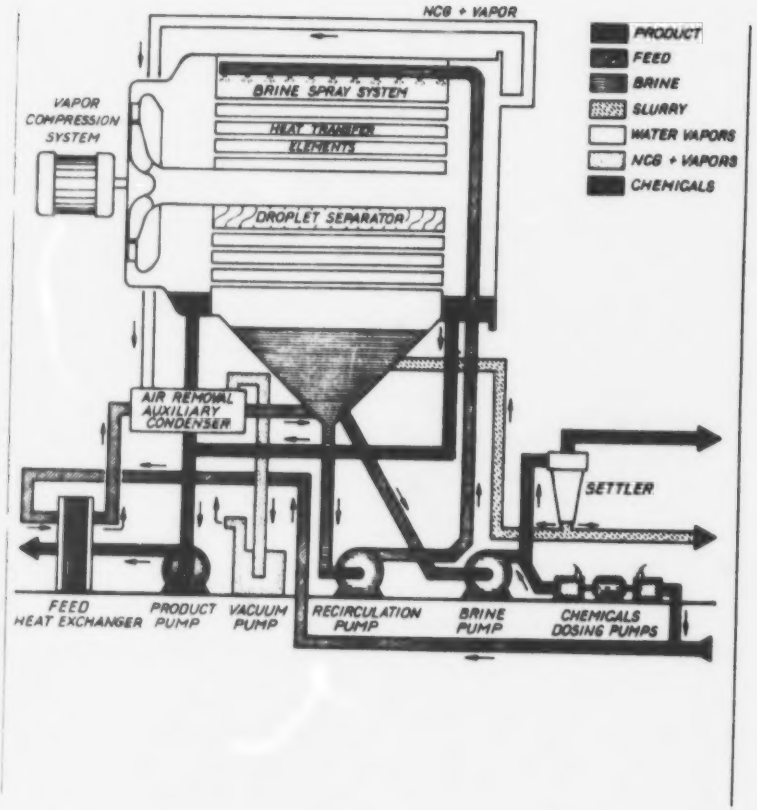
Two test runs are described to demonstrate the concentrator capability

Concentrating Sea Water up to 25% TDS	
Feed to Concentrator	Sea Water 4% TDS No Suspended Solids
Concentrated Brine Outlet	25% TDS about 5% TSS (Total Suspended Solids)
Product	10 ppm TDS

Concentrating Tap Water 1000 PPM up to 30% TS (Total Solids)	
Feed to Concentrator with anlysis	tap water 1000 ppm TDS 100 ppm Ca^{++} 40 ppm Mg^{++} 320 ppm HCO_3 20 ppm HS_2O_3 260 ppm $SO_4^{=}$ 200 ppm Cl_2
pH =	7.5 and No Suspended Solids
Concentrated Brine Outlet	24% TDS 6% TSS 30% TS
Product	10 ppm TDS

Heat Transfer surfaces remain clean after long periods of operation and coefficients of performance are steady and high

HORIZONTAL TUBE BRINE CONCENTRATOR



SELECTING THE RIGHT CONCENTRATOR

Concentrators can be driven either by a vapour compressor or steam (live or waste). Compressor size limits the vapour compression concentrator to about 1000 ton vapour/day above which multi-effect units must be used. However, when steam is available even small units can use multi-effect configurations.

A wide range of concentrators is available to meet specific requirements of any project. The following table is an example for cooling tower blowdown applications.

Capacity Tons of Vapours/day	Brine Concentration T.S.	Driving System	Number of Effects	Specific Consumption KW hr per ton vapours	Specific Consumption Kg fuel No. 6 per ton vapours
100-300	10%	Compressor	1	15—20	—
	20%	Compressor	2	18—24	—
	30%	Compressor	2	20—26	—
300-1000	10%	Compressor	1	14—18	—
	20%	Compressor	2	16—22	—
	30%	Compressor	2	18—25	—
1000-6000	10%	Steam	14	4	7
	20%	Steam	12	3.5	7.5
	30%	Steam	10	3	8

OPERATION OF THE VAPOUR COMPRESSION BRINE CONCENTRATOR

The incoming feed is pretreated with a minute dose of scale crystals-growth modifiers and passed through the product feed heat exchanger, where the discharged product heat is recuperated.

The heat is generated in the unit itself, a converted form of the mechanical energy supplied to compress and circulate the fluids. No separate makeup heat source is needed.

The feed is mixed with recirculated brine and sprayed on the outside of a bundle of horizontal heat transfer elements especially tailored for the purpose of concentrating solutions. The evaporting brine descends in thin films upon the outer face of the tubes, causing condensation to take place inside. The vapors evolving from the brine are drawn through a droplet separator, compressed and discharged into the tubes for condensation. The condensate is a salt-free product, while the concentrated brine is far above the scale saturation limit. The heat transfer surfaces are kept clean due to a unique seeding technique which combines prevention of calcium sulfate and silica together with calcium carbonate scale. No acid treatment to break down the carbonates is needed in the process.

The brine leaving the concentrator is turbid, but by use of a settler and, if necessary, by injection of a coagulant aid, the brine is split into two streams. The main stream is a clear brine while the minor stream is a slurry containing the scale crystals, calcium carbonate, sulfate and silica.

The clear highly concentrated brine solution contains valuable constituents as a by-product of the process. These constituents may be retrieved by crystalization, evaporation or other means, as the case may be.

Non-Condensible Gases are first concentrated in an auxiliary condenser and then exhausted by means of a rotary vacuum pump.

a new concept in multi-effect distillation

at low temperatures

MED

AQUAPORT MED is a completely new development in the field of desalination — a proven process which offers the maximum promise for lowest cost distilled water.

Commercially offered for the first time in 1967, over 130 desalination plants based on the AQUAPORT evaporator-condenser have been installed and operated world-wide. Within a few years after the construction and initial operation in 1974 of the first large-scale, commercial AQUAPORT MED plant — a 3800 ton/day facility in Eilat, Israel — IDE commissioned five 2000 ton/day units on Kish Island in the Persian Gulf. Impressed with their performance, the Iranian Government orderd five more similar plants in 1978.

The same year, following an intense competition with the world's desalination giants, IDE was selected by the U.S. Virgin Islands Water and Power Authority to supply three 4730 ton/day AQUAPORT MED plants for the islands of St Thomas and St. Croix. Excellent cost-effectiveness plus proven performance and reliability gave IDE the edge in the world-wide competition.

Today, IDE is responsible for the design, construction and commissioning of the world's largest MED desalination plant. This 10 MGD plant will operate with exhaust steam from a 50 MW power plant turbine located in Ashdod, Israel. It will produce fresh water from the sea at costs lower then any other type of desalination plant.

More Water for Less Money

In dual purpose, power and water production combination plants, the AQUAPORT MED achieves energy costs lower than those of any other known distillation, reverse osmosis or freezing process for seawater desalination.

AQUAPORT MED has by far the industry's highest Economy Ratios — the weight ratio of distillate produced to

heating steam consumed — of plants operating at maximum brine temperatures below 75 C (167°F). Economy Ratios of 14:1 with 10 ata steam or 9:1 with 0.3 ata "low-grade" steam from a back pressure turbine are available

Proven Reliability

Operating with maximum brine temperatures of less than 75 C (167 F), AQUAPORT MED employs harmless, non-corrosive polyphosphate feed additives which reduce scale and corrosion to a minimum. Dangerous and corrosive acids are not required. Low temperature operation permits extensive use of corrosion proof polypropylene and PVC plastic piping.

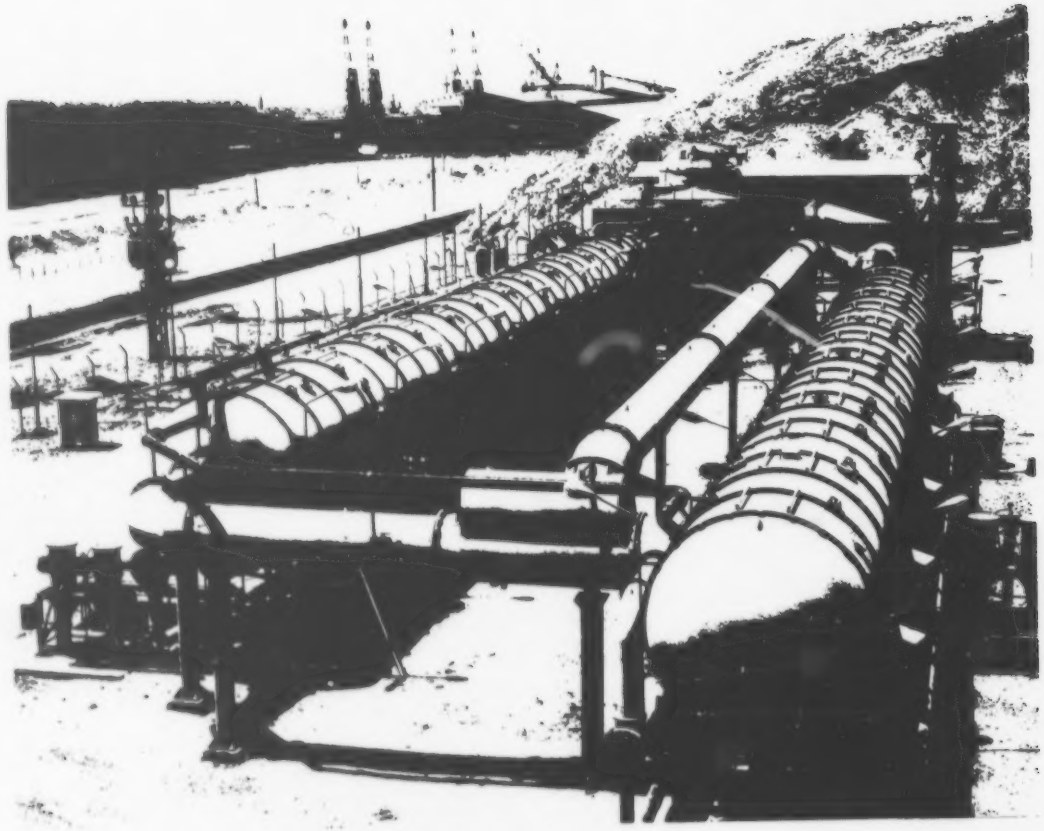
Requiring only simple controls, few relatively small pumps, virtually no moving parts and serviceable standard components, few and easily trained workers are needed for plant operation and maintenance.

Inherently Stable and Load Following

Fully automatic, the system is capable of operation at any capacity from 40 to 120% of normal rating purely as a function of steam supply rate. Because of its wide capacity range and unmatched inherent load following characteristics, AQUAPORT MED is the ideal solution for dual purpose, power and water production plants.

Cost Effectiveness

High Economy Ratios, low energy costs, competitive plant prices, minimal personnel requirements and proven on-line availability make AQUAPORT MED the most cost-effective method of desalination, today and in the years ahead.



Aquaport MED: A Better System

Unparalleled Efficiency

[illegible]

Low Temperature Minimum Scale and Corrosion

[illegible]

[illegible]

Low Energy Cost and Heat Source Versatility

[illegible]

Easy Capacity Regulation

[illegible]

Stable Automated Operation

AQUAPORT MED is inherently stable, requiring few controls and minimal operating personnel.

The liquid flow in all the effects is independent of pressure and temperature gradients, and is virtually unaffected by seasonal variations. Production never suffers from the flow irregularities characteristic of other types of plants, such as short-circuiting, liquid flooding, and reduced flow rate due to scaling are completely eliminated in the AQUAPORT MED. Capacity and flexibility for use are dependent only on the number of effects, steam pressure and steam supply rate.

Highest Reliability, Lowest Maintenance

AQUAPORT MED's simple no chemical design and rugged construction promote trouble-free operation and minimal maintenance. All AQUAPORT's are equipped with components of reliable design and highest quality, approved by leading international manufacturers.

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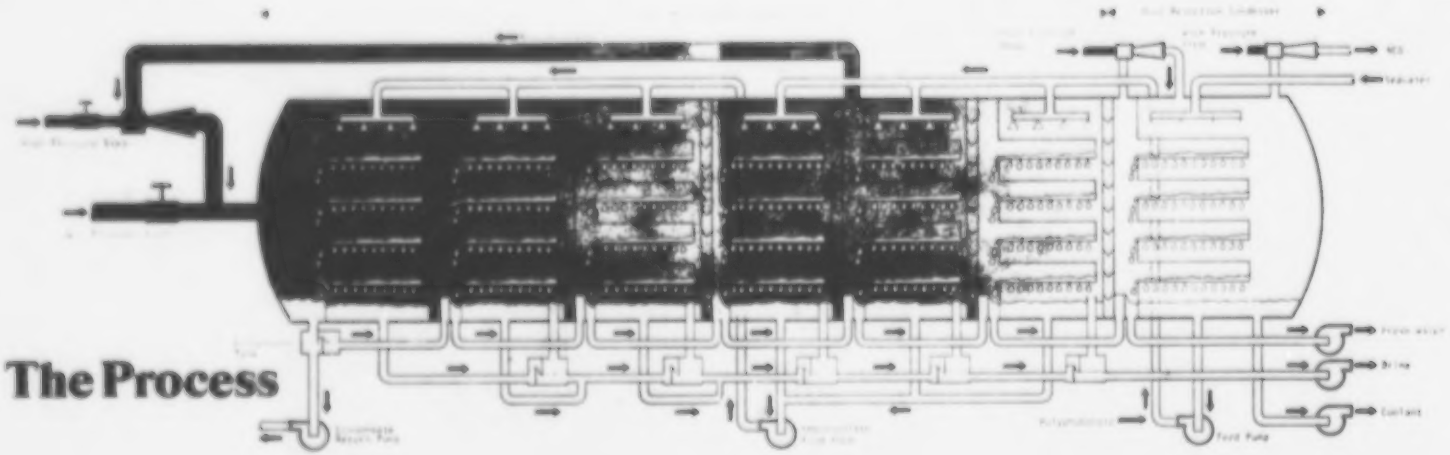


The Process

Multi-Effect Distillation is the most practical and least expensive method of producing large quantities of fresh water from the sea. The AQUAPORT MED process is by far the most efficient and cost-effective system of this type. Characterized as Low Temperature, Horizontal Tube, Falling Film Multi-Effect Distillation, AQUAPORT MED — like other systems in the AQUAPORT series — is based on the unique IDE evaporator condenser which uses specially selected aluminum alloy tubes for maximum thermodynamic efficiency and minimum cost.

Heat Recovery and Rejection

A train of identical, interchangeable evaporator condenser effects forms the Heat Recovery Section of AQUAPORT MED. The process delivers up to 14 times more distillate by weight than required motive steam — a most impressive Economy Ratio.

Latent heat given off by the motive steam is re-used in successive effects, with each step taking place at a slightly lower temperature-pressure liquid-vapor equilibrium point. Finally, in the Heat Rejection Condenser, latent heat remaining in the system is rejected by using it to raise the temperature of incoming seawater.

Seawater Feed

Incoming seawater, de-aerated and preheated in the condenser is divided into two flows. One acts as coolant, and eventually returns to the sea, the other becomes feed for the distillation process.

The feed is treated with a harmless polyphosphate additive to inhibit scaling, then fed into the lowest temperature group of Heat Recovery Effects. A spray nozzle system distributes it over the top rows of tubes in each effect. As the feed flows in thin films down each bank of tubes, part of it vaporizes as it absorbs the latent heat released by the motive steam inside the tubes.

The remaining feed, now slightly concentrated, is pumped to the next group of effects, which operate at a higher temperature. There the spray procedure is repeated, the remaining feed being pumped onward again until it leaves the hottest group of effects as concentrated brine.

Motive Steam Energy Supply

Almost any source of steam can be used to power the AQUAPORT MED. Motive steam of 1 atg or less is throttled down to 0.35 atg; above 3 atg, steam is reduced to a steam jet ejector which recompresses and recycles vapor from the cooler end of the plant in order to achieve a substantially higher Economy Ratio.

The steam is supplied to the tubes of the hottest effect. There it condenses, giving up its latent heat to the salt water flowing over the outer surface of the tubes. While condensation is taking place on the inside of the tubes, a nearly equal amount of evaporation is occuring on the outside. After passing through a brine droplet separator to maintain purity of the distillate, the vapor is drawn into the tubes of the next effect, which is operating at a slightly lower temperature and pressure.

The evaporation-condensation process is repeated along the entire series of effects, each of which contributes a significant amount of additional distillate. From the last effect, all the remaining vapor is liquefied in the Heat Rejection Condenser by sea water coolant.

The Distillate

Fresh water from the first effect is collected in a condensate tank. Part of this distillate is returned to the steam generator, the excess, above the original quantity of motive steam, flows into the first of a series of special chambers which collect the distillate from each effect. Since the vapor space of each collector is ducted to the cooler condensing section of the next effect, part of the distillate flashes off, cooling the remaining product stream while recovering heat and returning it to the main body of Heat Recovery Effects. The flowing product stream is thus cascaded and flash cooled at stages, the last effect is drawn off, necessarily the total efficiency of the process. The cooled distillate is finally discharged to storage by the product delivery pump.

The product is totally pure water. It is fresh, potable and soft, averaging only 20 ppm of dissolved solids.

Brine and NCG Disposal

The concentrated brine from the hottest effect is, like the distillate, cascaded and flash cooled to recover its heat. After cooling, it is returned to the sea via the brine pump.

Non-Condensible Gases (NCG) are bled from each tube and flow collectively from one effect to the next. They are eventually concentrated at the coolest end of the Heat Rejection Condenser, and are finally evacuated by a steam jet ejector or mechanical vacuum pump.

The Plant

Rugged construction

Simple mechanical design

Few moving parts

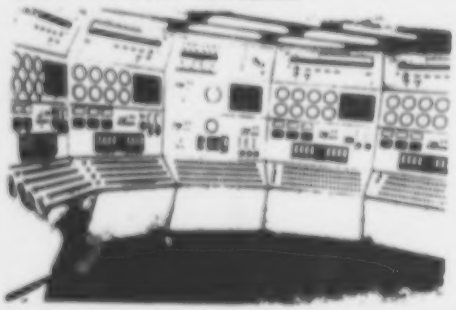
Factory assembled effects

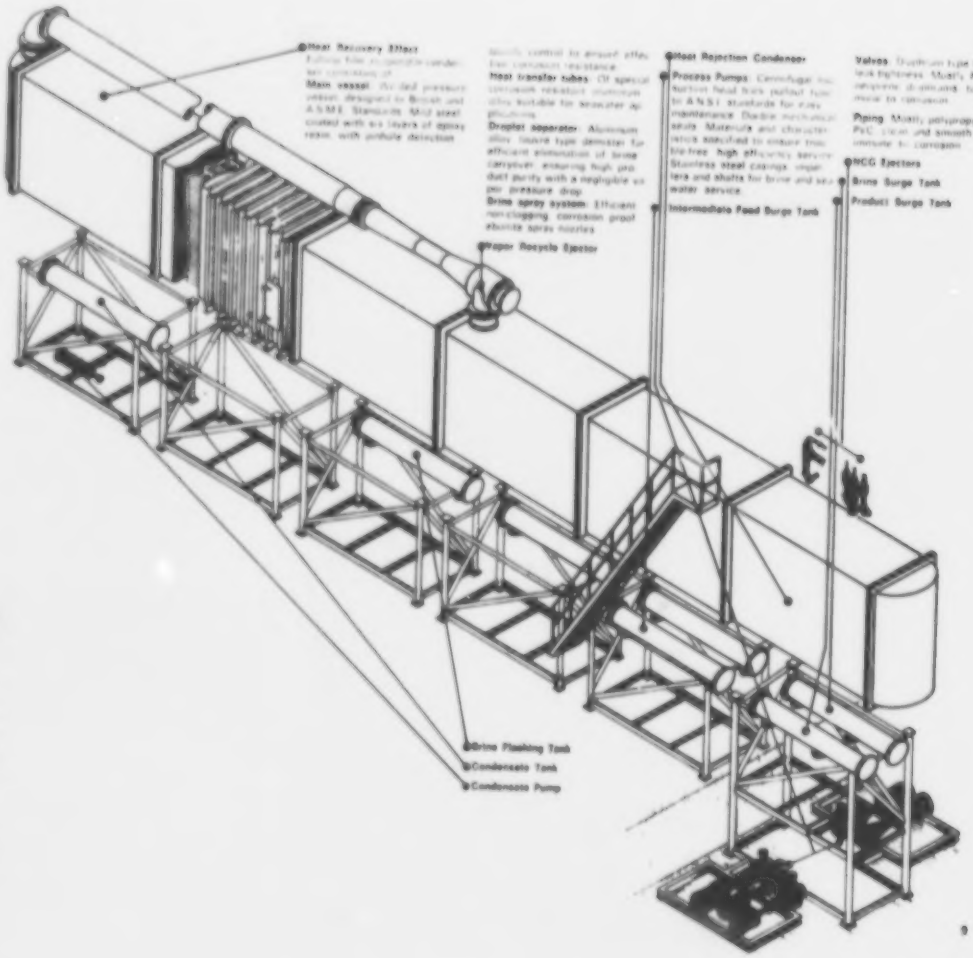
Easy site erection

No insulation required

Non-corrodable polypropylene & PVC piping

Control Controls, Instrumentation and Electrical Panel. Containing complete electrical system, push-button motor starters and controls. A central display of all instrumentation and controls allows easy supervision of plant operation. Instrumentation and controls connected to an integrated sequence sensitive safety alarm and shutdown system.
All instrumentation are of high quality and reliability to ensure steady operation with a minimum of supervision.





Saving through efficient combinations:

Aquaport MED and Electrical Power Plants

The AQUAPORT MED is the seawater distillation plant of choice for combination with:

- Steam turbine power plants
- Diesel engine power plants
- Gas turbine power plants

These low or zero energy cost waste heat sources can be employed to significantly reduce the cost of desalinated seawater.

Steam Turbine

Steam-powered electricity generating stations and AQUAPORT MED are ideally suited for each other. Turbine exhaust steam pressures as low as 0.2 ata (60°C, 140°F) can be used with the AQUAPORT MED in contrast to other types of distillation plants requiring higher temperature (120°C, 248°F) and pressure steam supply. This results in low or energy costs allocated to water production with AQUAPORT MED since the steam has been more fully expended in the turbine, giving greater power generation for a given fuel energy input.

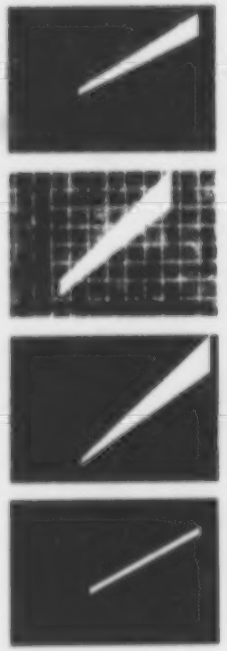
AQUAPORT MED has the built in advantage of broad-range load following capability, automatically adapting output to steam supply over a span of 40-120% of nominal capacity. In contrast to other types of distillation plants, no dump condensers are required and no steam is wasted during peak-load hours. Additionally, no high-cost auxiliary steam is needed during off-peak periods.

Diesel Generators and Gas Turbines

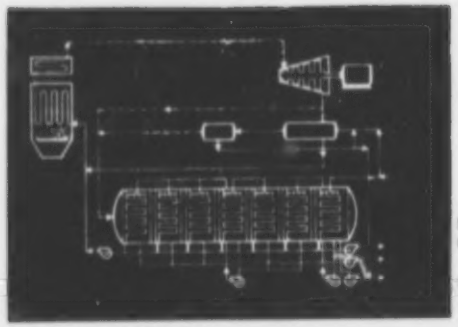
Waste heat from diesel generators and gas turbines may be utilized to produce steam for the AQUAPORT MED. A simple heat exchanger or waste heat boiler can enable the production of desalinated water at near zero energy cost. The waste heat from a diesel generator of 15 MW output can supply enough steam to produce 4000 tons of water daily. Similarly, a 15 MW gas turbine generator rejects sufficient heat for an average daily water supply of 7000 tons.

"Total Energy" Desalination Facility

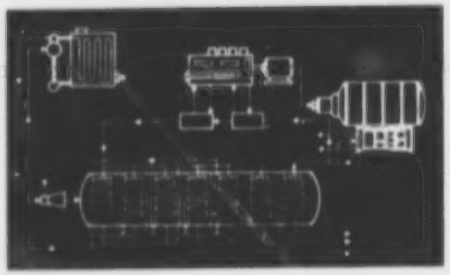
Up to 80% of the fuel energy input to a diesel-powered generating plant can be utilized in the production of pure water. This is accomplished by combining two AQUAPORT models. The steam-driven AQUAPORT MED and the electrically-powered AQUAPORT VC (Vapor Compression). The diesel generator supplies electricity directly to the AQUAPORT VC unit, while the AQUAPORT MED plant uses diesel waste heat from lubricating oil, cooling water and exhaust gases streams.



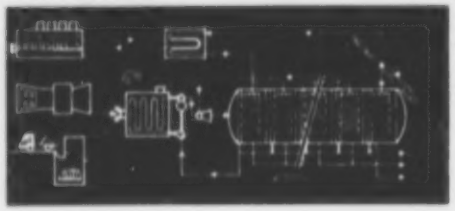
Water production rates with waste heat and solar energy sources



Steam turbine power desalination plant



Waste heat desalination plant



Total energy desalination facility

SPECIAL ENERGY CONSERVATION PLANTS

Industrial Waste Heat

Petrochemical plants, glass and ceramics factories, municipal incinerators, beverage distilleries, plastics factories and a host of other industries can provide desalinated water as a primary by-product with AQUAPORT MED. Heat exchangers, waste heat boilers or stack gas heat absorption bundles can transform waste heat into usable steam for AQUAPORT MED installations.

Solar Energy

Solar ponds and flat-plate or tubular solar collectors can efficiently provide hot water of up to 80°C. AQUAPORT MED's unique low temperature heat requirements make both these sources practical for distillation of seawater.

Geothermal Heat

Hot water from geysers and springs, steam from fumaroles, hot rock deposits, stable volcanic activity, and other geothermal sources can be readily adapted to the requirements of AQUAPORT MED units.

Bringing Down the Cost of Water

The end cost of a cubic meter of desalinated water is dependent upon a large number of factors. A few of these are beyond the control of the manufacturer or the user: land acquisition cost, local labor rates, local taxes. But the vast majority of expenditures contributing to the final cost of pure water are definitely lower with AQUAPORT MED.

Initial Investment — An AQUAPORT MED plant, with low-cost aluminum alloy tubing, modular construction and simple control system, costs less to buy, less to install than competitive plants of comparable output.

Lowest Energy Cost — The use of low-grade steam means lowest possible energy cost. The possibility of alternative energy sources — solar, geothermal or waste heat — can reduce energy costs to that required for pumping only.

Energy contributes over 50% to the cost of desalinated water in both single purpose (water only) and dual purpose (water plus electricity) applications, the MED offers lower energy costs than are possible with high temperature MSF or other type distillation plants.

Single Purpose Plants. Economy Ratios (weight ratio of product water to heating steam consumed) of up to 14:1 are possible with MED plants operating at a maximum brine temperature of only 75°C (167°F).

These Economy Ratios are much higher than available in MSF plants of comparable cost and size and are achieved by use of a steam jet ejector vapor recompression cycle (see graph). With vapor recompression, advantage is taken of the surplus energy potential available in the steam of a conventional low pressure (Bata) boiler to substantially increase the Economy Ratio while still introducing motive steam to the first effect at a pressure of only 0.35 ata (73°C, 163°F).

Dual Purpose Plants. In dual purpose applications, energy costs chargeable to IDE's plants are less than half the costs charged to high temperature distillation plants. Even with a steam supply at only 73°C (163°F), the AQUAPORT MED can operate at Economy Ratios comparable to or even better than those of high temperature MSF plants of similar size which require 120°C (248°F) steam.

The economic value of 73°C (163°F) temperature turbine steam is almost 70% lower than that of 120°C (248°F) steam (see graph) since it has been more fully expended in the turbine and produces more electrical power for a given steam input to the turbine.

Independent studies of energy costs in dual purpose plants show that the AQUAPORT MED achieves costs lower than those of any other known distillation, reverse osmosis or freezing process for seawater desalination (see table).

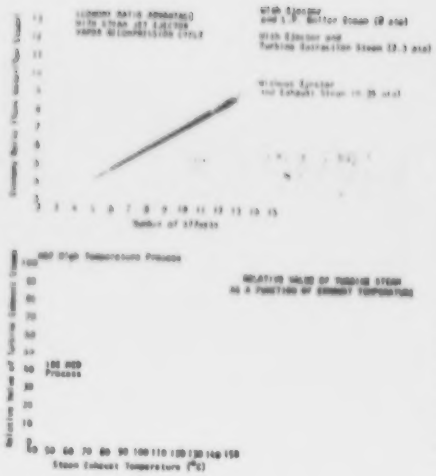
Reduced Labor Costs — AQUAPORT MED's fully automated operation and low maintenance profile reduce staff requirements to a bare minimum.

High Plant Load Factor — Continuous operation at full plant capacity and high on-line availability are features of the AQUAPORT MED.

The AQUAPORT MED operates at unparalleled low temperatures reducing scaling and corrosion to a minimum. Scaling and corrosion are behind 90% of all problems plaguing conventional high temperature 90°C to 120°C (194°F to 248°F), distillation plants and causing reduction in plant capacity and availability.

Quick start-up and broad-range load following capability also maximize production, minimize water costs.

Low Maintenance Costs — With low temperature operation and minimal corrosion and scaling, maintenance costs with AQUAPORT MED are low because of reduced component failure, fewer parts replacements and smaller required spare parts inventory.



ENERGY COSTS FOR SEAWATER DESALTING PROCESSES *

Process	Maximum Brine Temp	Energy Source	Economy Ratio klbs Water/kBtu	Btu/lb Water	Cost of Heat $/MMBtu	Cost of Water $/kgal	Pumping Energy kwh/kgal	Pumping Cost $/kgal	Total Energy Cost $/kgal
Distillation Single Effect		Waste Heat	0.95	1053	0.00	0.00	15.35	0.75-1.75	0.75-1.75
Distillation MSF	90°C 195°F	Turbine Extraction Steam @ 110°C (230°F)	8	125	0.00	0.00	8.10	0.40-0.50	0.40-0.50
Distillation MSF	120°C 250°F	Turbine Extraction Steam @ 130°C (275°F)	12	83	1.71	1.10	5.0	0.30-0.40	1.40-1.50
Distillation Multiple Effect	120°C 250°F	Turbine Extraction Steam @ 130°C (275°F)	15	67	1.71	0.85	4.6	0.20-0.30	1.15-1.25
Distillation Multiple Effect	120°C 250°F	Boiler Steam (Single Purpose)	15	67	4.00	2.10	4.6	0.20-0.30	2.50-3.00
Reverse Osmosis		Electricity 45 kwh/kgal	54	18.9	10.00	2.25	Included		2.25
Freezing		Electricity 50 kwh/kgal	49	20.5	10.00	2.50	Included		2.50
Vapor Compression		Electricity 60 kwh/kgal	30	30.0	10.00	3.00	Included		3.00

* From "Energy Costs of Various Desalting Processes" by Black Veatch Consulting Engineers, for Pure Water (1974). [illegible]

Brine Fuel Oil [illegible] $15.00/Bbl
Boiler Steam 600°F @ 5.4 [illegible] $/MMBtu
Power @ 10.0 kwh

World's Largest MED Desalination Plant

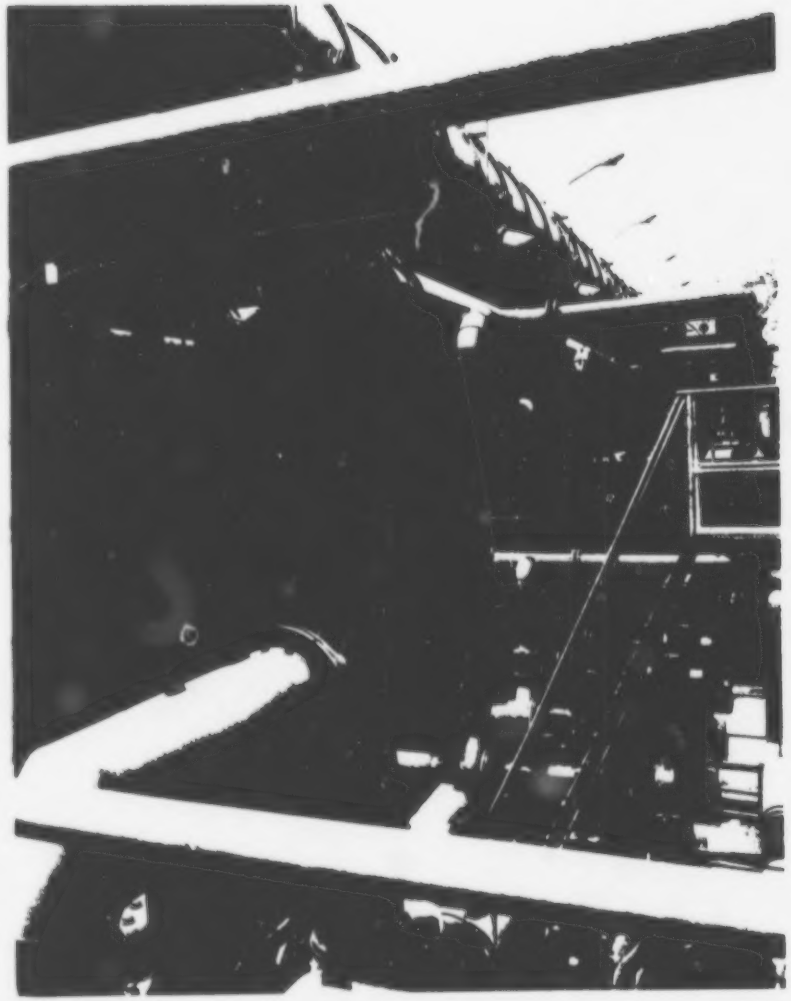
In 1979 IDE started construction of the world's largest MED desalination module at Ashdod, Israel. Utilizing back pressure turbine exhaust steam from an adjacent 50 MW electrical power plant, the giant AQUAPORT MED unit will produce 37,500 tons/day of pure distillate from the waters of the nearby Mediterranean Sea.

Design of the new plant was begun following evaluation of IDE's Eilat installation by the governments of Israel and the United States. The Eilat plant is a 12-effect system which provides 3,800 tons of water daily to the Red Sea resort town's 20,000 inhabitants, 18 major hotels, and a number of tourist facilities. The plant enjoys unprecedented efficiency, 99% on-line availability and an Economy Ratio approaching 12:1.

Highly impressed by the performance of the Eilat AQUAPORT MED plant and IDE installations in Iran, the United States government is taking an active role in the financing and development of the giant dual purpose plant. In return for technical knowledge it will gain, the USA is participating to the extent of $ 20 million of the projected $ 55 million total project cost.

Field erected because of its size, the Ashdod AQUAPORT MED module will be almost nine meters in diameter and 110 meters long. Its design calls for 14 Heat Recovery Effects and a Heat Rejection Condenser. Operating on low-grade 0.4 ata, 78°C (165°F), back pressure turbine exhaust steam and a maximum brine temperature of 74°C (165°F), its predicted Economy Ratio is 10.6:1.

Water costs in 1980 dollars, including amortization, for this type of plant in sizes of 37,500 to 375,000 tons/day should be about $ 0.40 per cubic meter, among the world's lowest prices for desalinated water of comparable purity.

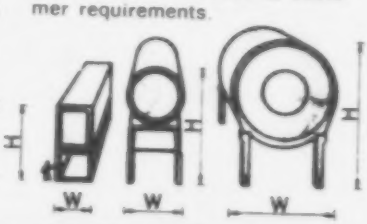


Aquaport MED Models and Specifications

AQUAPORT MED units are manufactured in a wide variety of nominal capacity ratings, ranging from 1,500 to 37,500 tons/day. A plant may be comprised of up to 10 units for a total output of up to 375,000 tons/day of pure potable water. This quantity is sufficient for the needs of a highly industrialized city with a population of 1,000,000.

In addition to AQUAPORT MED, the table below shows a listing for AQUAPORT MEVC plants. These differ from the MED only in the addition of a vapor recyling system for use with input steam pressure of 3 ata and above to achieve higher economy ratios at a lower specific energy cost.

The table below details the technical specifications for several typical units. It must be borne in mind that IDE can manufacture all AQUAPORT models to customer requirements.



Model No.	MED 2000	MEVC 2000	MED 5000	MEVC 5000	MED 37,500
Nominal capacity (tons/day)	2000	2000	5000	5000	37,500
Number of heat recovery effects	12	10	12	12	14
Economy ratio (kg distillate/kg steam)	8.6	10	8.6	11.5	10.5
Seawater supply rate (tons/hr)	460	450	1500	1000	11,000
Seawater supply temperature (°C)	25	25	25	25	25
Motive steam pressure (ata)	0.35	8	0.35	8	0.4
Steam flow rate (tons/hr)	9.7	8.3	24.2	18.1	150
Process power consumption (kw)*	120	100	250	250	2050
Specific power consumption (kwh/ton)	1.5	1.2	1.2	1.2	1.2
Brine temperature, maximum (°C)	70	70	70	70	70
Vapor recycle ejector (Yes/No)	NO	YES	NO	YES	NO
Dimentions (m) L	70	60	90	90	110
W	4	4	6.5	6.5	9
H	7.5	7.5	11.5	11.5	14
Shipping weight, approximate (tons)	260	170	350	350	1500
Shipping volume, approximate (m^3)	960	640	2200	2200	**

* Not including seawater supply power ** Field erected

The issue of this publication does not constitute an offer and the right is reserved to alter designs and/or specifications at any time without notice.

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BATEMAN ENGINEERING LTD.
P.O.B. 18041 TEL-AVIV ISRAEL. CABLES: HATPALA. TELEX: 33747. HEAD OFFICE: [illegible], R&D 417171
NEW TELEX: 33590

DESALINATION PLANTS REFERENCE LIST

Over 120 AQUAPORT Vapour Compression and Multi-Effect Distillation units ranging in capacity from 30 to 4,000 m^3/day each, have been sold throughout the world including, Spain, the Canary and Balearic Islands, Italy, Venezuela, Peru, Iran, United States and Israel. Typical of these are the plants listed below.

OWNER	LOCATION	TYPE-SIZE OF UNITS
"Hocasa"-Hotel San Antonio	Lanzarote, Canary Islands, Spain	*VC-200 m^3/day
Cabildo de Lanzarote	Famara, Lanzarote, Canary Islands, Spain	VC-350 m^3/day
Caja Insular de Ahorros de Gran Canaria	La Santa, Lanzarote Canary Islands, Spain	VC-400 m^3/day
Jandia Playa Hotel	Fuerteventura, Canary Islands, Spain	VC-450 m^3/day
La Aldea de San Nicolas Tolentino	Gran Canaria Canary Islands, Spain	VC-250 m^3/day
Cabildo de Fuerteventura	Puerto de la Rosario Canary Islands, Spain	VC-500 m^3/day
Municipality of Galdar	Galdar, Canary Islands, Spain	VC-500/200 m^3/day
Hierro-Peru	San Nicolas, Peru	VC-500 m^3/day
Instituto Nacional de Obras Sanitarias	Los Roques Venzuela	VC-75 m^3/day
Imperial Iranian Air Force	Kish, Iran	VC-200 m^3/day
Imperial Iranian Air Force	Bushire, Iran	VC-250 m^3/day
Imperial Iranian Air Force	Bushire, Iran	VC-300 m^3/day
Imperial Government of Iran	Bandar Langeh, Iran	VC-500 m^3/day
Kish Island Development Organization	Kish Island, Iran	**MED-2,000 m^3/day
Imperial Iranian Navy	Bandar Abbas, Iran	MED-2,000 m^3/day
Israel Defence Forces	Ophira, Israel	VC-450 m^3/day
Dead Sea Works, Ltd.	Dead Sea, Israel	VC-450 m^3/day
Mekoroth Water Company	Eilat, Israel	MED-4,000 m^3/day
V.I. Water & Power Authority	U.S. Virgin Islands	MED-4,735 m^3/day

* VC-Ambient Temperature Vapour Compression Distillation
** MED-Multi Effect Distillation

15.4.79

Consider RCC for its systems engineering approach

Resolving challenging waste and process stream management problems for clients is an important service at RCC. (1) We analyze your needs and design a system to meet them. (2) supply and install the equipment. (3) train the operators, and (4) start the system. Clients still rely on us for such services as parts-replacement expediting. Our customers call this total system responsibility the best in the business.

We're fully prepared to help you determine your requirements in the specific application of the Brine Concentrator or any other waste treatment system.

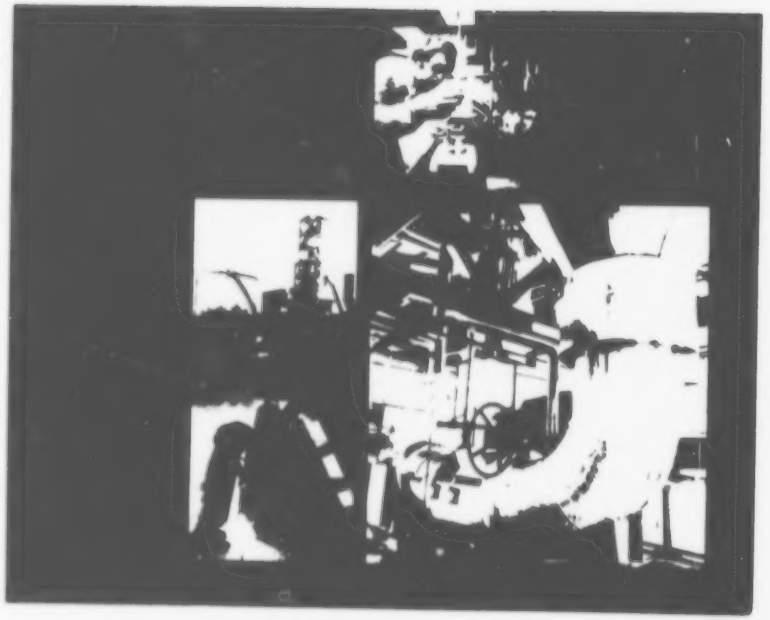
Resources Conservation Co
P.O. Box 1786
Seattle, WA 98124
206-628-2400

Resources Conservation Co

Brine Concentrator systems

Wastewater volume reduction

Energy-efficient resource recovery



Unique process requirements call for innovative solutions

Industrial water management frequently requires treatment of aqueous streams fabricated with inorganic salts and organic matter. As these materials precipitate, conventional water treatment equipment is rapidly scaled and fouled.

In contrast, Resources Conservation Co. (RCC) Brine Concentrators operate at supersaturated concentrations without scaling, eliminating system fouling and allowing pure product water to be recovered continuously. Corrosion is minimized through the use of titanium and other advanced-technology materials.

Scale-free operation increases reliability

Brine Concentrators are vertical, tube-in-shell evaporators. Through a process of preferential precipitation, the system forces precipitating calcium sulfate and silica to build on existing seed crystals in the process stream instead of crystallizing as scale on heat-transfer surfaces.

The systems designed and installed by RCC are unsurpassed in high-performance energy-efficient operation. They concentrate industrial wastes or process streams into liquids and recover up to 98% of the water.

The system's high concentration capability greatly reduces or eliminates the need for evaporation ponds and is a substantial contributor to industry's efforts in meeting zero-discharge requirements. RCC has power experience in concentrating cooling tower blowdown and other industrial wastes. In the process, the maximum amount of pure water is recovered for reuse.

Our technology has been employed to treat waste streams from power generating plants, effluents from pulp and paper mills, discharges from petroleum and chemical streams, effluents from sulfuric processes and brackish waters.

RCC offers Brine Concentrators in many sizes, with unit capacities up to 840,000 gallons (4,000 gal/min) and in system combinations to satisfy greater processing needs. Models are adaptable to both new and existing installations.

The RCC Brine Concentrator is usually specified as a vapor-compression evaporator, but it is also available in a multieffect configuration. Although the vapor-compression model requires less operating energy, the multieffect design may be a cost-effective alternative in plants where excess steam can be used as the energy source.

RCC Brine Concentrators offer many cost-effective advantages

Because an RCC system prevents scaling and resists corrosives, its online availability consistently exceeds specifications. The Brine Concentrator can handle a wide variety of feed streams in an energy-efficient manner. It returns an extremely high ratio of pure, reusable water and minimizes disposal costs of concentrated saturated wastes.

Long, trouble-free service. Much of the credit for the Brine Concentrator's noncscaling operating dependability is due to an advanced-technology design. Special steel alloys, titanium, and the most dependable components are used to ensure a long effective service life. Materials for all components are especially resistant to corrosion and are specified to accommodate the chemistry of each particular application.

The system's control console has a mimic display for realtime monitoring. It is designed for unattended, fail-safe operation. These features and the system's easy accessibility for maintenance result in reduced operating costs.

High, pure-water recovery rates. Even after the circulating slurry has reached supersaturation, the Brine Concentrator will continue to recover pure water at rates averaging 98%.

Product water TDS averages 2 ppm and is suitable for use as boiler makeup. The low TDS distillate reduces the demineralizer load, thereby decreasing chemical treatment costs.

The system's high product water recovery rate could save on source water needs. Such reduction offers significant economies in sizing and space requirements for source water pipes and pumps in new installations.

98% pure water recovery stream in operation

Each of these Brine Concentrators is selected to process 275,000 gal/d cooling tower blowdown (at 3x), recover at least 98% of the input as pure water, and use only 90 kWh of energy for each 1,000 gal of high precipitation. In actual performance, each unit has rejected feed rates as high as 269,000 gal/day, recovered 98% of the input as pure water, and maintained operation at less than 90 kWh for each 1,000 gal of feed. Left to right: RCC Brine Concentrators installed at the Star Iron Tech, Inc., and Huntington Electric Power generating stations.

Process flow through a vapor-compression system

The schematic shows the process flow for the Brine Concentrator in its principal design—the vapor-compression configuration.

Incoming suspended solids large than 50 microns are removed by equipment in the Brine Concentrator system. The waste stream goes into a feed tank, where it is heated to hold acidity (pH) between 5.5 and 6.5 for decarbonating. The acidified waste stream is then pumped through a heat exchanger (higher rates is denser it into the mixing point. After passing through a separator (2) to remove carbon dioxide, nitrogen, and oxygen, the waste stream combines with a high concentrate in the circulating slurry (3). The forty-fold concentrate, recycled from the sump (4) is pumped through a heat exchanger (5) and then into the circulating system. The system maintains the supersaturation of the fluid by controlling the rate of the feed stream. The circulating slurry is pumped through a vapor-compression system (6) where the slurry is concentrated to the point of saturation. The saturated slurry is then pumped to the separator (7) where the concentrate is separated from the vapor. The concentrate is then recycled through the circulating system. The vapor is compressed (8) and returned to the circulating system (9) to provide the heat for the evaporation process. The condensate is then pumped through a heat exchanger (10) to provide heat for the feed stream. The condensate is then pumped through a heat exchanger (11) to provide heat for the circulating system. The condensate is then pumped through a heat exchanger (12) to provide heat for the feed stream. The condensate is then pumped through a heat exchanger (13) to provide heat for the circulating system. The condensate is then pumped through a heat exchanger (14) to provide heat for the feed stream. The condensate is then pumped through a heat exchanger (15) to provide heat for the circulating system. The condensate is then pumped through a heat exchanger (16) to provide heat for the feed stream. The condensate is then pumped through a heat exchanger (17) to provide heat for the circulating system. 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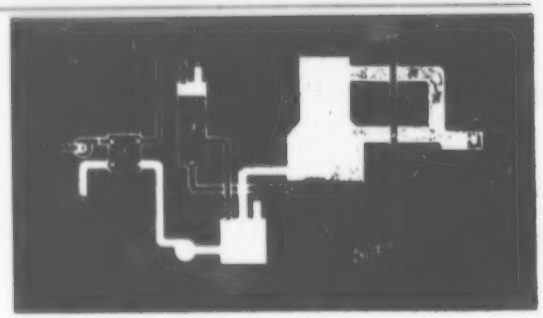
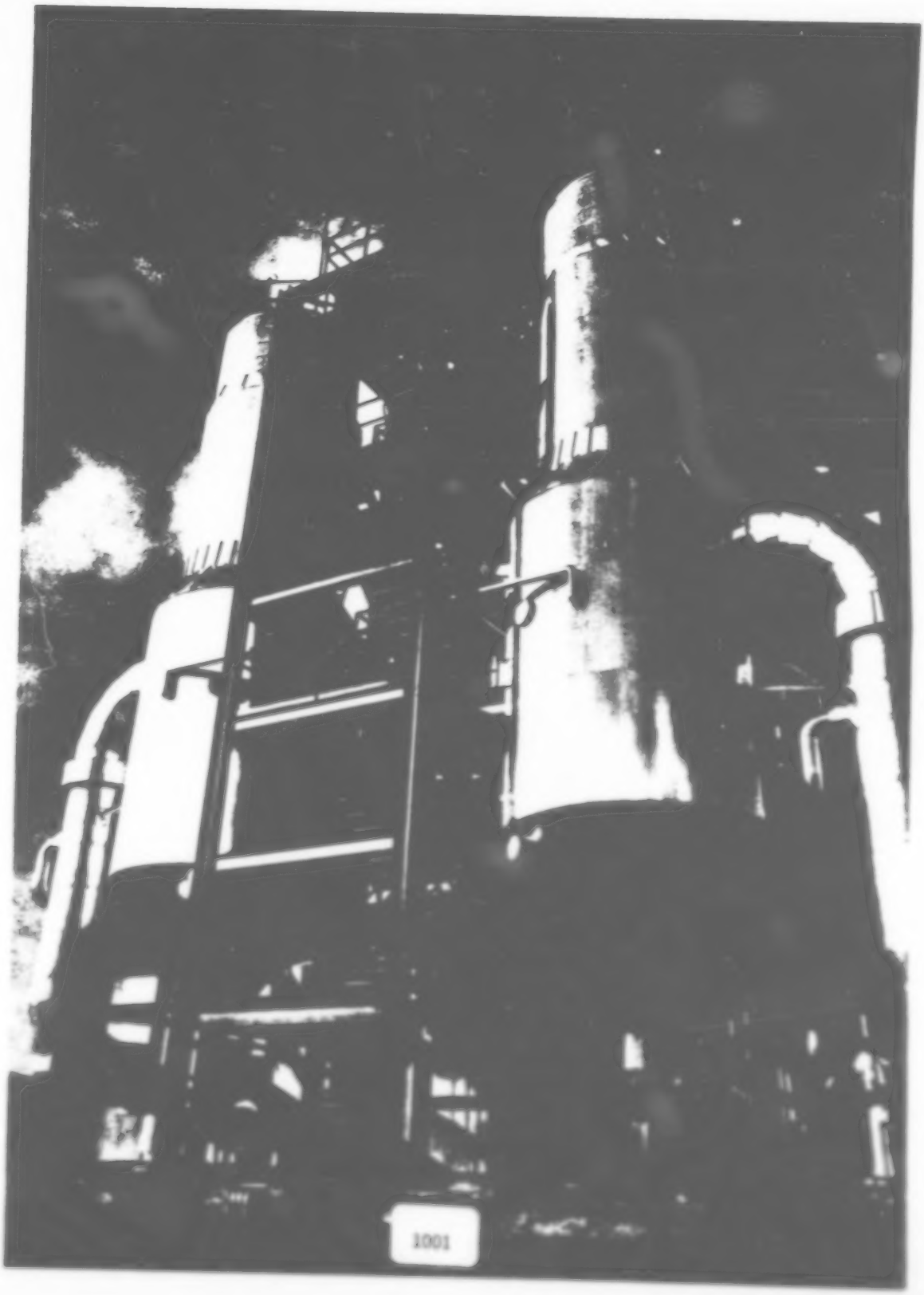



1001

Treating combined wastes can greatly reduce disposal costs

The Brine Concentrator easily handles the highly concentrated wastes from cooling towers, demineralizers, boilers, ash sluice systems, flue-gas scrubbers, and chemical processes. In many combined applications, highly concentrated streams are reduced to a slurry about 2% of their original volume. This waste can easily be crystallized in a small solar pond or dryer. At one power generating station, a Brine Concentrator permitted a planned holding pond to be reduced from 530 acres to only 11 acres. Brine Concentrators are lower in capital and life-cycle costs than solar ponds, which are often considered as the only treatment alternative.

Substantial energy savings

In the vapor-compression configuration, the Brine Concentrator needs only 29 to 37 Btu/lb to concentrate typical cooling tower blowdowns and other waste and process streams. This converts to an electrical energy requirement of from 70 to 90 kWh per 1,000 gal of feed. Conventional evaporators consume from 200 to 400 Btu/lb of feed processed.

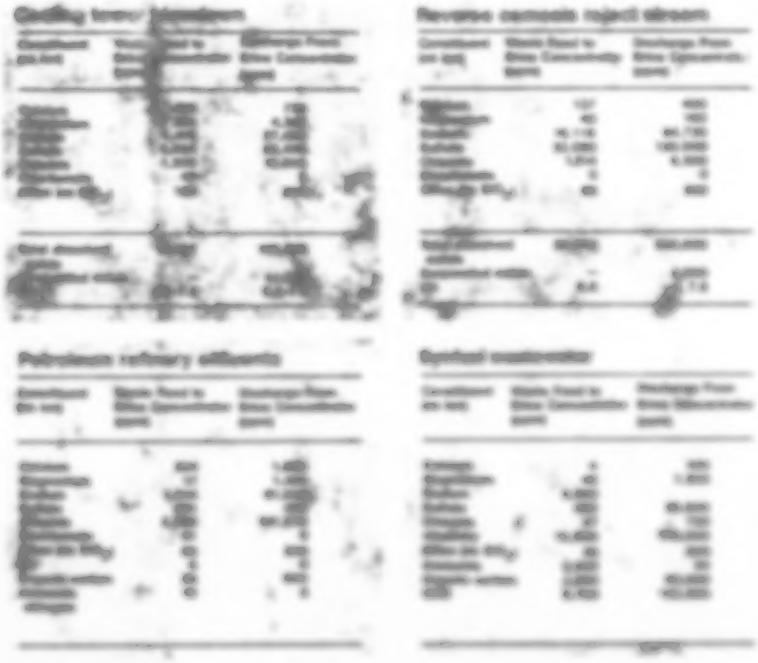
Usually, RICC vapor-compression Brine Concentrators are driven by steam compressors powered by electricity, but other power sources may be used to satisfy unique requirements. When customer plant steam is abundant, a multieffect Brine Concentrator offers special advantages.

A variety of wastes can be cleaned

The system's chemistry and operation can be adjusted to accommodate substantial variations in the quantity and chemical compositions of the TDS in waste and process streams. The stream chemistry examples illustrate the wide variety of wastes and other waters the system can efficiently process. Although total solids in the Brine Concentrator range from 115,000 ppm to over 350,000 ppm, the distillate contains less than 10-ppm TDS.

Brine Concentrator adapts to handle a variety of wastes

Top left: This is a typical cooling tower blowdown waste stream concentrated by a Brine Concentrator that recovers more than 98% of the water for reuse.
Bottom left: In this example, ash sluicing waste has been processed by a Brine Concentrator with 98% of the waste stream recycled.
Top right: This is an example where reverse osmosis waste has been reduced by 75%.
Bottom right: In this case, 95% of a waste stream from an oil or shale retorting plant is recovered for reuse.



Brine Concentrator Performance

RESOURCES CONSERVATION COMPANY EVAPORATOR INSTALLATIONS

Location	Concentrators at each station	Activation date	Total gal/d	Feed TDS (mg/L)	Concentrate TDS (mg/L)	Concentrate SS (mg/L)
Montana	2	Aug 1976	576,000	5,200	127,000	72,000
	1	Oct 1976	327,000	3,400	121,500	75,100
Colorado	3	Jun 1978	1,000,000	6,100	170,400	68,100
	2	Jan 1980	575,000	14,100	115,000	28,100
	2	Dec 1980	648,000	21,896	204,640	27,210
New Mexico	1	Mar 1975	253,000	5,800	191,900	123,100
	1	Jul 1978	432,000	12,000	202,700	80,700
Utah	1	Jul 1975	280,000	3,600	68,000	73,000
Arizona	1	Oct 1975	270,000	10,500	202,000	73,000
	2	Feb 1981	1,152,000	10,500	195,000	120,000
Florida	1	Jul 1981	418,000	7,538	326,700	16,100
Texas	1	April 1982	396,000	4,220	94,000	107,000
South Dakota	1	Sept 1980	665,000	2,936	90,800	56,200

Typical Wastewater Concentrated With A Brine Concentrator

Electric Utility Wastewater	Feed (Saturated With CaSO4)	Concentrated Brine	Ratio
Total Solids (mg/l)	1960	238,210	2
Flowrates (GPM)	227	2	225
Water Recovery Rate			>99%
Oil Refinery Wastewater			
Total Solids (mg/l)	4,200	208,000	50
Total Organics (mg/l)	35	960	7
Flowrates (GPM)	250	4	156
Water Recovery Rate			>99%
Oil Shale Wastewater			
Total Solids (mg/l)	15,300	447,000	34
Total Organic Carbon (mg/l)	1,830	26,000	545
Flowrates (GPM)	1,630	67	1,253
Water Recovery Rate			>99%

43RD ANNUAL MEETING

INTERNATIONAL WATER CONFERENCE

PITTSBURGH, PENNSYLVANIA

OCTOBER 25, 26, 27, 1982

ZERO DISCHARGE AT NORTHWEST ALLOYS, INC.

A CASE HISTORY

NED P. SWANSON, STAFF MECHANICAL ENGINEER

NORTHWEST ALLOYS, INC.

ADDY, WASHINGTON 99101

F. MARK SITTIG, STAFF ENVIRONMENTAL ENGINEER

ALUMINUM COMPANY OF AMERICA

PITTSBURGH, PENNSYLVANIA 15219

DOUGLAS A. AUSTIN, MANAGER - INDUSTRIAL SALES

RESOURCES CONSERVATION COMPANY

SEATTLE, WASHINGTON 98[illegible]

ZERO DISCHARGE AT NORTHWEST ALLOYS, INC. - A CASE HISTORY

Northwest Alloys, Inc., a wholly-owned subsidiary of the Aluminum Company of America, is located in Addy, Washington approximately 60 miles north of Spokane. The plant produces two important alloying metals, magnesium and silicon. Construction of the plant began in October, 1973 with the first magnesium being produced in March, 1976 and the first silicon metal in July, 1977. The rated yearly capacity of the plant is 24,000 tons of magnesium and 16,500 tons of silicon. The plant employs over 400 people and is located on a plant site of 240 acres.

Addy, Washington was chosen as the plant site because of its massive beds of dolomite, the raw material used in the magnesium production process, and of quartzite, which is required to produce ferrosilicon and silicon.

MAGNETHERM PROCESS

Northwest Alloys, Inc. uses about 400,000 tons of dolomite and 100,000 tons of quartzite annually. Conservative estimates indicate that there is at least a 15 year supply of these minerals at this location.

The magnetherm process is used to produce magnesium and Northwest Alloys is the only plant in the United States to use this European technology. In the process, dolomite is crushed, screened and

APPENDIX A

Table A1

Plant Water Balance Before Systems Revisions

Bldg. No.	Equipment	Quantity Used (GPM)
102	Blower Cooling	3
104	Recirculating System Makeup	20
108	Air Compressor Cool[illegible]	9
110	Fan Bearings Cooling	16
044	Air Compressor Cooling	5
372	Sanitary Clarifier Discharge	14
205	Recirculating System [illegible]keup	20
202	Crucible Wash System	15
218	Electrode Curing	2
044	Laboratory X-Ray Cooling	3
201	Elbow Cleaning Equipment Cooling	10
	Miscellaneous	8
	Sub Total	125
	Annual Run Off to Sto[illegible] Lake	35
	Total to Storm Lake	160

APPENDIX A

Table A2

Water Balance with Slag Granulation After Conservation Methods

Water Generating Processes

Bldg.No.	Description	Quantity Used (GPM)
104	Recirculating System Blowdown	3
205	Recirculating System Blowdown	34
202	Recirculating System Blowdown	2
372	Sanitary Clarifier Effluent	15
	Sub Total	54
	Annual Run Off to Storm Lake	35
	Total to Storm Lake	89

Water Consuming Processes

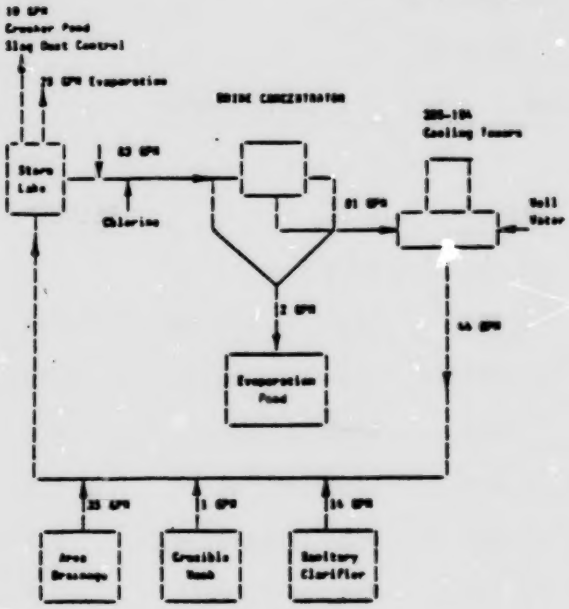
To Slag Granulation	70
Natural Evaporation	2
Dust Control	17
Total From Storm Lake	89

APPENDIX A

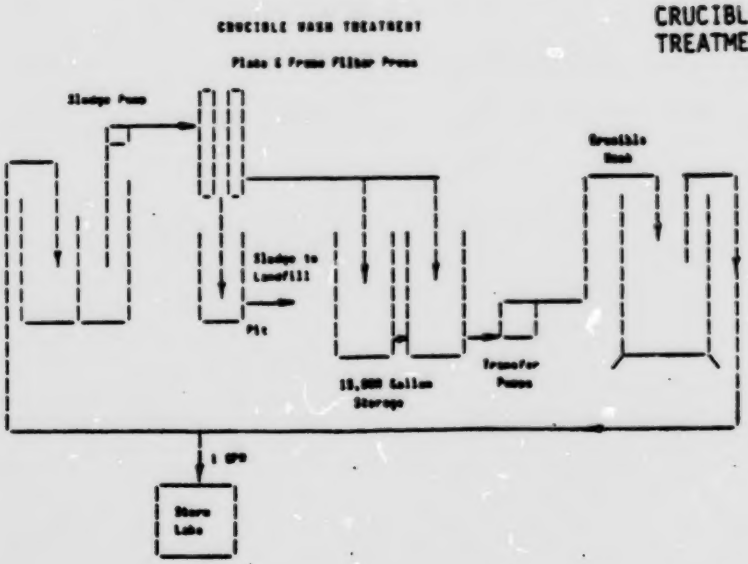
Table A3

CHEMICAL COMPOSITION OF CRUCIBLE CLEANING WATER

TESTS	RESULT:	TESTS	RESULTS
Sodium, mg/l	1,800	Turbidity, JTU	330
Potassium, mg/l	1,400	Specific Gravity	1.036
Calcium, mg/L	750	Aluminum, mg/l	19
Magnesium, mg/l	240	Ammonia, mg/l	474
Chloride, mg/l	5,800	Fluoride, mg/l	1.3
Sulfate, mg/l	780	Iron (total), mg/l	9.1
Total Dissolved Solids, mg/l	12,000	Manganese, mg/l	0.9
Suspended Solids, mg/l	2,200	Nitrate, mg/l	5.7
Elect. Cond., (μmhos/cm)	15,200	Phosphate, mg/l	0.8
pH	9.8	Zinc, mg/l	1.4
M.O. Alkalinity, (mg/L as $CaCo_3$)	490	Boron, mg/l	0.1
P. Alkalinity, (mg/L as $CaCo_3$)	380	Cyanide, mg/l	0.01
Silica, mg/l	15		



OPTION 10
CURRENT WATER BALANCE



CRUCIBLE WASH
TREATMENT

APPENDIX C

BRINE CONCENTRATOR OPERATING COSTS

	1981 4 th Qtr.	1982 1 st Qtr.	1982 2 nd Qtr.
Operating Labor	$ 9,976	$10,170	11,975
Outside Services	-	4,682	1,650
Supv. Tech. & Cler.	4,200	4,800	4,800
Repair & Maintenance	15,422	17,085	10,347
Power	12,0[illegible]	18,453	17,548
Operating Supplies	1,987	445	988
Burden:			
Taxes	551	570	230
Insurance	32[illegible]	321	321
Depreciation	36,249	36,249	36,249
O.T. Premium	813	813	813
Schedule Premium	312	312	312
TOTAL COST	$81,872	$93,900	85,233
GALLONS PROCESSED (10^3)	5,691	9,100	8,600
COST PER THOUSAND GAL.	$14.39	$10.32	$9.91

From: D. G. MURRAY

To: MR. L. E. GIBSON

1982 August 10

RE: MONTHLY WATER REPORT FOR JULY 1982

- Bldg. 104 RCW operated well for the month. The system remains sterile with the decreased Biocide feed.

- Bldg. 205 RCW operated well for the month. Chemical treatment change based on alkalinity done 07-13. Appears to be operating well aside from minor difficulty in determining proper pH and alkalinity ranges for this RCW system. Microbio counts remain Ø with the decreased Biocide feed.

- Bldg. 205-C multi-media side stream filter was down 07-09 thru 07-15 due to a malfunctioning solenoid operated Chemix makeup valve. Back on line 07-16 with an average NTU of 2.0.

- T&J Diving Service sludge pumped Bldg. 205 Hot Well 07-10/11, discovering ~four (4) feet of material and fine sludge on the pump impeller side of the weir.

- Bldg. 108 HWS operated well this month.

- Bldg. 375 Brine Concentrator operated at 98.9% uptime with eight (8) hours downtime due to a sample being cut from the D.A. vessel for lab analysis by RCC. Averaged 106.6 KWH/10^3 gallons water processed. Total product water for June was 3.87 x 10^6.

- Production Wells average gpd		140,600
- STP average gpd		--
- Bldg. 104 average makeup gpd	(potable)	55,522
	(distillate)	18,720
- Bldg. 111 Pelletizer average gpd		1,186
- Bldg. 202 Crucible Wash average makeup gpd		2,067
- Bldg. 205 average makeup gpd	(potable)	34,245
	(distillate)	100,800
- Bldg. 375 monthly average distillate gpd		119,426
		(83.0 gpm)
- Bldg. 375 uptime average distillate gpd		120,988
		(84.0 gpm)

D. G. MURRAY

DGH:mp

Attachment

(30)

Northwest Alloys, Inc.

LURGI

Lurgi Express Information

T 1315/3.79

Lurgi Umwelt und Chemotechnik GmbH
– Thermal Processes Division –
Gervinusstrasse 17-19
P.O.B. 119 181
D-6000 Frankfurt am Main

Freshwater from the Sea

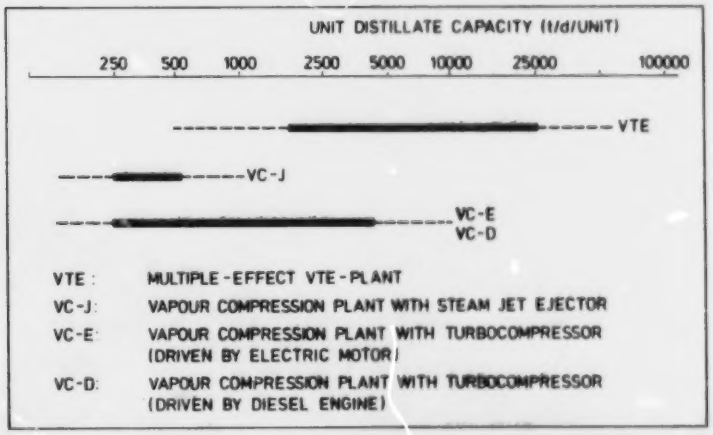
Vapour Compression Evaporation

1. INTRODUCTION

Fresh water is not available everywhere and not always in sufficient quantities. However, it can be obtained from sea, brackish or river water.

The plants needed for this purpose are designed by us in accordance with our own know-how, delivered, erected (also on turnkey basis) and commissioned.

Our know-how relies on the construction of more than a hundred evaporation plants working by the "VERTICAL TUBE EVAPORATION (VTE) SYSTEM", which offers many advantages in the desalting of sea, brackish or river water.



Types of LURGI seawater desalination plants

The multiple-effect VTE process is chiefly used for large plant capacities. For medium-size capacities, LURGI has developed another new conceptual design for seawater desalting plants. These seawater desalination plants with vapour compression (VC), benefit from the experience gained from evaporation plants working with thermal vapour compression (steam jet vapour compressor - VC-J) or with mechanical vapour compression (turbocompressor - VC-E or VC-D).

They can be built with a capacity of up to 4,000 tpd in one unit.

2. FEATURES OF THE VAPOUR COMPRESSION PROCESS

The vapour compression process for seawater desalting meets to a very high degree the present-day demands for low energy consumption at low investment costs, as well as for high availability, thanks to a clear set-up and ease of operation. The plants can be employed wherever electrical energy or fuel oil (EL) is available.

Mechanical vapour compression plants are distinguished by the following features:

- a very small process water intake quantity (2 to 3 t/t of fresh water) since no cooling water is needed.

- low process water treatment costs owing to the small water quantities involved.

- a very low energy consumption

  VC-E: 14 to 18 kwh/t of fresh water
  VC-D: 3 to 4 kg of fuel oil (EL)/t of fresh water

- a high purity of the distillate obtained (less than 8 ppm TDS).

- a high availability, due to carefully selected corrosion-proof materials and minimal scaling, owing to the low operating temperature.

- low operation and maintenance labour costs, thanks to automatic operation and the use of plant components having been tested over the years. Special care is exercised in selecting the compressor.

- pretreatment of the seawater with both additives and sulphuric acid

- turbocompressor drive by electric motor or Diesel engine at option

- a large range of variation of the distillate quantity

- low requirements for erection labour and short erection time due to extensive premounting of the plants

- small volume of civil work

- autonomous operation of the plant possible by its own power generation set

Thermal vapour compression plants are characterised by:

- complete pre-assembly, supply as a package unit

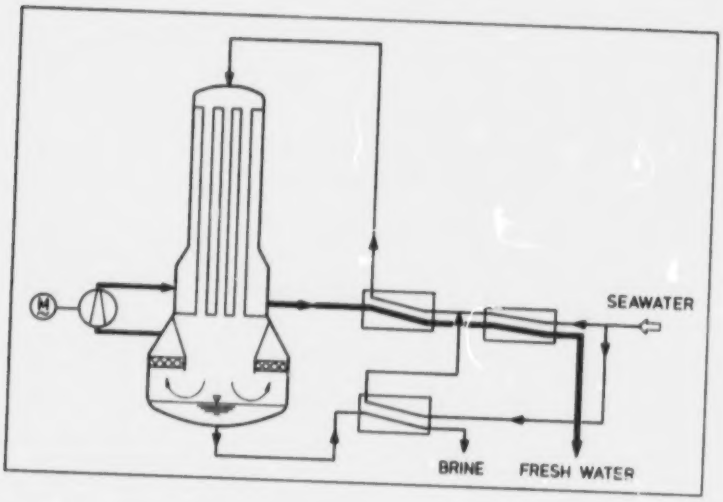
- very low investment costs

- unproblematical operation due to simplicity of plant set-up

- autonomous operation of the plant possible by its own power generation system

3. PRINCIPLE OF THE PROCESS

3.1 MECHANICAL VAPOUR COMPRESSION
- TURBOCOMPRESSOR DRIVEN BY ELECTRIC MOTOR



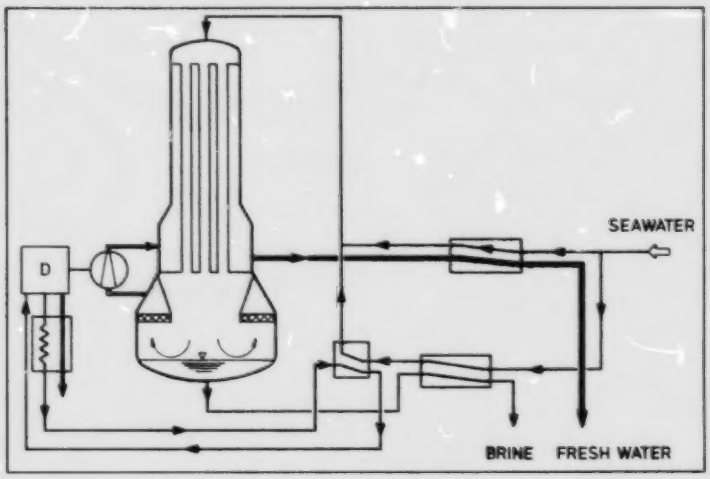
After mechanical and chemical pretreatment, the seawater is heated to the evaporation temperature (60 to 80°C) in plate heat exchangers in countercurrent to the distillate and brine and enters the evaporator at the top. Evenly distributed over the tube plate of a vertically disposed tube bundle, it flows down as a film inside the tubes. The tubes are heated with steam on the outside, so that water is evaporated from the seawater film.

The vapour given off from the seawater is compressed polytropically in a turbocompressor and re-introduced into the evaporator as heating steam.

The steam condenses on the outside of the tube walls and, after heat exchange with the process water, it is obtained as salt-free condensate suitable for processing into drinking water or for direct use.

Plants with a capacity of up to 1200 tpd are furnished with one evaporator. For larger plant capacities, two or three evaporators are connected in series.

3.2 MECHANICAL VAPOUR COMPRESSION
- TURBOCOMPRESSOR DRIVEN BY DIESEL ENGINE

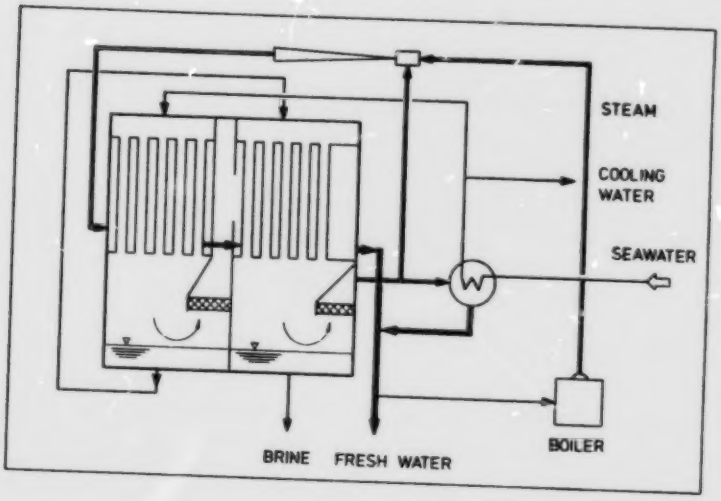


Under this process variant, the heat of the waste gases from the Diesel engine and of the cooling water is employed in addition to the distillate and brine heat for heating the process water. This process has been conceived for autonomous operation and is remarkable for the low costs it requires under partial load.

3.3 THERMAL VAPOUR COMPRESSION WITH STEAM JET EJECTOR

After the seawater has undergone mechanical and chemical pretreatment, it is heated in stages to the evaporation temperature (60 to 80°C) in the condenser and preheaters and subsequently reaches the first evaporator at the top, where it is evenly distributed over the tube plate of a vertically disposed tube bundle and flows down as a film

inside the tubes. The tubes are heated with steam on the outside, so that water is evaporated from the seawater film.



The vapour given off from the seawater, serves as heating steam in the second evaporator effect.

Part of the vapour produced in the second evaporating effect is compressed to a higher pressure in a steam jet ejector, employing steam from a steam boiler and is used to heat the first evaporating effect.

The other part of the vapour is condensed in the condenser, thus heating the process water, and is collected as saltfree condensate, together with the steam having condensed on the outer wall tubes of the evaporator. Part of this condensate returns to the steam boiler, whereas the remaining part is available for processing into drinking water or for direct use.

4. PRETREATMENT OF THE SEAWATER

At certain temperatures, untreated seawater will chiefly precipitate

calcium carbonate
calcium sulphate
magnesium hydroxide

on the heating surfaces.

Calcium carbonate is formed at low temperatures by thermal decomposition of hydrocarbonate. At higher temperatures (above 80°C), the hydrogen carbonate hydrolyses preferentially and results in the formation of magnesium hydroxide.

In fact, scale deposits on the heating surfaces reduce the output distillate and might increase the specific energy consumption.

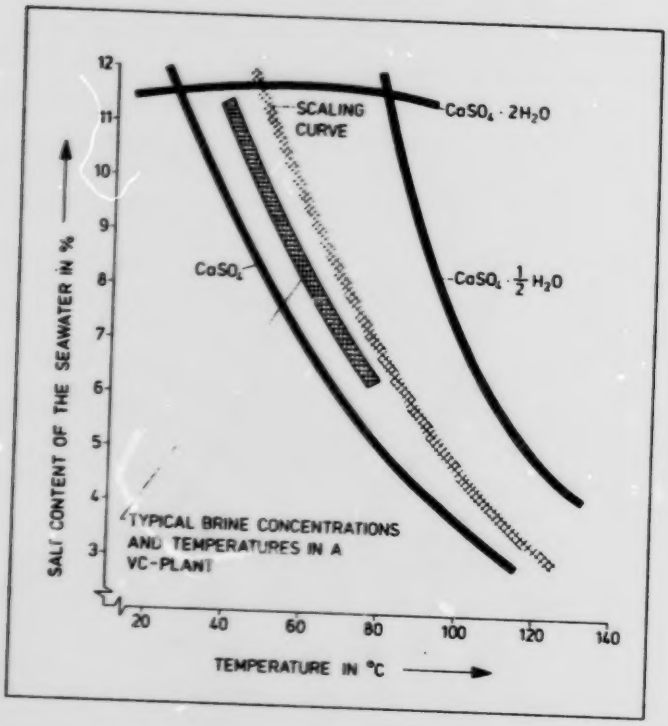
The LURGI VC process eliminates magnesium hydroxide deposition by using evaporation temperatures below 80°C.

For the elimination of calcium carbonate scaling, two methods can be adopted:

1) Treatment of the seawater with additives (e.g. polyphosphate or polymeric carboxylic acids). These additives are to keep the calcium and magnesium carbonates in solution and thus prevent deposition on the heating surfaces.

   Experience has shown that scaling cannot be eliminated entirely. However, the deposits are loose and may be readily dissolved by a suitable acid (e.g. aminosulfonic acid); it is therefore advisable to flush the plant at certain intervals.

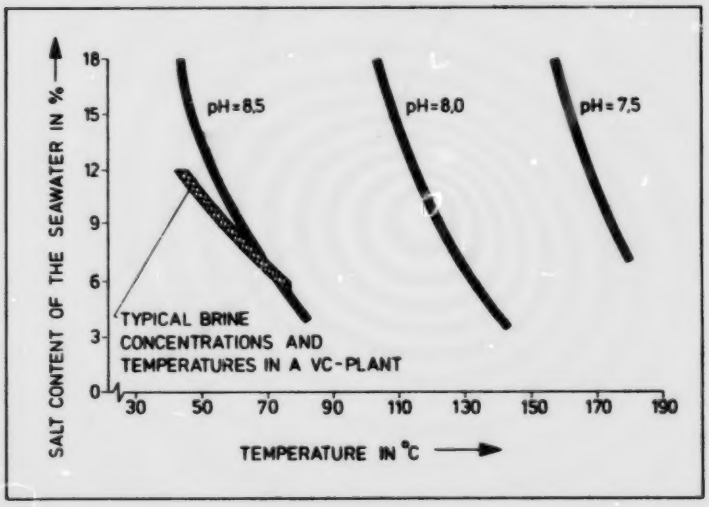
There is no fear of calcium sulphate deposits in VC plants either, because the temperature and concentration of the brine during distillation always remain below the calcium sulphate scaling curve, which runs between the saturation curves of the anhydride and hemihydrate.



Solubility of calcium sulphate

2) Treatment of the seawater with sulphuric acid. The sulphuric acid reacts with the hydrocarbonate forming calcium sulphate and carbon dioxide. The latter is drawn off completely from the seawater in a vacuum degasser.

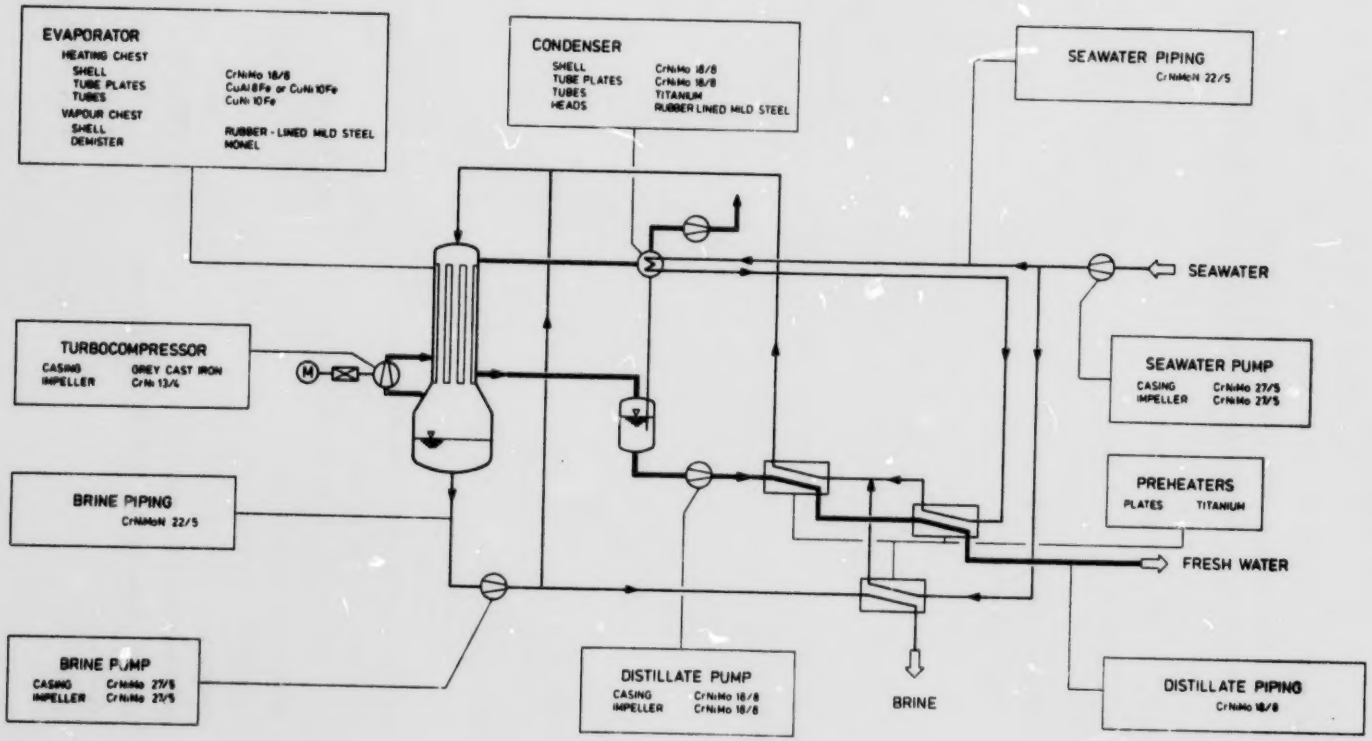
The acidified and degassed seawater is adjusted to a pH value of 7.5 by means of sodium hydroxide before it enters the evaporator. This pH value ensures that, at the concentrations and temperatures prevailing in the VC plant, no magnesium hydroxide precipitates.



Solubility of $Mg(OH)_2$ in seawater

5. CONSTRUCTION MATERIALS

Reliability and availability are indispensable features of plants to producing drinking water and service water. We guarantee these features by careful selection of construction materials and testing. The metal laboratory of METALLGESELLSCHAFT, Frankfurt/Main, our parent company, assists us in these matters.



SELECTION OF CONSTRUCTION MATERIAL DEMONSTRATED FOR A VC-PLANT

6. CAPACITY RANGE AND SPACE REQUIREMENTS

We supply VC plants of 250 to 4,000 tpd in one stream. The capacity range of the plants with thermal or mechanical vapour compression is broken down as follows:

Thermal vapour compression:

250 and 500 t/day

Mechanical vapour compression:
(with Diesel engine or electric motor drive, at option)

500 to 1,300 t/day with one evaporator
1,300 to 2,700 t/day with 2 evaporators in series
2,700 to 4,000 t/day with 3 evaporators in series

The plants are equipped for outdoor installation and premounted to the largest possible extent.

Thermal vapour compression plants are sold as package units.

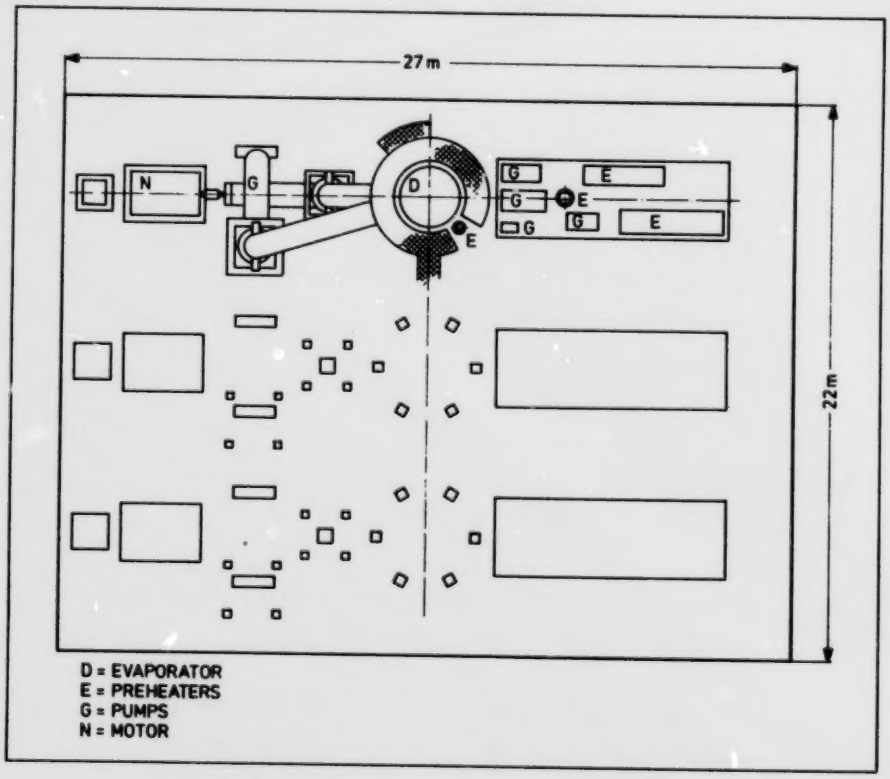
Technical Data

Mechanical Vapour Compression Plants

- salinity of brackish/seawater, in TDS	15,000 to 60,000 ppm
- salinity of the brine, in TDS	65,000 to 110,000 ppm
- salinity of distillate, in TDS	$\leq$ 8 ppm
- seawater temperature	up to 50°C
- seawater quantity:	
distillate output	3 : 1 to 2 : 1
- evaporation temperatures	60 to 80°C
- energy consumption /ton of distillate	
VC-E	14 - 18 kWh
VC-D	3 - 4 kg fuel oil

Thermal Vapour Compression Plants

- salinity of brackish/seawater, in TDS	15,000 to 60,000 ppm
- salinity of brine, in TDS	up to 80,000 ppm
- salinity of distillate, in TDS	$\leq$ 30 ppm
- seawater temperature	up to 45°C
- seawater quantity : distillate output	5 : 1
- evaporation temperatures	70 - 75°C
- energy consumption /t of distillate	
fuel oil	12 - 14 kg
electric energy	2.5 kWh

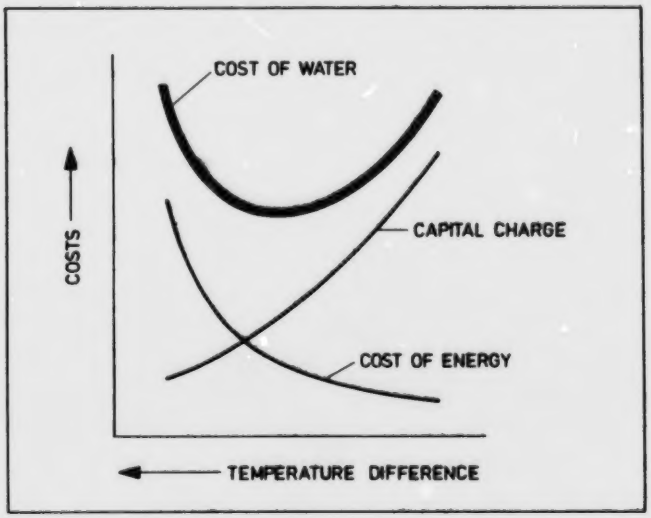


Space requirements of a 3-line VC-E plant installed outdoors, capacity: 3 x 1000 t/d

7. HOW MUCH DOES A TON OF DISTILLED WATER COST?

The water price is determined decisively by energy and capital costs. They depend on the effective temperature differential in the evaporator of the desalination plant.

The sum of energy and capital costs is reduces to a minimum value at a given temperature difference, depending on the local cost factors.



Water costs

The Price of one Ton of Water

produced in a single-effect VC-E seawater desalination plant with a distillate output of 500 tpd

salinity of seawater	45,000 ppm TDS
salinity of brine	70,000 ppm TDS
distillate	8 ppm TDS
operating period per annum	8,000 h

Consumption per m^3 of distillate:

electrical energy	18	kWh
additive	0.015	kg

Amortization period: 10 years at 8 % interest.

7.1 Plant Cost

		D M
a) VCE plant f.o.b. without seawater intake structure and drinking water treatment system, electric drive (approx. 80 % premounted)		1,520,000.--
b) Freight charges		.....
c) Final field erection	approx.	100,000.--
d) Foundation (civil work and engineering)	approx.	50,000.--
e) Commissioning	approx.	10,000.--
f) Spare parts for 2 years (approx. 5 % of a)	approx.	76,000.--
	approx.	1,756,000,--

7.2 Capital Charges

8 % interest for 10 years

f = 0.149

= 0.149 x 1.756.000 = DM 259,888.--

7.3 Costs per m^3 of Fresh Water — D M

7.3.1 Capital costs

$$K = \frac{259.888.--}{8000 \times 500/24} = 1.559$$

7.3.2 Energy costs

Price DM 0.07/kWh

Consumption 378 kW

(K = 5 - 6)

$$E = \frac{378 \times 0.07}{500/24} = 1.270$$

7.3.3 Chemical costs

$Na_5P_3O_{10}$; price DM 2400.--/t

consumption 5 ppm

$= 5\ g/m^3 \times 65\ m^3/h = 0.325\ kg/h$

$$C = \frac{0.325 \times 2400}{1000 \times 500/24} = 0.037$$

7.3.4 Cost of manpower

- inspection 1/2 h every 4 h
  = 1 h / shift
- 3 + 1 man / shift
- hourly wages DM 15.-- / h
- social security contributions 70 %

$$P = \frac{15.-- \times 1.7 \times 1,333 \times 0.5}{500/24 \times 4} = 0.204$$

7.3.5 Maintenance cost

D M

4 % of the plant cost /annum

$$W = \frac{1.520.000 \times 0.04}{8000 \times 500/24} = 0.365$$

Total cost per ton of distillate

Amortization	DM 1.56	(45.3 %)
Utilities and auxiliary materials	DM 1.31	(38.1 %)
Manpower	DM 0.20	(5.8 %)
Maintenance	DM 0.37	(10.8 %)
	DM 3.44	(100 %)

8. TREATMENT OF DRINKING WATER

Seawater distillate is not drinking water. It lacks the minerals required by the organism, human and animal. To obtain a chemically and bacteriologically flawless drinking water that does not damage the pipe network, the freshwater has to be processed.

For processing, the following treating methods have proved successful:

- aeration
- salinification to approx. 300 ppm by adding seawater
- acidification with carbon dioxide
- passing over dolomite or mixing with caustic lime, in order to obtain a calcium hardness of at least 1 mval/kg
- protective chlorination up to a chlorine residue of 0.2 to 0.3 ppm.

9. PRODUCTION OF BOILER FEED WATER

The distillate from a VC plant is processed into boiler feed water at very low costs, because of the residual salt content of the distillate, which is already low.

For large waterspace boilers and circulation boilers up to an operating pressure of 64 bar, softening by cation exchange resins in the sodium form is sufficient. The total hardness of the distillate is thus reduced to values smaller than 0.01 mval/kg.

For circulation boilers above an operating pressure of 64 bar, as well as for once-through boilers and injection water for steam desuperheaters demineralisation is effected directly in mixed bed exchangers. A mixed-bed exchanger consists of a filter bed with a mixture of strongly acid cation exchanger and strongly basic anion exchanger.

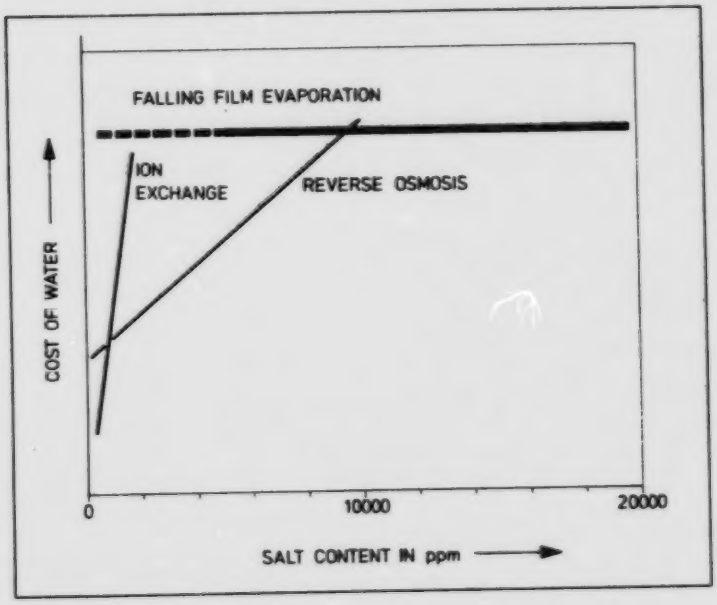
In those cases where a water-steam cycle exists, i.e. condensate is returned as boiler feed and the distillate from the VC plant is used solely as make-up water, condensate processing and distillate demineralization can be combined accordingly. To this end, mostly candle filters, precoated and unprecoated, are employed for condensate filtration, followed by mixed-bed exchangers for demineralizing the distillate and condensate.

10. WHEN IS THE VC PROCESS APPLIED?

For the desalination of brackish, river and seawater, various processes are available:

- distillation process
- freezing and hydration process
- electrodialysis
- reverse osmosis and
- ion exchangers

In addition to the reliability and applicability, the costs of the final product produced - service or drinking water in this instance - play a decisive part in the selection of a process. A comparison of the costs associated with the processes most frequently used - distillation, reverse osmosis and ion exchange - reveals an interesting function between the distillate price and the salinity of the water under treatment, at the present level of technology.



Water costs of different types of desalting plants

As a salinity of up to 500 ppm, water produced by ion exchange techniques is definitely the cheapest. For salinities ranging between 400 and 10,000 ppm, the use of plants working by the reverse osmosis principle should be given serious consideration. Above a salinity of 10,000 ppm, the distillation processes have been and still are unbeaten regarding their economics.

VC plants can be employed very economically where plant capacities of up to 4,000 tons per day and line are involved.

Thermal vapour compression plants with capacities of up to 500 tpd are remarkable for their

- low investment costs
- low construction and erection costs
- low operating and maintenance costs

while their consumptions are higher. They are particularly suited as water supply units for construction sites.

Mechanical vapour compression plants are designed for minimum energy consumptions and offer the same advantages as VC-J plants at somewhat higher investment cost.

They are very versatile in application, e.g.

- as plants for the production of boiler feed water in power plants
- as drinking and service water production plants for capacities of up to 4,000 tons per day and train
- as extension of existing desalting plants since in this case, the cooling water can be re-used as process water for the VC plant.

  Thus, no costs arise for a new seawater intake structure and for seawater treatment.

REFERENCE LIST

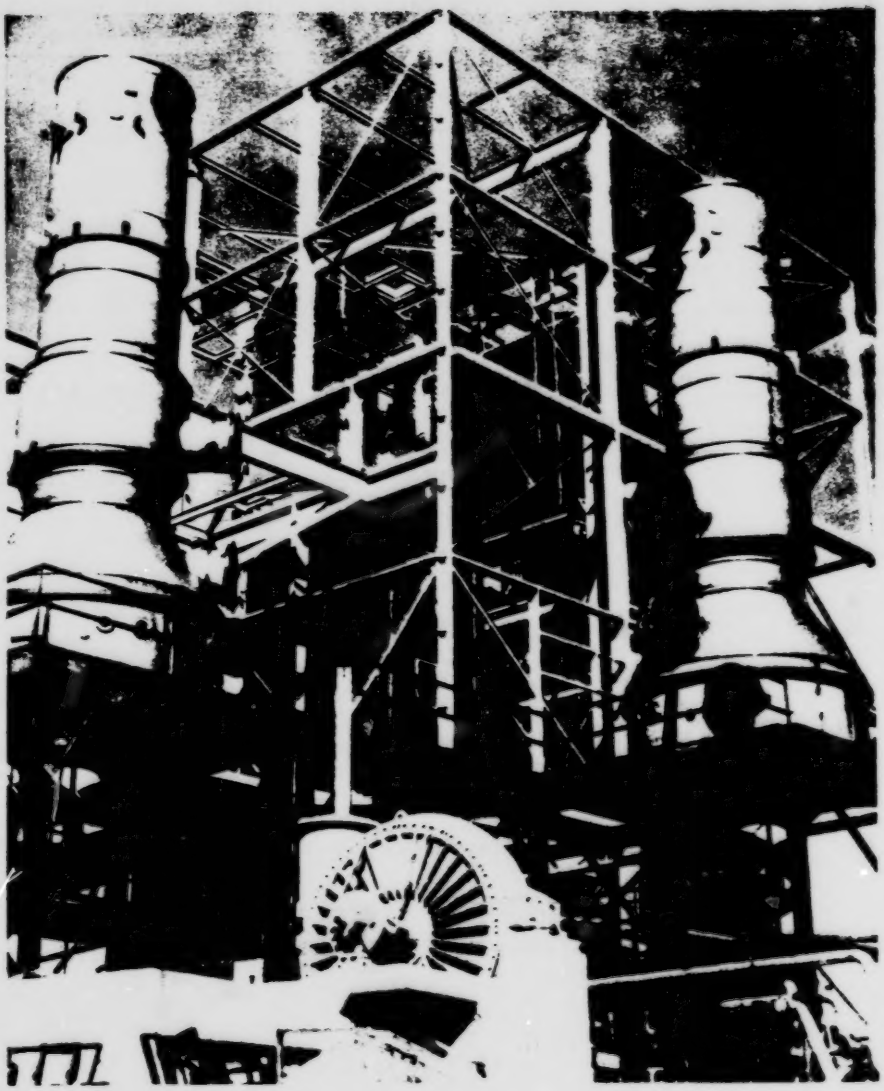
Client/Location	Type	Feed Material	Effect	Capacity of water evaporation/ distillate
SUOMEN SOKERI Helsinki/Finland	A	sorbite	1	9,6 t/d
CELULOSA Y PAPEL Michoacan/Mexico	A	sulfate waste liquor	7	1 800 t/d
OLEOCHIM, Belgium	A	glycerine water	2	168 t/d
BENCKISER Ludwigshafen/Germany	A	citric acid	4	230 t/d
BENCKISER Ladenburg/Germany	A	tataric acid	4	82 t/d
MAIZENA Krefeld/Germany	A	glucose	2	190 t/d
EPIDC DACCA/Pakistan	A	sulfate waste liquor	4	550 t/d
NETTINGSDORFER PAPIERFABRIK Nettingsdorf/Austria	A	sulfate waste liquor	6	1 440 t/d
HACO Gümlingen/Switzerland	A	coffee-solution	2	48 t/d
PROTUCASA Lanzarote/Spain	A	seawater	10	150 t/d
KLÖCKNER WERKE Bremen / Germany	A	brackish water	8	2 400 t/d
KRAFTWERK UNION Bushehr/Iran	A	seawater	10	2 400 t/d
NUCLEAR RESEARCH CENTRE Karlsruhe/Germany	B1	contaminated water	1	100 t/d
NUCLEAR RESEARCH CENTRE Karlsruhe/Germany	B1	contaminated water	1	100 t/d

Client/Location	Type	Feed Material	Effect	Capacity of water evaporation/ distillate
BOISE CASCADE Salem/USA	B1	sulphite waste liquor	3	3 000 t/d
GEORGIA PACIFIC Bellingham/USA	B1	sulphite waste liquor	3	1 900 t/d
KRAFTWERK UNION Bushehr/Iran	B1	seawater	1	500 t/d
KRAFTWERK UNION Bushehr/Iran	B1	seawater	1	500 t/d
BMFT Lanzarote/Spain	B2	seawater	1	500 t/d
ZELLWOLLE LENZING Lenzing/Austria	B3	sulphuric acid	1	60 t/d
SVENSKA RAYON Älvenäs/Sweden	B3	sulphuric acid	1	100 t/d
COTONIFICIO TRIESTINO Gorizia/Italy	B3	sulphuric acid	1	100 t/d
GLANZSTOFF GMBH Köln/Germany	B3	sulphuric acid	1	72 t/d
TECHMASHIMPORT Moscow/UdSSR	B3	sodiumsulfate	1	100 t/d
TECHMASHIMPORT Moscow/UdSSR	B3	sodiumsulfate	1	100 t/d
MASINIMPORT Bukarest/Rumenia	B3	sodiumsulfate	1	90 t/d
CHEMIEFASER LENZING Lenzing/Austria	B3	sodiumsulfate	1	130 t/d
GODREJ SOAPS Bombay/India	B3	glycerine water	2	50 t/d

Client/Location	Type	Feed Material	Effect	Capacity of water evaporation/ distillate
JAHRES FABRIKKER Norway	B3	glycerine water	2	80 t/d
OLEOCHIM Belgium	B3	glycerine water	2	180 t/d
NOURY Emmerich/Germany	B3	glycerine water	2	72 t/d
AARHUS OLIEFABRIK Aarhus/Denmark	B3	glycerine water	2	72 t/d
GLYCHEM Singapore	B3	glycerine water	2	30 t/d

PLANT TYPE

A	Multiple Effect Vertical Evaporation	(VTE)
B	Vapour Compression Evaporation	(VC)
B1	Mechanic Vapour Compression driven by Electric Motor	(VC-E)
B2	Mechanic Vapour Compression driven by Diesel Engine	(VC-D)
B3	Thermal Vapour Compression with Steam Jet	(VC-J)



Vapour compression evaporation plant
for spent sulphite liquor (under construction)
Client: Boise Cascade, Salem, USA
Capacity of water evaporation: 3000 t/day
Commissioned: 1972

SEAWATER DESALINATION WITH VERY LOW ENERGY CONSUMPTION

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ABSTRACT

A desalination process is presented, employing a combination of VTE and MSF processes. A new development of compact titanium plate heat exchangers permit the vertical arrangement of 55 effects within a pressure housing 34 m height, with a 2,5 x 3,2 m base. This tower unit provides a fresh water output of 5000 m^3/day with a Performance Ratio of 40 (tons of fresh water per ton of supplied steam).

INTRODUCTION

A large scale prototype desalination plant has been developed based on a new patented plate heat exchanger design. This plant, operating as multiple effect process (vertical tube evaporation VTE + multi stage flash MSF) has been erected at Bavaria Anlagenbau GmbH, near Munich. A total process capacity of 5000 m^3/day can be reached by simply doubling the prototype's cross section width.

The plant's most important advantages are the extremely low energy consumption (Performance Ratio > 40 by thermodynamic evaluation) and improved operating characteristics.

Specifically this unique design offers:

1. A large number of effects because of compact heat exchanger design, their arrangement and economic production technique.
2. An effect interconnecting baffle system avoiding external pipework.
3. A Performance Ratio > 40, because 55 VTE effects and 75 MFS stages are combined, operating from 130 °C down to approx. 30 - 35 °C.
4. Maximum corrosion resistances as all heat exchangers are manufactured of titanium and all internal chamber surfaces in contact with seawater are made of monit.

5. Minimized scaling, as brine is passed only once through the plant housing and operation with reduced pH-values does not attack the titanium and monit structures.
6. Easily interchangeable VTE-evaporators that can be slid into and out of pressure housing.
7. Front and rear hydraulic operated covers giving immediate access to the heat exchangers. An inflatable sealing ensures pressure-tight housing covers.

PROCESS DESCRIPTION

(see Fig. 1)

There are 5 main components:

1. Preheater (1)

   Seawater pumped through the preheater to the top VTE effect (2) of the box is heated up to 130 °C. Heating energy is supplied partly by condensing vapors from the MSF stages (3) and partly from the VTE effects (4).

2. VTE-evaporator effects (5)

   They are forming the pressure chamber boundaries together with the vapor guiding baffles (6) and MSF flash stages (7).

   Over 55 effects the pressure drops from approx. 2,9 bar at the top to approx. 0.05 bar vacuum over the bottom effect.

   For the sections of normal and vacuum pressure the VTE plate side offers an extended cross section to accomodate the dropping vapor density. Because of a reduced VTE heat transfer surface, the average driving temperature is increased to have optimum adaption to the geometric and thermodynamic conditions.

   Brine is flashed at each VTE effect inlet point (8)

followed by the falling evaporation as the brine passes vertically downstream.

Starting from the top, seawater of 130 °C enters the first VTE-effect (2) and is evaporated by heating steam of 3 bar, 132 °C (A) which is supplied to the VTE effect plate side. The steam condenses and forms the initial fresh water passing down the 75 MSF effects (7).

Brine and fresh water vapors leave the VTE effect on the tube side.

The brine (15) collects on top of the following VTE-effect which is covered by water distribution elements (8). These elements serve to throttle and to accumulate the brine to a defined level. This insures equalized brine falling film characteristics in the tube profiles of the VTE evaporator below.

The fresh water vapors, (10) having left the VTE evaporator tubes are forced to stream horizontally via the baffle plates (6) and the centrifugal separators (11) to enter the next VTE-effect at the plate side and the preheater's tube side for condensation. The condensation causes a suction effect continuously drawing vapor to the condensation surfaces.

By entering and passing the VTE via both plate-side ends, the vapors experience a minimum pressure loss. Inside the VTE-plate -side structure the condensate runs off vertically (14) due to gravity and accumulates for horizontal discharge (13) in the lowest plate cross section.

In the VTE effect the vapor's heat of condensation is used as heat of evaporation on the tubeside for vapor generation. The temperature difference corresponds to the pressure drop at the brine throttling plate (8).

3. Baffles (6) with centrifugal separators (11).

As described above vapors are guided to the next following VTE effect plate side. Brine droplets are separated from the vapors by the centrifugal effect resulting from the radial baffle-forced vapor flow.

4. MSF-flash effects (7)

Condensate effluents from the VTE effects and from the corresponding preheater sections are accumulated to be flashed into the next pressure chamber for increased heating steam availability in the preheater section below.

For the 12 lower VTE effects the corresponding MSF effects are divided up into several pressure steps (12) in order to provide elevated temperature differences between condensate and seawater in the preheater section below - for optimum use of the available heat transfer area.

5. Run-off system (not shown in Fig. 1)

Brine collected over the VTE effects (15) and in the centrifugal separators (11) is passed down to the next pressure effect by means of a run-off system, acting as soon as a maximum liquid level is reached.

6. Inert gas discharge (17)

Inert gases are exhausted selectively by means of VTE internal scondary condensation of remaining vapors, along the lowest plate cross section of the VTE evaporator (13) starting as the midpoint of the VTE plate length (16).

TABLE 1:

Data of the DVT-process

Consumption data

Inlet seawater, preheated			370	t/h
	temperature	approx.	35	°C
	pressure		8	bar
	total salinity TDS	"	400000	ppm
Heating steam to 1. VTE effect			5.2	t/h
	temperature		132	°C
	pressure		2.9	bar

Performance data

Distillate water			210	t/h
	temperature	approx.	36	°C
	pressure		0.07	bar
	flexibility		40-100	%
Seawater concentration factor			2.3	-
Performance ratio p.r.			>40	-

VTE-evaporator:

an all-welded plate heat exchanger of patented profile structure (Fig.2) with plates of 0.2 mm titan-palladium material.

In the vertical passage the facing plate profiles form double fluted tube channels of 330 mm length and 5 mm hydraulic diameter (Fig.3). The tube profiles are intersected every 36 mm by horizontal tube interconnecting channels which act to equalize pressure and concentration of fall-film evaporation.

In the horizontal passage all the facing plate profiles form plates with sinuous flow channel characteristics providing a short condensate film run-off length (Fig.4).

TABLE 2:

VTE-evaporator data

No. of tubes per VTE effect	18 520	
Heat transfer area per VTE effect (in medium press.section)	491	m^2
Heat transfer surface per m^3 evaporator vol.	200 - 290	m^2
Heat transfer surface per kg titanium	1.1	m^2
Average heat transfer coefficient	4180	W/m^2K
Average temperature gradient per effect	1.74	K
Average temperature difference	1.0	K

Preheater

The preheater is designed with parallel plate heat exchanger units using the same plate profile and tube channel length as the VTE effect but without the double flute tube structure used in the tube profile. 0.4 mm titan-palladium plate elements are used.

As vertical upstream seawater is pumped through the plate side (Fig.4) it generates a sinuous turbulent flow characteristic.

In the horizontal passage product vapors condense in the tube profiles and the condensate runoff follows the tube interconnecting channels as vertical downstreams (Fig.5).

The condensate is discharged into the adjoining MSF chamber along a preheater pressure effect subdivision boundary (9). This boundary is formed by modification in the plate profile structure, creating a tight

contact between facing plates due to the pressure of seawater passing through the plate side.

TABLE 3:

Preheater data

No. of tubes	759 000	-
No. of pressure effects	75	-
Heat transfer area	8200	m^2
Heat transfer surface per m^3 preheater	220	m^2
Heat transfer surface per kg titanium	0.5	m^2
Average heat transfer coefficient	4250	W/m^2K
Average temperature difference	0.8	K
Maximum pressure (seawater inlet)	8	bar

LETTER SYMBOLS IN THE PROCESS DIAGRAM, FIG. 1:

A steam inlet 132 °C
B seawater inlet
C distilled water outlet
D brine outlet
E residual steam to final condensor
F inert gases to vacuum pump

numbers shown in Fig.1 are explained in the text.

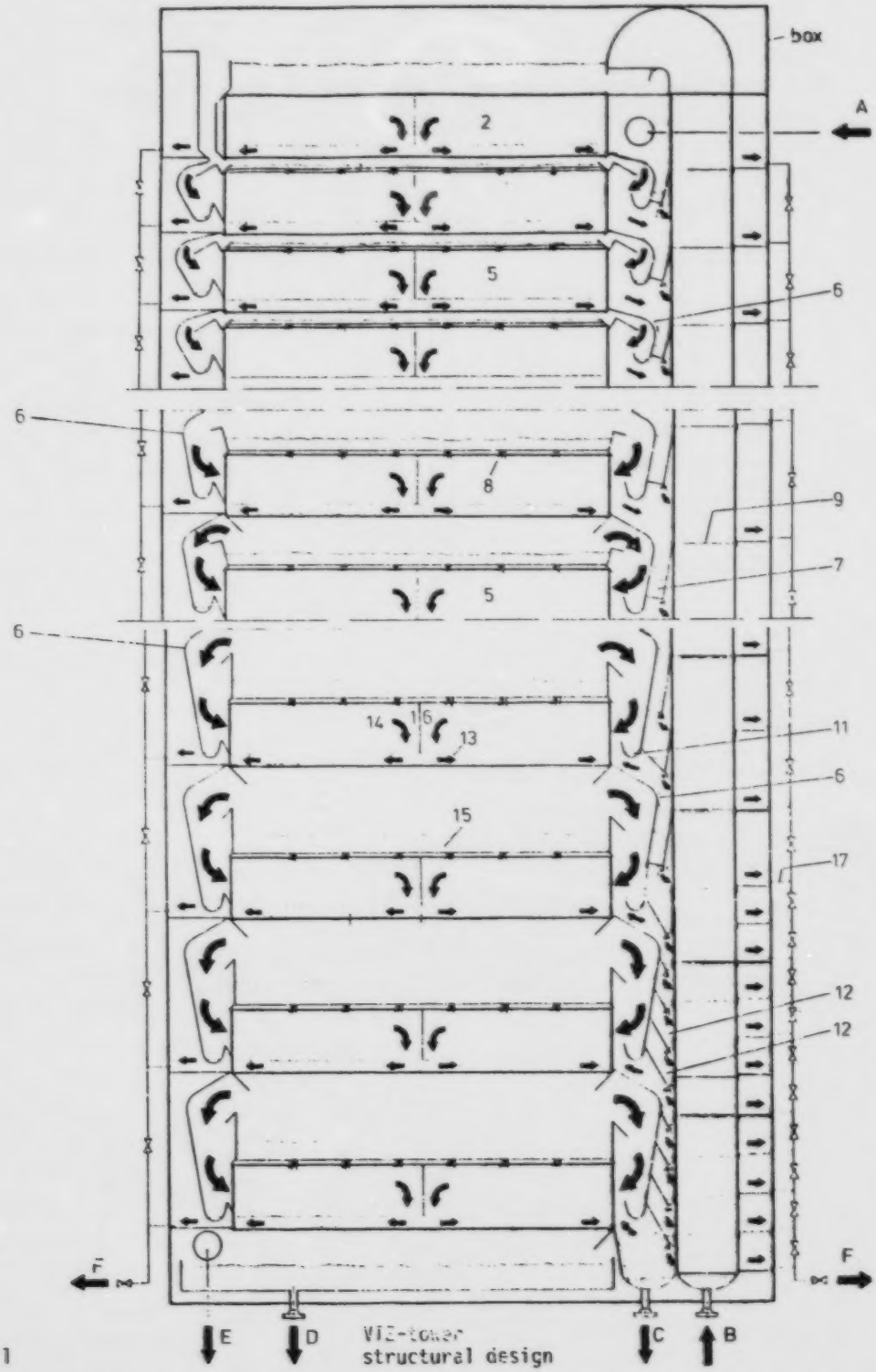


Fig. 1 VIE-tower structural design

plate-side

tube side

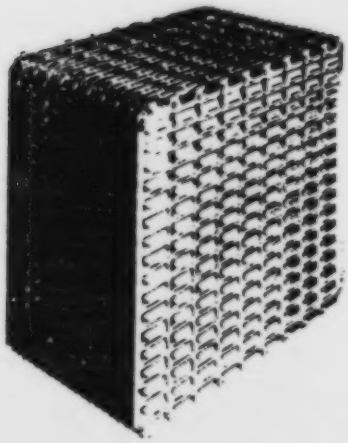


Fig. 2 Plate heat exchanger element showing tube profile structure

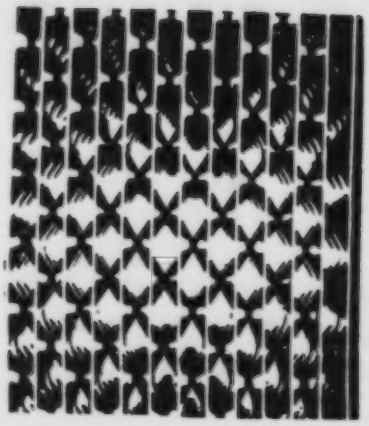


Fig. 3 Tube-side flow channel cross section

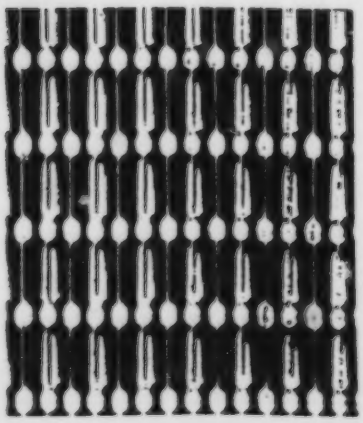


Fig. 4 Plate-side flow channel cross section

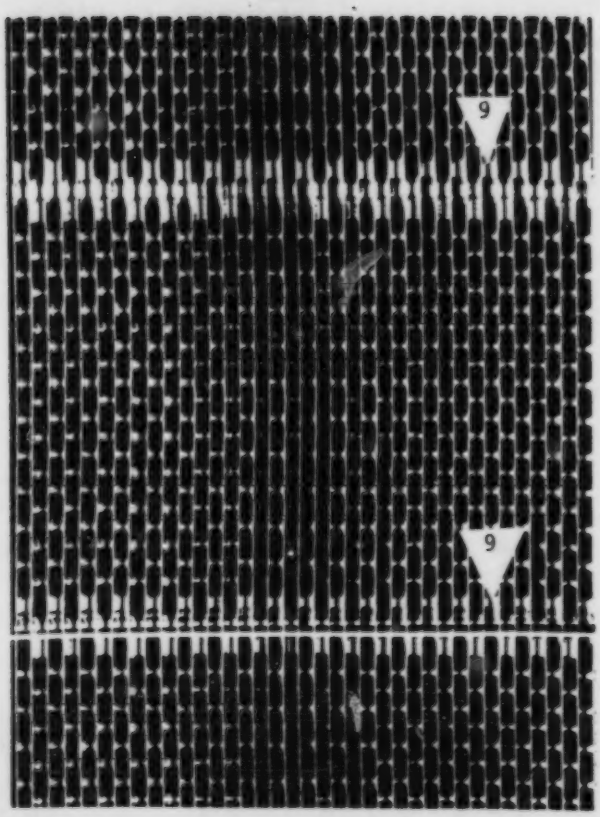
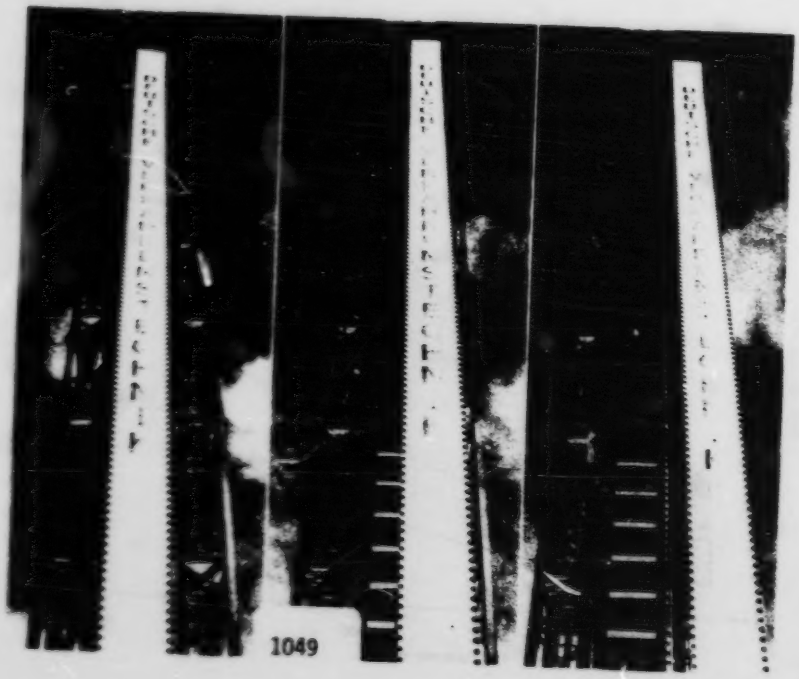


Fig. 5 Preheater's tube-side condensate cross section showing a pressure effect boundary (9):
There, facing profile plates form a tight contact from the pressure of seawater passing through the plate-side.

dvt VTE-MSF DISTILLATION PROCESS
a breakthrough in performance and design

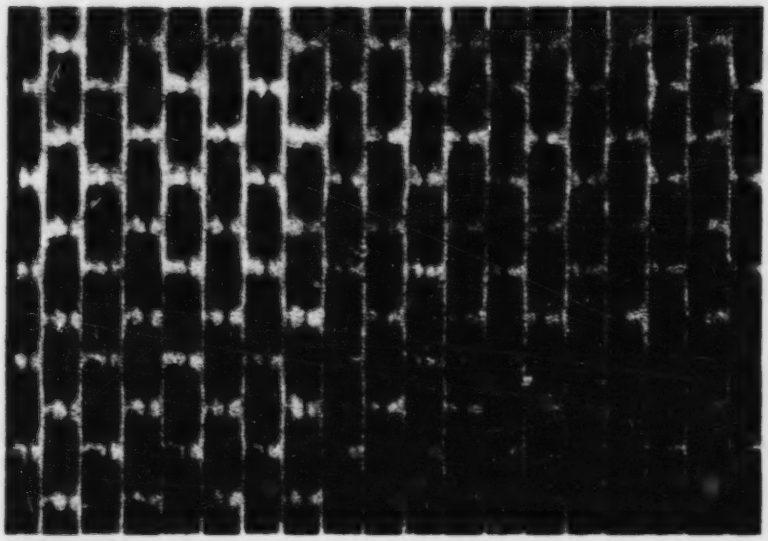
- minimum energy consumption:
  performance ratio of 40 (to fresh water per to heating steam) realised by the compact high performance BAVEX exchanger design arranged in 55 vertical VTE effects.
- extended plant life time:
  high quality materials as 0.2 mm thin titan palladium plates for the BAVEX VTE, and 0.4 mm thin monit plates for the BAVEX MSF condensor ensures
- corrosion free operation
- operation free of scaling:
  acid dosing for scale control not hazardous for the BAVEX exchangers made of titan and monit. Once through brine circulation.
- compact design:
  units for capacities of 10000 m^3/day will only require a ground area of 20 sqm. The height of the desalination tower reaches 35 m. There is no external effect interconneting pipework.
- competitive investment costs:
  compact prefabricated design, high efficent use of raw materials for the automatisized BAVEX exchanger production.
- reduced maintenance time:
  VTE effects are installed as a slide in and pull out system. Acess is given by hydraulicly locked tower front-doors (see photographs below) with inflateable sealing.



Opening of hydraulic locked tower front-door

dvt

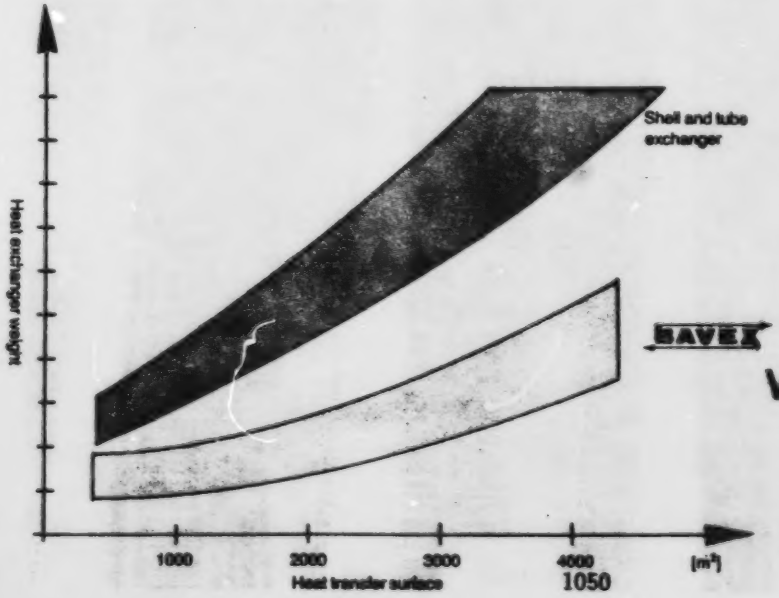
The patented BAVEX hybrid exchanger as core element for the new VTE-MSF design



BAVEX

vertical view through the tube side cross section. The plate side flow path is seen as sinuous flow channels.

Weight and Material Consumption of BAVEX compared with tube & shell exchangers.



Development and operating experience with BAVEX Hybrid heat exchangers have shown that almost all advantages of plate type and tube & shell type exchangers have been optimized in one innovative heat transfer system. Conventional tube & shell type exchangers with Cu-Ni-tubes in seawater services are being replaced by hybrid exchangers of MONIT stainless steel or titanium.

Advantages of BAVEX hybrid exchangers are especially:

- Lifetime of MONIT approx. 5 times longer than Cu-Ni materials in seawater services and chloride solutions
- Lifetime of titanium not limited by corrosion as seawater services have shown.
- Less plot area required and less weight
- High heat transfer rates and low pressure drop
- Economic prices due to automic fabrication although high quality material is used.

Deutsche Verfahrenstechnik

Graf-Adolf-Straße 68
D-4000 Düsseldorf 1
West-Germany

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Telex 8 587 739

Pretreated Seawater is pumped through the preheater (2)* to the top of the tower (1)* while it is heated by condensing vapors from the MSF stages (11) and the VTE-effects (7).

By external steam (3) the seawater is reaching its final temperature of 130 °C and is evaporating in the top VTE-effect (1) to form brine and the initial fresh water vapors.

The brine passes through the tube side of all 55 VTE effects as once through vertical downstream. From effect to effect the pressure and temperature is dropping to reach vacuum pressure and about 30 °C at the bottom of the tower.

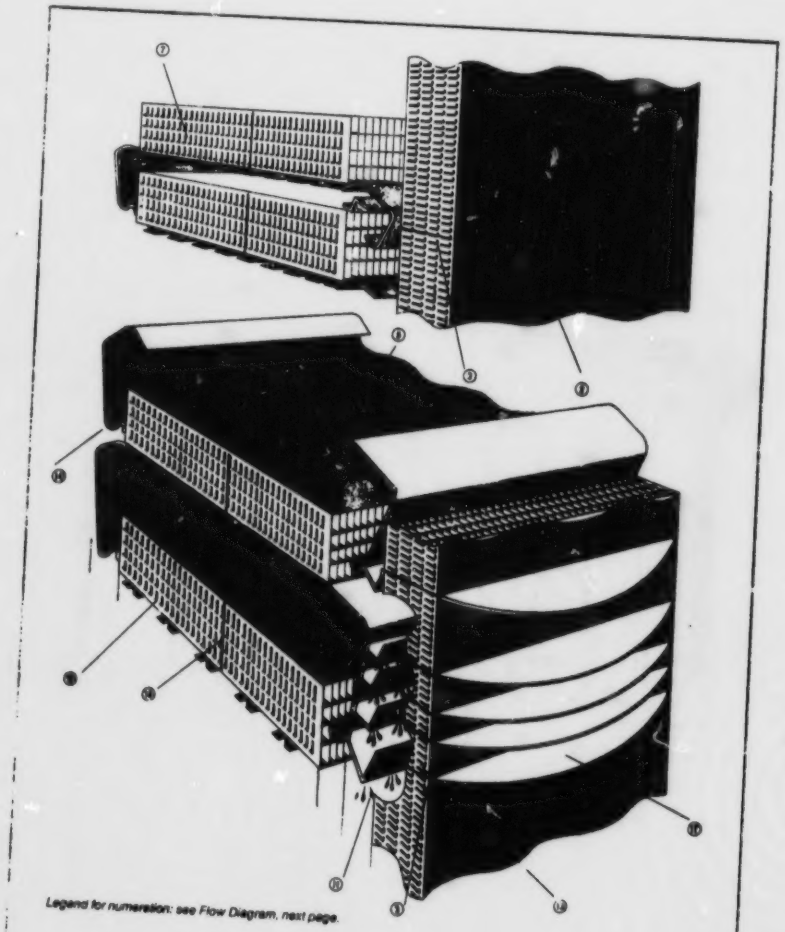
Fresh water vapors are evaporating from the brine falling film in each VTE effect (7). In the next following VTE effect below these vapors are condensed on the plate-side and provide the heating energy in this VTE effect to cause new vapors forming from the evaporating brine on the tube side. The new vapors have a reduced temperature and pressure level and repeat the same process again in the following VTE effects.

The condensates (15) produced by each VTE effect runs off into the MSF stages (10). There, from stage to stage the condensate is flashed (11) to provide heating steam for the preheater (2).

Along the low pressure VTE effects the MSF stages are divided up into several flashing steps (12) to provide vapors on elevated temperature levels for preheating.

Inert gases are exhausted selectively by secondary condensation of vapors along the lowest plate cross section of each VTE effect (15).

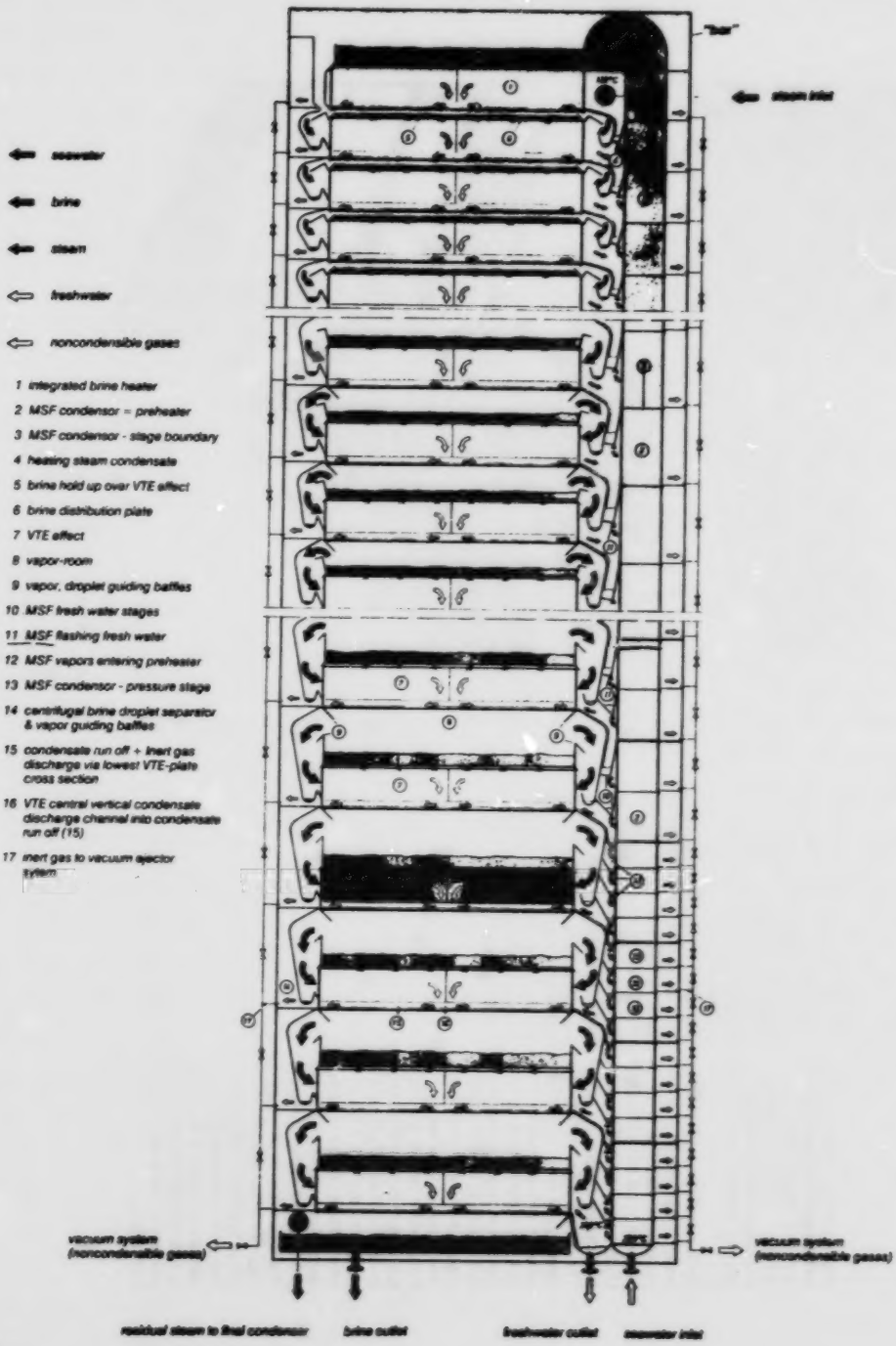
* numbers refer to Flow-Diagram next page.

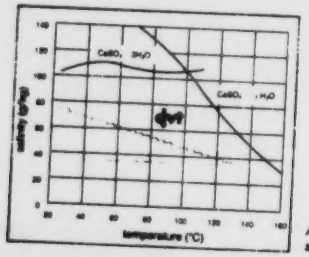


Legend for numeration: see Flow Diagram, next page.

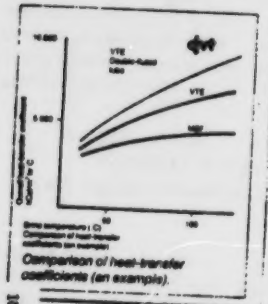
Principle of heat-exchangers and guiding-panels

dvt VTE-MSF Process – Flow Diagram

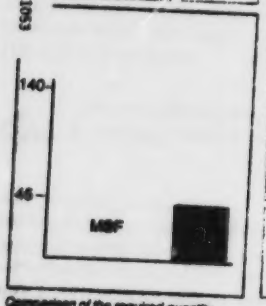




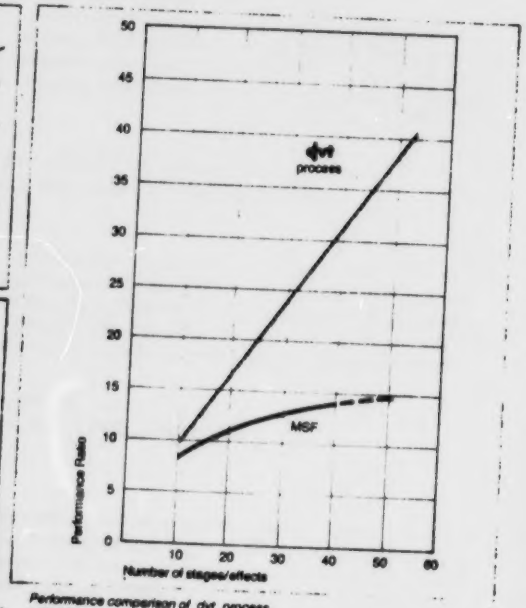
Approximate solubility limits for calcium sulfate in seawater.



Comparison of heat-transfer coefficients (an example).



Comparison of the required quantity of e.g. titanium and monit for the MSF- resp. plant (10.000 m³ / d).



Performance comparison of dvt process with MSF.

dvt VTE-MSF Process – data table for comparison with MSF

		dvt VTE-MSF	conventional MSF
Performance Data			
Performance Ratio kg H_2O/kg steam		40	6–12
Feed - Product ratio m^3/m^3		1.1–2	2
Electrical power requirements KWh/m^3		1.5–2	3–5
Acid dosing	%	70	100
Fouling rate		low - falling film once through	high - brine recycle corrosion products
Corrosion		extremely low — titanium — monit* — once through	very high — carbon steel — Cu-Ni — brine recycle
Technical design data			
Process Flow Scheme		vertical once through	horizontal brine recycle
Process temperature range °C		130–30	120–30
Max. boiling-point elevation °C		0.9	1.2
Seawater Concentration factor		1.0 (130 °C) 2.4 (30 °C)	~ 2.0 (120 °C) ~ 3.0 (30 °C)
Heat transfer surfaces-materials		VTE: BAVEX-titan MSF: BAVEX-monit*	shell & tube - Cu-Ni
Number of VTE effects		55	—
MSF stages		75	10–35
Economics			
Investment Costs	%	100	100
Energy Costs Steam	%	25	100
Energy Costs Electricity	%	50	100
Maintenance & Labor	%	50	100

*** Monit:** Especially developed for seawater services and chloride solutions. Monit is a ferritic stainless steel titanium stabilized with extra low carbon and nitrogen contents. Corrosion resistance of Monit was prooved by extensive tests in seawater of the Arabic Gulf region

typical composition of Monit in %:

C	0.025
Si	0.5
Mn	0.5
Cr	25.0
Ni	4.0
Ti	0.4
Mo	4.0
N	0.025

dvt MSF desalination tower – flash chambers instead of VTE's

The advantages of the vertical tower concept and of the BAVEX heat exchanger are also avalable for the MSF process. Through 70 flash chambers the brine experience as vertical downstream minimized non equilibrium flash losses, resulting in a performance Ratio of 15 - a competitive alternative to the RO-process. A separate broschure of the "dvt-MSF tower" is avalable.

dvt VTE-MSF waste water-treatment tower – "zero-waste discharge"

The VTE process design applied for waste water treatment, for example treatment of the brackish water discharge from RO plants, will concentrate the brine over 25 effects. The brine discharge as waste stream will drop to approx. 10% of the feed water stream. This application of the dvt VTE-MSF process solves brine discharge and pollution problems or increases the fresh water capacity for remote locations.

1054 VEX - MSF condensor and BAVEX brine heater for retubing and increasing performance of existing MSF units

The BAVEX exchanger blocks of non corrosive monit or titan material can economically replace old, non efficient or corroded conventional tube & shell condensors and brine heaters in existing MSF plants. Improvements in the Performance Ratio and capacity are to be experienced due to the higher surface density of the BAVEX-system. A separate broschure of the "BAVEX-Evaporators, Preheaters and Concentration Plants" is avaiable.

dvt VTE-MSF process - powered by solar collector field

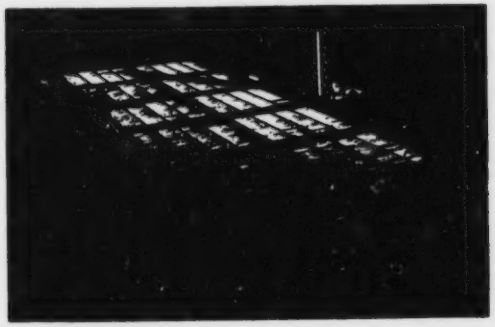
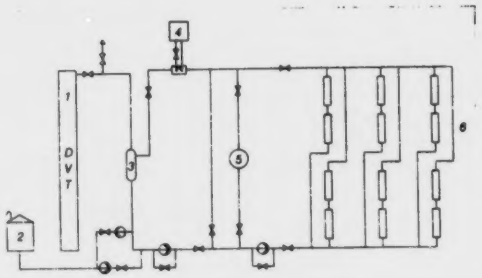


Photo of a model, showing the required collector area for a 10000 m³/day desalination tower including night storage capacity.

The high performance ratio of the dvt VTE-MSF process – increased by a factor 4 to 5 compared to conventional MSF-makes the concept of a large scale solar powered desalination plant feasible. Investment cost for solar collector field compared to desalination plant costs will drop to a ratio of approx. 1:1.



Legend

1 DVT VTE/MSF tower
2 Fresh water storage tank
3 Flash steam vessel
4 Steam boiler (make-up system)
5 Hot water storage tank
6 Solar collector fields

Flow-Diagram solar powered dvt – VTE-MSF desalination tower.

W. L. GORE & ASSOCIATES, INC.
GORE
MEMBRANE DISTILLATION DIVISION
3773 KASPAR STREET • P. O. BOX 1980
FLAGSTAFF, ARIZONA 86002
602/526-3038

JAN 9 1984

January 4, 1984

Hans Von Michaelis
Randol International Ltd.
7510 W. Mississippi Ave. #210
Lakewood, CO 80226

Dear Mr. Von Michaelis:

At present our membrane distillation devices are being used in two pilot plants for production of drinking water from seawater. We have not yet provided water for boiler makeup or battery water.

Although we believe our process has value for chemical concentration, this has not yet been tried except in laboratory-scale systems. We are currently testing our modules to ensure their durability.

I have enclosed a technical paper for your information. Feel free to call me or to visit our Ft. Myers, Florida pilot plant if you have further questions.

Sincerely yours,

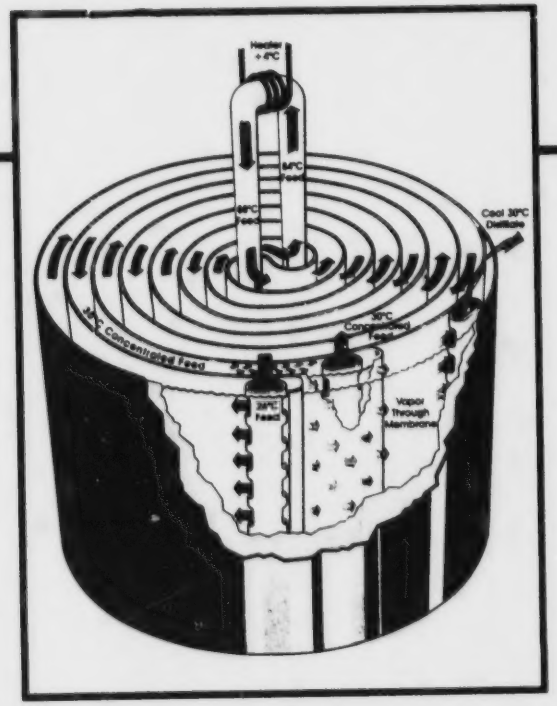
David W. Gore

David W. Gore

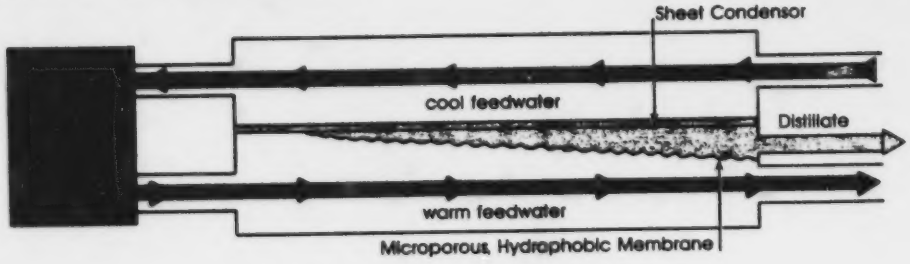
enclosure
cc: Bill Rose

The Module

Salty or brackish water, at ambient temperatures, enters the spiral channel. It is progressively heated as it flows toward the center. A slight amount of heat (4°C) is then added, the feedwater flows along a GORE-TEX Membrane, and water vapor passes through the membrane, condenses, transfers the heat of vaporization and condensation to incoming water, then is forced out as pure distillate. The spiral design of the module makes it compact, strong, and efficient. *Note:* Temperatures are variable depending on (1) size of still/length of flow channel; and (2) applied energy.



The Process



The Advantages

High Purity Distillate

Low in dissolved solids
Low in particulates

Low Cost for Energy

Can use low temperature heat
Uses high temperature heat efficiently

Simple to Operate

Compact design
No moving parts
Automatic operation
Warm protection

Flexible

Adjustable for different conditions
Adjustable for different capacities
Can use sea water, brackish water, or other feedwater
Multiple systems

Durable

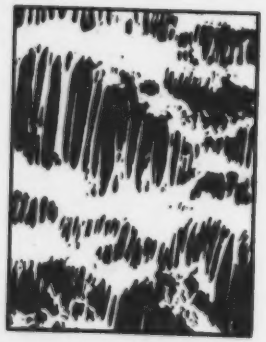
Membrane is [illegible]
Less of [illegible]

Exceptional Value for Small Installations

Can be scaled [illegible]

1056

The Membrane



This new process for the production of pure water is made possible by the development of GORE-TEX® Expanded PTFE (above, magnified 1500 times). GORE-TEX Membranes are microporous (completely impermeable to all particulates above .2 microns in size, including bacteria); chemically inert (immune to virtually all chemical attack, including concentrated chlorine solutions); hydrophobic (impermeable to water) and yet permeable to water vapor. These membranes are non-contaminating and are not subject to aging or decay.

GORE

W. L. GORE & ASSOCIATES, INC.
Membrane Distillation Division
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Telephone: 602/526-3038

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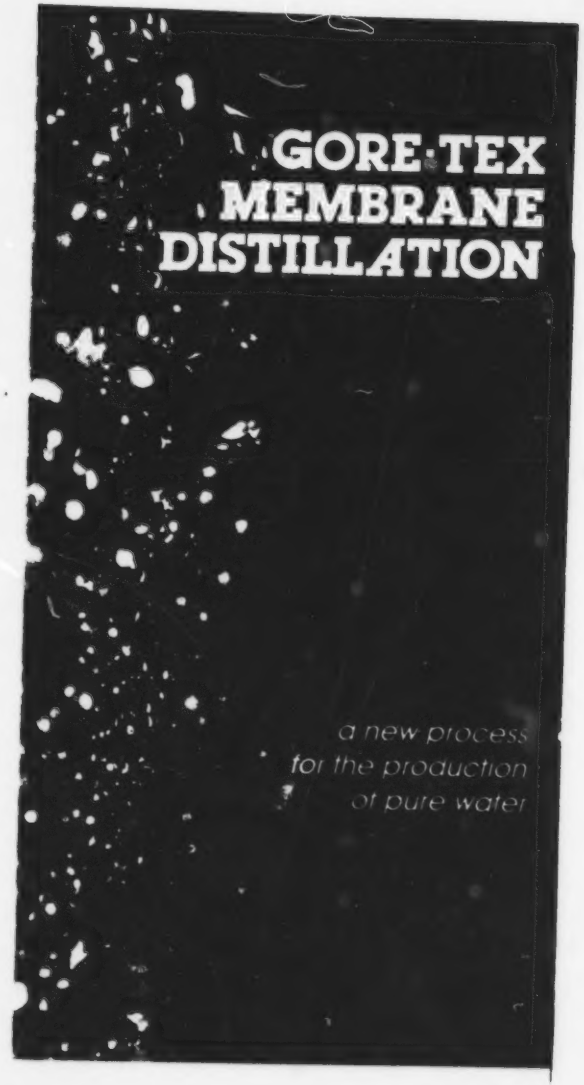


GORE-TEX® MEMBRANE DISTILLATION

David W. Gore
Distillation Project Manager

W. L. Gore & Associates, Inc.
3773 Kaspar
Flagstaff, Arizona 86001

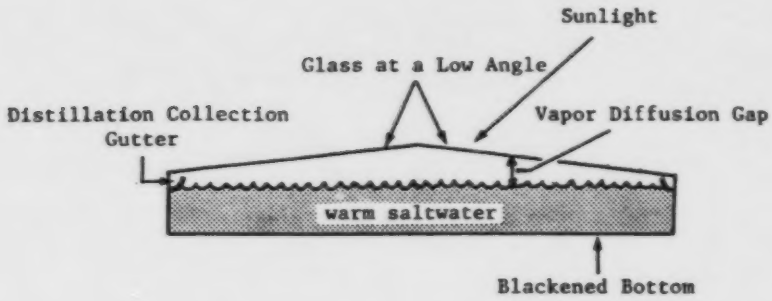
Introduction

Distillation usually involves three steps. First, the feedwater is boiled, often violently. Water vapor and feedwater mist flow in the absence of air across a space, through a demister which removes most of feedwater droplets, and on to a relatively cool condenser surface. In the final step, the water vapor is condensed into distillate, which is drawn off.

The fundamental simplicity of distillation is compromised by the need for complete removal of all noncondensible gases. By leaking into vessels and blanketing the condensor surface, even small amounts of air seriously cut distillate production. Vacuum pumps, strong pressure vessels, deairing devices, and specially-constructed feed recirculation pumps are all necessitated by the harmful effects of noncondensible gases.

A number of distillation processes have been proposed which eliminate the need for creating a vacuum. Hodges[1] built an air/vapor system which moved the air along with the water vapor. Basin-type solar stills use this same principal, but circulate the moisture-laden air through natural convection rather than by mechanical means. Another approach using narrow vapor gaps does not rely on moving humid air, but rather on diffusion of water molecules through still air. Devices operating in this way have been called "diffusion stills."[2] A basin-type solar still (see Figure 1) acts as a diffusion still if the feedwater surface is close enough to the glass to suppress convection.[3]

Figure 1: Basin-type Solar Diffusion Still



In diffusion stills, water does not boil but evaporates non-violently at the feedwater surface. In principal then, demisters are unnecessary in diffusion stills. Since virtually no feedwater mist is formed, one might expect the distillate to be unusually pure.

These alternative approaches to distillation have not been commercially successful. They either require considerable energy to pump air/vapor mixtures, lack the means to recover the latent heat energy, or produce little water, considering the inherent capital cost of the device.

Membrane Distillation

One finding of the study of diffusion stills was that the length of the "diffusion gap" between the evaporating and condensing surfaces was crucial. Production per unit area per unit time was found to be inversely proportional to the diffusion gap distance. Unfortunately, there was no way to bring the evaporating and condensing surfaces close together without causing contamination of the distillate by the feedwater.

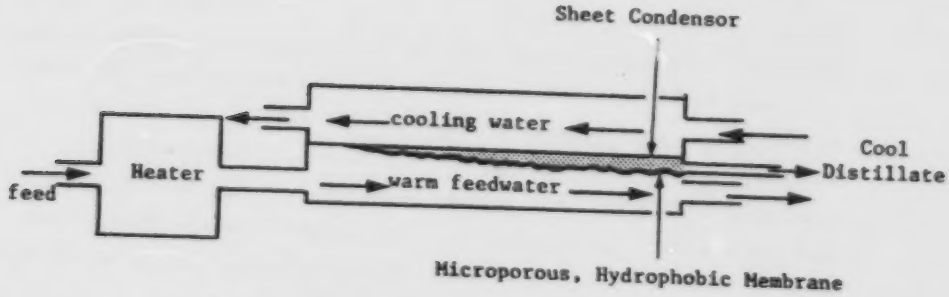
Certain hydrophobic, microporous membranes show the surprising property of allowing easy passage of water vapor, but of completely blocking flow of liquid water. Surface tension of the water prevents its passage through the sub-micron pores of the hydrophobic material. As an example, a Gore-Tex® membrane

made of polytetrafluoroethylene (PTFE) can be 80% porous and yet resist entry of water at 40 psi pressure.

If one of these microporous PTFE membranes is placed between the evaporating feedwater and the condensing surface, the danger of distillate contamination is eliminated. In fact, one side of the PTFE membrane can make contact with the feedwater while the other side is in contact with the distillate. The diffusion gap distance then becomes the thickness of the microporous PTFE membrane. Since these membranes can be made as thin as 25 microns (.001"), the productivity of such a device can be many times that of other sorts of diffusion stills. The limitation on productivity becomes not the membrane thickness but the means of supplying heat to the feedwater/membrane interface and removing the heat of condensation from the membrane/distillate interface.

Figure 2 shows a device which supplies heat to the feedwater/membrane interface by means of heated feedwater which passes across one side of the membrane. Part of this feedwater evaporates, and water vapor from the feed diffuses through the microporous hydrophobic membrane and condenses on the other side when it comes into contact with the relatively cool distillate. The distillate in turn is cooled by an impermeable sheet of metal or plastic which forms one wall of a chamber through which cooling water is passed.

Figure 2: Use of Two Bodies of Water at Different Temperatures



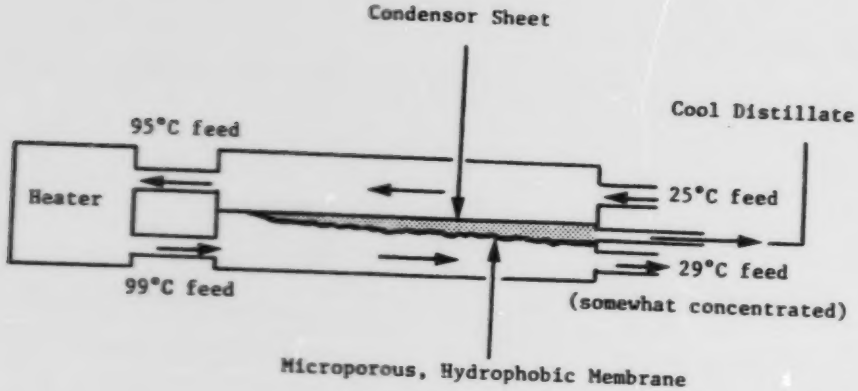
Heat of condensation must be removed rapidly from the membrane/distillate interface. This requires a minimally thin distillate layer. Use of a strong, supportive condensor sheet and proper placement of the distillate outlet allow the warm feedwater flow to "milk" the distillate from the membrane distillation module and keep the distillate layer minimally thin at all times.

If we measure the average temperature in the warm feedwater channel and in the cooling water channel, and make the simplifying assumption that these correspond to the feedwater/membrane interfacial temperature and membrane/distillate interfacial temperature respectively, then we have a measure of productivity. For the ambient temperature range, a device such as that shown in Figure 2 will produce about 12.3 liters/m^2 day per torr of vapor pressure difference across the membrane (.3 gal/ft^2 day torr). If 4% NaCl feedwater is 30°C and the cooling water 20°C, this vapor pressure difference is 13.7 torr, and the membrane distillation module produces 168 liters/m^2 day (4.11 gal/ft^2 day). This invention clearly holds promise for making use of ambient-level temperature differentials for the production of desalted water.

Recovery of Latent Heat

For many applications "free" thermal energy is not available. To the extent that heat energy is expensive, it is necessary to recover the heat of condensation for re-use. Figure 3 shows schematically how this can be done in membrane distillation. Fresh feedwater enters the module cold but is progressively warmed by the condensor sheet, so that it emerges from the module quite hot. The heater boosts this feedwater temperature slightly, and the heated feedwater passes back through the module on the membrane side, gradually losing its heat through evaporation. The feed finally emerges somewhat concentrated and only slightly warmer than it was when it first entered the module. The distillate flows from the unit nearly completely cooled by the fresh feedwater.

Figure 3: Recovery of Latent Heat in Membrane Distillation



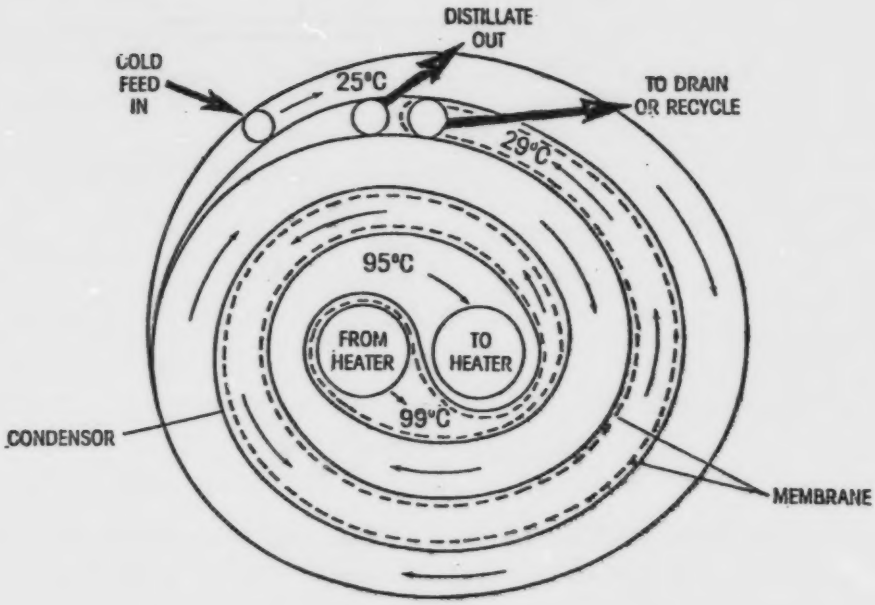
The performance ratio f of the device in this example is:

$$f = \frac{(.8)(95 - 25)}{(99 - 95)} = \frac{(.8)(70)}{(4)} = 14$$

The factor of .8 allows for the fact that from 5% to 20% of the heat transfer is due to thermal conduction rather than to evaporation and condensation of the water. The exact value of this factor (called "membrane efficiency") depends on the feedwater salinity, the temperature drop across the membrane, the average temperature of the system, and the speed of the feedwater flow. As the feed is pumped faster, the stagnant boundary layer of cool, evaporating feedwater at the membrane interface is reduced in thickness, increasing both the membrane efficiency and the productivity.

One difficulty with a linear membrane distillation device such as shown in Figure 3 is that the feedwater channels must typically be one hundred feet or more in length. The module is made much more compact by wrapping the channels into a spiral configuration so that the hot end is at the center and the cold end is at the outside (see Figure 4). This eliminates the need for insulation and bracing, since a spiral is both compact and resistant to moderate internal pressures.

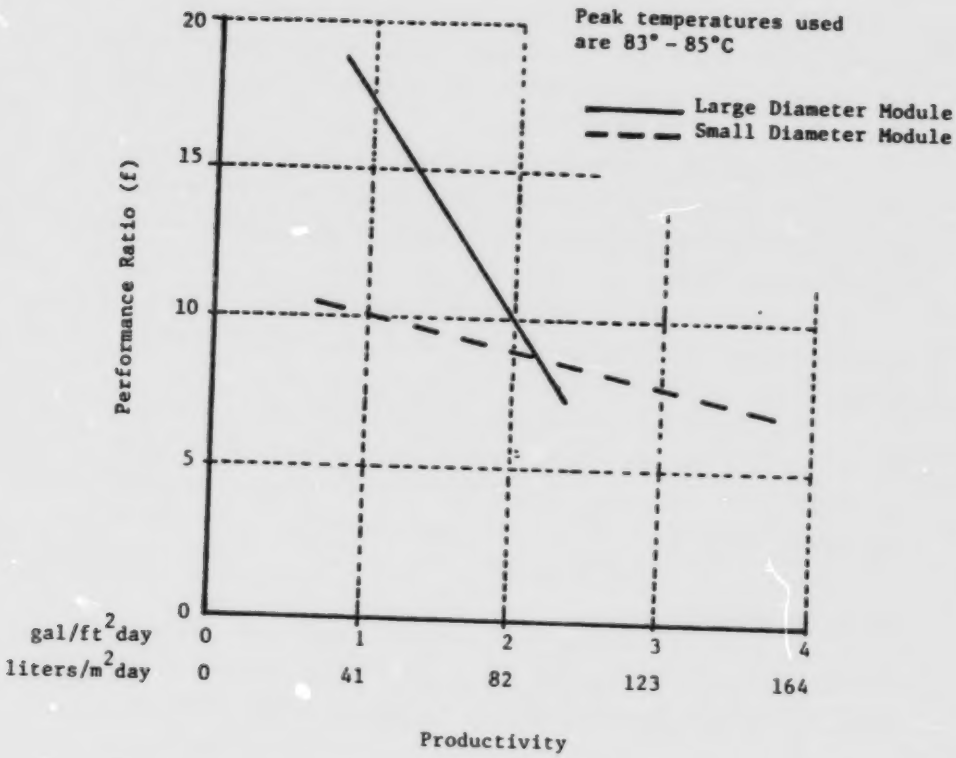
Figure 4: A Spiral-Wound Membrane Distillation Module



A membrane distillation module does not exhibit a fixed performance ratio or a fixed productivity. Instead, there is a tradeoff relationship between the two (see Figure 5). The particular values depend on channel length and geometry, upper and lower feedwater temperatures used, feedwater salinity, and membrane type.

Points on the curve are selected by varying the feedwater flow rate, with higher flows increasing productivity but decreasing the performance ratio.

Figure 5: Performance Ratio and Productivity Tradeoffs



In general, higher performance ratios are achieved by lengthening the flow path of the feedwater. For a spiral-wound module, this results in a module of larger diameter. Increasing the axial length of a spiral-wound module does not change the tradeoff of unit productivity and performance ratio, but increases the distillate production, heat requirements, and feedwater requirements in proportion to the axial length increase.

Spiral-wound modules built to date have achieved performance ratios of 14.2 combined with productivities of 71.2 liters/m^2 day (1.74 gallons/ft^2 day). Considerable improvement on this can be expected as the technology matures.

Advantages of Membrane Distillation

Because the feedwater does not boil, and since the vapor passes through pores of .2 to .45 micron size, the distillate emerges sterile, free of particulates, and very low in dissolved solids. Distillate resistivities of 1 megohm-cm have been measured while using 4% NaCl solution as feedwater.

Substantial productivities can be achieved using ambient-level temperature differences. This allows use of oceanic thermal energy and inexpensive solar energy collection schemes such as shallow solar ponds.

The ability of membrane distillation systems to operate effectively at ambient pressures greatly simplifies their design and operation. This has particular value in small installations and in locations where engineering resources are scarce.

Recovery of latent heat within a single module allows construction of small highly efficient units and modular system organization for larger installations.

The module is flexible in operation, so that it can "load follow" to make best use of variable sources of waste heat. This flexibility also means that productivity can be adjusted to demand and performance ratio can be varied with the changing cost of energy.

Commercial Availability

Spiral-wound modules are now being tested in Ft. Myers, Florida, to ensure the reliability of the current design. Modules producing 250 GPD and 1,500 GPD will be available next year.

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[1]Carl N. Hodges, T. Lewis Thompson, John E. Groh, and Donald H. Freiling, "Final Report-Solar Distillation Utilizing Multiple-Effect Humidification," Solar Research Laboratory, University of Arizona (January 31, 1966), OSW Report No. 194 (May, 1966), 155 pages.

[2]Peter Kroeger, "Diffusion Still Analysis," OSW Report No. 99 (April, 1964).

[3]M. N. Bahadori and F. E. Edlin, "Improvement of Solar Stills by the Surface Treatment of the Glass," Solar Energy, 1973, Vol. 14, pp. 339-352.

[4]Gore-Tex® is manufactured by and is a registered trademark of, W. L. Gore & Associates, Inc. of Elkton, Maryland, U.S.A.

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DS-S09	TRIPOD™ II Monitor & Control — Membrane/RO **INPUT:** Feedwater chemistry, pretreatment system, membrane configuration. **OUTPUT:** Operator prompts for efficient control of process streams and chemical dosage. Displays plant performance critical data and economics of fouling.
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*Specification sheets available upon request.

RQ Associates Consultants
P.O. Box 1205 Teaneck, N.J. 07666 201-692-1640

March 23, 1984

Mr. Hans von Michaelis
Randol International, Ltd.
21578 Mountsfield Drive
Golden, Colorado 80401

Dear Mr. von Michaelis:

As Bruce Watson indicated, you had discussed with him the possible use of our services in applying Desalination Technology to the metallurgical processes.

At Bruce Watson's suggestion, I have enclosed an outline of my professional background. I have eighteen years' experience in the membrane area, involving the development, design, and application of the membrane processes. The applications have included not only brackish water treatment, but industrial water reuse applications.

As Bruce Watson may have mentioned, we have formed a team to offer our services to those wishing to evaluate the evaporation and membrane processes. We would be very much interested in applying our Desalination expertise to the treatment of metallurgical streams and would look forward with interest to working with you in this area.

Thank you for your consideration. If there are any further questions, please do not hesitate to call.

Sincerely yours,

Robert M. Quinn

RQ:lm

WATSON DESALINATION FOUNDED 1978
8710 BARNETT ST. MANASSAS, VA. 22110 (703) 361-7333 • TELEX [redacted]
791840

CURRICULUM VITAE

NAME:

Bruce Morgan WATSON

POSITION:

Principal Engineer

EDUCATION

Queen's University, Kingston, Ontario
B.Sc. (Mechanical Engineering), 1952

Royal Naval Engineering College, Plymouth, England
(Marine Engineering Specialist) 1954

SUMMARY OF QUALIFICATIONS

Twenty-three years' theoretical and practical experience in almost all aspects of seawater desalination technology, with particular emphasis on diagnosis and correction of operational problems related to scale, corrosion, heat consumption and water production.

Conceptual designs, feasibility studies and economic evaluations of single-purpose and multi-purpose facilities.

Special expertise in: (a) use of empirically-derived relationships between the scale and corrosion potentials of plant streams and their composition, and (b) application of currently available countermeasures via process adjustments and chemical treatment.

Instruction of operating and laboratory staffs of more than thirty desalting facilities, in well over a dozen countries, in control techniques to minimize fuel consumption, scale and corrosion.

Market and technology assessments.

Broad range of personal and professional contacts throughout the desalting industry, worldwide. Previous resident assignment in Middle East.

Preparation of microcomputer software packages for use by station operating engineers and chemists to calculate from plant data: scale potentials, heat and material balances, fouling, and all resulting economic parameters by which to adjust type of treatment, cleaning intervals, etc.

CONCEPTUAL DESIGNS, FEASIBILITY STUDIES AND COST ESTIMATES / SCALE AND CORROSION DIAGNOSIS & CONTROL
OPERATIONAL TROUBLESHOOTING AND COST REDUCTION / STAFF INSTRUCTION / MARKETING & TECHNOLOGY CONSULTATION

CHAPTER 19

FREEZING FOR DESALINATION AND COOLING

The basic principles of refrigeration equipment for desalination by freezing is provided by SCHUTTE (1983).

At first, Randol started off this investigation with the idea that since some deep underground mines require cooling as well as water treatment, that the two processes might be combined in an energy-efficient manner. Discussions with South African mining company experts pointed out that as yet no perfect means has been developed to pump ice slurries underground without problems of the crushed ice consolidating and clogging lines, etc.

Tom Wolfe of the Resources Conservation Co. pointed out that the other distillation processes require much less energy than does freezing. Heat used was recovered in the process to preheat incoming feed so the process of distillation is more efficient energywise than expected.

Theo Stielau, before retiring from Delkor Technik of Johannesburg, indicated that his company had found more efficient large-scale freezing equipment which could reduce the cost of making ice considerably. He did not elaborate, but Delkor can be contacted as follows:

DELKOR TECHNIK PTY LTD.
Post Office Box 39744
Bramley 2018
South Africa
(011) 643-6751
Errol Amm, Director

No commercial operations were encountered where water is desalinated by freezing.

DESALINATION: A SOUTH AFRICAN PERSPECTIVE

C.F. SCHUTTE

Senior Adviser:
Water Research Commission

FREEZING

9.1 Introduction

Desalination by means of freezing is based on the natural phenomenon that ice crystals are made up of pure water. Any impurities such as dissolved solids are excluded from the crystals and therefore when melted, the ice crystals yield pure water. Freezing resembles distillation in that a change of phase is involved but it has a number of advantages over distillation : it requires the transfer of less energy; needs almost no pretreatment and has minimal corrosion problems. Despite these advantages and research and development work since the 1950's seawater desalination by freezing has not become a commercial success. However, there still is potential for the development and use of freezing as a desalination process.

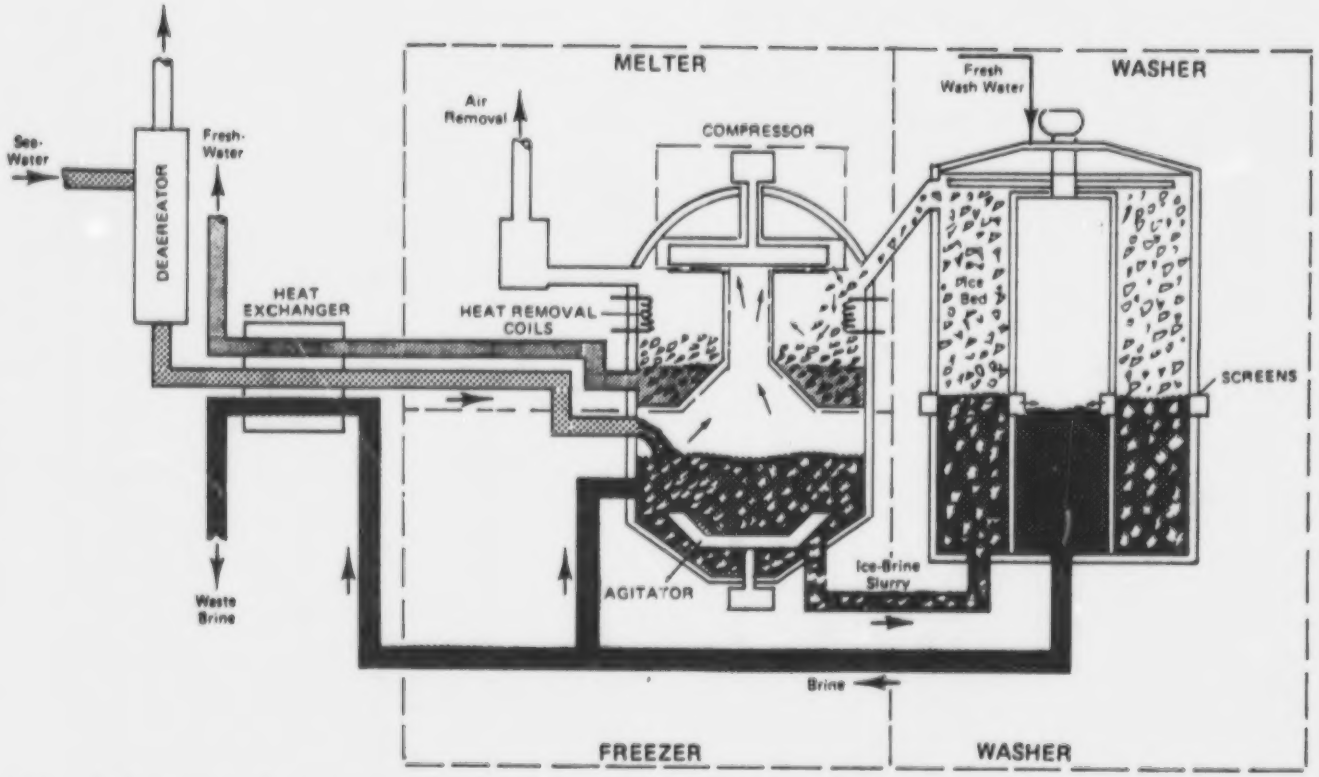
Problems encountered in freezing include handling and separation of the ice-brine slurry and washing the ice crystals free of salts.

9.2 Elements of the freezing process

There are four basic elements in all freezing desalination processes viz freezing, washing, melting and heat removal.

Freezing or formation of ice crystals may be accomplished by either of two methods; direct or indirect freezing.

In the direct process freezing is effected by flash evaporation of water at reduced pressure. The vapour formed absorbs its heat of vapourization from the remaining liquid. This cools the water below its triple point and ice crystals begin to form and release their heat



Notes: 1. The combined freezer (crystallizer) and melter in one vessel is a unit called a hydroconverter.
2. The compressor utilizes thin flexible metal blades. It is built specifically for the high-volume, low-pressure conditions found in the VFVC process.

FIGURE 9 1Schematic diagram of a freezing desalination plant using the vacuum-freezing vapor-compression (VFVC) process. (USAID 1980)

of crystallization to reheat the water back to its triple point so that more water can vapourize. These processes of boiling and freezing take place simultaneously in the freezer with feedwater being added and ice slurry and vapour being withdrawn. The vacuum-freezing vapour compression direct process has been developed to the stage where a commercial unit was produced.

Figure 9.1 gives a schematic illustration of the process (USAID 1980).

In the indirect freezing process, freezing is accomplished by vapourization of an immixible refrigerant such as freon in direct contact with the feed water. The pressure in the freezer is maintained below the boiling pressure of the refrigerant (but not of the water) so that the refrigerant vapourizes. In vapourizing, the refrigerant removes its heat of vapourization from the water causing part of it to freeze. The advantage of using a secondary refrigerant is that it vapourizes at a much higher pressure than water and hence the freezer can operate near ambient pressures. The specific volume of the vapour produced is much less than that produced in the vacuum-freezing direct process. This allows the use of standard commercial compressors, reducing capital cost and operation and maintenance problems. A process configuration is given in figure 9.2 (USAID 1980)

9.3 Practical application

Application of freezing processes for water desalination is still limited to pilot scale. One 375 m^3/d vacuum-freezing vapour compression plant was built and sold but the plant did not operate continuously and was later removed because of financial problems experienced by the owner.

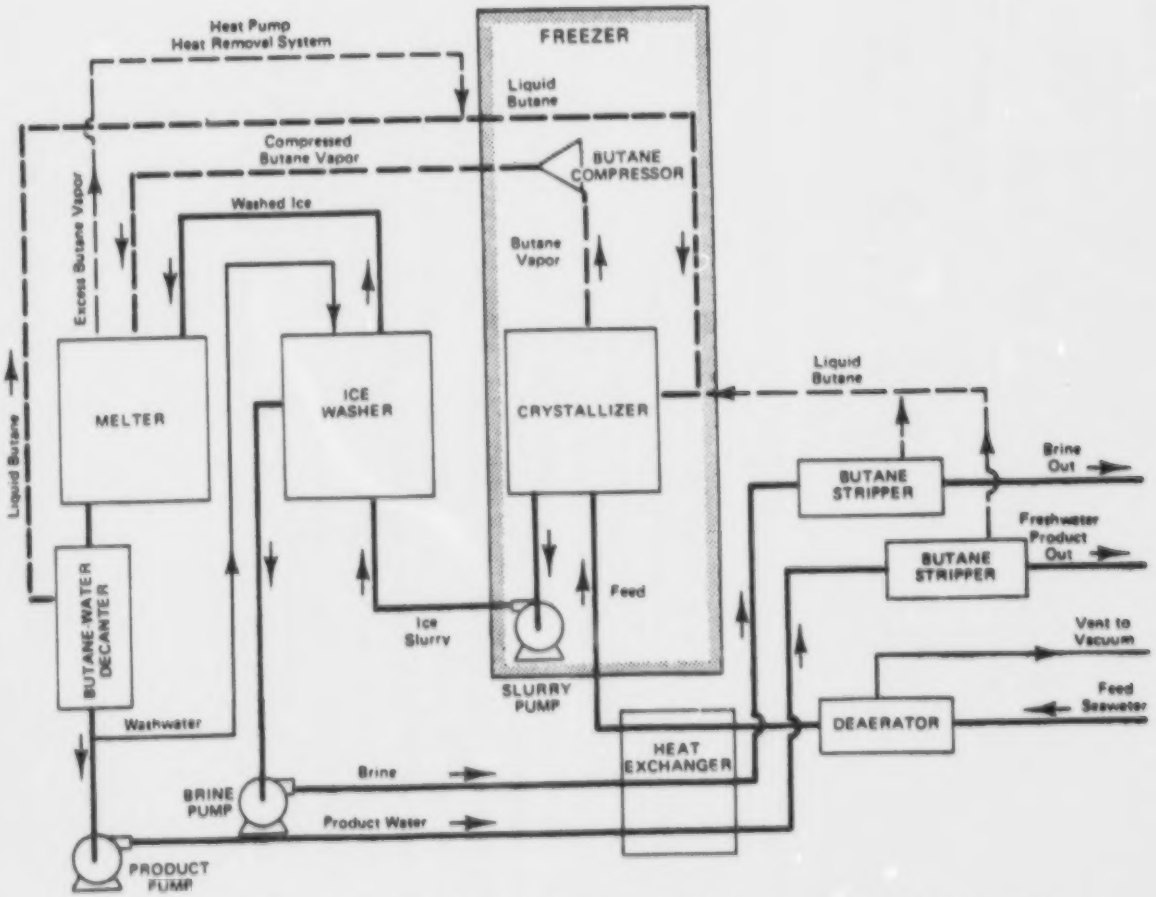


FIGURE 9.2 Block diagram of a secondary-refrigerant freezing process for desalting seawater. (USAID 1980)

CHAPTER 20

CRITICAL COMPARISON OF DESALINATION PROCESSES

From an applicability point of view, it is clear that in mine-mill environments, desalination processes should, if at all possible, be avoided altogether. These processes are not inexpensive and usually contribute little to the profitability of an operation. Nor are they all that easy to design, operate, and maintain.

Given that all else fails and desalination cannot be avoided, selection of the appropriate desalination process would vary considerably from case to case, depending on:

- Nature and Volume of the Effluent to be Treated
- Alternatives Available for Brine Discharge/Disposal
- Purity of Water Required
- Operator and Maintenance Skills Available
- Power Costs
- Climate

In general for very low TDS solutions requiring desalination, ion exchange processes may prove to be the more cost effective means of desalination. Here we are talking about solutions with 120 mg/l TDS and below, or where only certain specific ions need to be selectively removed.

Where solutions above about 150 mg/l TDS up to 10,000 mg/l need to be desalinated, which covers the range in which most acid mine drainage and mill tailings effluent fall, then R.O. or EDR membrane processes appear attractive. However, scaling and pretreatment requirements for these waters may favor the seeded slurry R.O. process of the Resources Conservation Company before all others because this avoids the need for pretreatment and employs a rugged, simple R.O. module (but many of them) rather than a smaller number of more sophisticated and correspondingly more sensitive membrane modules.

At concentrations in excess of 10,000 mg/l, often evaporative desalination processes are called for and, again, for minewater-type feed solutions, seeded slurry thin-film evaporators may be considered. There are several types of distillation systems that can be considered as discussed in the previous chapter. The relative ease of operation and startup of the alternatives is compared from one to the other and with R.O. in Technical Presentation 750-3550 by Aqua-Chem, Inc. below, who also compare a variety of other parameters, albeit for seawater desalination.

A useful comparison of desalination technologies was prepared by the Bechtel Group, Inc. of San Francisco for the Metropolitan Water District of Southern California by ROGERS, et al. (1983). This comparison is reasonably current and, although an apology is made for the poor quality of the copy, the information contained in it is reasonably useful in making a comparison.

Conclusions made in this investigation include:

1) The technologies of desalination are complex and difficult to evaluate for all possible applicabilities--each has its own niche, and the boundary of its niche would change as the nature of the parameters change.

2) Companies involved in one of the technologies, e.g., evaporation, may well be much less experienced in other desalination technologies, e.g., membrane desalination or ion exchange and vice versa. They make the best case for their own product, often without understanding the merits of the alternatives.

3) The assistance of a skilled and experienced consultant in making comparative analysis and selections of equipment and suppliers for desalination would be highly recommended.

4) Several pilot tests to demonstrate R.O., EDR, and evaporation for particular applications have failed--i.e., pilot testing is highly recommended ahead of designing or ordering a full-scale plant.

5) Mine-mill solutions are not the same as seawater as far as their desalination process parameters are concerned--nor are the brine disposal alternatives.

6) In mine-mill applications, consideration can be given to inserting desalination processes as a means of concentrating valuable ions as well as for water recovery.

7) Combinations of more than one desalination process may be the best solution to a problem. A systems approach is essential in selecting and sizing desalination processes--again, unless these can be avoided.

8) The RCC seeded slurry R.O. and evaporation process summarized below overcomes the serious limitations on desalination presented by most mine-mill effluents.

PROCESS SELECTION GUIDE TO SEAWATER DESALTING

TECHNICAL PRESENTATION
750-3550

WATER TECHNOLOGIES DIVISION
aqua-chem, Inc.

INTRODUCTION

As desalting technology advances, old processes change and new ones are developed. This paper presents a comparison of the current commercial seawater desalting processes including mechanical vapor compression (MVC), thermo-compression (TC), multiple effect (ME), once-through multistage flash (MSF-OT), brine recirculation multistage flash (MSF-BR), and reverse osmosis (RO).

These processes are compared on the basis of maintenance and operating complexity and capital and operating costs. The comparison is based primarily on the experience of the authors and the company that they represent.

The goal of the paper is to help users and planners answer the question, "What process is best for me?" Although some of the comments are applicable to all size plants, the paper is directed primarily to plants less than 2,000,000 GPD capacity. Plants using a combination of processes or hybrid systems are not considered.

PART I PERFORMANCE COMPARISON

A comparison of desalting processes on the basis of ease of operation, complexity and maintainability is necessarily a subjective analysis. However, we have tried to quantify our rationalization and to substantiate our conclusions as much as possible.

Ease of Operation and Startup

Table 1 ranks the desalting processes from the easiest to the most difficult from an operation and

Ranking Easy to Difficult	1 RO	2 MSF-OT	3 TC	4 MVC	5 MSF-BR	6 ME
Start up Sequence	1) Fill flush/ suckback tank 2) Start seawater 3) Commission pre-treatment syst 4) Check SDI 5) Start high pressure pump 6) Adjust flows and pressure	1) Start seawater flow 2) Start blowdown 3) Commission vacuum syst 4) Start steam to heater 5) Start cond pump 6) Commission chemical system 7) Start dist pump 8) Commission top temperature ctl 9) Adjust plant to full capacity	1) Start seawater flow 2) Set makeup flow 3) Start transfer pump(s) 4) Start blowdown pump 5) Commission vacuum system 6) Commission chemical system 7) Start steam to compressor 8) Start dist pump 9) Adjust plant to full capacity 10) Set top temperature ctl	1) Check Lube Oil & comp safeties 2) Start recycle 3) Start recycle pump 4) Start blowdown pump 5) Start heating source 6) Commission chemical system 7) Set pH control 8) Bring plant to press & vent 9) Start comp at part capacity 10) Start dist pump 11) Adjust plant to full cap	1) Start seawater flow 2) Fill evaporator 3) Start recycle pump 4) Set makeup flow 5) Start blowdown pump 6) Commission vacuum system 7) Start steam to heater 8) Start cond pump 9) Commission chemical system 10) Set pH control 11) Start dist pump 12) Commission top temperature ctl 13) Adjust plant to full cap	1) Start seawater flow 2) Fill evaporator 3) Start transfer pumps 4) Set makeup flow 5) Start blowdown pump 6) Commission vacuum system 7) Start steam to first effect 8) Start cond pump 9) Commission chemical system 10) Set pH control 11) Start dist pump 12) Adjust plant to full capacity 13) Adjust top temperature ctl
Startup Time	1/2 - 1 hr.	2 - 3 hrs.	2 - 3 hrs.	2 - 3 hrs.	3 - 4 hrs.	3 - 4 hrs.
Critical Operating Parameters	1) pH 2) Module press 3) Reject flow 4) Chemical dosage	1) Top temperature 2) Chemical dosage 3) Heater pressure	1) Steam condition 2) Operating press 3) Seawater flows 4) Chemical dosage	1) Operating press 2) Brine conc 3) Compressor 4) Capacity 5) pH	1) Top temperature 2) Brine conc 3) pH 4) Heater pressure	1) Top temperature 2) Brine conc 3) Effect flow 4) pH

Table 1. Ease of Operation and Startup

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aqua-chem
WATER TECHNOLOGIES DIVISION
P.O. BOX 421
MILWAUKEE, WISCONSIN 53201 U.S.A.

startup standpoint. It is fairly easy to see from the table why the processes are ranked the way they are on the basis of the startup sequence. It is not as readily apparent that the same ranking is applicable during normal operation.

Actually, none of the processes should be difficult to operate once they are operating. There are only three to five critical operating parameters which must be controlled closely to avoid rapid deterioration of the plant's performance. Probably the most difficult task in the operation of any desalination plant is the determination of the cause of a problem when it occurs.

In an RO plant the quality of the seawater or improper pretreatment should be suspect when problems occur. In a thermal process improper chemical treatment or venting, for instance, can cause reduction in capacity or corrosion or both. In any case, it is important for operators to log plant performance and for the owners to have qualified supervisors who can interpret the data to determine the source of a problem.

We do not feel there is a significant difference in the degree of operational difficulty between the processes. The table does show a significant difference in the startup time of the different processes. Startup time will vary substantially depending on the ability of the operators and the size of the plant. The times shown are based on average size plants and experienced operators. The times also are for the startup of only one train. If a plant consists of multiple trains, the trains are usually started up in series. In most installations startup time does not represent a very significant factor because the plants are on line continuously. It would be a significant factor, however, if the plant were to be shut down and started frequently.

We have not addressed the question of the difficulty of commissioning a new plant. This again will vary considerably with the process, quality of water, and size of the plant. However, this should be the responsibility of the plant's supplier who should thoroughly check out the plant and train the operators before the plant is turned over to the owner.

Complexity

Table 2 ranks the processes from the least to the most complex based on a comparison of the number of controls, alarms, chemical systems, other systems, and pumps as well as our experience with these processes. The simplified process diagrams, Figures 1 thru 6, will help the reader relate to Table 2.

Ranking Least to Most	1 RO	2 MSF-OT	3 TC	4 MSF-RH	5 MVC	6 MEE
Controls	1) Membrane pressure 2) Reject flow 3) Acidight 4) Shutdown flush	1) Top temperature 2) Brine flow 3) Cond level 4) Dist level 5) Blowdown level	1) Top temperature 2) Makeup flow 3) Transfer level 4) Dist level 5) Blowdown level	1) Top temperature 2) Brine recycle 3) Makeup flow 4) Cond level 5) Dist level 6) Blowdown level 7) Acidight	1) Top temperature 2) Makeup flow 3) Cond level 4) Dist level 5) Blowdown level 6) Evaporator level 7) Acidight	1) Swap press 2) Makeup flow 3) Acidight 4) Dist level 5) Blowdown level
Monitoring Alarms	1) pH hi/lo 2) Chlorinator 3) pH temperature 4) Pump bath press 5) Membrane pressure 6) Reject stand 7) Permeate stand 8) Permeate press	1) Top temperature 2) Cond purity 3) Dist purity 4) Feed front fdr	1) Top temperature 2) Steam temp 3) Makeup flow 4) Dist purity	1) Top temperature 2) pH hi/lo 3) Cond purity 4) Dist purity	1) Top temperature 2) pH hi/lo 3) Cond purity 4) Dist purity	1) Swap press hi/lo 2) Lube oil press 3) Lube oil temp 4) Comp vibration 5) Dist purity 6) pH hi/lo 7) Dist purity
Chemical Systems Required	1) Acidight 2) Pres inject 3) Chlorinator clean	1) Scale control 2) Acid cleaning	1) Acid cleaning	1) Acidight or Scale Control	1) Acidight	1) Acidight
Other Systems	1) Sanitization/flush 2) Cartridge fdr 3) Rehabilitation	1) Vacuum system 2) Desuperheater 3) Condition pump	1) Vacuum system 2) Desuperheater 3) Dist pump	1) Vacuum system 2) Deaerator 3) Desuperheater 4) Condition pump	1) Vacuum system 2) Deaerator 3) Desuperheater 4) Condition pump	1) Lube oil system 2) Gear box 3) Dist pump 4) Grade Hi
Large Rotating Machinery	1) High pressure	1) Blowdown 2) Condensate 3) Blowdown	1) Brine transfer 2) Blowdown 3) Distillate	1) Recycle 2) Blowdown 3) Condensate 4) Distillate	1) Feed pump 2) Blowdown 3) Transfer pumps 4) Condensate 5) Distillate	1) Compressor 2) Recycle 3) Blowdown 4) Distillate
Other Systems Which Could Be Required	1) Chlorinator 2) Dechlorinator 3) Sodium Hfm 4) Polyphosphate 5) Potassium	1) Ammonia	1) Scale control 2) Dist washer 3) Dist cooler 4) Reboiler	1) Ammonia 2) Acid cleaning	1) Ammonia	1) Ammonia

Table 2. Complexity Comparison

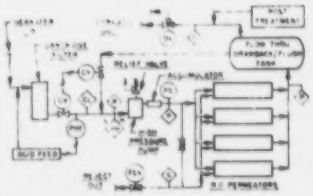

Figure 1. Reverse Osmosis (RO)

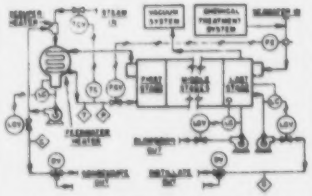

Figure 2. Multistage Flash Once Through (MSF-OT)

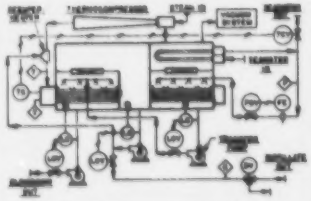

Figure 3. Thermocompression (TC)

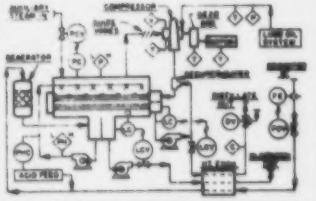

Figure 4. Mechanical Vapor Compression (MVC)

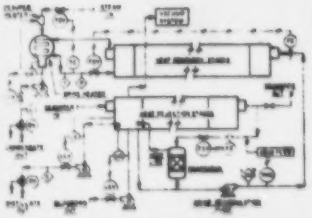

Figure 5. Multistage Flash Brine Recirculation (MSF-RH)

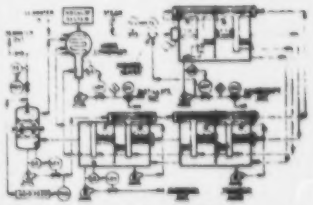

Figure 6. Multiple Effect

In our evaluation we have not taken into account the seawater intake or brine disposal. A supply of seawater is required for all of the processes although the quantity will vary considerably. The mechanical vapor compression process requires approximately two times as much seawater as distillate produced, whereas, reverse osmosis requires approximately three times as much and the other processes eight to ten times. The brine disposal system, including seawater return in some cases, is common to all of the processes. Here again, the MVC process has the smallest brine flow followed by RO, while the other processes have considerably larger flow rates. Since the complexity of these systems can vary wildly from site to site we have chosen not to consider them in our evaluation. Each user will have to make his own evaluation of the impact of the seawater intake and brine disposal.

Likewise, the quality of the seawater supply was not evaluated because it, too, will vary widely. The quality of the seawater has little impact on the complexity of thermal processes as long as the designer takes it into account and chooses proper operating temperatures and concentration levels. On the other hand, the quality of the seawater can greatly influence the complexity of reverse osmosis systems particularly in the area of pretreatment as shown in Table 2 under the heading, "Other Systems Which Could Be Required".

It is common practice for suppliers of reverse osmosis systems to recommend that the user obtain his seawater supply from beach wells. Experience shows that beach wells normally produce a good quality seawater at a relatively constant temperature and, therefore, minimize the amount of pretreatment required. Our evaluation reflects this practice and assumes the seawater supplied is of such a quality.

All of the thermal processes require a steam supply which is not required by reverse osmosis systems. The quantity of steam required by the MVC process, however, is very small compared to the other thermal processes.

It is believed that the ranking given the processes is reasonable, although the differences between some may not be very great. The degree of difference in complexity of the processes is left to the opinion of the reader.

Maintenance

It is not possible to quantify the subject of maintenance when comparing the various desalting processes. In Table 3 they are ranked, based on experience, from the process requiring the least to the most maintenance. The following discussion attempts to justify this ranking by discussing each process in turn.

Ranking	Process
1	TC
2	MSF-OT
3	MSF-BR
4	RO
5	ME
6	MVC

Table 3. Maintenance Comparison

The TC process is ranked as the easiest to maintain primarily because it is usually a very low temperature plant. Therefore, even though TC is a thin film process, there should be very little scaling. Occasional acid cleanings will be required because some scaling will occur, but such occurrences should be very infrequent, probably less than once a year. Also, because of the low temperature, corrosion problems should be minimal even with steel shell materials. The number of pumps and controls are few and, since the compressor has no moving parts, it requires very little maintenance. The process becomes slightly more complex and requires more maintenance if a reboiler is needed to prevent condensate contamination of the distillate or if a distillate sterilizer is required.

The MSF-OT process is ranked second, primarily because it is a non-acid process. Corrosion may be a problem particularly in the hot end where the gases will be released, but this problem can be minimized by using proper materials, lining, and venting. Here again, the number of pumps and controls are minimal. The plant will have to be acid cleaned periodically, probably two to four times per year, depending on the type of scale control chemical used, the top operating temperature, and the quality of the seawater.

The MSF-BR process is ranked third behind the MSF-OT process because it has more pumps and controls and because it is typically an acid plant. If the plant uses a non-acid chemical for scale control, maintenance should be very similar to the MSF-OT process. History has shown that maintenance of acid plants has been relatively high because of corrosion problems and the difficulty in keeping the pH control system operating properly. These problems can be lessened by using better materials, more extensive linings and better operator training.

The reverse osmosis process has been ranked fourth, although there is not much experience by which to judge this process. It is reasonable to assume corrosion problems and maintenance will be less than the early MSF-BR acid plants, due to the materials of construction used in this process and the low operating temperatures. Nevertheless,

there are a number of reasons which lead us to believe that maintenance will be greater than modern MSF processes. The process normally uses acid for scale control and, thus, will have the same problems keeping the pH system functioning properly. There are many permeators in an RO plant each with corresponding connections, compression fittings, instrument connections, etc. Flow, conductivity and pressure drop data must be checked regularly for each rack in each block. Eventually the modules will have to be replaced on a more or less routine basis. The high pressure pump will probably require more maintenance than the usual centrifugal pumps used in the other processes. The RO plants are typically furnished in multiples of smaller capacity trains, although this has its advantages, it also multiplies the equipment involved and increases the amount of maintenance required.

The ME process has been ranked fifth because of the reported and known problems which have occurred in these film-type evaporators(1). These plants are typically acid treated for scale control and, thus, are subject to potential corrosion problems. The ME process typically uses a thin film evaporator with evaporation occurring on the liquid surface. These plants are more prone to scaling problems due to concentration gradients, and maldistribution of brine over the heat transfer surface(2). Controls and instruments are similar to MSF plants, but there are additional pumps to transfer the water between effects.

The MVC process has been ranked last because of the previously mentioned difficulty of scale control with thin film, acid treated evaporators and because of the added maintenance associated with the compressor and support equipment. Many of the problems associated with MVC plants have been caused by corrosion and misoperation, but nevertheless are real.

It is our opinion that any of the processes can achieve an acceptable level of maintenance if the process, materials of construction, and operating conditions are selected to suit the application, the seawater, and the quality of operators and supervision. On the other hand, any process can be a maintenance headache if it is misapplied or if it is not properly operated and maintained.

PART II COST COMPARISON

Economy

The economy, defined as the pounds of distillate produced divided by the energy input expressed in thousands of Btu's, is an accepted and convenient means of comparing the energy efficiency of desalination plants. Table 4 shows, roughly, the practical economy (E) range of the seawater desalination processes discussed in this paper, with TC and MSF being at the low end of the E range and RO being at the high end.

The TC process is ideal for the end-user who has high pressure steam which he intends to use for evaporation. Rather than reduce the steam pressure through a control valve for use in a MSF or ME evaporator, it can be reduced through a thermocompressor which boosts the E at a relatively small capital cost. The TC process is normally used with a multiple effect evaporator having two or more effects and, therefore, is really a combination TC/ME process. By using a large number of effects, economies greater than 10 can be achieved.

The TC process is used to improve the E of desalination plants when operating at low temperatures, 165°F or lower. There is little or no advantage to using a TC process at higher temperatures. The available temperature difference is small because of the low operating temperature and, as a result, heat transfer surface requirements become very large at high economies. Therefore, the top practical economy is about 10 although this would be quite expensive compared to MSF (3).

The maximum practical economy for a MSF evaporator is about 12. Of course, higher economies are theoretically possible and some have been built, but there are several problems associated with them. As the E is increased, the number of stages must be increased. Thus, the stage temperature differential decreases and losses such as boiling point elevation (BPE), pressure drop through the condenser and entrainment separators and, especially, flash suppression become significant. This decreases the designer's margin of error. The practical maximum number of stages is between 40 and 50 making the cost of MSF plants prohibitive at economies greater than 12.

Process	TC	MSF-OT	MSF-BR	ME	MVC	RO
Economy (Lb/1000 Btu)	3-10	3-12	3-12	10-15	17-33	30-200
Type of Energy	Hi Press Steam	Lo Press Steam or Hot Water	Lo Press Steam or Hot Water	Lo Press Steam or Hot Water	Elect. or Hi Press. Steam	Elect.
Practical Top Operating Temp (°F)	120-165	170-240	190-250	185-240	170-215	32-100

Table 4. Economy, Energy and Temperature Comparison

Table 4 shows that the range for a ME is between 10 and 15. ME evaporators are in service with economies well below 10, but the practical low-end boundary is fixed at 10 because of the advantages of MSF with respect to ME in low E applications. As mentioned in Part I, the MSF process is ranked higher than ME on the basis of simplicity and ease of operation. ME does not offer any significant advantages with respect to MSF at lower economies, but, the ME process has overriding advantages at economies above 10. Since there is no flash deviation in the ME process, temperature differential losses are limited to BPE, which is easily predicted, and to small pressure drop losses through vapor ducting and entrainment separators. So, compared to MSF, the designer is left with a much greater margin of error as E is increased.

PR	MSF	ME
12	1.0	.85
10	1.0	.88
5	1.0	.92

Table 5. Relative Evaporator Costs

Another advantage of ME, with respect to MSF, is the capital cost savings which is directly proportional to the E. Table 5 shows the relative savings as a cost ratio of ME/MSF. The exact value of these ratios is less important than the fact that the savings does exist and that it will increase as E increases.

The ME, MSF, and TC processes use heat energy at an elevated temperature and then, after a series of effects or stages release the energy to a heat sink. Thus, the initial investment of latent heat of vaporization is finally lost from the evaporator plant to the heat sink. In contrast, a MVC evaporator continually recycles the latent heat of vaporization using a vapor compressor (heat pump). Mechanical energy is usually input at the rate of 30 to 50 Btu/lb of distillate compared with 70 to 360 Btu/lb of distillate for a comparable ME or MSF evaporator.

The E of a MVC plant is proportional to the pressure differential (or polytropic head, in compressor jargon) developed by the compressor. The following equation demonstrates how the E of a MVC depends on the compressor's polytropic efficiency (η poly), polytropic head (H poly) measured in feet of steam, and the motor efficiency (η M).

$$E = \frac{7.7 \times 10^6 \, (\eta \text{ poly}) \, (\eta \text{ M})}{\text{H poly}}$$

Example: H poly = 20,000 ft
η poly = .77
η M = .9

$$E = \frac{7.7 \times 10^6 \times .77 \times .9}{20{,}000} = 27$$

The polytropic head for a commercially available, single-stage, centrifugal compressor ranges from 6,000 to 40,000 feet. The range typically employed for evaporation is 16,000 to 26,000 feet. Thus, the practical E for MVC processes ranges from 17 to 33.

The E of the RO process without power recovery ranges from about 30 to 140. As the following equation demonstrates, it depends primarily upon the pressure required across the membranes (Δ P expressed in PSI), the recovery rate (R), the efficiency of the pumps (η P) and the motors (η M), and the specific gravity (SG) of the feed.

$$E = \frac{3.37 \times 10^6}{(SG)} \times \frac{\eta \text{ P} \times \eta \text{ M} \times \text{R}}{\Delta \text{ P}}$$

Example: R = .35
ηP = .80
ηM = .95
Δ P = 900 psi
S.G. = 1.03

$$E = \frac{3.37 \times 10^6 \times .80 \times .95 \times .35}{900}$$

E = 96.7 lb/1000 Btu

The preceeding equation is valid for a one pass system without power recovery (PR). The E will be decreased somewhat by the addition of a second pass. Power recovery, on the other hand, will substantially increase the E of an RO plant. Relatively high energy exists in the RO blowdown stream which constitutes 65 to 85% of the feed stream and is at a pressure which is only 5% or so below that of the feed pressure. Power recovery turbines are commercially available with 65 to 85% efficiency and serve to reduce the energy consumption of the plant by as much as 45%, boosting E by 80% (4).

Type of Energy Used and Its Value

ME and MSF use low pressure steam, at 50 psig or less, or hot water. TC uses high pressure steam at 70 psig or higher. Either electricity via an electric motor or high pressure steam via a turbine can be used to drive a mechanical vapor compressor, although an electric motor is normally used. RO uses electricity. Table 4 summarizes the type of energy required for each process.

The economy is a useful comparison for plants that use an identical energy source but, since it doesn't account for the value of the energy consumed, it is not always a useful measurement when comparing plants that use different energy sources. A MVC evaporator may have a capital cost equal to and an E three times that of a MSF plant, but MSF will be the more economical process if the value of the energy to run the MVC is more than three times that of the MSF. The point being that the economy is only truly meaningful when it is examined together with the cost of the energy source.

In most cases it is very difficult to evaluate the true cost of electrical or thermal energy and everyone goes about their evaluation differently. However, some fundamental truths hold. For instance, the transformation of energy makes the final, useful Btu or KW more expensive due to energy conversion inefficiencies. Thus, the closer a desalination plant can get to the root source of energy -- that is, the fewer the transformations -- the less expensive the energy.

For example, a single purpose thermal plant would require a boiler supplying steam exclusively for the desalination plant. With a boiler efficiency of 90%, a gallon of fuel having a heating value of 150,000 Btu would yield 135,000 Btu's of useful energy. But if the desalination plant uses electricity as its energy source the fuel would first have to be converted to electrical energy. If the electrical energy is generated with a diesel generator at 25% efficiency, a gallon of fuel would yield only 37,500 Btu's of useful energy. Therefore, the electrical energy would cost 3.5 times as much, on a Btu basis, as the steam for a single purpose plant. Table 6 helps to compare the different desalting processes on this basis.

This comparison is valid only for single purpose plants. When dual purpose plants are used, the value of energy consumed will be considerably lower than the energy cost of fuel oil on a Btu basis and, in many cases, the user has waste heat available to operate a desalting process. Each case should be considered on its own merits. The user should evaluate what the various sources of energy cost and compare the desalting processes on the basis of these costs.

Process	E Lb/1000 Btu	Btu/ 1000 Gal.	KW/1000 Gal.	Form of Energy	Gal Oil/ 1000 Gal.
RO With PR	150	55,533	16.3	Electrical	1.48
RO Without PR	90	92,555	27.1	Electrical	2.47
MSF-OT,MSF-BR,ME	10	833,000	243.9	Steam	6.17
MVC	27	308,520	90.3	Electrical	8.23
TC	5	1,666,000	487.8	Steam	12.34

Table 6. Energy Requirements for Single Purpose Plants

Capital Costs

The capital cost of a plant is influenced by numerous variables, but, of these, the two most important are capacity and economy.

Economy should be chosen to yield the lowest unit cost of water. The cost of water can be defined as dollars per thousand gallons and is proportional to capital cost (installed plant cost, financing package, depreciation, etc.) and inversely proportional to operating cost (energy, chemical and spare parts cost, staff salaries, etc.). The capital cost varies directly with economy; operating cost varies inversely with economy. Therefore, the optimum economy is the one for which the combination of capital and operating cost yields the lowest cost of water.

Capacity, more so than any other variable, is under the control of the end user. The easiest way for an end user to cut capital cost (and total cost of water) is by reducing the capacity. Thus, it is extremely important that accurate water needs be determined. On the other hand, it is also important for the user to realize that the cost of, say, doubling the capacity of a plant, during the planning stage, will not double the cost. In fact, the cost will only be increased by about 50%. Doubling plant capacity after the initial capacity has been installed, however, will about double the cost of the total plant. This phenomenon is known as economies of scale and leads to a very useful relationship known as the six-tenths power rule.

If the cost of Evaporator A is known and the cost of Evaporator B, which has twice the capacity, but is identical in every other respect, is unknown, the cost of Evaporator B can be estimated by using the six-tenths power rule:

$$\text{Cost Evap B} = \left(\frac{\text{Capacity Evap B}}{\text{Capacity Evap A}}\right)^{.6} \times \text{Cost Evap A}$$

$$\text{Cost Evap B} = 2^{.6} \times \text{Cost Evap A} = 1.5 \times \text{Cost Evap A}$$

An equation of the same general form can be used to estimate the impact of economy on an otherwise identical plant. That is, if the cost of Plant C with E of 6 is known and we want to determine the impact of changing the E to 10 (Evap C'), then the following equation applies:

$$\text{Cost Evap C'} = \left(\frac{\text{E Evap C'}}{\text{E Evap C}}\right)^{.7} \times \text{Cost Evap A}$$

$$\text{Cost Evap C'} = \left(\frac{10}{6}\right)^{.7} \times \text{Cost Evap C} = 1.43 \text{ Cost Evap C}$$

The cost of an RO plant also follows a similar pattern with changes in capacity. The economics of scale, however, are less noticeable due to the fact that they have already been realized by the membrane manufacturer and are reflected in the price of the membranes which account for about 50% of the plant's cost. The value of the exponent is about 0.9 and therein lies the reason why RO lends itself to modular design. That is, subplants, whose size ease shipping and installation and whose independent operation mitigate unscheduled shutdowns, can be built at about the same price as one large RO plant.

These power rules yield good approximations and are useful tools during the study phase of a project. (Note that the value of the exponents will change somewhat from manufacturer to manufacturer.)

Two other capital cost variables, top operating temperature and material selection, are also important. Top operating temperature is a major consideration in the case of evaporators and it affects different evaporation processes in different ways.

The advantage of a higher top operating temperature in MSF and ME plants is that it increases the total temperature differential across the plant. Since the heat transfer surface is inversely proportional to the temperature differential, the capital cost of the plant is reduced (capital cost follows the six-tenths power rule with respect to surface area) with higher temperatures. The disadvantage of a high operating temperature (especially if it makes acid treatment necessary) is the increase in equipment failure due to corrosion. Unfortunately, this disadvantage is not as easy to quantify because it has a long-term effect that is obscured by chemical treatment as well as maintenance and operator skill. As the temperature is increased, though, one can be certain that the corrosion potential is also increased and corrosion, over the long run, can cancel the initial cost savings.

The top operating temperature of the once-through MSF process is limited by the temperature sensitivity of the non-acid scale control chemicals. High temperature additives make operation up to 240°F possible. The practical range is from 190 to 240°F. The brine recirculation MSF process's top temperature is limited by sulfate scale precipitation and its minimum operating temperature is the point where the additional capital cost exceeds the chemical treatment savings with respect to MSF-OT. Its practical range is about 170 to 250°F. ME's top temperature is also limited by sulfate scale precipitation; its practical range is about 170 to 240°F.

The same advantages and disadvantages apply to MVC, but the capital cost savings are realized in a different way. If the operating temperature is lowered in a MVC evaporator, the specific volume of the stream increases, making a larger size compressor necessary to handle the increased volumetric flow rate. For example, a plant having a volumetric flow rate of 40,000 ACFM at 212°F would have a volumetric flow rate of 95,364 ACFM at 170°F. This would make a larger compressor necessary, one that would cost approximately 60% more. Since the compressor is a very substantial cost component of the total system, the user should study carefully the benefits versus the costs of lowering the maximum brine temperature in a MVC plant. The practical top operating temperature range is 170 to 215°F.

The cost of a TC plant is not greatly affected by changes in the top operating temperature. The compressor is relatively inexpensive and changing its size will not significantly impact the total plant cost. The plant cost may, in fact, be reduced by lowering the maximum brine temperature since the evaporator vessel can then be constructed of less expensive materials such as carbon steel, without danger of excessive corrosion. The practical top operating temperature range is 120 to 170°F.

RO operates at ambient temperature and the only limitations are those set forth by the membrane manufacturers to protect the membrane materials and ensure maximum membrane life. A summary of the practical top operating temperature range for the different processes appears in Table 4.

As mentioned, material selection has an important impact upon the cost of a desalination plant. The material selection decision, however, becomes easier in the case of small evaporators. Evaporators with less than 200,000 GPD capacity are often constructed of copper-nickel simply because the cost savings of carbon steel is not sufficient to warrant the added corrosion risk. Table 7 shows the savings realized by constructing typical MSF vessels of carbon steel instead of copper-nickel.

Capacity GPD	Relative Plant Cost (Carbon Steel Cu-Ni)
70,000	95
200,000	90
1,250,000	86

Table 7

The selection of the tubing material is another important cost decision in selecting an evaporator process. Titanium tubes, for example, are much more expensive than Cu-Ni 90-10 tubes, but they should give the user a much longer life, particularly if acid is being used for scale control. Economic compromises in the material selection process must be studied carefully in the light of the potential for long-term deleterious effects.

Materials used in a RO plant are more straightforward and usually consist of aluminum bronze or stainless steel for the high pressure pump, stainless steel for high pressure piping, and PVC or RFP for low pressure piping. Iron bearing metals should be avoided in the feedwater system because iron fouls the membranes.

Two other capital cost factors worth mentioning are standard design and overspecification. The sixth-tenths power rule is not applicable in the case of standard versus custom-designed plants. For example, the six-tenths rule suggests that two half-size plants together will be 30% more expensive than a full size plant. But the rule does not hold if the half-size plants are standard and the full-size plant is a custom-made product. In fact, the two standard-size plants may be cheaper!

Normally the designer has complete control of the geometry or configuration of a plant. Economy, capacity, process type, even space allowances can be specified by the end user, but it is the designer alone who creates the geometry and a creative designer can substantially reduce costs. When users specify such things as cross-tube or long-tube design or tube diameter, they limit the packaging flexibility of the designer. Cross tube plants have been successful, long-tube plants have been successful and tube diameters of 3/8 inches and up have been successful. The end user should be careful not to overspecify because, in the end, it is the user who is penalized by costlier plants.

Capital cost decisions for RO plants are quite different from evaporators. Capital cost is affected by capacity, product water purity, use of power recovery, recovery rate and, probably most of all, by feed pretreatment.

A second pass may be required if the feed salinity is relatively high (greater than 40,000 ppm) or if a product water purity in the 70 ppm range is desired or both. This will add on the order of 15% to the capital cost of the plant. Power recovery units add to the capital cost of the plant, but usually have a payback period of 2 to 3 years.

The recovery rate affects the size of the feed intake, the pretreatment system, the RO pump and, ultimately, the capital cost. The capital cost decreases as the recovery rate is increased. As the recovery rate is increased above 20%, acid treatment of the feed becomes necessary to prevent scale. There is some uncertainty about the long-term affects of acid upon the materials in an RO plant. Thus, as is the case with evaporators, decisions to effect short term savings in capital cost may, in the long-run, result in diseavings.

The feed pretreatment system depends on the feedwater quality, its consistency and the quality of the operators and supervisors. Its cost varies with its complexity. A sophisticated system, which includes media filters, centrifuge cleaners, chlorinator, etc., may, cost as much as the RO membranes themselves, especially in smaller capacity plants.

Table 8 compares the relative capital cost of desalination processes on a $/GPD basis. The break point between large and small plants is about 250,000 GPD. The comparison is valid for plants with the same capacity, in addition, the ME, MSF and TC pressures were assumed to have the same economy. The comparison is based on the cost of equipment only, F.O.B. factory.

Process	TC	MSF-OT	MSF-BR	ME	MVC	RO
Relative Cost on a $/GPD Basis						
Small Plants	2.6	2.1	2.3	2.0	2.6	1.8
Large Plants	1.3	1.0	0.9	0.9	1.4	1.4

Table 8. Capital Cost Comparison

The table can be used to determine the relative $/GPD cost of different processes. For example, a million GPD RO plant will cost about 40% more than a MSF-OT, but a 100,000 GPD RO plant will cost about 15% less than an MSF-OT plant.

It is believed that the comparison is reasonable although one should realize that the differences may vary in actual circumstances. For instance, market competition, installation cost, seawater intake and disposal systems, shipping costs, etc. will have a considerable impact on the final installed capital cost differences.

Auxiliary Consumables

The section entitled "Type of Energy and Its Value" discussed the energy consumed by each process for separation of salt from water. Table 9 presents the auxiliary consumables, that is, approximate consumption of chemicals and auxiliary electricity.

Chemical consumption is expressed in pounds consumed per 1000 gallons of product water. The dosage rates and thus the consumption is dependent primarily upon the top operating temperature and brine concentration. The terms Poly, HTA and Acid stand for polyphosphate, high temperature additive and sulfuric acid, respectively.

Electrical consumption is expressed in KW per 1000 gallons of product water. The consumption does not include compressor power in the case of MVC or high pressure pump power in the case of RO - these are considered primary energy consumptions. The electrical consumption does not account for unusual intake or return requirements. The electrical consumption includes the electricity which is consumed within the battery points of the plant for feed, distillate, condensate, blowdown, recycle, and transfer pumps.

The flash plant electrical consumption is valid for a long tube design, the consumption will be about 30% higher for a cross tube plant.

Table 9 also lists cleaning and conditioning chemicals required for the various processes. The consumption of these chemicals will vary significantly from site to site and, therefore, no attempt was made to quantify this consumption.

Process	Top Temp (°F)	Chemicals		Electricity KW/KGAL	Cleaning/ Conditioning Chemicals
		lb/KGAL	Type		
MSF-OT	185 230	.18 .14	Poly HTA	14 13	HC1 or Sulfamic HC1 or Sulfamic
MSF-BR	185 230 250	.085 .12 2.5	Poly HTA Acid	17 16 15	HC1 or Sulfamic HC1 or Sulfamic
ME	185 240	.033 2.16	Poly Acid	7 8	HC1 or Sulfamic
TC	150	.056	Poly	5.0	HC1 or Sulfamic
MVC	170 215	.034 2.04	Poly Acid	5.0 5.0	HC1 or Sulfamic
RO (30% recovery)	N/A	1.9	Acid	2.0	Ammoniated Citric PTB Formaldehyde Detergent

Table 9. Auxiliary Consumables

Conclusion

The purpose of this paper is to provide the user of seawater desalination equipment with a better understanding of the factors which are important to process evaluation and selection. No attempt has been made to give absolute costs for equipment, utilities or water because these figures vary widely and change frequently.

The evaluation of a process should involve the factors discussed; that is, maintenance, operating complexity, operating costs and capital cost. Each user must also analyze his particular situation taking into account product water use, quality of seawater, site location, installation cost and intangibles such as the quality of operating personnel and supervision.

Each process has advantages and disadvantages and the final process decision should be based on achieving the desired reliability while minimizing the unit cost of water.

ACKNOWLEDGMENT

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DESALINATION TECHNOLOGY

Report on the State of the Art

Submitted to the Metropolitan Water District of Southern California

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Leon Awerbach - Project Manager Bechtel Group, Inc. Feb 1983

BACKGROUND

SUMMARY

Large quantities of water are required throughout the United States for agricultural, industrial, and residential use. Providing the necessary water supply presents a problem in many cases, particularly in Southern California where the local water supply is inadequate to meet local needs. As a result, it has been necessary to import water into this area from distant sources.

Southern California has a large potential water supply in certain brackish groundwater basins and in the Pacific Ocean. These supplies have not been developed in the past because of the high cost of desalination compared to the cost of alternative sources. As water needs continue to grow, it will become increasingly expensive to develop new sources of imported water and desalination may become cost competitive.

This report has been prepared as a resource document for use by The Metropolitan Water District of Southern California in planning the District's present and future involvement in desalination projects. The report presents the current technical and economic status of alternative desalination processes for seawater, brackish water, and wastewater reclamation.

STATUS OF DESALINATION

It is now technically feasible to generate large volumes of water of suitable purity by the desalination of brackish water and seawater. During the past two decades, over 2.24 million acre-feet per year (Af/y) (2 billion gallons per day (gpd)) of desalination capacity has been installed throughout the world. Although there have been "growing pains," the plants, ranging up to 300,000 Af/y in one location and comprising single trains of over 11,200 Af/y (10 million gpd), have performed reliably, delivering water of high purity at a cost which is acceptable in the regions where the plants have been built.

On a worldwide basis, there are a very large number of small desalination plants serving hotels, condominiums, and small industrial establishments. Even if we limit the discussion to plants of 28 Af/y (25,000 gpd) capacity and larger, the present number of plants worldwide still exceeds 2,200. Figure 1-1 shows the distribution of this number of plants according to the size of the desalination plant. Notice that only 10 percent of the plants (those having capacities of 1,000 Af/y or larger) account for more than 80 percent of the world's installed capacity.

The large plants are required primarily in water-starved areas, where they are the primary source of supply. Figure 1-2 indicates that the greatest installed capacity is in the Middle East and North Africa. Since plants in the Middle East have capacities of up to 268,800 Af/y, it is not surprising that the Middle East accounts for two-thirds (66 percent) of the worldwide installed-plant capacity. The strong showing of Europe and the United States, two normally nonarid regions, indicates that *local* needs may exceed economically available water supplies even in such temperate regions, thereby justifying the use of desalination.

Figure 1-3 shows the wide diversity of processes currently employed for desalination. The predominance of multistage flash (MSF) plants is explained in part by the early use of MSF in Kuwait and subsequently in Saudi Arabia, after which these users issued repeat orders for a technology with

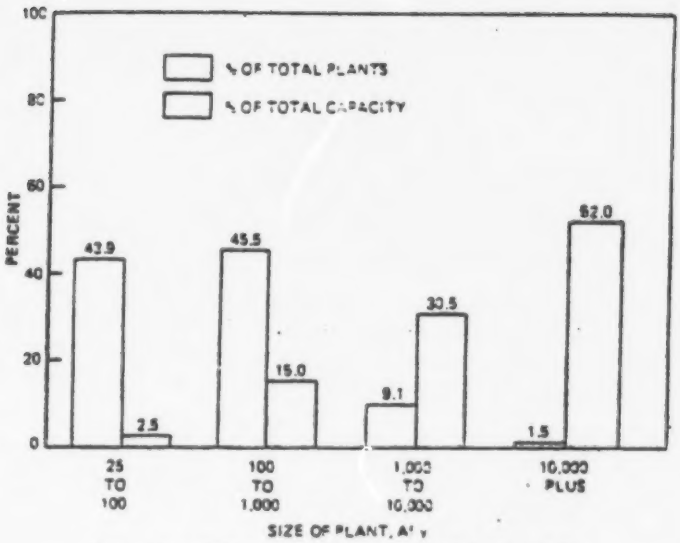


Figure 1-1 DESALTING PLANTS WORLDWIDE
(Grouped According to Plant Size)

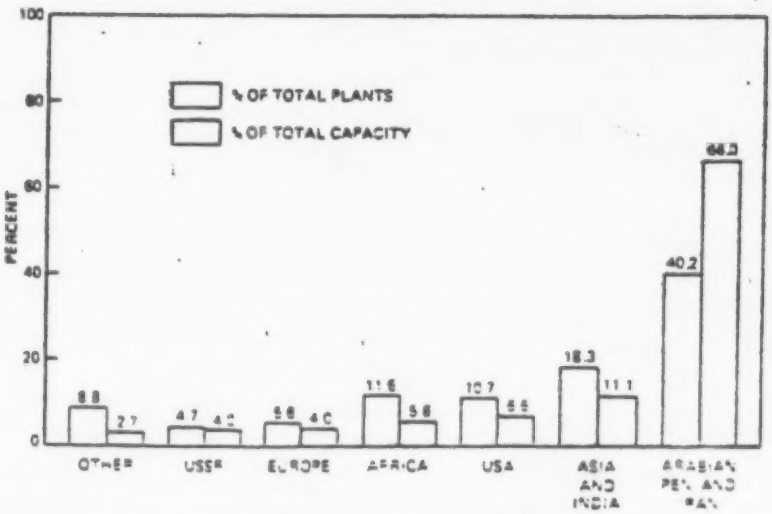


Figure 1-2 DESALTING PLANTS WORLDWIDE
(Grouped According to Geography)

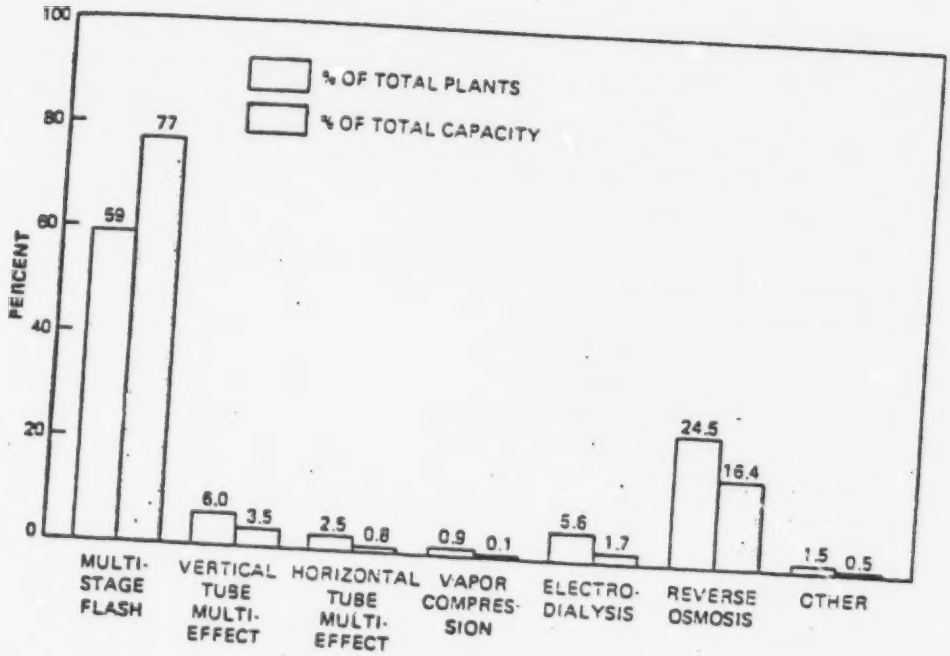


Figure 1-3 DESALTING PLANTS WORLDWIDE
(Grouped According to Type of Process)

which they were familiar. For the future, it is believed that multiple-effect distillation will supplant MSF plants due to better energy efficiency. Note in Figure 1-3 the increasing use of reverse osmosis (RO). This process is employed primarily for seawater desalination in plants less than 5,000 Af/y and desalting brackish water. Electrodialysis (ED) has historically competed with RO for brackish water desalting in the past but has been hindered by membrane fouling problems. Since introduction of the electrodialysis reversal (EDR) in the early 1970's, the ED process has to a large extent eliminated this problem making ED truly competitive with RO.

Figure 1-4 groups the world's desalination plants according to the type of feedwater. Most of the large-scale projects in the Middle East have used seawater, a practically limitless resource. The largest brackish water desalting project supplies the city of Riyadh, Saudi Arabia. The Wellton-Mohawk desalination project at Yuma, Arizona, now coming on stream, desalts 80,000 Af/y of agricultural return flows. The desalination of municipal and industrial wastewaters is a comparatively minor but expanding activity at present in the United States and other advanced countries.

Section 5

TECHNICAL COMPARISON OF PROCESSES

This section discusses a number of important technical considerations that should be involved in the selection of a desalination process. These considerations include:

- Purity of the product
- State of development of the process
- Insensitivity to feedwater total dissolved solids (TDS)
- Pretreatment requirements
- Necessary skill of operators
- Maintenance requirements
- Stability under design conditions
- Flexibility of the process
- Reliability of the process

PURITY OF THE PRODUCT

Any one of the distillation processes can produce comparatively pure water. Manufacturers typically submit bids containing warranties that the TDS will be less than 25 mg/l and, in some bids, less than 10 mg/l. The reverse osmosis (RO) membrane process, on the other hand, can attain about 500 mg/l from a seawater source in a single pass. From a brackish water source, a 90 percent reduction in TDS is commonly attained. Electrodialysis (ED) can perform about as well with a brackish feed but has not succeeded in desalting seawater on a commercial scale.

Equally important is the selectivity of the process for specific contaminants. It is apparent that at least a fraction of the volatile impurities will be carried over into the product by a distillation process. ED cannot remove from the feed any material that is not ionized. Consequently, the removal of silica is zero. RO, although not an electrolytic transport process, is sensitive to the ionic nature of the contaminants, removing more effectively those with a higher charge. Calcium (Ca^{++}) is removed far better than sodium (Na^{+}), and sulfate (SO_4^{--}) better than chloride (Cl^{-}). A nonionized material such as dissolved carbon dioxide (CO_2) or boric oxide (B_2O_3) is not removed at all; that is, its concentration in the permeate is identical to that of the feedwater. These specific contaminants can be ionized to a degree and, hence, partially removed by raising the feed pH; however, many membranes are sensitive to alkaline conditions and would disintegrate in a short time at a high pH.

Desalination by freezing results in almost pure ice crystals, but the adhering brine that is not removed by rinsing contributes impurities to the product. Contaminants are rejected regardless of ionic charge. Because of the low temperature of operation, many volatile impurities remain behind in the reject stream.

STATE OF DEVELOPMENT OF THE PROCESS

All of the variants of the distillation processes discussed in the preceding section are fully developed and have been in successful commercial use for a number of years. The membrane processes, RO and ED, have processed brackish waters in sizable modules for over 10 years; however, seawater ED is not

yet available. One seawater RO plant has been in operation for the past 6 years and another for 4 years, and a number are now coming on line. Freezing desalination, while yielding excellent results in pilot plant equipment, has yet to be installed in a moderately large, commercial plant.

Improvements continue to be made in all these processes. In distillation, the emphasis is largely on the reliability of components and the control of corrosion. (See the subsection, "Maintenance Requirements.") In membrane processes, the present effort centers on membrane reliability, new membranes, and on membrane sizing, a method of upgrading deteriorated membranes based on established textile sizing procedures.

INSENSITIVITY TO FEEDWATER TDS

Although the "minimum theoretical work" of distillation is roughly proportional to feed concentration, the total energy consumption is almost the same for seawater or very dilute brackish water. The membrane processes, on the other hand, experience a sharp increase in energy demand as the feedwater concentration rises. For RO, the pump pressure required by a brackish feedwater is 250 to 400 pounds per square inch (psig), for seawater 800 to 1,000 psig. The ion migration and other problems with ED are even more serious. Not only does the ED ion transport current increase with dissolved salt concentration, but a high salinity concentrate stream increases back-diffusion of solute, to a large extent negating the desalting action of the electric current. In addition, very high salinities short-circuit the current through the flow ports, thereby "burning" the edges of the membranes and the electrodes. These problems have tended to limit the application of ED to feedwaters of low TDS. In freezing desalination, increased salinity of the feed lowers the freezing point of the brine, thereby increasing the energy consumption. In addition, a high-salinity feedwater will yield a less pure product water than a feed of low salinity.

PRETREATMENT REQUIREMENTS

Large objects must be eliminated from any feedwater stream. To this end, ocean surface intakes are equipped with trash racks and screens. An alternative is the construction of sea wells, which strain the seawater through the naturally occurring sand of the seashore. These wells remove not only kelp and marine organisms but also fine suspended matter that cannot be tolerated by RO membranes. In contrast, distillation plants are indifferent to moderate amounts of silt. If the silt loading is excessive, its removal by means of hydrocyclones is adequate for distillation plants. For both RO and most distillation plants, it is mandatory to chlorinate the feed: preferably by shock chlorination, a treatment that destroys microorganisms and, in the case of open intakes, also the shellfish, which could lodge in the tubes of distillation plants, either blocking the flow or inducing erosion by generating eddies downstream from the obstruction. In general, this concern is minimal in those horizontal tube plants where the brine is sprayed on the outside of the tubes because deposits on the exterior of the tube do little harm and are easily removed.

The formation of scale can be a serious obstacle to the successful operation of a desalination plant. Scale deposits impose a barrier to the transfer of heat in a thermal process, coat and even pierce membranes in a membrane plant, and obstruct flow passages and "freeze" valves in any kind of plant. One of the most common scale formers is calcium carbonate ($CaCO_3$), which deposits when

carbon dioxide (CO_2) is released from the feed by boiling or by CO_2 transfer across a membrane, as described previously:

$$Ca(HCO_3)_2 \longrightarrow CO_2 + H_2O + CaCO_3$$

One of the oldest methods for the prevention of scale is the acidification of the feed with a mineral acid. This technique, however, requires the storage and handling of a potentially dangerous substance and, if not carefully controlled, may induce rapid corrosion of metallic plant components. Scale control additives have been tested for the prevention of carbonate scaling with varying degrees of success. For RO plants, the transfer of CO_2 across the membrane makes the use of acid in combination with additives the best method at present. For distillation processes that operate below 240F, high-temperature additives show promise. Multistage and multi-effect plants at temperatures not exceeding 195 F have successfully used sodium polyphosphate for a number of years.

Even plants using acid for the prevention of carbonate scale require sodium hexametaphosphate (SHMP) or one of the newer additives to prevent the deposition of calcium sulfate, a common problem in brackish water and all seawater.

RO, in general, requires thorough pretreatment to avoid deposits that might decrease the product flux or, in extreme cases, could completely destroy the membranes. Particular care in feed preparation is required when desalting surface or wastewaters (e.g., agricultural drains). As an example, the Yuma desalination plant of the U.S. Bureau of Reclamation incorporates the following pretreatment steps:

- Straining through a trash rack
- Chlorination
- De-silting in a settling basin
- Softening, coagulation, and settling in a reactor-clarifier
- Supplementary chlorination
- Filtration through a dual-media filter
- Dechlorination by passage though a bed of activated carbon or, preferably, by the addition of bisulfite
- pH adjustment with sulfuric acid
- Injection of anti-scalant additive
- Passage through a 5-micron or 10-micron cartridge filter

The RO plant of the Orange County Water District furnishes an example of an adequate process and careful operation that yields satisfactory results with a wastewater feed. There, a secondary sewage effluent is pretreated by softening, coagulation, activated carbon, and dual-media filtration prior to RO desalination. Successful operation has been reported.

For seawater, several of these steps may be omitted if the intake consists of sea wells or a Ranney well (a well terminating in a number of laterals).

Reports indicate that in contrast to RO, ED with reverse polarity can operate safely for extended periods without acids or additives. This is equally true for the freezing process. Silica, which deposits damaging scale from some feedwaters in other membrane processes, is reported to do no harm in ED plants with reverse polarity.

NECESSARY SKILL OF OPERATORS

At present, no operating experience is available for commercial-scale freezing desalination plants. The other processes discussed in Section 4 present a wide spectrum of requirements for operator education and training. At one end of the spectrum, reverse polarity ED, low-temperature multi-effect distillation, and low-temperature vapor compression require very little operator attention or skill. High-temperature distillation requires careful attention to scale control and corrosion prevention methods. The most demanding process is RO, for which operators must be trained in all the pretreatment steps. A dedicated and skillful crew is necessary to ensure satisfactory RO plant performance. Ignorance or indifference can result in the catastrophic failure of any process.

MAINTENANCE REQUIREMENTS

In every well-operated plant, even those which inject acid into the feed stream, scale and other contaminants will deposit slowly. When the heat transfer drops below a predetermined value in a distillation plant or when the product flux or purity drops to a preset value in a membrane plant, cleaning as outlined below is initiated:

- In distillation plants, inhibited acid is circulated through the system. This can be done without shutdown, but with no water production. A high-temperature system will require cleaning at intervals of 3 to 6 months, provided no serious maloperation has occurred. A low-temperature plant must be cleaned at intervals of 6 months to 2 years. In an MSF plant, the scaling rate can be substantially reduced by continually circulating sponge balls through the tubes during plant operation, a process that involves an increase in investment.
- For an RO system, a detergent/suspending agent solution is circulated through the feed side of the plant. If the elements are loaded with scale to the point that the cleaning process is ineffective, the elements must be removed from their pressure vessels and soaked in a tank of cleaning solution. Should this fail to solve the problem, the membrane elements must be discarded and replaced by new ones.
- Although polarity reversal is quite effective in eliminating scale formation in ED, either deposits on the membranes or other problems may require maintenance. Prior to shutdown, the trouble spots are located by measurement of inter-cell potential drop. Then the stack is disassembled and dirty membranes are cleaned by manual scrubbing. Membranes showing burns or fractures are replaced. Defective electrodes are removed for replating.

Should an RO system exhibit an increase in flux accompanied by a drop in product purity, there is reason to suspect local imperfections in one or more membranes. The maintenance procedure consists of circulating a sizing solution of a composition determined by the membrane material. The sizing solution fills the microscopic voids and, if successful, permits the continued use of the membrane.

The maintenance of an RO pretreatment system requires specialized skills because of the numerous and intricate subsystems involved. The most troublesome one from the standpoint of corrosion is the acid injection section where the localized dilution of a strong acid occurs. Maintenance in this area can be held to a minimum by constructing the in-line mixer and the mixing pipe spool of high-alloy materials. The RO vessels themselves are seldom a problem since they are constructed of stainless steel or fiber-reinforced plastic; however, connectors to the elements have experienced corrosion and maintenance problems, requiring upgrading to high-nickel stainless steel.

In contrast, the shells and internals of high-temperature distillation plants may corrode rapidly unless constructed of, or clad with, corrosion-resistant alloys. Heat transfer tubing may also be a source of serious trouble. Even the more costly alloys, such as aluminum-brass, copper-nickel and titanium and its alloys, may have a comparatively short life under some conditions of operation. Maintenance consists of welding "patches" on the vessel and plugging or replacing defective tubes, both operations requiring equipment shutdown and the use of skilled laborers. Where low-temperature distillation is used, however, corrosion is almost eliminated. The carbon steel vessels are protected by a multilayer internal coating of cured organic material. The heat transfer surface is formed from Alloy 5052, a seawater-resistant alloy of aluminum. Should a perforation occur in a tube of a low-temperature multi-effect distillation plant, there is no effect on product purity since the pressure on the product side is greater than that on the brine side. In all processes, maintenance is required on pumps and rotating equipment.

STABILITY UNDER DESIGN CONDITIONS

All the desalination processes described in this report are quite stable under design conditions. Two possible sources of instability are the vapor compressor in a VC plant and the control equipment in any desalination plant. It is safe to assume that a reliable manufacturer of vapor compression equipment will design a compressor to operate in the stable range. The balance of this or any other system can become unstable if the control system exhibits positive feedback characteristics. The most annoying (and perhaps damaging) is the improper control of flow in a circulating loop, resulting in surging, but this is seldom a problem in a well-designed control system.

FLEXIBILITY OF THE PROCESS

The purchaser of a desalination plant will ask two questions:

- Can I achieve more than the rated output if needed?
- To what degree can I cut back on the plant production?

As for the first question, it must be remembered that the supplier is not obligated to provide overcapacity beyond the contracted value. However, it is possible to increase the output of an ED cell simply by increasing the current through the cell, making certain not to exceed the maximum specified by the manufacturer. For an RO plant, an increase in applied pressure, if permitted by the pumps, will yield a greater product flow, but at the expense of shortened useful membrane life. The output of a VC plant can be increased only if the compressor motor and the compressor itself have been overdesigned. A higher output from a thermal distillation plant requires an increase in prime steam tem-

perature and flow, preferably with an increase in brine recirculation rate. A higher steam temperature increases the danger of scale formation in the prime heater, even if the pumps permit an increase in recirculation rate. In summary, a 10 percent increase is possible for MSF, 25 percent for MED; a substantial production increase in the other processes is questionable.

The answer to the second question depends on the desalination process. For ED, unlimited turndown is possible, accompanied by an improvement in product purity, but an increase in specific energy consumption. Alternatively, an ED plant can be turned on and off, as needed, with no harmful effects. For RO, on the other hand, a decreased feed pressure cuts down product flow but is detrimental to product purity. In addition, there are definite limits to minimum and maximum flow through RO elements. Turndown of a VC plant lowers the energy efficiency and, even more seriously, may lead to instability of the compressor. MSF can tolerate, in general, a turndown of about 10 percent, below which the operation becomes unstable or ceases to function entirely. Multi-effect distillation (MED) output can be reduced substantially without instability or energy penalty, except for the wasted power of the recirculating pumps. It has been demonstrated that the multi-effect evaporator design can readily accept a 40 to 45 percent turndown, which is achieved rapidly in response to changes in the steam supply. When a desalination plant is built using a number of modules, as is sometimes done for increased reliability and flexibility, one or more modules may be shut down as the need dictates. A prolonged shutdown, however, requires precautionary measures. An unlined carbon steel plant, such as those frequently used in distillation processes, requires nitrogen blanketing, together with the addition of an oxygen scavenger to the brine to minimize corrosion of the steel. For an RO plant, a protracted shutdown requires that the brine in the system be replaced with product water containing a bacteriostat such as formaldehyde.

RELIABILITY OF THE PROCESS

Each of the desalination processes reviewed in this report must be considered as a system that includes the requisite pretreatment steps. Any interruptions attributable to problems with pretreatment will affect the reliability of the entire system. On this basis, the most dependable desalination processes are the ones requiring the fewest and simplest pretreatment steps. From the standpoint of interruptions of the desalination process due to the pretreatment train, the most-serious problems can be anticipated from RO as applied to surface waters and wastewaters (although RO brackish water plants have generally performed well). On the other hand, the processes requiring the simplest pretreatment and, hence, exhibiting the greatest reliability are reverse polarity electrodialysis and low-temperature distillation. The reliability of each of the three broad categories of commercial desalination processes is evaluated below.

Distillation Processes

Serious problems have been encountered in multistage flash plants, particularly those operating with pH control of scale. Operator inattention or defective instrumentation has been responsible for wide swings in pH. Insufficient dosage of acid permits scale deposition, and excess acid leads to catastrophic corrosion of tubes and evaporator shells. Even a well-operated plant is difficult to control since the target pH is on the knee of the pH-vs-dosage curve. One alternative for good scale control with moderate corrosion is the injection of scale control additives. Another source of difficulty is the chlorination required as biocide. The chlorine reacts with the bromides in seawater, liberating bro-

mine, which severely corrodes the venting system. Successful removal of both scale and marine organisms from heat exchange tubing has been achieved by circulating sponge balls through the plant (the Taprogge process), but at considerable increase in complexity and plant investment. Further corrosion problems are introduced by hydrogen sulfide (H_2S), which results from organics present in some seawater sources. Shutdowns for the repair of corrosion damage are frequent and become increasingly so with time.

Greater reliability is exhibited by the low-temperature distillation plants, both VC and multi-effect. Although still faced with the problems of marine growths, they suffer less from corrosion, and scale formation is easily controlled. In contrast with the high-temperature distillation plants, these low-temperature systems have been reported to operate from 6 months to 2 years before a short interruption for on-line cleaning is necessary. For the plants that operate at lower temperatures, an organic coating applied to the chamber interiors provides long-term protection to carbon steel. Multi-effect plants tubed with aluminum-alloy heat-transfer tubing experience a uniform tube corrosion rate of about 0.5 mil per year and show no sign of crevice corrosion or stress corrosion cracking even in the presence of considerable amounts of H_2S. Thus, almost no operating time is lost for retubing or for the patching of vessel shells.

The RO Process

For the RO process, the estimate of reliability is dependent on the type of feed. In general, plants supplied with brackish well water have an excellent on-stream factor if properly operated and serviced. Seawater plants have experienced a number of interruptions; however, the seawater application is relatively new, and its problems are expected to be gradually solved. At the other extreme, a high degree of reliability cannot be predicted at this time for the processing of surface waters or wastewaters by RO unless very thorough pretreatment is provided.

The ED Process

Improvements are being made in all desalination processes. In ED, the early problems of scaling and attack on the electrodes have been overcome by the introduction of reversing polarity. (See Section 4.) Recent plants using reverse polarity ED for the desalination of brackish water are performing well and exhibit a satisfactory on-stream factor. It should be emphasized again that ED is not currently offered for seawater desalination and that its reliable application to wastewaters requires careful attention to the control of bacteria and membrane contaminants such as iron in solution.

SUMMARY OF THE TECHNICAL COMPARISON OF PROCESSES

Table 5-1 summarizes the evaluation discussed in the preceding subsections. Under each criterion, a number has been assigned to represent the rating of each process as follows: 3 — a highly satisfactory process; 2 — a process that is only fair in meeting a particular criterion; 1 — a process that does not perform well or one that is troublesome; 0 — a criterion that has not yet been demonstrated for the particular process.

A rating system covering a wider range of grades, for example, 0 to 10, does not appear to be justified because of the difficulty of breaking down each criterion into finer degrees of performance.

Table 5-1

TECHNICAL COMPARISON OF PROCESSES

Process	Purity of the Product	State of Development	Insensitivity To Dissolved Solids of Feed	Pretreatment Requirements	Necessary Skill of Operators	Maintenance Requirement	Stability Under Design Conditions	Flexibility	Reliability of the Processes	Sum of Ratings
Multi-stage flash distillation (seawater only)[a]	1	3	3	2	2	1	3	1	2	20
Multi-effect distillation (seawater only)										
Vertical tube, high temp[a]	1	2	3	1	2	1	3	1	2	20
Horizontal tube, low temp[a,b]	3	2	3	3	3	2	3	3	2	24
Vapor compression distillation[c]	3	3	2	2	2	2	3	2	1	22
Reverse osmosis										
Seawater	2	2	2	2	2	3	3	3	2	21
Brackish well water	2	3	1	2	2	3	3	3	1	22
Surface or wastewater	2	2	1	1	1	1	3	3	1	15
Freezing desalination[d]	1	0	3	3	0	0	0	0	0	7
Electrodialysis										
Seawater	Not currently available for seawater desalination									
Brackish water or wastewater	2	3	2	2	3	2	3	3	1	21

Ratings:
- 1 - Highly satisfactory process
- 2 - Fair
- 3 - Low quality or troublesome
- 0 - Performance not demonstrated

Notes
(a) Not competitive for brackish water.
(b) Technically superior to membrane process for some wastewaters
(c) Large units sold predominantly for wastewater concentration.
(d) Pilot plant tested on seawater and some industrial concentration processes to date

The sum of the ratings for each process provides a basis for selection by the prospective purchaser. It has been assumed that each of the technical considerations is weighted equally. Under some circumstances, the purchaser of a desalination plant may be justified in attaching greater importance to one or more of these criteria, leading to a different ranking of the processes than the one shown here. The reader should note that a zero rating does not indicate a failure but, instead, that the process has not yet advanced beyond the pilot plant stage. In addition, commercial ED has not been developed for seawater desalination. Freezing and seawater ED, however, may be considered for future development.

It is apparent that a process may have a high rating for some applications and yet be a questionable choice for others. For example, Table 5-1 shows that RO merits serious consideration for the desalination of brackish well water but may encounter troublesome problems in the treatment of some surface waters or wastewaters. In general, the highest overall rating is shown for seawater desalination by multi-effect distillation in low-temperature plants of the horizontal tube type.

In some applications, the use of a process of slightly inferior numerical rating but lower overall cost may be justified. (See the discussion of economics in Section 6.)

Section 6

ECONOMIC COMPARISON OF PROCESSES

This section first develops a generalized estimate of the investment required for each type of process. The base case involves a plant to yield 5,000 to 6,000 acre-ft/yr (Af/y) of desalinated water. For each process, the cost of the product water is then estimated including major cost components:

- Capital
- Energy
- Operation and maintenance (including applicable G&A)
- Chemicals and general supplies
- Membrane replacement (reverse osmosis and electrodialysis only)
- Filter replacement (where used)

The capital investment estimates are based on a review of current studies in the desalting field and recent awards for actual plants. The costs include minimum allowances for site-specific items, but no particular site has been assumed. The desalting plants do not include a boiler for thermal processes that require steam heating. Steam requirements are handled as a utility — part of the operating costs.

The basis for the estimates of the cost of water is as follows:

- Plant life — 20 years
- Interest rate — 10 percent
- Insurance — 2 percent
- Cost of electricity — $0.06/kWh

The designations "single-purpose" and "dual-purpose" reflect the source of steam for the thermal processes. The cost of steam for a single-purpose plant is assumed to be $6/million Btu, representative of costs incurred in generating steam by burning an oil fuel. For a dual-purpose plant, where steam is extracted from a nearby steam-electric power generating facility, the costs range from $2.50/million Btu for steam at 50 psia (about 280F) to $0.32/million Btu for steam at a pressure of 5.5 inches of mercury (about 130F).

Both capital investment and cost of water estimates are intended as comparative costs among themselves and should be used only to determine cost trends. For a specific project where the site and the feedwater have been identified, the cost of produced water may vary considerably from those presented here. A site-specific analysis could result in a change in the relative ranking of some of the processes. The final choice of a process will depend upon those items mentioned above as well as the energy availability and cost at the time, the economic climate, the projected inflation rates for various categories of costs, and the social, legal, and environmental constraints at the proposed plant site.

In developing estimates of water costs, the annual water production was reduced from the daily design capacity to account for plant downtime. The stream factor (percentage of time the plant is running) for the processes considered ranges from 75 to 95 percent. Table 6-1 lists the estimated stream factors for each process and feedwater. The provision of storage facilities may be important for isolated facilities. For a large, flexible system such as the Metropolitan Water District and associated

agencies, it does not appear to be necessary and, consequently, the cost of storage tanks was neglected in this report.

Tables 6-2 and 6-3 summarize the capital investment requirements for seawater and brackish/wastewater desalting plants. The costs are presented as unit investments, i.e., dollars per Af/y plant capacity, for a plant in the size range of 5,000 to 6,000 Af/y. These costs are also presented in the form of bar charts in Figures 6-1 and 6-2.

Table 6-1

STREAM FACTOR ASSUMED FOR EACH PROCESS

Plant Type	Feed	Stream Factor (Percent)
Multistage flash	Seawater, acidified	75
Multi-effect vertical tube	Seawater, acidified	85
Multi-effect horizontal tube, low temperature	Seawater, no acid	95
Multi-effect horizontal tube	Wastewater	95
Vapor compression, low temperature	Seawater, no acid	95
Vapor compression	Wastewater	85
Reverse osmosis	Seawater	85
	Brackish water	92
	Wastewater	85
Electrodialysis	Brackish water	95

Table 6-2

COMPARATIVE INVESTMENTS FOR SEAWATER DESALINATION PLANTS

(5,000 to 6,000 Af/y Capacity) (6 × 10⁶ m³/year

(AF - 20,999 m³/day)

Plant Type	$/Af/y (4th Quarter 1982)
Single-Purpose Plants	
Multistage flash[a]	6,700
Multi-effect vertical tube[a]	5,900
Vapor compression, low temperature[b]	4,200
Reverse osmosis:	
1-pass hollow fine fiber	3,300
2-pass spiral wound	3,600
Dual-Purpose Plants	
Multi-effect flash[a]	6,700
Multi-effect:	
Vertical tube[a]	5,900
Horizontal tube[c]	5,100
Horizontal tube, low temperature[d]	4,600

(a) Performance ratio of 12 (see Sect. 3), acid added, steam temperature = 250F

(b) Low energy use (38 kWh, 1,000 gal). ~10 kwh/m³

(c) Performance ratio of 6, no acid, steam temperature = 180F

(d) Performance ratio of 2.85, no acid, steam temperature = 135F

Table 6-3

COMPARATIVE INVESTMENTS FOR BRACKISH WATER DESALINATION PLANTS
(5,000 to 6,000 Af/y Capacity)

Plant Type	$/Af/y (4th Quarter 1982)
Brackish Water Feed	
Reverse osmosis	760
Electrodialysis:	
2,000 mg/l feed	1,300
3,500 mg/l feed	1,750
Wastewater Feed	
Reverse osmosis[a]	940
Vapor compression[b]	4,400
Multi-effect horizontal tube, low temperature[a]	4,400

(a) For municipal wastewater.

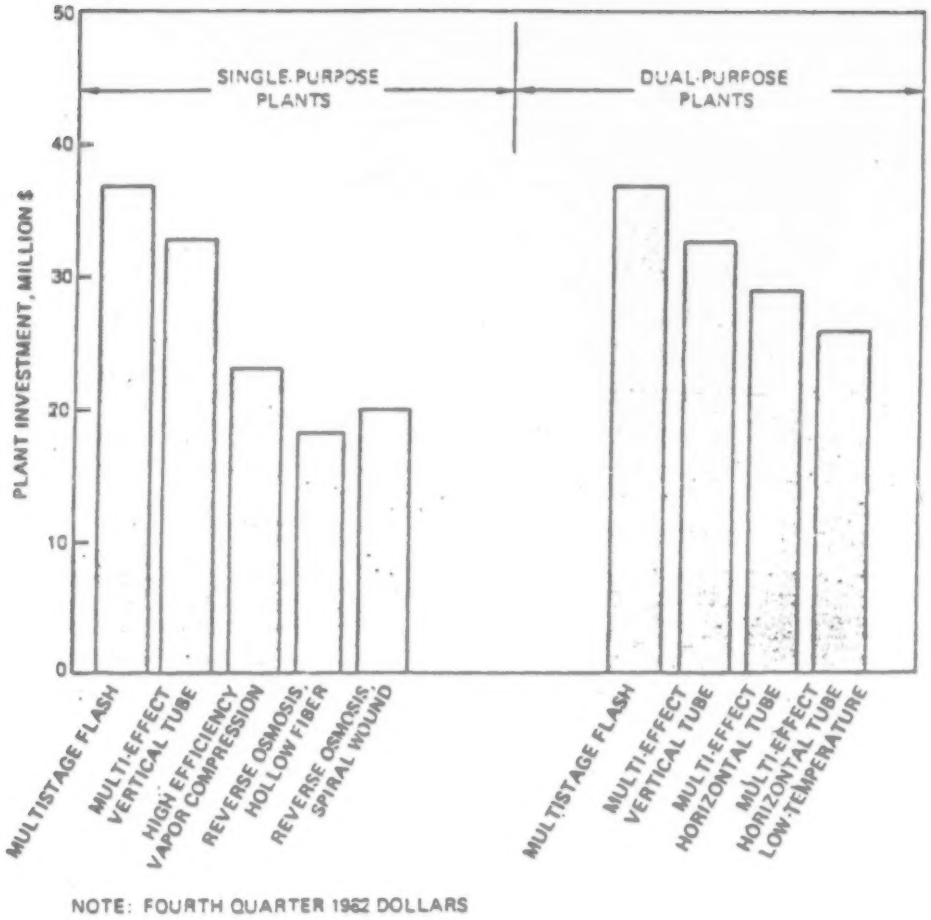
(b) For cooling tower blowdown (industrial wastewater) concentration.

It is apparent that for seawater, the lowest plant investment is represented by the reverse osmosis (RO) process using either hollow fibers or the spiral wound configuration. This is equally true for brackish water. For the latter, electrodialysis (ED) is a close second, its investment cost depending on the salinity of the feed.

The costs of producing water, expressed as $/Af, are shown in Table 6-4 with a breakdown of three categories of costs — (annualized) capital, energy, and other (including labor, operating supplies, and maintenance materials). Table 6-4 indicates that for a single-purpose plant supplied with a seawater feed, the lowest cost of product water is achieved by the high-efficiency low temperature vapor-compression plant. When the supply is brackish water, however, the lowest water cost is achieved by either ED or RO. As in the case of plant investment, product cost from ED is influenced by the composition of the feed as shown by the difference in water costs for 2,000 and 3,500 mg/l wellwater.

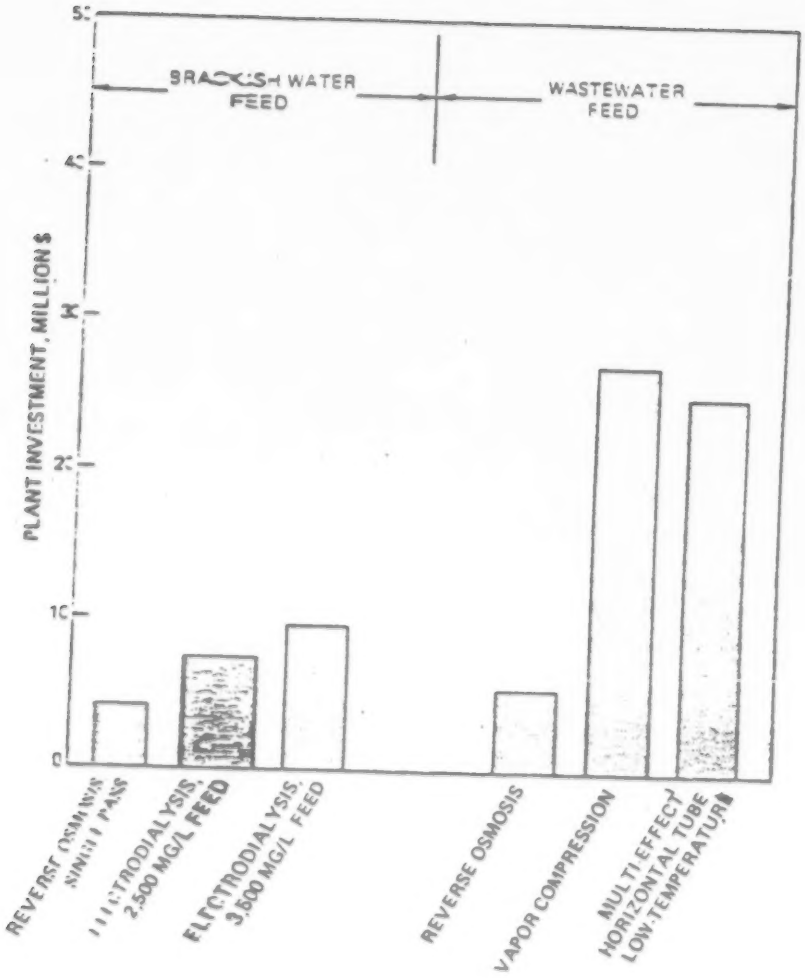
The effect of energy cost is shown clearly by the economic advantage of coupling a distillation plant with a power plant in a dual-purpose plant. This can be seen by comparing the single- and dual-purpose plant costs in Table 6-4 for multistage flash and multiple-effect vertical-tube plants. In the case of seawater desalination, the lowest overall cost is achieved by coupling a multi-effect horizontal low-temperature desalter with a power plant. The heat that would normally be rejected to the power plant condenser provides a low-cost source of energy for desalination.

The contribution of each of the major cost components to the product water cost is summarized in Table 6-4, and is presented in Figures 6-3 through 6-10 inclusive for seawater feed, and Figures 6-11 through 6-16 inclusive for brackish water and wastewater. These cost components are for a plant size



NOTE: FOURTH QUARTER 1982 DOLLARS

Figure 6-1 INVESTMENT REQUIRED FOR SEAWATER DESALINATION – 5,600 ACRE-FT/YEAR (5 mgd) INSTALLED CAPACITY



NOTE: FOURTH QUARTER 1982 DOLLARS

Figure 8-2 INVESTMENT REQUIRED FOR BRACKISH WATER AND WASTEWATER DESALINATION – 5,600 ACRE-FT/YEAR (5 mgd) INSTALLED CAPACITY

Table 6-4

COMPARATIVE ESTIMATES DESALTED WATER COSTS[a]
(5,000 to 6000 Af/y Capacity)

Plant Type	$/Acre Foot			Total Cost of Water
	Capital Costs[b]	Energy Cost	Other Costs	
	Percent of Total Cost			$/Af
Seawater Feed				
Single-Purpose Plants[c]				
Multistage flash	42	52	6	2,900
Multi-effect vertical tube	37	58	5	2,600
Vapor compression, low temperature	42	52	6	1,400
Reverse osmosis[d]	33	36	31	1,600
Dual-Purpose Plants[e]				
Multistage flash	57	35	8	2,200
Multi-effect:				
Vertical tube	54	38	8	1,800
Horizontal tube	49	42	9	1,500
Horizontal tube, low temperature	58	34	8	1,200
Brackish Water Feed				
Reverse osmosis	28	41	31	390
Electrodialysis, 2,000 mg/l feed	51	30	19	370
Electrodialysis, 3,500 mg/l feed	50	32	18	500
Wastewater Feed				
Reverse osmosis[f]	26	33	41	570
Vapor compression[g]	31	65	4	2,300
Multi-effect horizontal tube low temperature[f][g]	56	36	8	1,100

(a) All costs in 4th quarter 1982 dollars

(b) Based on 10%, 20 years plus 2%/yr insurance cost

(c) Steam cost $6/million Btu

(d) RO with energy recovery

(e) Steam cost ranges from $2.50/million Btu to $0.32/million Btu

(f) Municipal wastewater feed

(g) Industrial wastewater (cooling tower blowdown) feed

of 5,000 to 6,000 Af/y. It is important to note that the value of the energy consumed is one of the major contributors to overall product cost.

To minimize the energy cost for the reverse osmosis plants, it is assumed that energy recovery is incorporated into the desalting plant. Energy recovery has not been assumed for the lower pressure brackish water plants, however, since the increased capital charges resulting from energy recovery equipment negates the savings in energy cost.

The plant investment and water costs discussed above are based on a plant of nominal 5,000-6,000 Af/y capacity. The economy of size is indicated by the data in Table 6-5, which shows unit plant costs for plants of 1,000, 5,000, and 12,000 Af/y. For each technology, the plant cost per Af/y of plant capacity tends toward a constant value as plant size increases, since desalination plants are of modular construction and a single desalination complex of large size is composed of a number of modules of smaller size. For example, for membrane plants, the individual modules may be as low as 100 Af/y, even for large installations. Distillation plants seldom exceed 7,000 Af/y in a single train. The largest commercial vapor compression distillation plant produces 970 Af/y.

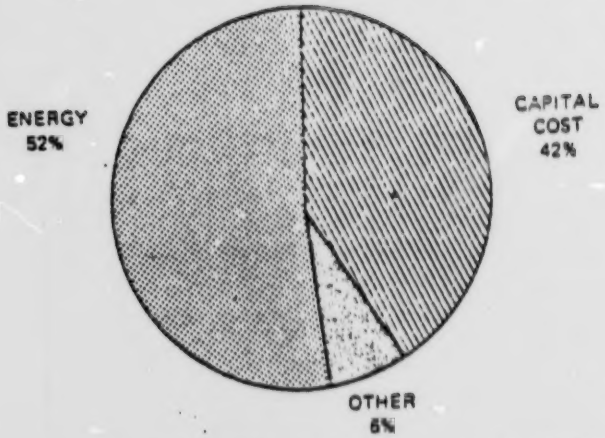
EFFECT OF BLENDING

One of the ground rules of this study was that the economics section should list the cost of water as produced and that MWD would calculate the cost of the blended product if such blending were desirable. Figure 6-17 is included to assist the reader in adjusting the water cost to allow for blending. For example, if a well water with 2,000 mg/l of dissolved solids is available, distillation product water at 10 mg/l can be blended to a 500 mg/l at a 25 percent reduction in the cost of distilled water product. An additional benefit of blending is the corresponding increase in usable water delivered by the plant. Thus, in the example cited above, a 5,600 Af/y desalination plant will deliver 7,400 Af/y of blended water containing 500 mg/l of total dissolved solids. Figure 6-17 permits cost calculations also for blending product waters of several other purities.

Table 6-5

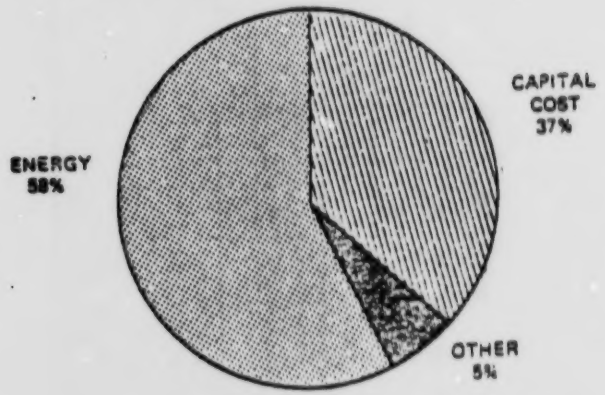
ESTIMATED EFFECT OF PLANT CAPACITY ON COST OF PRODUCED WATER

Process	Cost of Produced Water Relative to Production Cost from 5,000 Af/y Plant		
	1,000 Af/y	5,000 Af/y	10,000 Af/y
All seawater processes	1.40-1.50	1.00	.85-.90
Brackish water processes			
RO and low-temperature multi-effect horizontal tube	1.30-1.35	1.00	.90-.95
EDR (electrodialysis reversal)	1.80-1.90	1.00	.85-.95



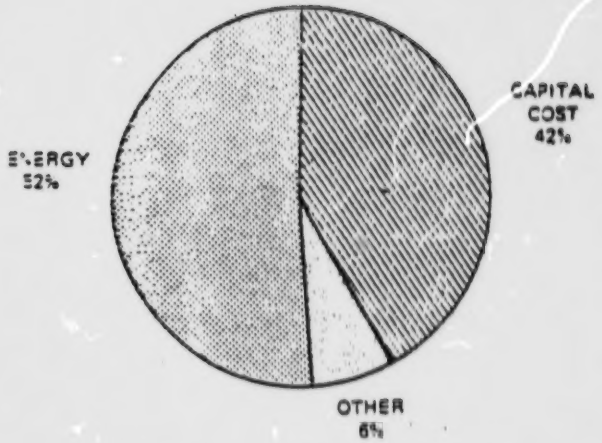
TOTAL COST OF PRODUCT WATER = $2,900 PER ACRE/FT

Figure 6-3 WATER COST FROM SEAWATER VIA SINGLE-PURPOSE MULTI-STAGE FLASH PLANT, ACID ADDED, SOURCE OF ENERGY – LOW SULFUR FUEL OIL (LAST QUARTER 1982 DOLLARS)



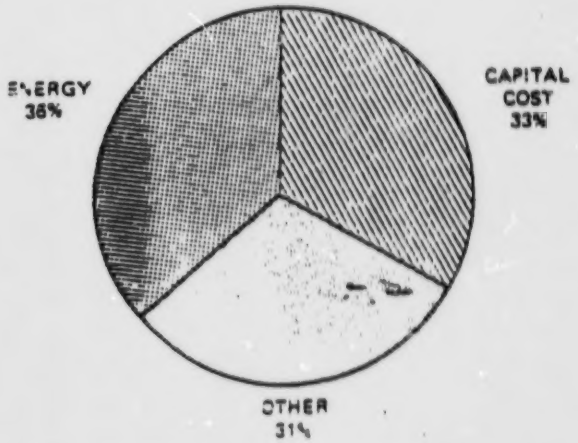
TOTAL COST OF PRODUCT WATER = $2,600 PER ACRE/FT

Figure 6-4 WATER COST FROM SEAWATER VIA SINGLE-PURPOSE MULTI-EFFECT VERTICAL TUBE EVAPORATION, ACID ADDED, SOURCE OF ENERGY – LOW SULFUR FUEL OIL (LAST QUARTER 1982 DOLLARS)



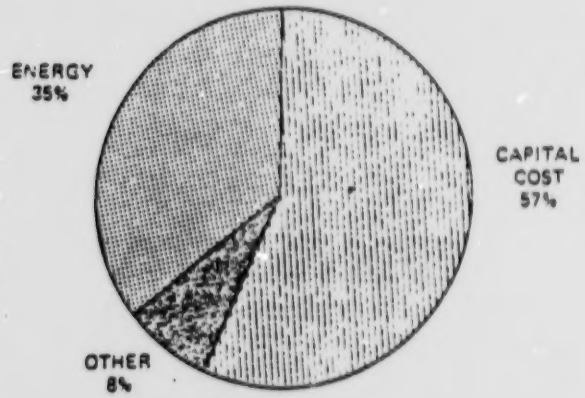
TOTAL COST OF PRODUCT WATER = $1,400 PER ACRE/FT

Figure 6-5 WATER COST FROM SEAWATER VIA DISTILLATION IN A LOW-TEMPERATURE VAPOR COMPRESSION PLANT (LAST QUARTER 1982 DOLLARS)



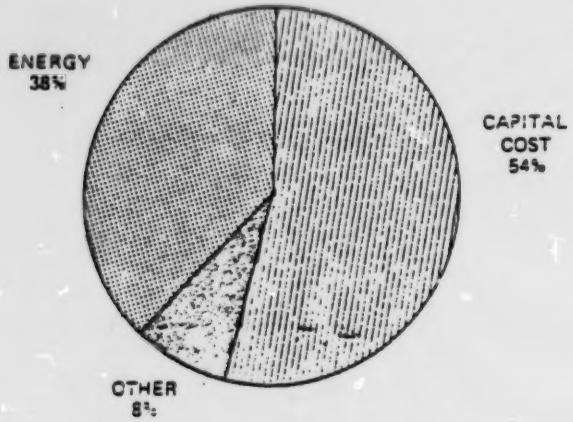
TOTAL COST OF PRODUCT WATER = $1,570 PER ACRE FT

Figure 6-6 WATER COST FROM SEAWATER VIA REVERSE OSMOSIS WITH ENERGY RECOVERY (LAST QUARTER 1982 DOLLARS)



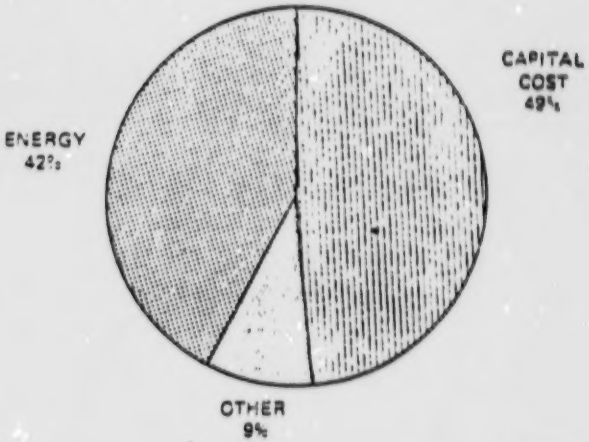
TOTAL COST OF PRODUCT WATER = $2,200 PER ACRE FT

Figure 6-7 WATER COST FROM SEAWATER VIA DUAL-PURPOSE MULTISTAGE FLASH PLANT, ACID ADDED (LAST QUARTER 1982 DOLLARS)



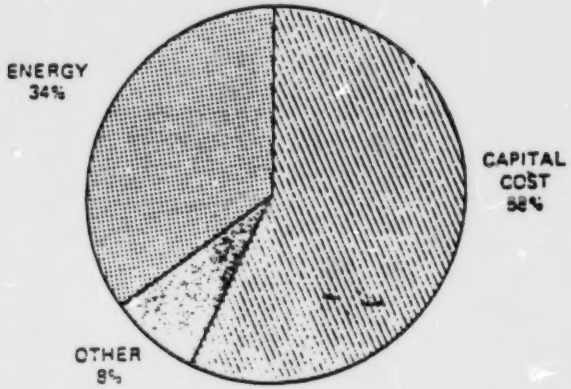
TOTAL COST OF PRODUCT WATER = $1,800 PER ACRE FT

Figure 6-8 WATER COST FROM SEAWATER VIA MULTI-EFFECT VERTICAL TUBE EVAPORATION IN A DUAL-PURPOSE PLANT (LAST QUARTER 1982 DOLLARS)



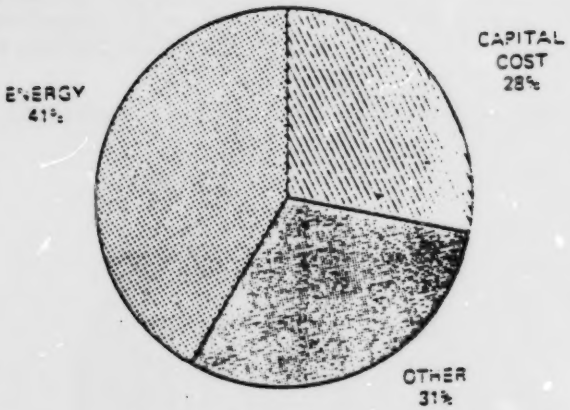
TOTAL COST OF PRODUCT WATER = $1,500 PER ACRE FT

Figure 6-9 WATER COST FROM SEAWATER VIA MULTI-EFFECT HORIZONTAL TUBE EVAPORATION IN A DUAL-PURPOSE PLANT (LAST QUARTER 1982 DOLLARS)



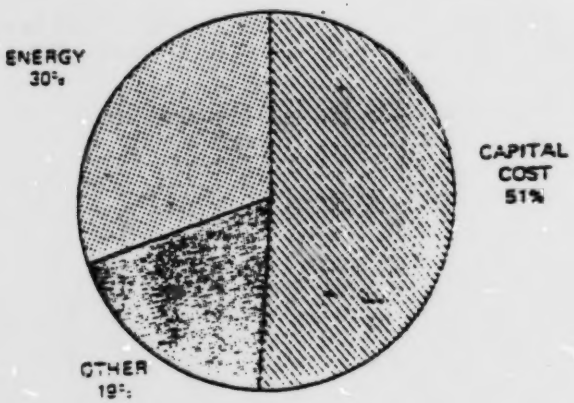
TOTAL COST OF PRODUCT WATER = $1,200 PER ACRE FT

Figure 6-10 WATER COST FROM SEAWATER VIA DUAL-PURPOSE MULTI-EFFECT HORIZONTAL TUBE, LOW-TEMPERATURE DISTILLATION (LAST QUARTER 1982 DOLLARS)



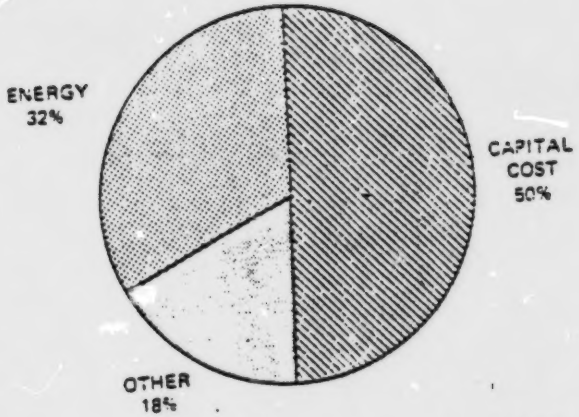
TOTAL COST OF PRODUCT WATER = $330 PER ACRE/FT

Figure 6-11 WATER COST FROM BRACKISH WELL WATER VIA REVERSE OSMOSIS, WITHOUT ENERGY RECOVERY (LAST QUARTER 1982 DOLLARS)



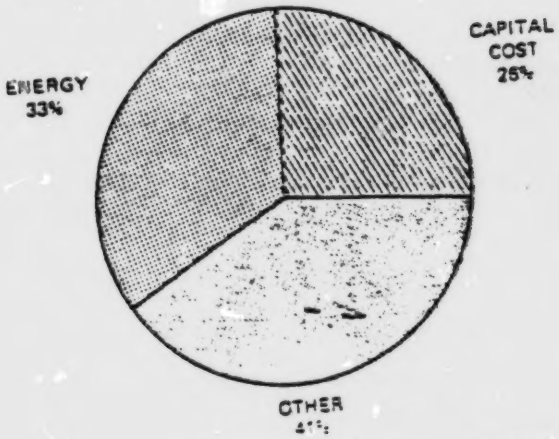
TOTAL COST OF PRODUCT WATER = $370 PER ACRE FT

Figure 6-12 WATER COST VIA ELECTRODIALYSIS WITH FEED TDS OF 2,000 MG/L (LAST QUARTER 1982 DOLLARS)



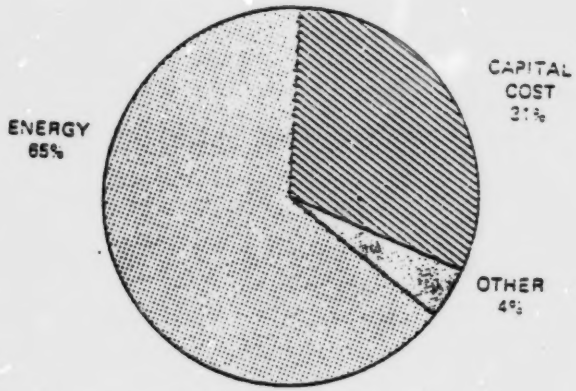
TOTAL COST OF PRODUCT WATER = $500 PER ACRE/FT

Figure 6-13 WATER COST VIA ELECTRODIALYSIS WITH FEED TDS OF 3,500 MG/L (LAST QUARTER 1982 DOLLARS)



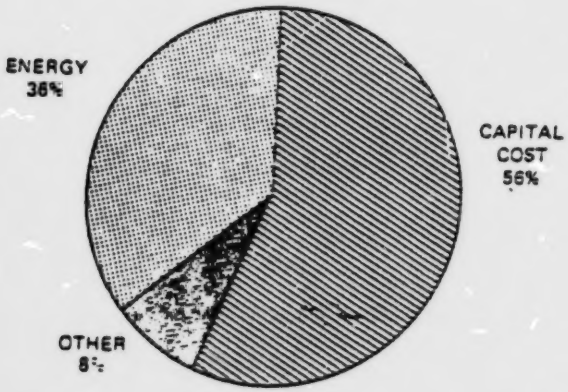
TOTAL COST OF PRODUCT WATER = $570 PER ACRE FT

Figure 6-14 WATER COST FROM WASTEWATER VIA REVERSE OSMOSIS, WITHOUT ENERGY RECOVERY (LAST QUARTER 1982 DOLLARS)



TOTAL COST OF PRODUCT WATER = $2,300 PER ACRE/FT

Figure 6-15 WATER COST FROM WASTE WATER VIA VAPOR COMPRESSION DISTILLATION IN A SINGLE-PURPOSE PLANT (LAST QUARTER 1982 DOLLARS)



TOTAL COST OF PRODUCT WATER = $1,100 PER ACRE FT

Figure 6-16 WATER COST FROM WASTEWATER USING A MULTI-EFFECT HORIZONTAL TUBE, LOW-TEMPERATURE, DUAL-PURPOSE PLANT (LAST QUARTER 1982 DOLLARS)

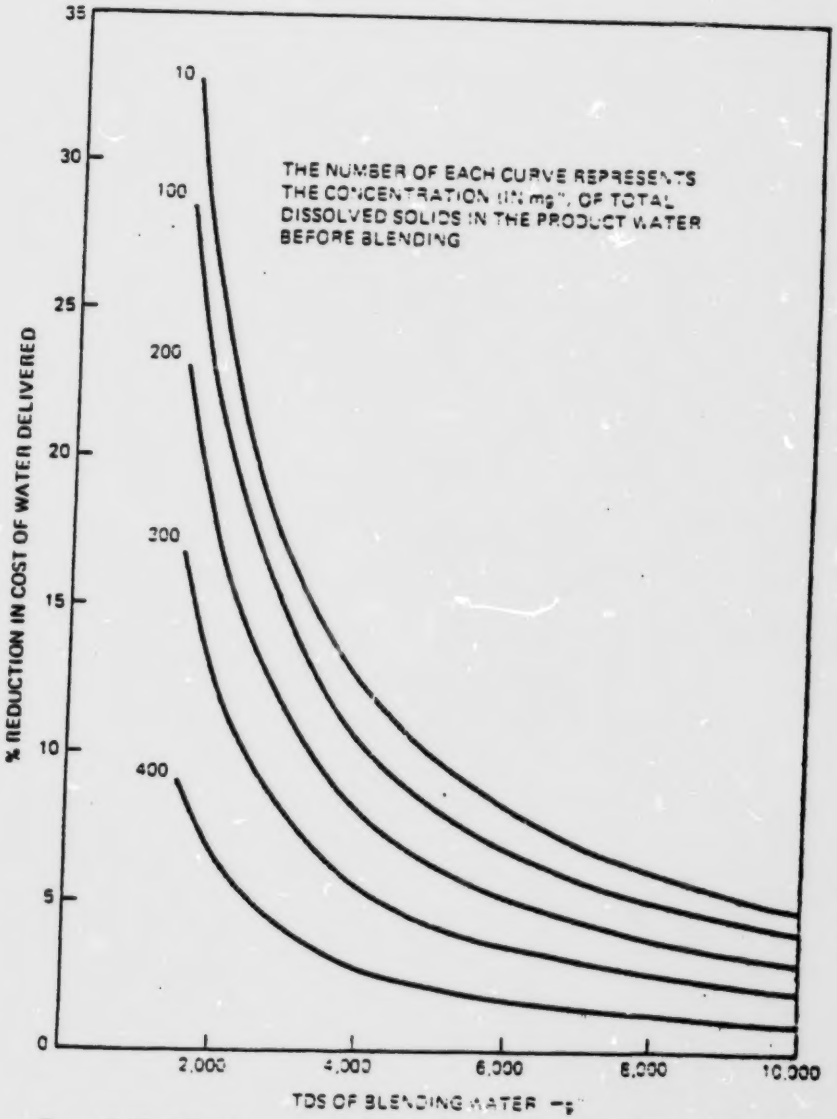


Figure 6-17 COST SAVINGS FROM BLENDING PRODUCT WATER OF DIFFERING PURITIES WITH BRACKISH WATER TO RESULT IN 500 mg/l IN THE BLENDED WATER

SEEDED SLURRY REVERSE OSMOSIS

AND

SEEDED SLURRY EVAPORATION

PRESENTED

AT

THE RANDOL WATER WORKSHOP

OCTOBER 21-23, 1984

R. Reams Goodloe, Jr.
Resources Conservation Co.
Bellevue, Washington
U.S.A.

I. "SEEDED" PROCESSES FOR CONCENTRATION OF AQUEOUS SOLUTIONS

The concentration of solutions containing low solubility salts is aggravated by the occurance of scale forming compounds in the solution being treated, whether in an evaporation based, or in a membrane process based, or a combination treatment plant. Although the solubility limits for many species commonly present in wastewaters can be slightly exceeded by use of additives such as dispersants or crystal modifiers, the practical effect of the presence of scale formers in process waters has been to either live with the scale (typically possible only in evaporation or electrodialysis reversal), or to design the system for normal operation below expected solubility limits of species present. In the majority of industrial wastewater processing applications, either alternative is not a desirable choice, since additional operating costs are involved for cleaning, or additional water recovery is not easily achieved.

Resources Conservation Company, of Bellevue, Washington, has developed a proprietary process to effectively control seeding parameters in evaporation equipment, and a patented process to effectively control seeding parameters in membrane equipment, to allow concentration of solutions many concentration factors beyond the solubility limits of commonly found scale forming compounds. Both processes are based on the widely known but less widely understood process of providing a more extensive and more favorable surface for scale deposition than the heating or membrane surface itself. Seed crystals of the scale forming ingredients themselves typically provide the most favorable surface for deposition of potential scale. Since calcium sulfate and silica are the most commonly encountered scale formers, RCC has used calcium sulfate as the base for co-precipitation of itself and other species when concentrating solutions. In evaporation systems, calcium sulfate is commonly found in the anhydrite form at the temperatures found in the equipment, and in membrane systems, calcium sulfate is found in the gypsum form.

RCC provided evaporation units incorporating this technology have been operating for more than ten years, with more units being added every year to the operating inventory. Operators have found that sustained scale free operation is possible, with equipment downtime for routine maintenance normally once every 10 to 18 months.

RCC has been developing the laboratory, pilot plant, and field testing data on seeding for membrane processes, in particular for use with reverse osmosis, for more than seven years. Currently known information on process parameters, and ongoing improvements in membrane technology, have given RCC the confidence to offer the seeded reverse osmosis (SRO) technology to potential users.

Since the technical risks of this new process can be minimized by on-site testing using currently available test modules, we expect to see commercial installations very shortly.

II. Seeded Slurry Evaporation

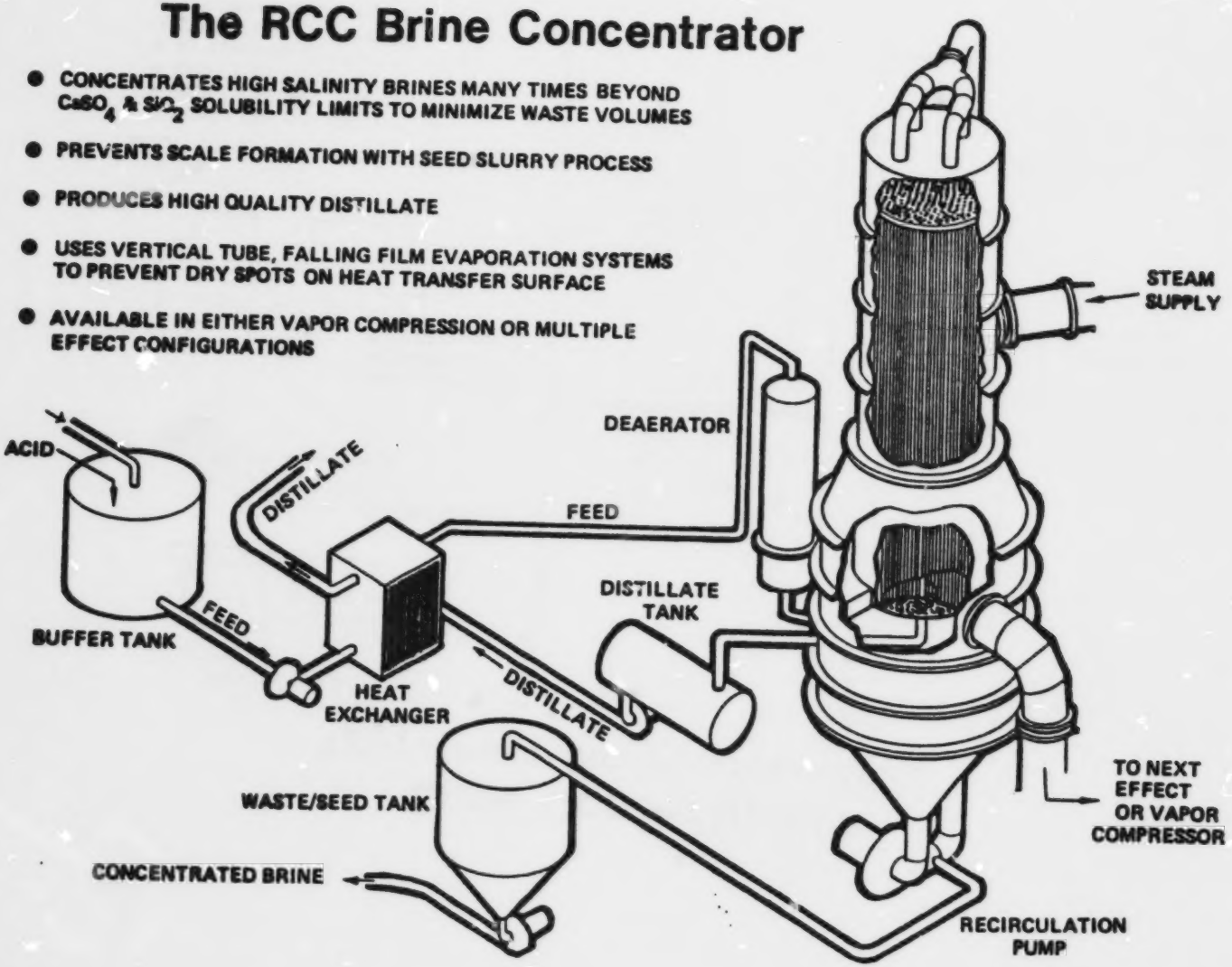
- Presentation Attached

III. Seeded Slurry Reverse Osmosis

- Presentation Attached

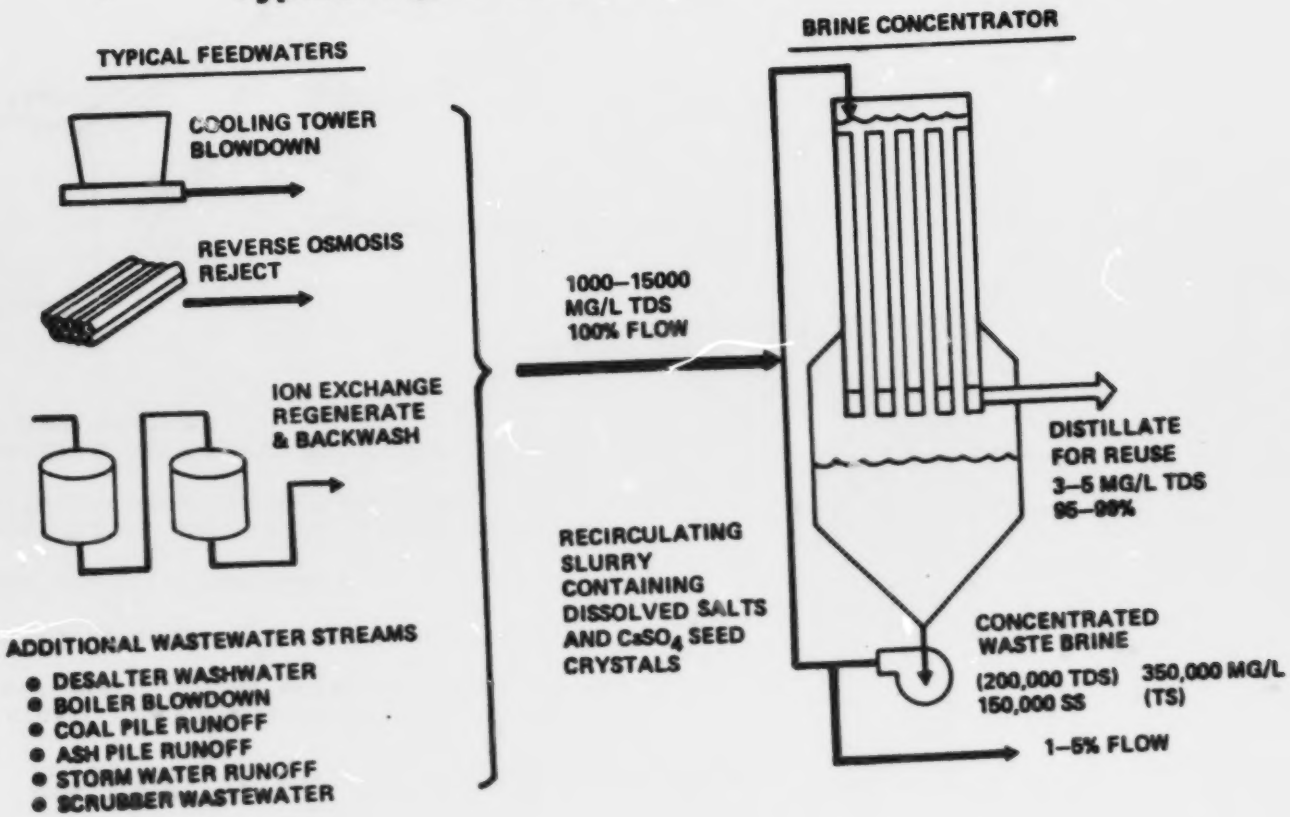
The RCC Brine Concentrator

- CONCENTRATES HIGH SALINITY BRINES MANY TIMES BEYOND $CaSO_4$ & SiO_2 SOLUBILITY LIMITS TO MINIMIZE WASTE VOLUMES
- PREVENTS SCALE FORMATION WITH SEED SLURRY PROCESS
- PRODUCES HIGH QUALITY DISTILLATE
- USES VERTICAL TUBE, FALLING FILM EVAPORATION SYSTEMS TO PREVENT DRY SPOTS ON HEAT TRANSFER SURFACE
- AVAILABLE IN EITHER VAPOR COMPRESSION OR MULTIPLE EFFECT CONFIGURATIONS



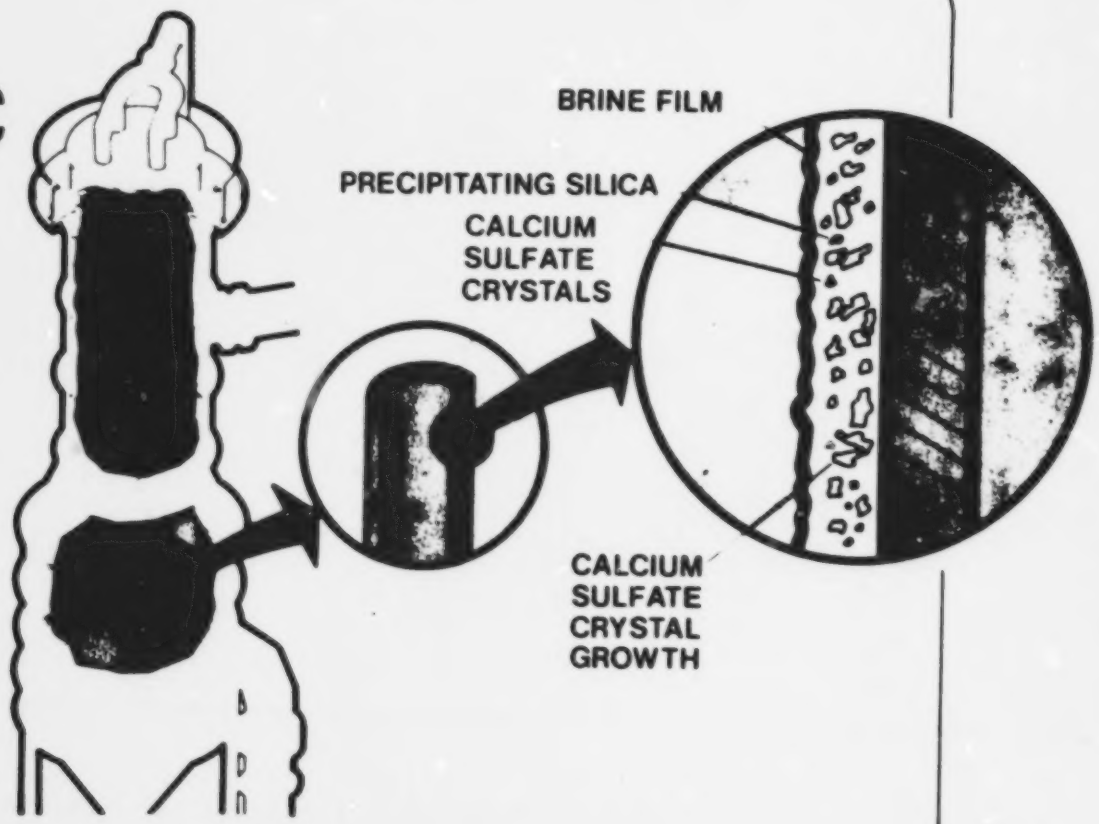
Brine Concentrator

Typical Input/Output Compositions

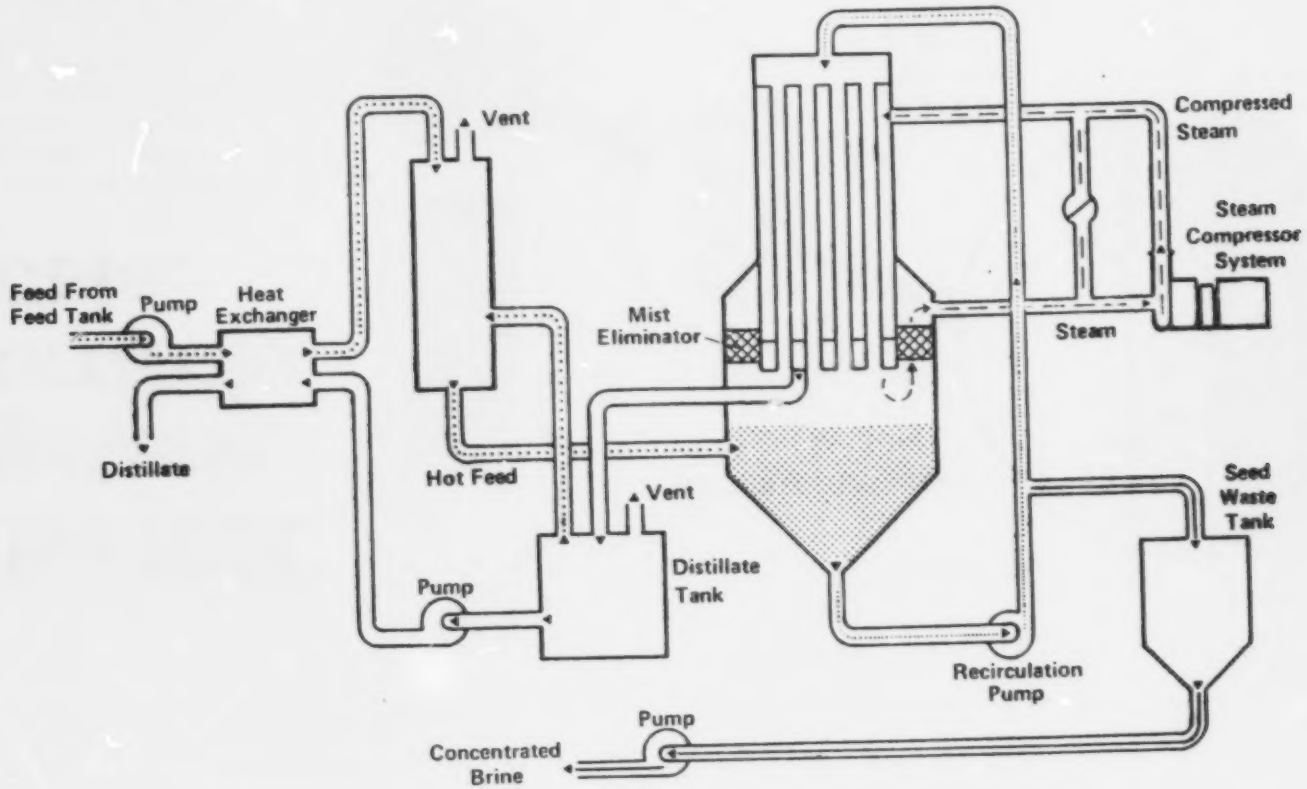


The RCC system controls scale.

The vapor compression evaporator employs a new seed-slurry technique to control scale. In essence it forces scaling material to build up on crystals in the brine instead of allowing it to cling to the tube walls as scale.

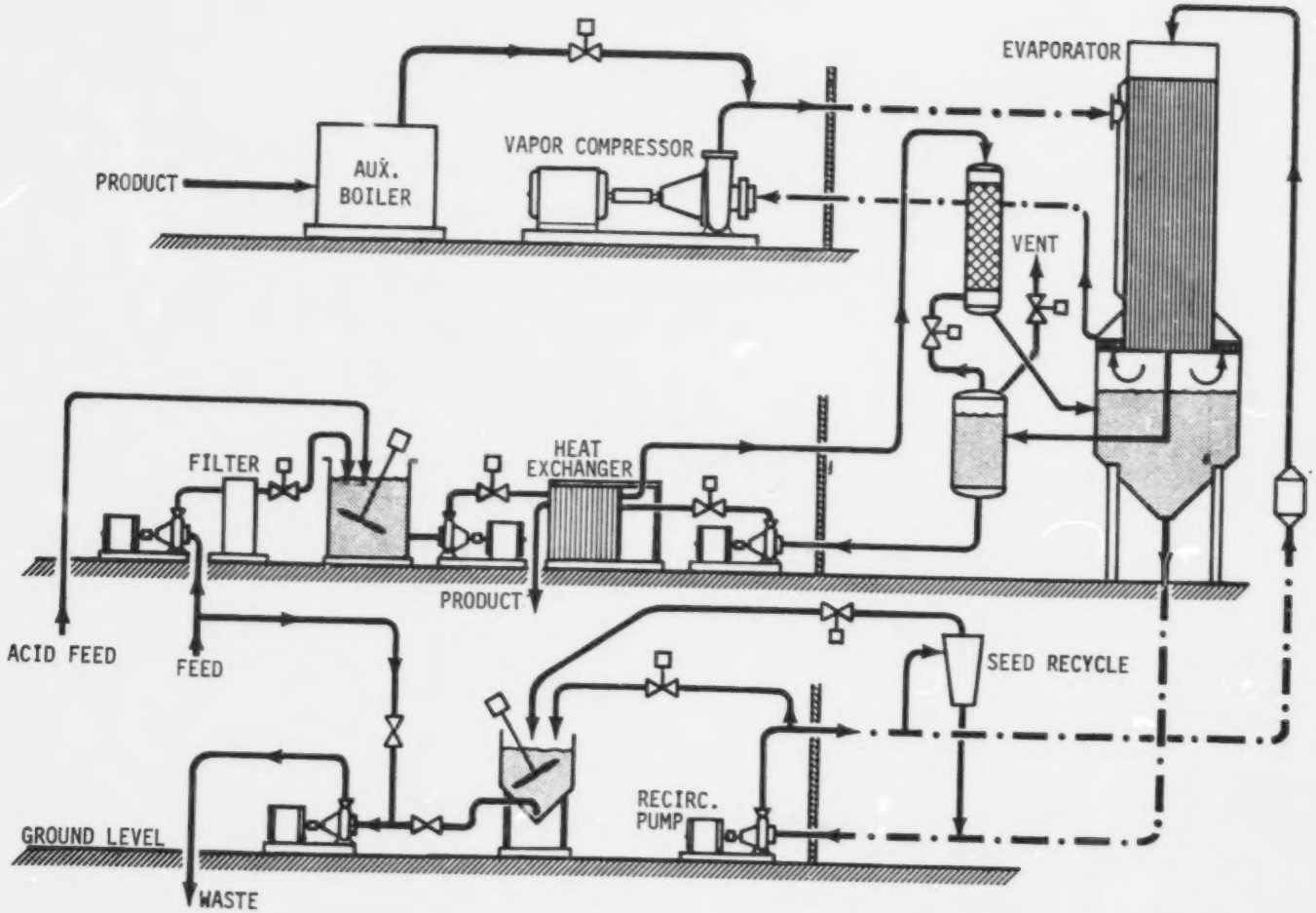


Brine Concentrator Flow Schematic



④

DESIGN & EQUIPMENT

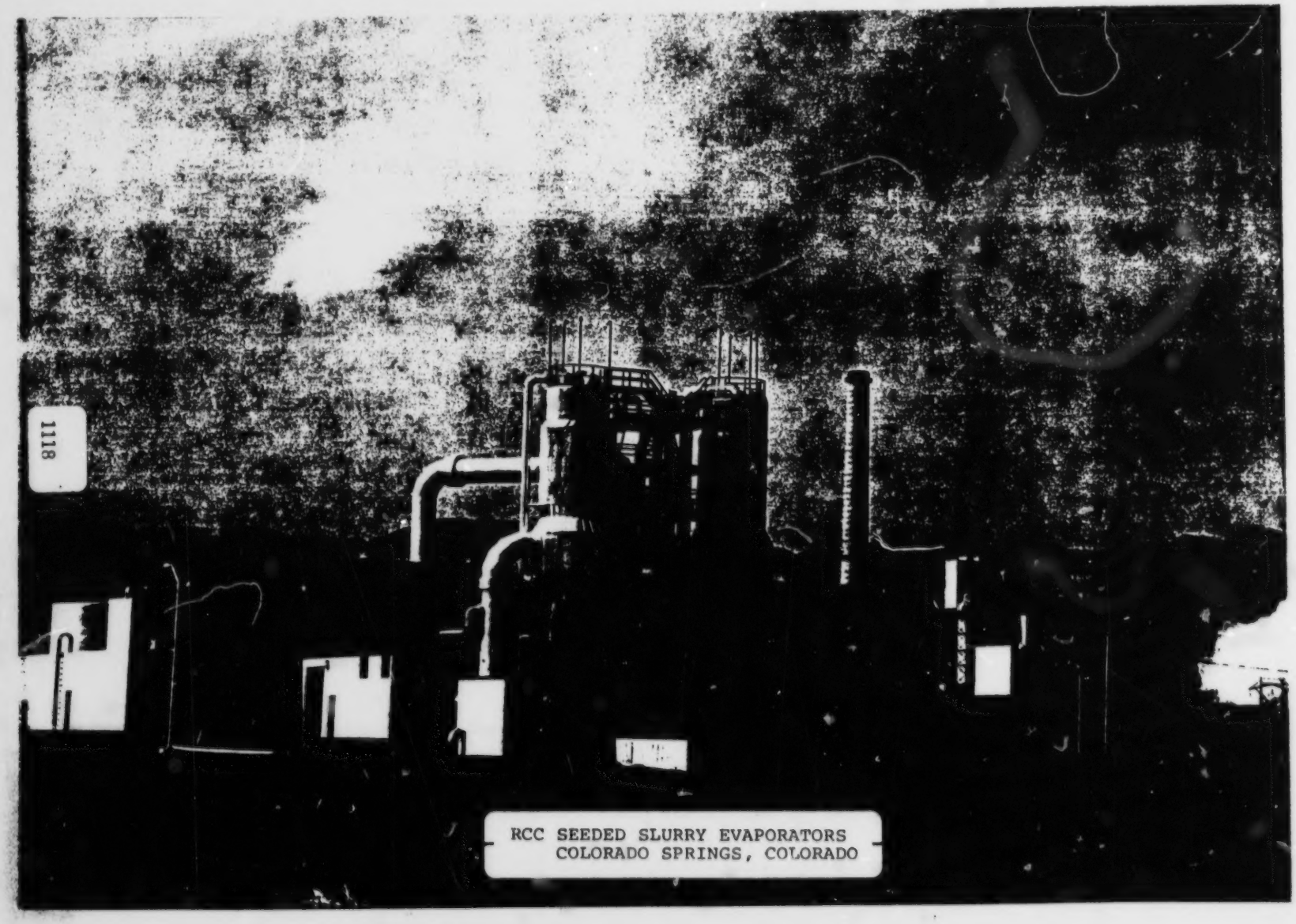


Brine Concentrator

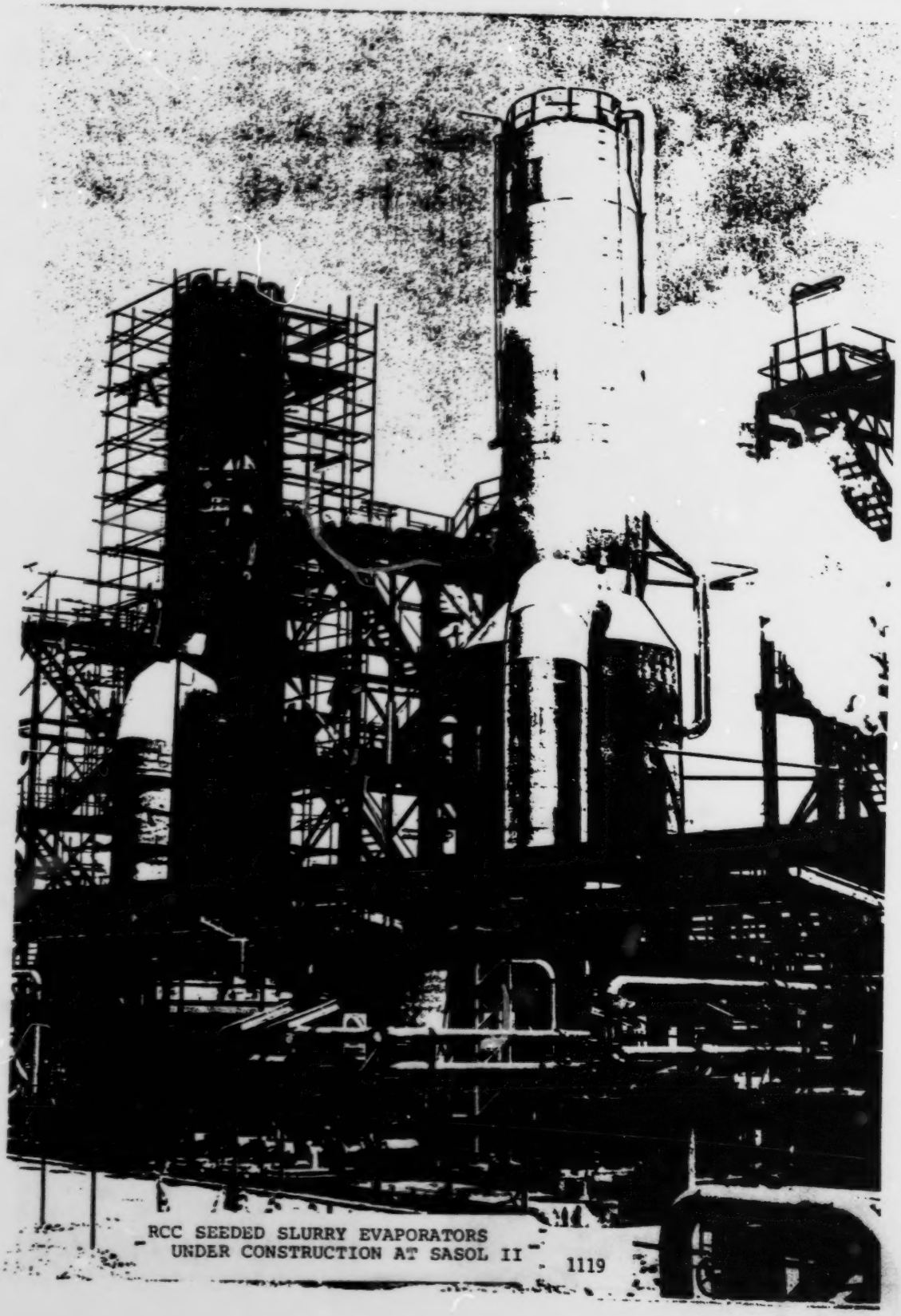
- Cooling Tower Blowdown
  - Can Recover 99% Of Waste As Product Water
  - Product Water Less Than 5 mg/l TDS
  - Insensitive To Changing Chemistry
  - Simple, Automatic Operation
  - Many Installations With Similar Feedwaters
  - Energy Use Less Than 21 KWH/m^3
  - Scale Free Operation
  - High Availability Proven
  - 30 + Year Lifetime Established
- Demineralizer Wastes
  - Can Process To Approximately 90% Recovery
  - Minor Chemical Addition Required. (Calcium)
  - Ammonia Stripping Necessary For Highest Purity Product

RCC Evaporator Design Features

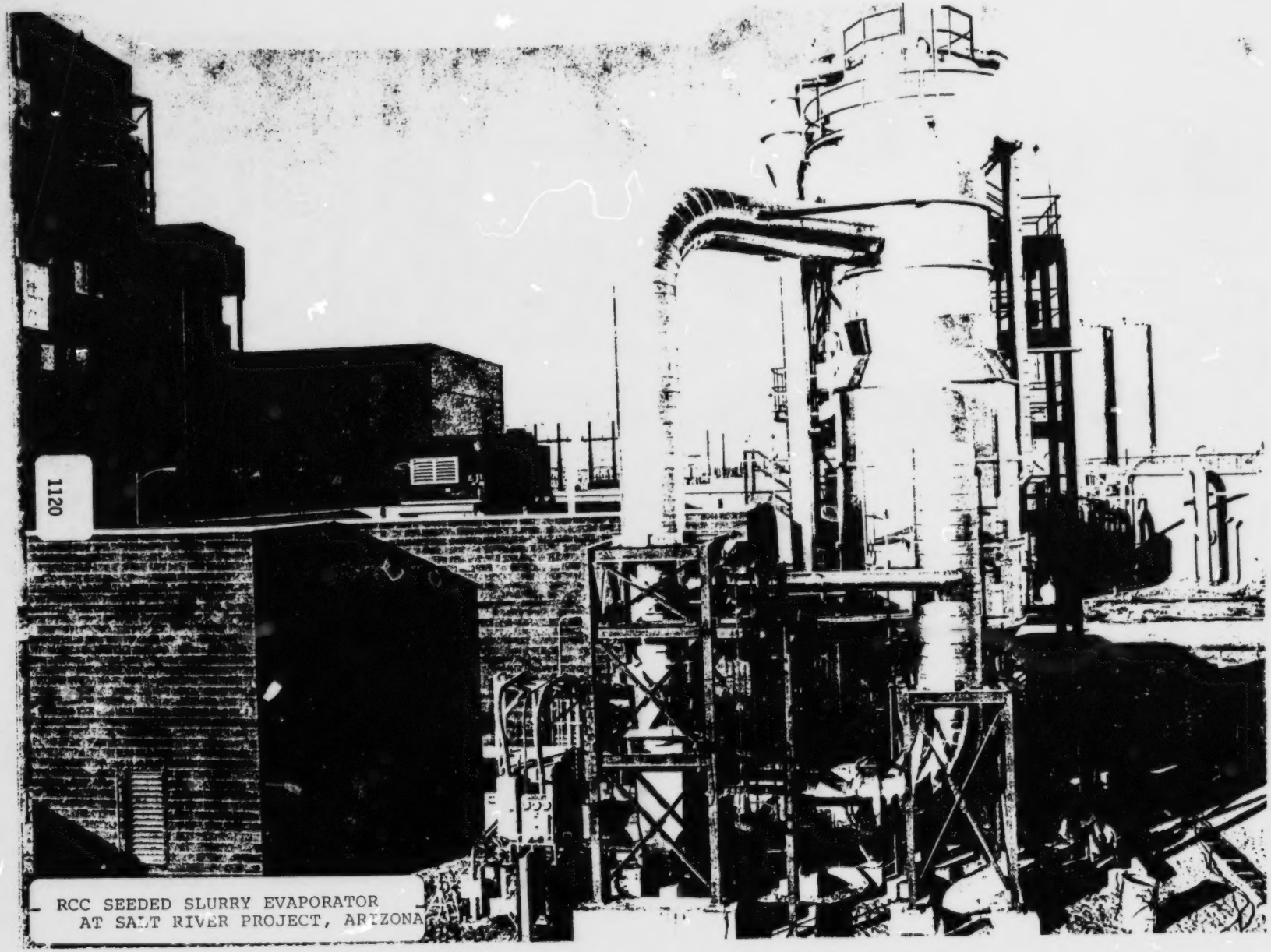
- Potential for Scaling and Fouling is Minimized
  - High Liquor Velocities in Critical Areas
  - Flow Distributors to Insure That All Tubes Are Completely Filmed
  - Proper Recirculation Rates to Insure Filmed Tubes and Low Extraction Rates
  - Effective Entrainment and Foam Control to Prevent Carryover (No Steam Side Fouling)
- Control System Eliminates Risk of Overshooting or Undershooting Desired Final Concentration
  - Reduces Evaporator Fouling (Sometimes Caused by Over Concentration)
  - Reduces Steam Consumption in Subsequent Operations (Often Caused by Low Product Solids)
- Compressor Installation Details Lead to Reliable Operating Performance
- Computerized Plant Evaluations Allow Optimum Selection of Components to Provide Stable Operating Conditions at Low Energy Consumption Rates



RCC SEEDED SLURRY EVAPORATORS
COLORADO SPRINGS, COLORADO



RCC SEEDED SLURRY EVAPORATORS
UNDER CONSTRUCTION AT SASOL II



RCC SEEDED SLURRY EVAPORATOR
AT SALT RIVER PROJECT, ARIZONA

SEEDED REVERSE OSMOSIS

A NEW WAY TO MEET ENVIRONMENTAL CHALLENGES

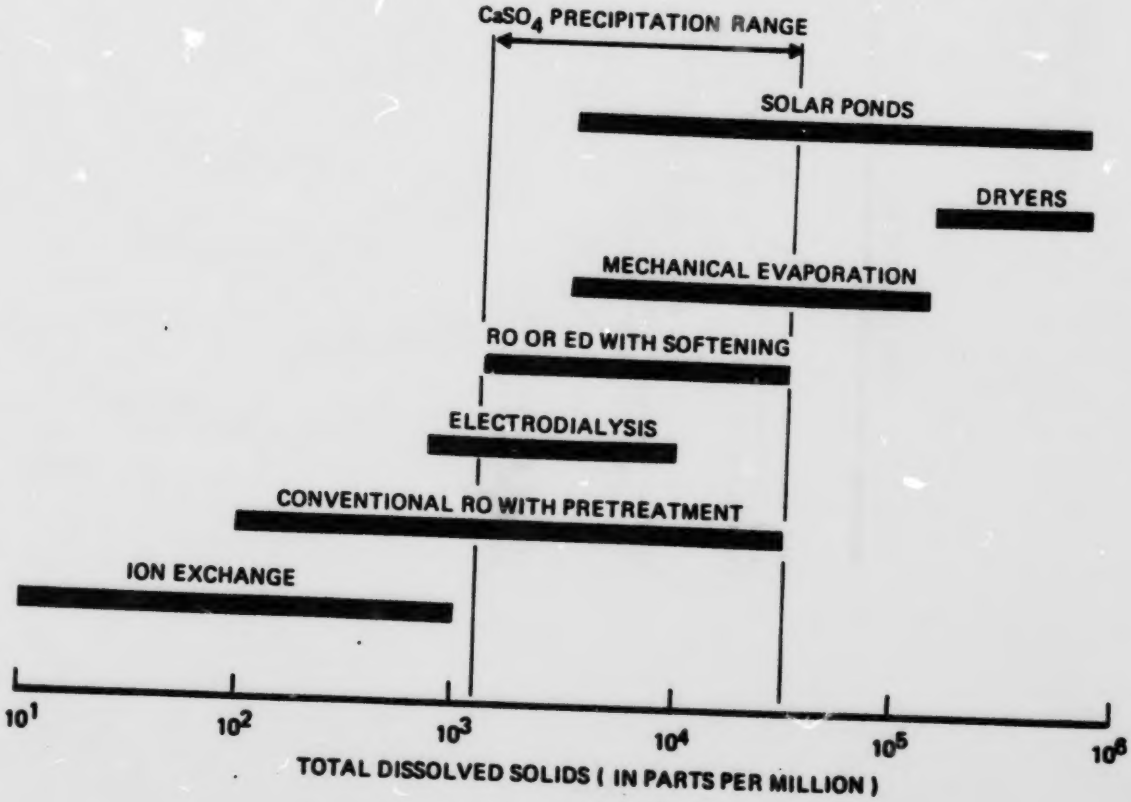
IN METAL PROCESSING

THE PROBLEM

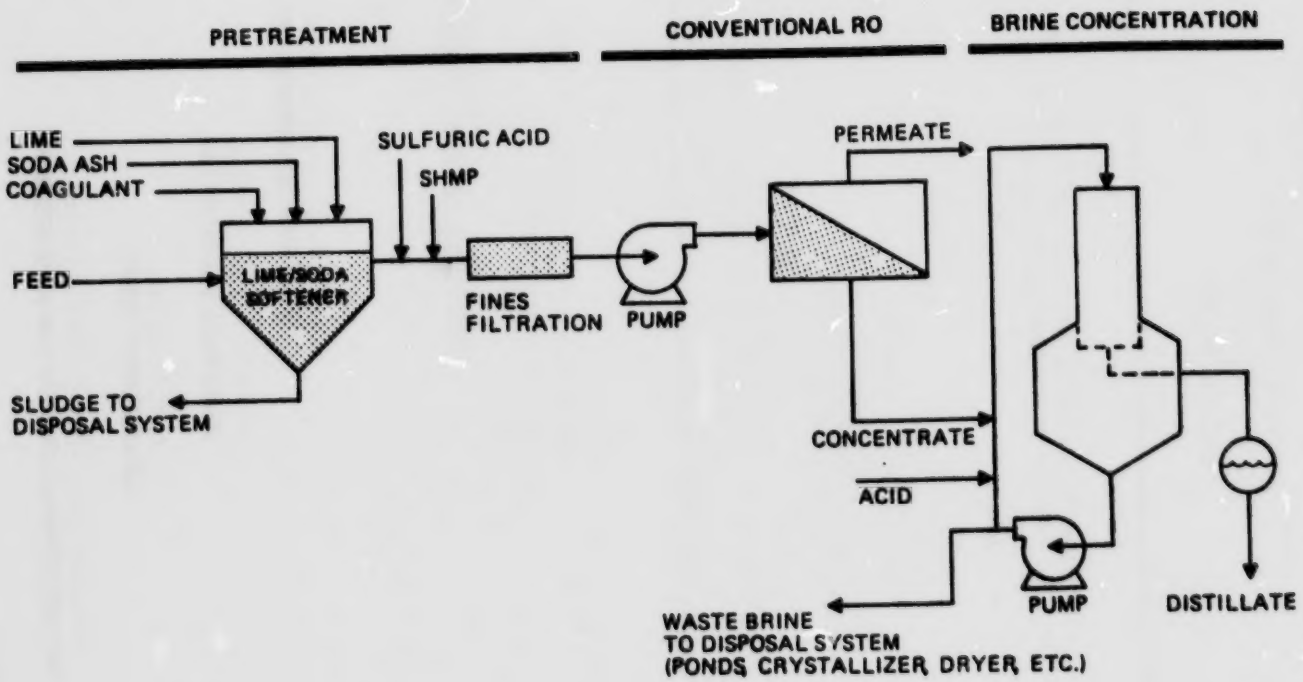
TREATMENT OF WATERS AT OR NEAR CALCIUM SULFATE SATURATION (OR OTHER SPARINGLY SOLUBLE SPECIES)

- COMPLEX
- COSTLY
- MANPOWER - INTENSIVE
- PRONE TO CHANGES IN CHEMISTRY AND TEMPERATURE

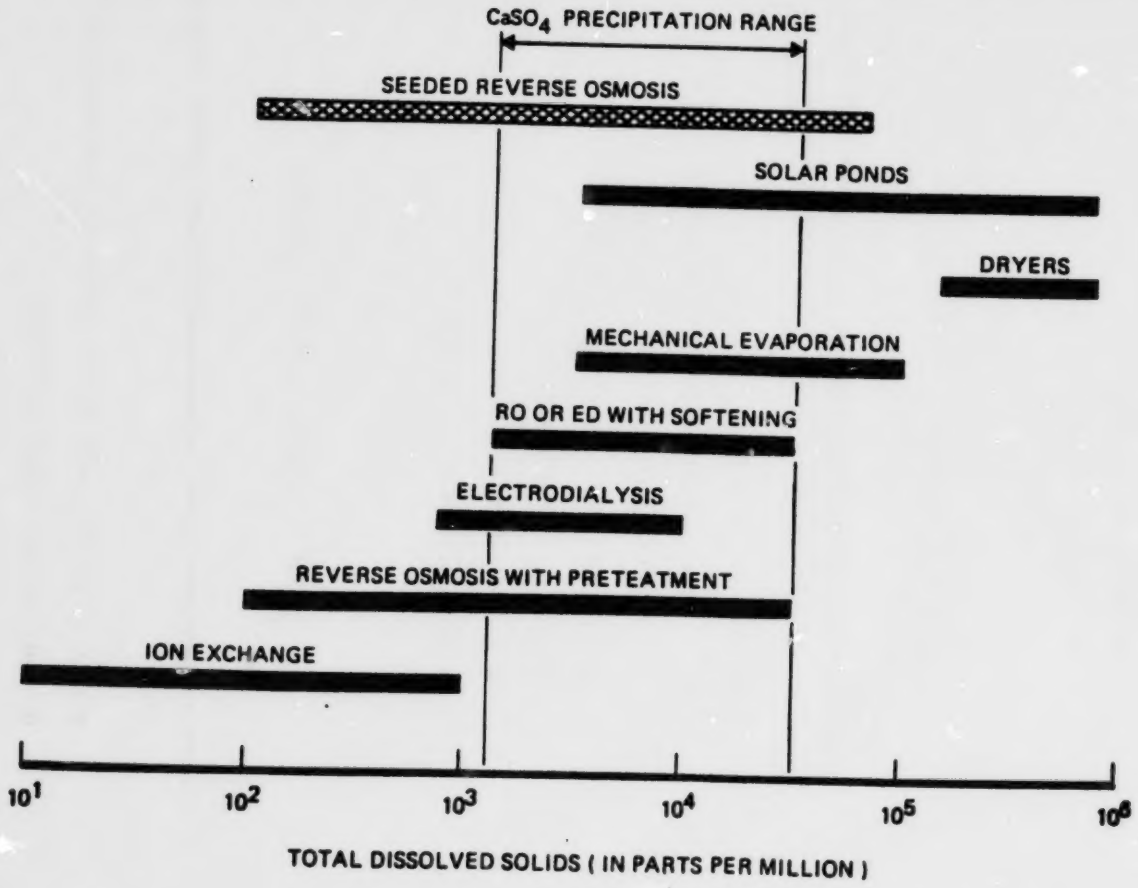
WASTEWATER TREATMENT PROCESS OPTIONS



CONVENTIONAL ZERO DISCHARGE WASTEWATER TREATMENT PLANT



WASTEWATER TREATMENT PROCESS ALTERNATIVE: SEEDED REVERSE OSMOSIS



SEEDED REVERSE OSMOSIS (SRO)

A SIGNIFICANT ADDITION TO TECHNIQUES AVAILABLE FOR DESALINATION AND FOR WASTEWATER VOLUME REDUCTION AND REUSE OF WATERS SATURATED IN CALCIUM SULFATE AND OTHER SPARINGLY SOLUBLE SPECIES.

- LOWER OPERATING COSTS
- ENHANCED RELIABILITY

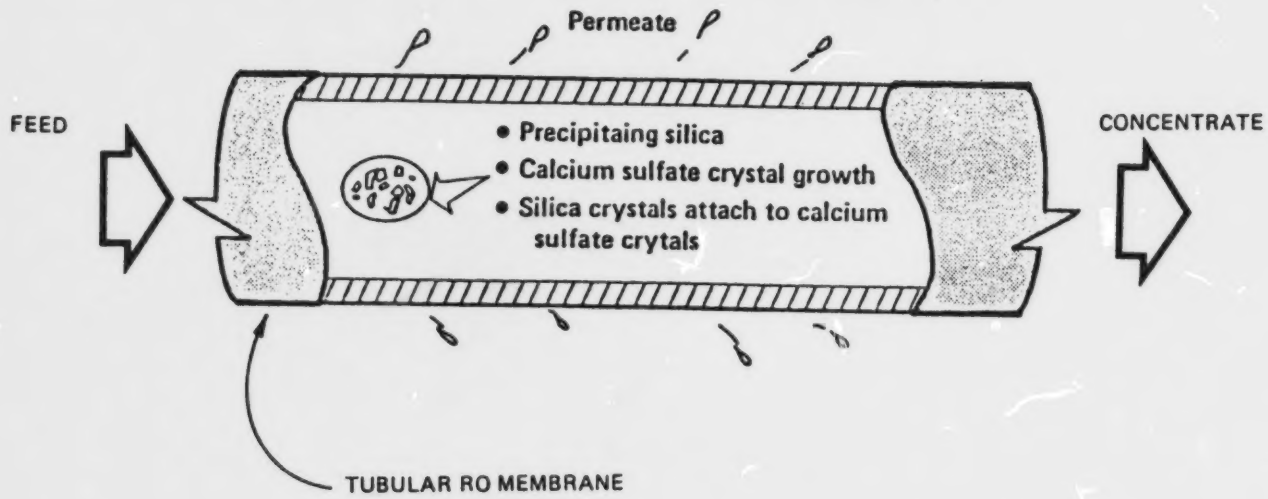
APPLICATIONS

- MINE DRAINAGE WATER
- METAL PROCESSING FACILITY WASTEWATERS
- ELECTRIC UTILITY PLANT WASTEWATER
- CHEMICAL AND PETROLEUM PLANT WASTEWATERS
- SYNFUEL PLANT WASTEWATER
- SALINITY CONTROL PROGRAMS
- AGRICULTURE WATER REUSE

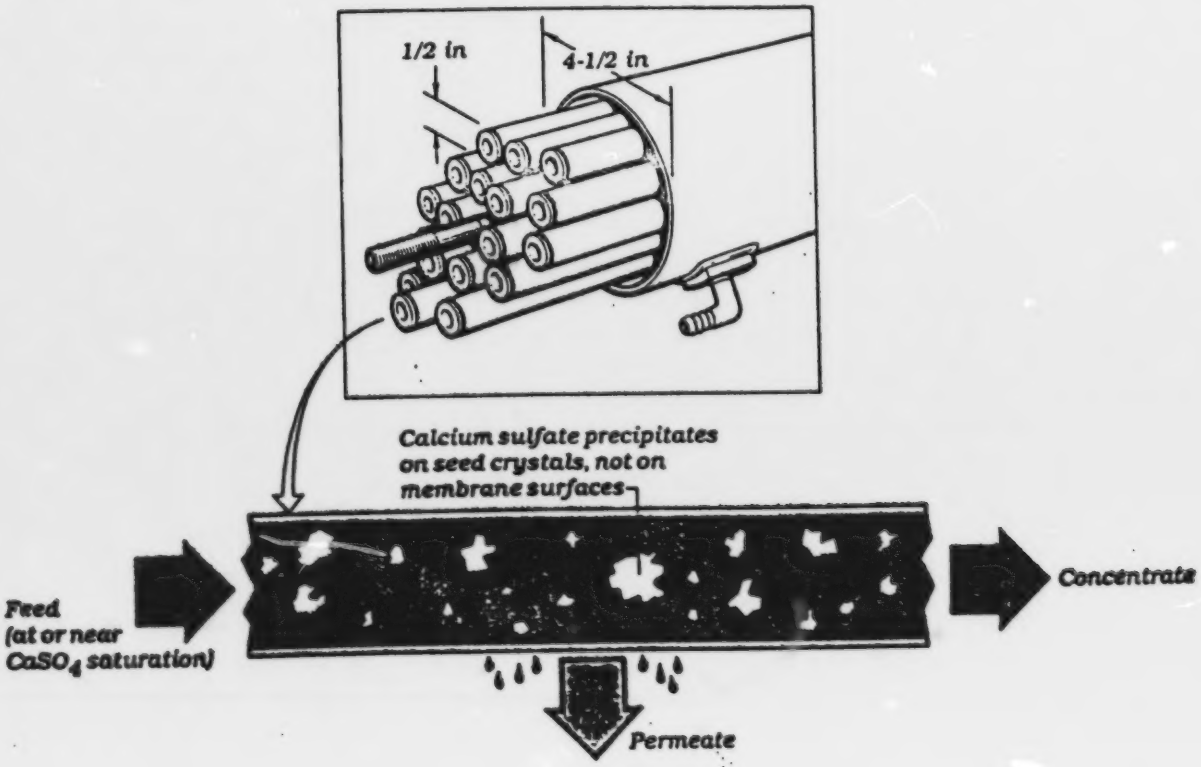
SRO CONCEPT DEVELOPMENT

- RCC EXPERIENCE WITH SEEDED SLURRY BRINE CONCENTRATOR
- SURVEYED MEMBRANE SUPPLIERS
- DEVELOPED PROCESS CONCEPT
- PILOT PLANT TESTING VERIFIED FEASIBILITY

SRO CONCEPT

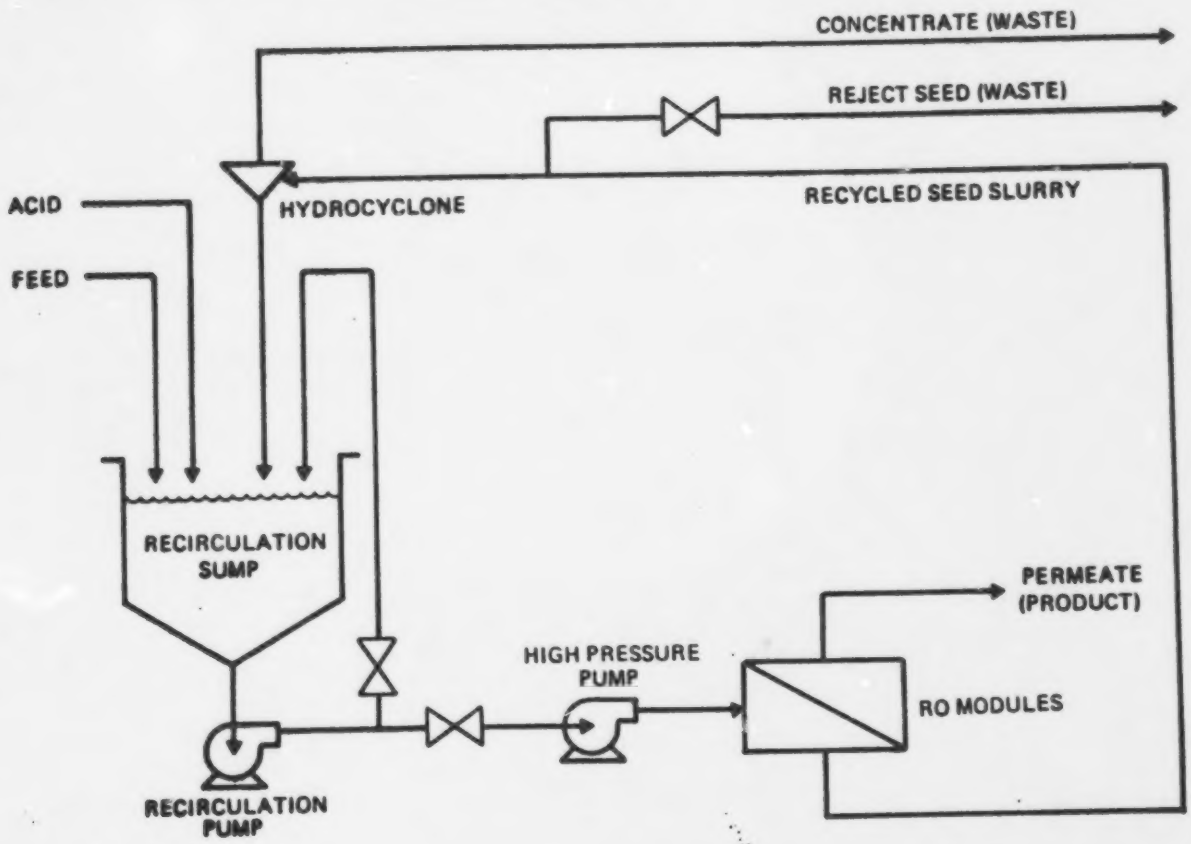

Permeate
FEED
CONCENTRATE
• Precipitaing silica
• Calcium sulfate crystal growth
• Silica crystals attach to calcium sulfate crytals
TUBULAR RO MEMBRANE

SRO CONCEPT

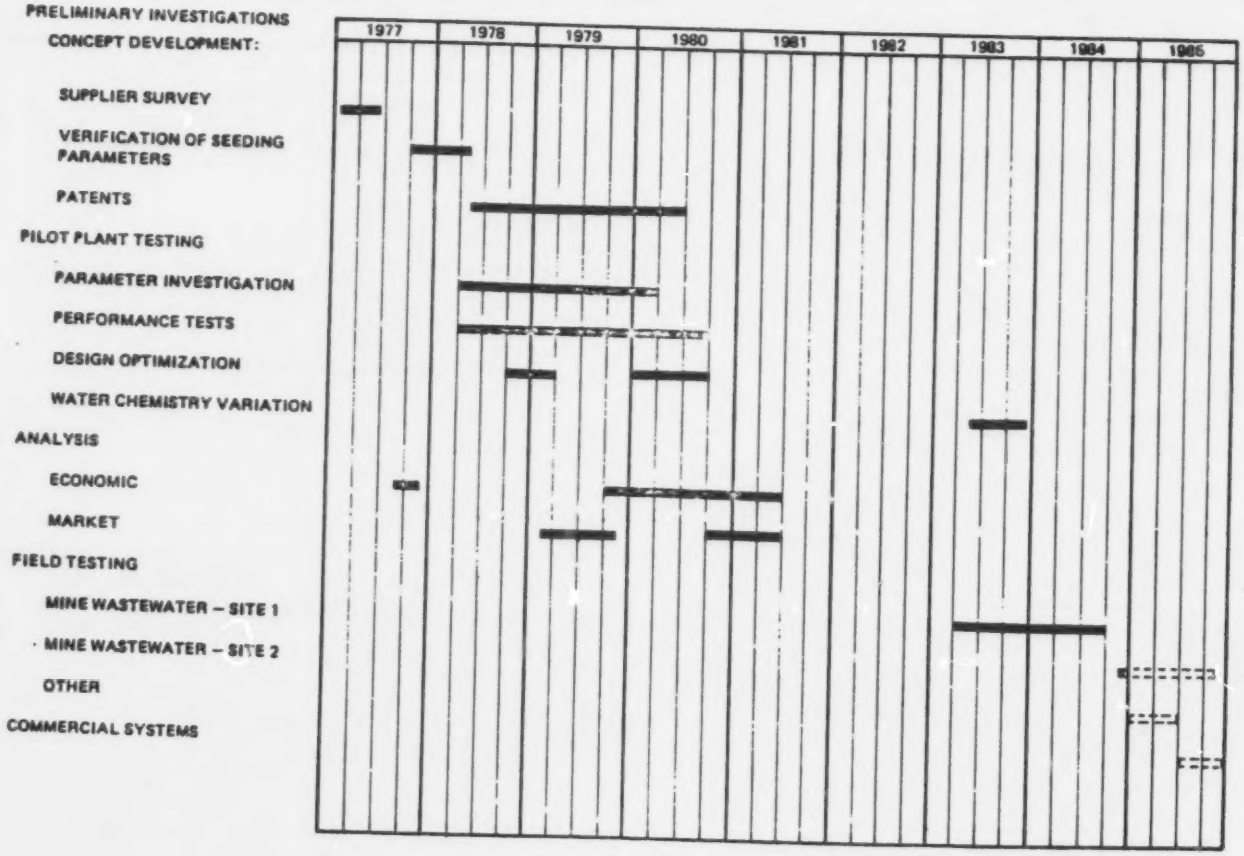

1/2 in
4-1/2 in
Calcium sulfate precipitates on seed crystals, not on membrane surfaces
Feed (at or near $CaSO_4$ saturation)
Concentrate
Permeate

SEEDED RO MEMBRANE MODULE

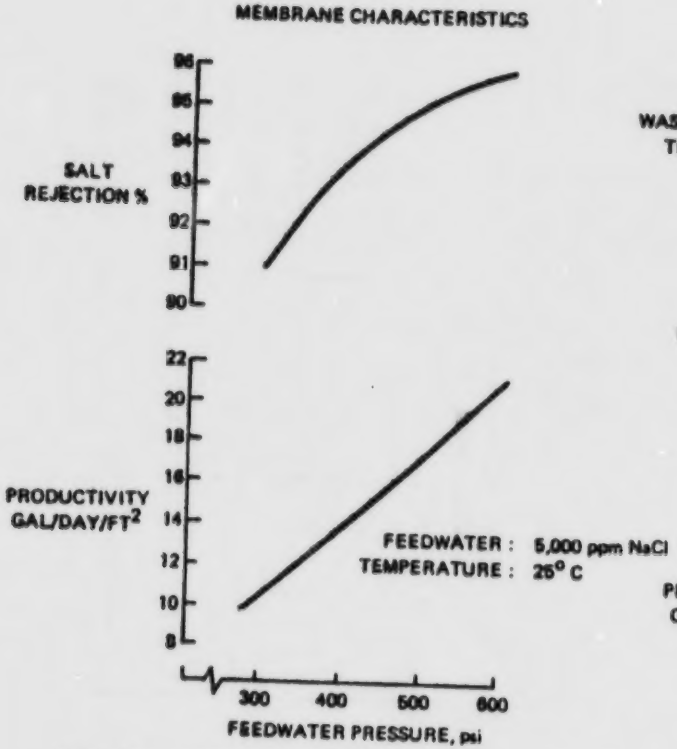
SYSTEM SCHEMATIC
SEEDED REVERSE OSMOSIS PROCESS



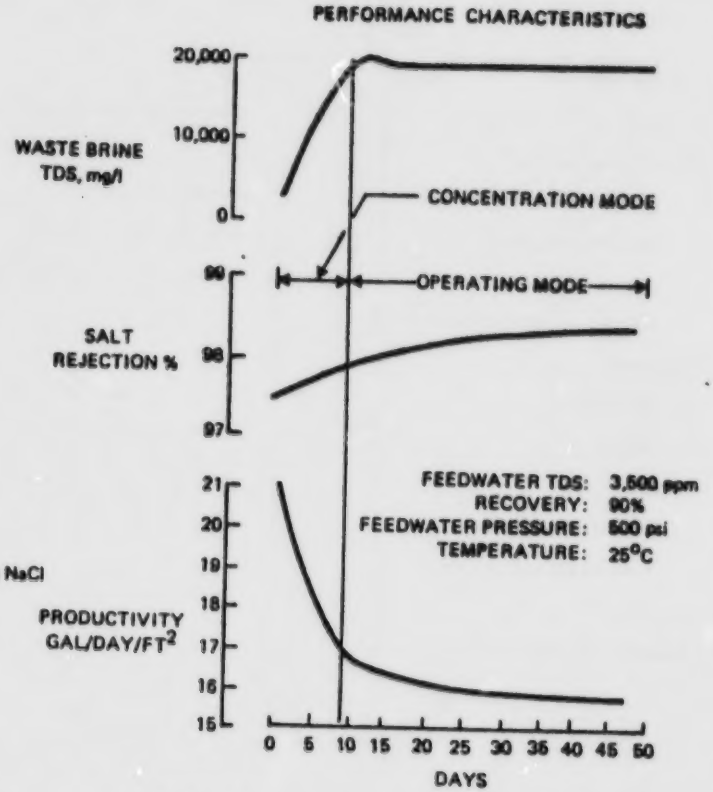
SEEDED RO DEVELOPMENT PROGRAM



TYPICAL SEEDED RO PERFORMANCE CHARACTERISTICS



PRODUCT WATER FLUX AND SALT REJECTION AS A FUNCTION OF FEEDWATER PRESSURE (ON 5,000 PPM SALT SOLUTION)



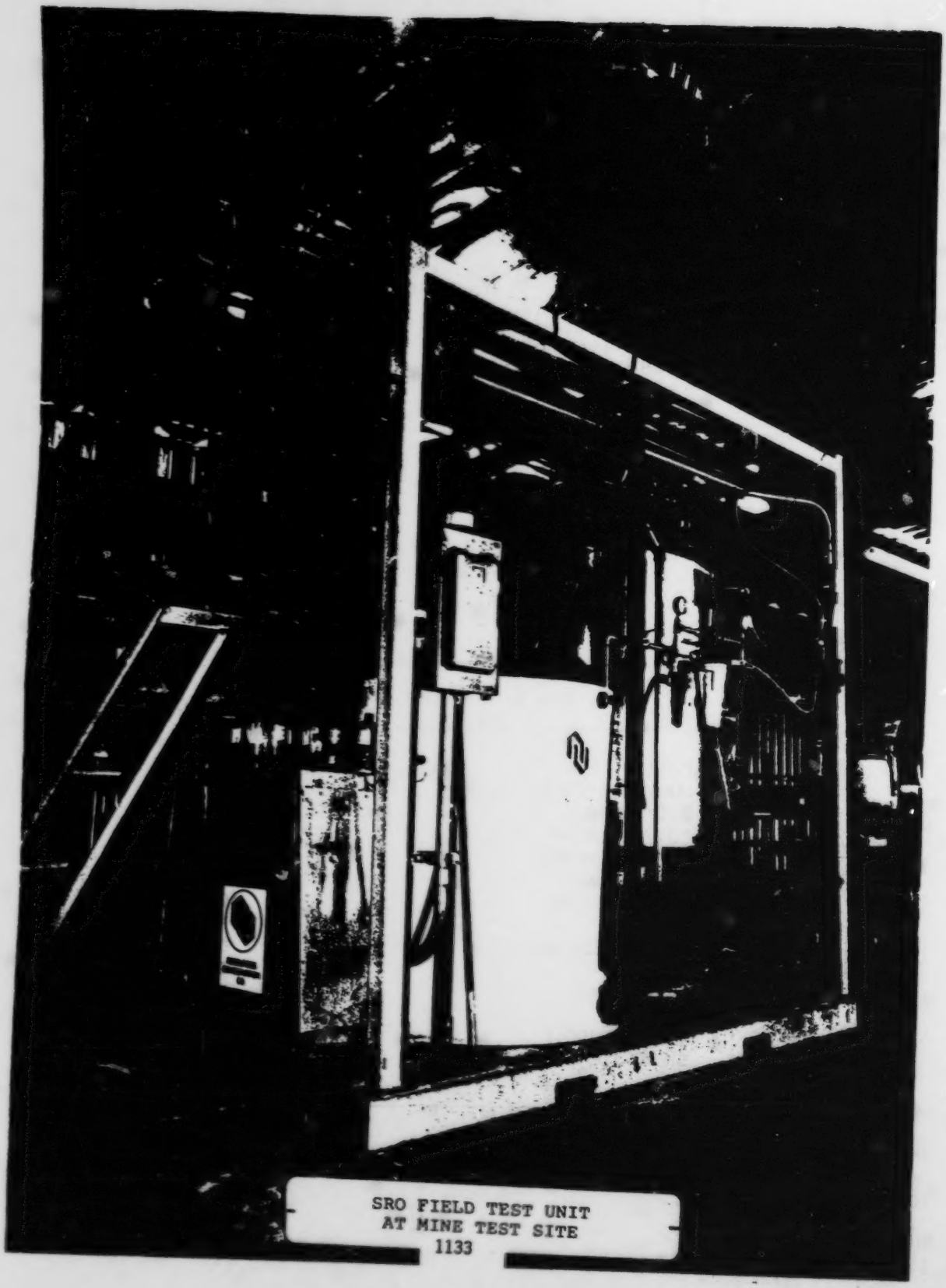
PRODUCT WATER FLUX AND SALT REJECTION OVER TIME ON SEEDED SALT SLURRY (WASTE BRINE TDS OF 3,500 PPM)

1130

PILOT PLANT TEST CONCLUSIONS

- Seed slurry concept verified for RO
- Over 8,000 hours of scale-free operation
- Parameters for scale-free operation defined
- Several waters tested under varying operating conditions
- Process shown to work on different RO modules

SEEDED SLURRY EVAPORATOR TEST UNIT
RESOURCES CONSERVATION CO



SRO FIELD TEST UNIT
AT MINE TEST SITE
1133

RAW MINE WATER – AUGUST 1983	
CALCIUM (Ca)	333 mg/l AS ION
MAGNESIUM (Mg)	120
SODIUM (Na)	132
POTASSIUM (K)	13
STRONTIUM (Sr)	2.6
BARIUM (Ba)	0.04
ALUMINUM (Al)	25
IRON (Fe)	6.4
MAGANESE (Mn)	8.4
ZINC (Zn)	2.1
NICKEL (Ni)	8.1
TOTAL ALKALINITY (TO pH 4.5)	NIL
(TO pH 3.7)	17.4
FREE AMMONIA (N)	8
NITRITE NITROGEN (N)	0.11
NITRATE NITROGEN (N)	8.2
CHLORIDE (Cl)	98
FLUORIDE (F)	1.2
SULFATE (SO4)	1825
TOTAL PHOSPHATE (P)	0.18
SILICA (SiO_2)	44
pH	4.24
CONDUCTIVITY AT 25°C, µS/cm	2650
SUSPENDED SOLIDS	56

RAW MINE WATER – FEBRUARY 1984	
CALCIUM (Ca)	404 mg/l AS ION
MAGNESIUM (Mg)	113
SODIUM (Na)	128
POTASSIUM (K)	11
STRONTIUM (Sr)	1.2
BARIUM (Ba)	0.08
ALUMINUM (Al)	46
IRON (Fe)	27
MANGANESE (Mn)	8
ZINC (Zn)	2
NICKEL (Ni)	6
SULFATE (SO_4)	1785
SILICA (SiO_2)	67

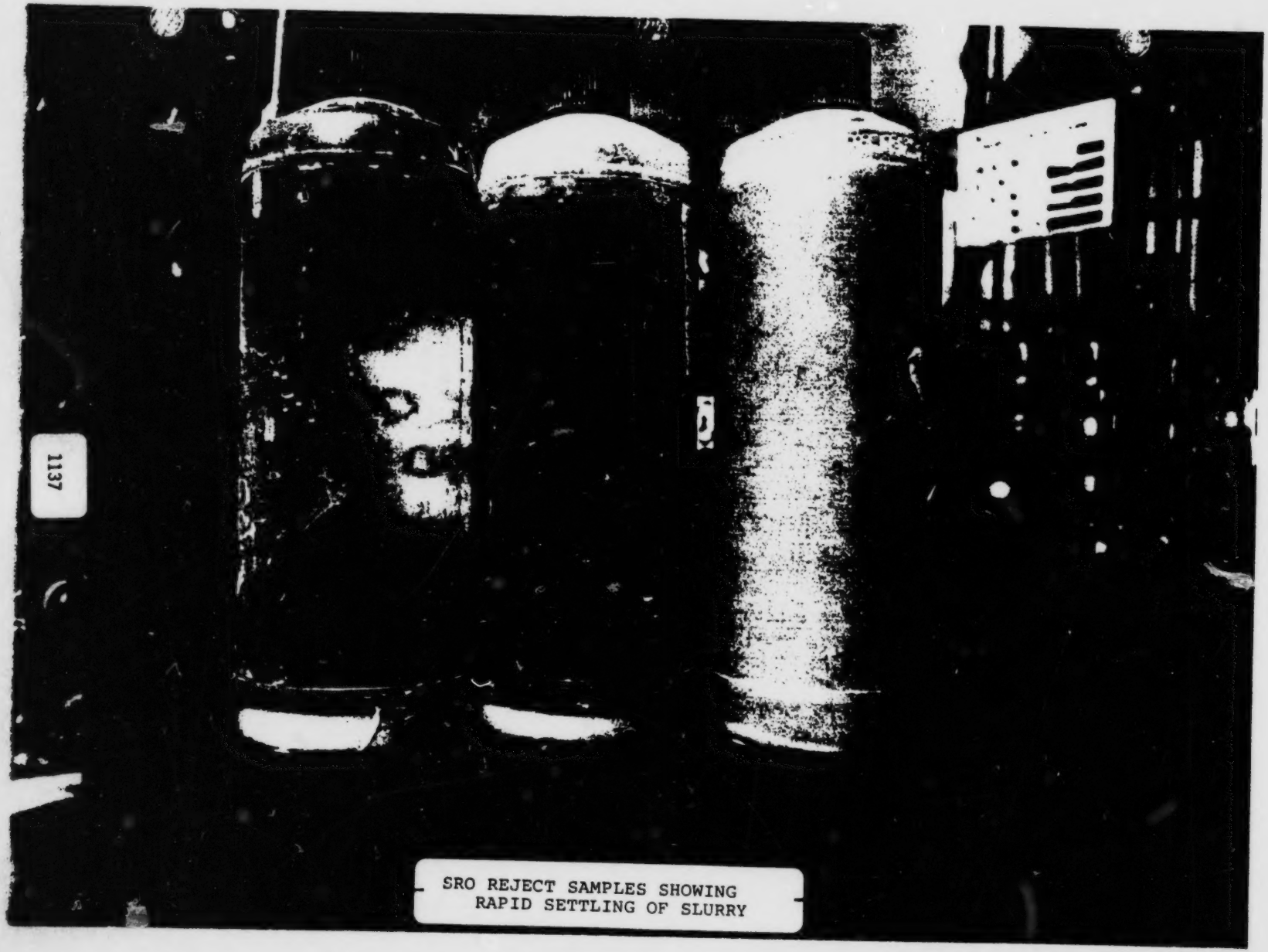
CIRCULATING SRO BRINE
AT MINE TEST SITE

	SUMP RECIRCULATION BRINE	PERMEATE
CALCIUM (Ca)	440 mg/l AS ION	10.9 mg/l AS ION
MAGNESIUM (Mg)	1025	9.3
SODIUM (Na)	1560	81
POTASSIUM (K)	66	3.6
STRONTIUM (Sr)	40	0.1
BARIUM (Ba)	0.45	< 0.02
ALUMINUM (Al)	280	0.5
IRON (Fe)	100	0.06
MANGANESE (Mn)	89	0.48
ZINC (Zn)	18.3	0.13
NICKEL (Ni)	72	0.30
TOTAL ALKALINITY (TO pH 4.5)	NIL	2.1
(TO pH 3.7)	38	12.8
FREE AMMONIA (N)	41	2.6
NITRITE NITROGEN (N)	0.08	0.11
NITRATE NITROGEN (N)	15.5	6.3
CHLORIDE (Cl)	380	50
FLUORIDE (F)	7.5	< 0.1
SULFATE (SO_4)	8250	112
TOTAL PHOSPHATE (P)	0.75	0.12
SILICA (SiO_2)	92	12.9
pH	4.44	5.22
CONDUCTIVITY AT 25°C µS/cm	12200	545
SUSPENDED SOLIDS	44050	< 1

PRECIPITATED SOLIDS		
SAMPLE DRIED AT 105°C PRIOR TO ANALYSIS		
LOSS ON IGNITION		
% LOSS TO 150°C	4.85	
150 – 450°C	1.73	
450 – 800°C	2.71	
800 – 1000°C	1.82	
ANALYSIS OF DRIED SOLIDS		
ACID INSOLUBLE (SILICACEOUS)	5.38%	
CALCIUM (Ca)	247,000	mg/kg
MAGNESIUM (Mg)	496	
STRONTIUM (Sr)	766	
BARIUM (Ba)	150	
ALUMINUM (Al)	8,238	
IRON (Fe)	2,343	
MANGANESE (Mn)	22	
ZINC (Zn)	32	
NICKEL (Ni)	200	
COPPER, COBALT, CHROMIUM, LEAD	25–34	
SULFATE (SO_4)	563,600	

FIELD TESTING CONCLUSIONS

- SRO CONCEPT VERIFIED FOR UNTREATED MINE DRAINANGE WATER
- 1.5 YEARS OF NON-SCALING OPERATION ACHIEVED
- MEMBRANES TOLERANT OF PARTICULATES AND COLLOIDAL MATERIAL
- SIGNIFICANT QUANTITIES OF METALS DID NOT AFFECT UNIT PERFORMANCE
- UNIT CAN BE OPERATED SUCCESSFULLY BY PERSONNEL INEXPERIENCED WITH RO
- RECOVERY OF 95% OF FEEDWATER CAN BE ACHIEVED



SRO REJECT SAMPLES SHOWING
RAPID SETTLING OF SLURRY

CONCLUSIONS

- SEEDED RO IS A TECHNICALLY FEASIBLE AND PILOT-PLANT-PROVEN TREATMENT FOR WATERS SATURATED WITH CALCIUM SULFATE.
- SRO IS MORE RELIABLE AND EASIER TO OPERATE THAN CONVENTIONAL RO WITH SOFTENING:
  - MINIMAL RELIANCE ON CHEMICAL SUPPLY
  - EASIER ADAPTATION TO FEED CHEMISTRY CHANGES
  - NO OPERATION OF SOFTENER SYSTEM
- ECONOMIC ANALYSIS INDICATES THAT –
  - SRO CAPITAL COST IS SUBSTANTIALLY LESS THAN CONVENTIONAL SYSTEM WITH PRETREATMENT, RO, AND EVAPORATION
  - SRO OPERATING COSTS ARE SUBSTANTIALLY LESS THAN CONVENTIONAL SYSTEMS WITH PRETREATMENT, RO, AND EVAPORATION

CHAPTER 21

DISPOSAL OF DESALINATION CONCENTRATE STREAMS

INTRODUCTION

Every desalination process produces a low TDS water product and a waste brine containing, in a concentrated form, the dissolved solids that were removed from the feedwater to make the desalinated product. In the case of ion exchange desalination processes, the concentrate may contain additional amounts of chemicals added to regenerate the loaded resin, although HENDRY (1983) has made a valiant attempt to show that this need not always be the case.

SCHUTTE (1983) summarized brine disposal alternatives, and Chapter 10 of his report is summarized below. It is clear, however, that each alternative is carefully qualified with one or more potential problems that must be avoided without saying how to avoid them.

Brine disposal remains an open questionmark in the U.S.A. today, although deep well disposal is a commonly practiced method for these and chemical industry wastes. However, very little has been written about desalination concentrate disposal. Regretably, virtually no cost data could be developed.

WATER RECOVERY

The water recovered by desalination processes is expressed as a percentage of the volume of feedwater. Water recoveries can be higher than 95% or lower than 25% resulting in brine volumes of less than 5% or more than 75% of the feedwater depending on the process employed, characteristics of the feedwater, and the goals of the desalination plant.

The most important factor which determines water recovery is the presence of scale-forming substances in the feedwater such as calcium carbonate, magnesium hydroxide, and calcium sulfate. When concentrations of these substances exceed their solubility limits as a result of the removal of pure water product, precipitation and scale formation results which usually seriously reduces the performance of the process. For this reason, feedwater is pretreated to remove these ions or to prevent them from precipitating by means of acid treatment, applying scale inhibitors or softening. In most desalination cases, however, especially those containing significant amounts of calcium sulfate, the only answer is to operate within the solubility limits of the compound. Even when scale inhibition is successfully applied, in almost all cases, the volume of brine may be reduced, but its concentration increases.

The seeded slurry reverse osmosis and seeded slurry evaporation processes are the only ways identified so far to avoid scaling and to enhance recovery while reducing the volume of brines yielding manageable solid precipitates in slurry form.

Water recovery in the desalination of seawater by reverse osmosis typically deteriorates from about 30% in newly installed modules to 20% for plants in which the membranes are approaching the end of their useful life. In distillation processes, water recoveries vary in the range of 40% to 60% for seawater feed.

Much higher recoveries are possible in the desalination of brackish waters where recoveries of 75% to 90% are typical and with seeded slurry R.O., a much higher recovery still, in the range of 95% plus can be achieved.

METHODS OF DISPOSAL

1) Sea Disposal

In coastal areas, disposal of brines does not present serious problems as they can be discharged to the ocean. However, that will be so only for brines generated by sea water desalination and where there are no toxic chemical or contaminants in the brines. Desalination of mine water or a mill effluent could well result in toxic brines that are not suitable for marine discharge--at least without further treatment. In any case, most mines are too far from the sea for this to practical in the first place.

2) Evaporation

In areas where there is a high net rate of evaporation such as in the dry parts of South Africa and the western interior of the U.S.A., disposal of effluents in evaporation ponds is the most cost-effective way of disposal. Where land costs are high, other methods may prove more cost effective. In the U.S.A., very often lined ponds are required which are expensive to install. Care must be taken to prevent seepage to groundwater aquifers and overflow or runoff to surface sources of water. In some cases, soil and subsurface conditions make a naturally impermeable pond floor. However, there are cases where evaporation ponds function better than theoretical evaporation rates would indicate because of invisible seepage. Many of these will be outlawed in the future and could cause problems with regulators.

In designing evaporation ponds that are lined, great care must be taken. The trip report on QUIVIRA MINING in Appendix I illustrates some of the unexpected problems that arise with lined evaporation ponds. Industry is still low on the learning curve in this area, and much care must be taken in the selection of lining material as well as the way it is applied. Consideration must also be given to the ultimate closure of the evaporation pond site in a stabilized way so that, in years to come, the concentrated salts cannot find their way into the environment.

3) Return to the Water Supply

Where boiler feedwater containing extremely low levels of dissolved salt is required and where available regional water is in short supply but relative low in TDS, then it is possible to use the regional water supply to recover say 10%-20% desalinated water and to return the "concentrate" which will have only 10%-20% higher TDS load than feed to the plant back to the regional water supply to be blended back with water supplied for other domestic or industrial uses. It is believed that the Electricity Supply Commission may apply this principle to some of their boiler feedwater treatment plant "concentrates." This is a very logical approach considering water conservation benefits and the avoidance of the need to dispose of brines. However, it has limited application in the tretment of mine-mill effluents.

4) Salt Water Sinks

In areas where large volumes of brine must be disposed of, the creation of a salt water environment in natural or artificial salt pans could greatly facilitate idsposal. This apparently is one of the alternatives under consideration for the disposal of brines from all kinds of desalination projects in the greater Witwatersrand area where there are major growing incentives to reduce the salt load in streams reaching the Vaal Dam.

5) Deep Well Injection

Brines are injected in wells to aquifers or rockstrata that are much deeper than any water source in the area to prevent any possibility of pollution. This a commonly used practice of the chemical industry in the United States.

In South Africa, deep defunct mines might be considered as a repository for brines provided contamination of underground waters could be avoided and provided that the old mine areas could be sealed to prevent brine flowing to active mines which are being dewatered, or where high salt content would enhance corrosion or cause other problems.

6) Further Processing

Further processing of brines in evaporator-crystalizers followed by spray drying producing a dry product is the recommended way of disposing of brines from desalination of many industrial effluents. At Rustenburg Refiners, a salable Na_2SO_4 product is produced which solves their brine disposal problem at the metallurgical plantsite.

7) Landfill Disposal of Solids

The seeded slurry reverse osmosis and evaporation processes yield brine slurries carrying crystalline precipitated salts which can be decanted easily to yield a "spadable" product for compact disposal. It was still too early to determine whether the precipitates in the seeded slurry R.O. process generated at ERPM (see trip

report in Appendix I for analysis) would pass the EP leach test for "hazardous" waste determination in the U.S.A. However, more information on this process can be requested from:

RESOURCE CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400

REFERENCES

HENDRY, B.A. (1983) Ion Exchange Processes for Chemical Recovery Combined with desalination. CSIR Symposium on Desalination: New Developments and Industrial Application, Pretoria, October 27, 1983.

SCHUTTE, C.F. (1983) Desalination: A South African Perspective. Water Research Commission, Post Office Box 824, Pretoria 0001, South Africa.

CHAPTER 22

APPLICATION OF DESALINATION AS A CONCENTRATING DEVICE IN EXTRACTIVE METALLURGY

Desalination techniques are not in use on any commercial scale operations as concentrating devices for metal values, except for some overlap in the use of ion exchange in selective metal recovery, for example, for uranium recovery.

It is believed that as membranes and system technologies are improved and particularly as effluent discharge regulations become more restrictive, there may be room for innovative applications of desalination techniques in resource recovery flowsheets. Removal or destruction of a pound of reagent costs a lot more than adding it to a solution in most cases. Therefore, methods to recover reagents may become sought after, just as in the case of metal finishing industries.

Potential applications for membrane technologies have been identified in two areas:

1) Recovery of Reagents in Reusable Form
2) Preconcentration of Metal Ions Before Recovery

RECOVERY OF REAGENTS IN REUSABLE FORM

- Various workers have experimented with the use of ED, for example, to recover reagent ions from spent solutions after the recovery of metal values in metallurgical processes. It is believed that the Council for Mineral Technology, MINTEK, in South Africa examined ED as a way of recovering sulfuric acid and ammonium hydroxide from spent metallurgical solutions containing ammonium sulfate. This research is either still in progress or has been terminated--no open file report on a successful process has been released.

- The magazine Galvanotechnik in West Germany described the application by a company, Linnhoff GmbH, of ED for the recovery of electrolyte from rinsewater in the metal finishing industry. In this process, 25 l/h of copper cyanide solution is recovered and returned to the plating bath from rinsewater containing 0.69 g/l Cu^{2+} and 0.34 g/l CN^{-}.

LINNEHOFF GmbH
Muhlenweg 15
D5870 Hemer
West Germany

- At an Australian nickel project that wishes to remain anonymous, high pressure reverse osmosis is used to upgrade $(NH_4)_2 SO_4$ from 10 g/l to 120 g/l in an effluent following ammoniacal leach at pH 5. Ultimately, a $(NH_4)_2 SO_4$ concentrated solution is generated which is disposed of as fertilizer. The company concerned declined to provide details on the R.O. system used and indicated a preference that the existence of the ammonium sulfate effluent be forgotten.

- Albany International has developed innovative new reverse osmosis membranes that allow ammonia to pass through readily while retaining base metal amine complexes which can be concentrated by a factor of 4-5 times in pregnant solution.

A copy of a draft evaluation of the benefits of using R.O. in the Sherritt-Gordon copper-nickel leading/precipitation process is inserted below. Although the assumptions and data are not refined, the concept appears intelligent. Randol International Ltd. believes that the new chemically resistant membranes developed by Albany International, if applied in tubular R.O. systems, would possibly be more appropriate as these avoid the possible need for filtration of solutions fed to the R.O. unit to avoid fouling by suspended solids. The albany International Ltd. membrane materials, however, allow a much wider operating pH range and are not as sensitive to high temperatures or Cl_2.

SEALED CELL ELECTRODIALYSIS

At the world conference on desalination held in Venice in May, 1983, ORA Kedem of the Weizmann Institute demonstrated a bench-scale sealed cell electrodialysis unit which used a slurry of carbon for elution transfer to enhance the movement of ions across a membrane in cell pairs. The following results were demonstrated for a NaCl solution in her laboratory cell stack:

Cf Feed	Cp Product	Output $m^3/m^2/d$	DC Energy $kW\ h/m^3$	Brine Concentration (ppm)	Volts/ Cell Pair
2,500	500	1.81	1.04	86,000	0.7
1,000	430	4.2	0.29	--	0.7
500	10	1.05	0.63	47,000	1.0
485	50	2.36	0.34	--	1.0
1,000	50	1.4	0.2	26,000	1.5
100	10	2.08	0.12	23,000	1.?

The very high brine concentration levels achieved and low energy consumption led to the thought that perhaps this process could be developed into a useful metallurgical concentrating device.

DEPT. OF MEMBRANE RESEARCH
The Weizmann Institute of Science
76100 Rehovot, Israel
Telex: 361900
Dr. Ora Kedem

REFERENCES

BENNETT, R.C. (1976) Ammonium Sulfate by Crystallization. Proc. Third National Conference on Complete Water Reuse, June 27-30, 1976, Cincinnati, Ohio.

Membrane Development Venture
921 Providence Highway
Norwood, Massachusetts 02062
Tel. 617 / 769-6310

ALBANY INTERNATIONAL

March 24, 1983

Mr. Hans von Michaelis
Randol International Ltd.
7510 West Mississippi #210
Lakewood, CO 80226

Dear Mr. von Michaelis:

It was a pleasure to meet you in Atlanca. As we agreed during our conversation, I am sending to you information on our membranes. Albany Interntional has developed a range of composite reverse osmosis hollow fiber membranes with unique properties. Our membranes can work in extreme pH's, at temperatures and under chemical conditions that no other known membrane system can afford. This seems to provide opportunities for their utilization in hydrometallurgical operations, where pH's can vary from very acidic to very basic, where fluid temperatures may be quite high, and where different oxidizing or reducing agents are present.

We belive that at least the following uses of our membrane in hydrometallurgy would be worth considering.

Concentration of Cations. Preliminary experiments show just in one stage we can easily increase concentrations of copper and nickel in a leaching stream 4-5 times;

Recovery of Ammonia. Our membrane is capable of passing undissociated ammonia while retaining metal ions which allows us to suggest its use in separating ammonia from ammoniacal leachate solutions, and in this manner avoid the high energy consuming recovery of ammonia by distillation;

Treatment of Waste Streams with Recovery of Values. This can become another area of utilization of our membrane. At present we are collaborating wih a major mineral acid manufacturer who has a serious environmental problem with waste ponding. We have demonstrated the feasibility of concentrating a dilute acid waste with our membranes to a level where the value of the concentrate pays for the process. Fresh water for reuse and control of environmental contamination are bonus benefits.

As I have already mentioned to you, we have developed other composite membranes which are able to enrich air to 50% oxygen in one stage quite economically. Oxygen enriching membranes can be useful in both pyrometallurgy and hydrometallurgy.

In summary, I'd like to say that there appears to be a lot of potential for using our membranes in metallurgical processing. We would be happy to run tests on streams of interest to the metal manufacturers at our expense. This can be done by them supplying us with actual samples (about 25 gallons) or by us modeling their composition in our laboratory, based upon information supplied by them.

Enclosed herewith is some literature describing Albany International Company, its Membrane Development Venture and some of the unique features of our membranes. We are looking forward to hearing about the progress of your survey.

Good luck.

Very truly yours,

Alla Kan

Alla Kan
Research Associate

AK/dl
Encl.

PRELIMINARY RESULTS OF AMMONIA RECOVERY REVERSE OSMOSIS PROCESS.

Two types of solutions were tested: The first one was a simulation of waste streams and contained 530 ppm of copper, 167 ppm of nickel and a total 5.4 gr/L of ammonia (both as ammonium ion and free ammonia).

The second solution contained a higher concentration of the ingredients: 9300 ppm of copper, 960 ppm of nickel and a total ammonia concentration of 70 gr/L. Both solutions were treated with calcium hydroxide to precipitate gypsum, which was filtered out before feeding the solution to the RO module at 400 psi.

The unit was operated to take about 80% of the feed volume through the membrane as permeate, thereby causing a four to five-fold concentration of metals in the concentrate, while 60-80% of the ammonia passed into the permeate.

The results of the test are presented in Table 1.

	Test I				Test II			
Metals (ppm)	Cu	Ni	Ca	NH_3	Cu	Ni	Ca	NH_3
Feed	9,280	960	580	58,700	530	167	542	5,070
Concentrate	54,720	5,590	2,780	36,400	1,970	634	2,060	7,610
Permeate	250	38	8	64,100	20	4	16.2	4,140
Rejection %	97.3	96.1	98.7	-9.4	96.3	97.3	97.0	18.3

To prevent calcium sulfate precipitation from the concentrate, a specific anti-precipitating agent was injected into the influent feed, which postponed crystallization for more than 1.5 hours and significantly decreased the possibility of membrane fouling with calcium sulfate.

These results allow us to suggest the incorporation of reverse osmosis into the hydrometallurgical process (figure 1). Probably there are several other points for introducing which could be discussed and tested later.

ECONOMICAL ESTIMATION OF SUBSTITUTION OF AMMONIA DISTILLATION FOR RO AMMONIA RECOVERY PROCESS.

A preliminary economic evaluation of the introduction of RO into the hydrometallurgical technology has been done to compare capital, operating, and energy expenditures for RO and adsorptive removal of ammonia from the flows.

Three categories of expenditures to consider in calculating the impact of RO on the cost of an overall process are: capital costs, which include the costs of the equipment, installation costs of this equipment and operating costs, which include labor, utilities, maintenance, insurance, taxes, etc.

Complete data specifying the current costs of hydrometallurgical equipment, its installation and operation are not readily available. However, reasonable approximations can be made by the following approach:

1. Most of the capital and operating costs obtained from manufacturers, catalogs of equipment, or reported in the literature were updated to 1982 using the Consumer Price Index as reported in "Monthly Labor Review", "Chemical Marketing Report", or "Survey of Current Business".

The operating economical parameters are presented in the table.

OPERATING ECONOMICAL PARAMETERS

Name	Unit	Parameter
Electricity	kWh	$ 0.065
Steam	10^6BTU	$ 4.1
Maintenance	% of Capital Costs	5%
Administration insurance, taxes	% of Capital Costs	7%
Labor	Hour	$12.5
Interest Rate	%	12%

2. Capital and operating costs were calculated per industrial unit with inlet flow of the leachate 30 gal/min. This unit works 350 days a year, 24 hours a day processing 15.1 x 10^6 gallons of leachate per year. Installation costs were assumed 25 percent of the capital costs. Depreciation time was assumed to be 10 years.

3. Electricity consumed by the conventional unit (figure 2), is derived from:

40 HP x 24 hr. x 350 days x 0.746 kW/HP = 251,000 kWh

The cost of electricity is:

251,000 kWh x 0.065 $/kWh = $16,600/year.

4. Cost of steam needed for ammonia evaporation was assumed $4.10/$10^6$ BTU, based on the cost of fuel oil and data obtained from the report, "Technical and Economical Feasibility of Membrane Technology", by Andrew M. Sandre of American Crystal Sugar Company, Moorhead, Minnesota.

The inherent heat of evaporation of ammonia from water is 34 kJ/mol or 32.2 BTU/mol. (Handbook of Analytical Chemistry, by Louis Meites, NY, 1963). Ammonia concentration in the leaching solution was assumed 227.1 gr/gal. Molecular weight of ammonia is17, therefore every gallon contains 13.3 moles ammonia, from which 80% or 10.6 moles are to be recovered. The energy consumed for that operation is 32.3 BTU/mol x 10.6 mol/gal = 341 BTU/gal of leaching solution.

The cost of steam consumption for ammonia evaporation was calculated:

$$341 \text{ BTU/gal} \times 15.1 \times 10^6 \text{ gal/year} \times \frac{\$4.10}{10^6 \text{BTU}} = \$21,110/\text{year}.$$

5. It is supposed that one worker can operate ten units during one 8-hour shift. The labor cost is assumed:

350 days/year x 24 hr/day x 12.5 $/hr. = 105,000 dollars per 10 units per year.

Per one unit the labor cost will be $10,500 per year.

The following tables represent the estimated costs of processing of 1,000 gallons of ammoniacal solution with the conventional method.

Capital and Installation
Costs of Conventional Hydrometallurgical
Ammonia Recovery Process

Cost Items	Units	Cost, $1982 per year
Capital Costs:		
LTV-evaporator	1	48,000
Packed Adsorption Tower	1	125,000
Centrifugated Filter-Mixer	1	18,000
Pump	3	3 x 4200 = 12,600
Auxiliary Equipment	1	4,000
Total Capital Costs		207,600
Installation Costs		51,900
Total Capital and Installation Costs		259,500

Operating Costs of Conventional
Hydrometallurgical Ammonia Recovery Process

Cost Items	Cost, $1982 per year
Operating Costs:	
Depreciation	25,950
Maintenance	11,000
Administration, insurance, taxes	15,400
Labor	10,500
Utilities:	
Electricity	16,600
Steam	21,110
Total Operating Costs	100,560

Assuming that one unit is processing 15.1×10^3 thousand gallons per year the processing cost for 1000 gallons of solution:

$100,560/year:15, 100 thousand gallons/year = 6.66 dollars per 1000 gallons of the ammoniacal solution.

5. Electricity consumed by the RO unit (figure 3) is derived from:

35HP x 24 hr. x 350 day x 0.746 kW/HP = 220,000 kWh.

The cost of electricity is:

220,000 kWh x $0.065/kWh = $14,300/year.

7. Cost of steam needed for ammonia evaporation from 8,640 gal/day of RO concentrate (instead of 43,200 gal/day of the initial solution):

$$341 \text{ BTU/gal} \times 3.02 \times 10^6 \text{ gal/year} \times \frac{\$4.10}{10^6 \text{BTU}} = \$4,220/\text{year}.$$

8. The labor cost assumed the same as the previous case, $10,500 per year.

9. Costs of Membrane Modules - Experimental results presented here were obtained on the preproduction size modules with the membrane area 30 sq. feet. As we estimated the commercial size modules would have 500-2000 sq.ft. membrane area with productivity 2-2.5 gal/sq.ft./day.

Our estimations show that the cost of the membrane system will be $1.60 per gallon per day during a year.

Therefore, the cost of membranes for the unit chosen for this estimation is:

43,200 gal/day x $1.6/gal = $69,120/unit.

The tables on the following page represent the estimated costs of processing 1,000 gallons of ammoniacal solutions with the RO process incorporated.

Capital and Installation Costs
of RO Ammonia Recovery Process

Cost Items	Units	Costs, $1982 per year
Capital Costs		
LTV evaporator*	1	14,000
Packed Adsorption Tower*	1	30,000
Centrifugated Filter-Mixer	1	18,000
Pump (5 HP)		4,200
Pump (4 HP)		3,600
Pump (1 HP)		1,000
RO Pump (8 HP)		6,000
Membrane Modules		69,120
Total Capital Costs		145,920
Installation Costs		36,480
TOTAL CAPITAL AND INSTALLATION COSTS		$182,400

*One can use evaporation - adsorption equipment, installed at the plant, not utilized in the full capacity or combine several batches.

Operating Costs of RO Ammonia Recovery Process

Cost Items	Costs, $1982 per year
Operating Costs	
Depreciation	18,240
Maintenance	7,660
Membrane replacement (assuming membrane life 2 years)	23,600
Administration, insurance, taxes	10,750
Labor	10,500
Utilities	
Electricity	14,300
Steam	4,220
Total Operating Costs	$89,270

Assuming that one unit processes 15.1 x 10^3 thousand gallons per year, the processing cost for 1000 gallons of solution is:

74,550:15, 100 thousand gallons/year = 5.91 dollars per 1000 gallons of the ammoniacal solutions which gives savings of .75 cents/1000 gallons.

Assuming nickel concentration in the solution of 10 gr/L or 83.7 pounds/1000 gallons, and yearly nickel production of 10,000 tonnes, the total savings introduction of RO only for the recovery of ammonia from the leachate can bring

$$\frac{10{,}000{,}000 \text{ kg/year } 0.75 \text{ dollar/1000 gal}}{0.452 \text{ kg/lb. x } 83.7 \text{ lb/1000 gal}} = \$198{,}200/\text{year.}$$

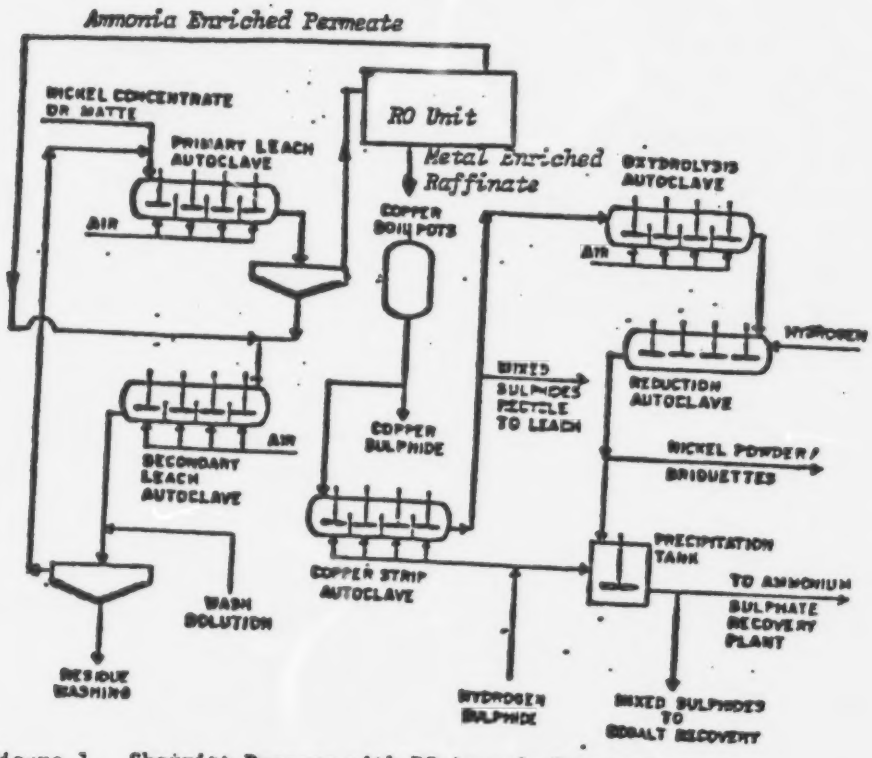
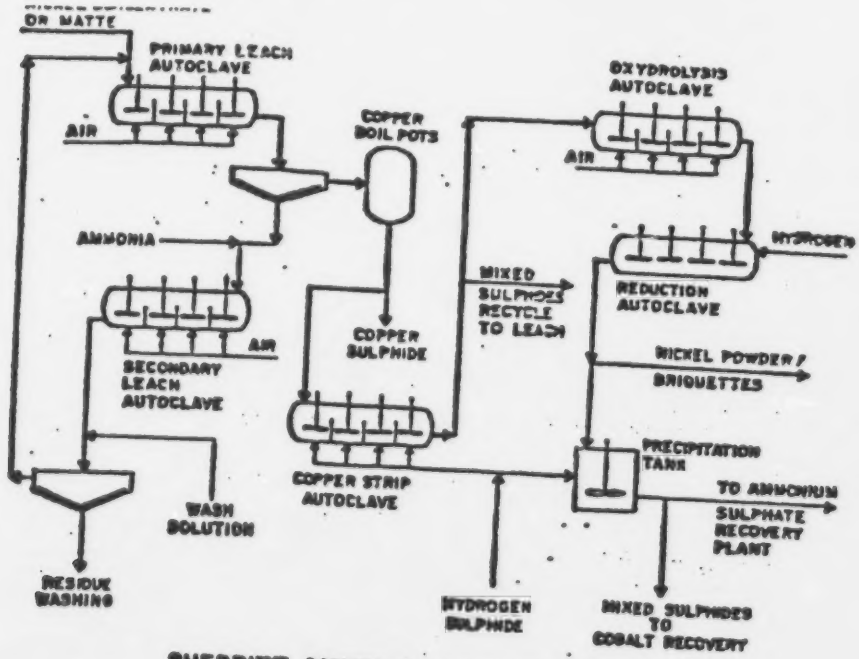


Figure 1. Sherritt Process with RO Ammonia Recovery Unit Incorporated.



SHERRITT AMMONIA LEACH PROCESS

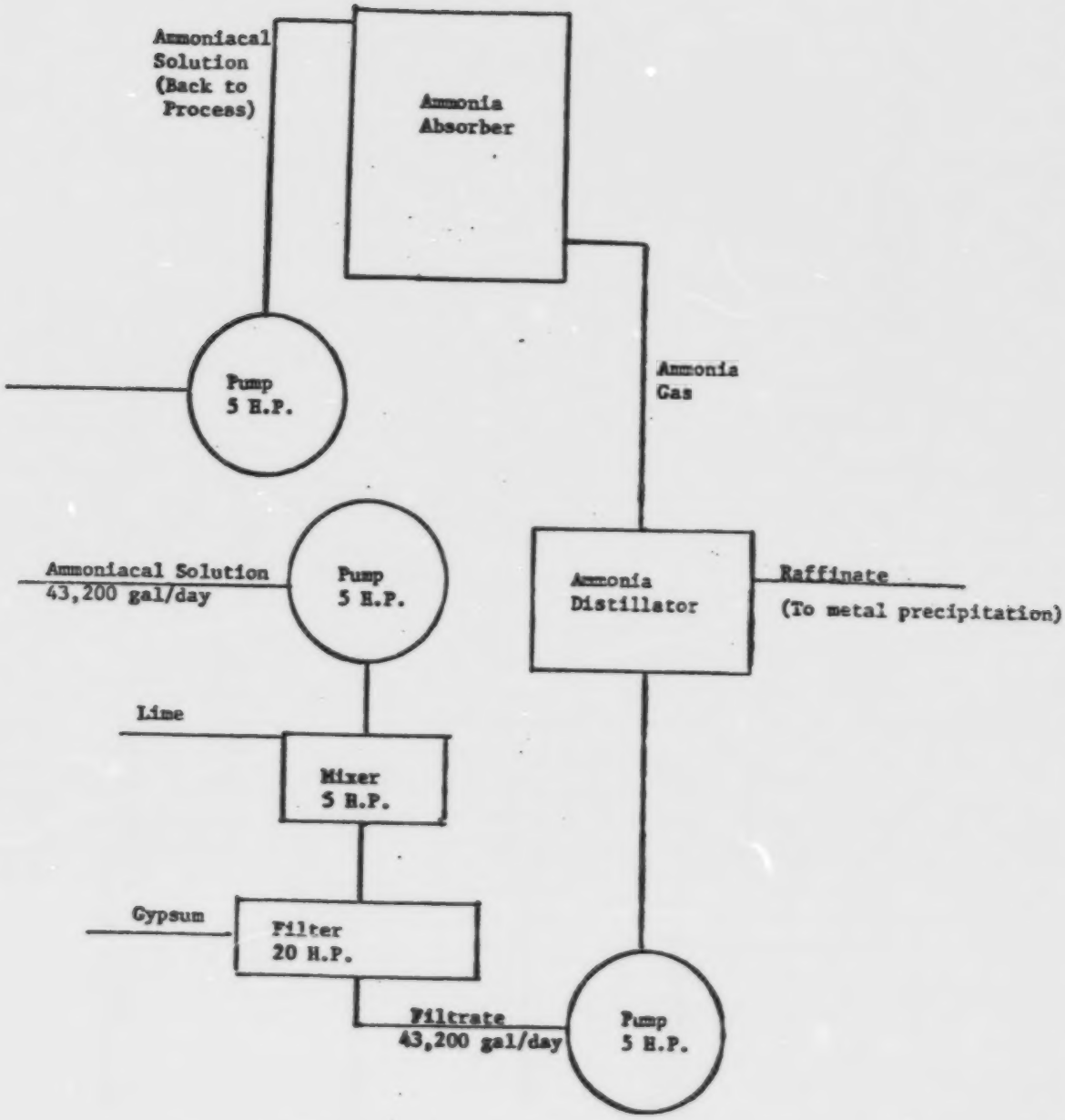


Figure 2. Conventional Ammonia Distillation Recovery

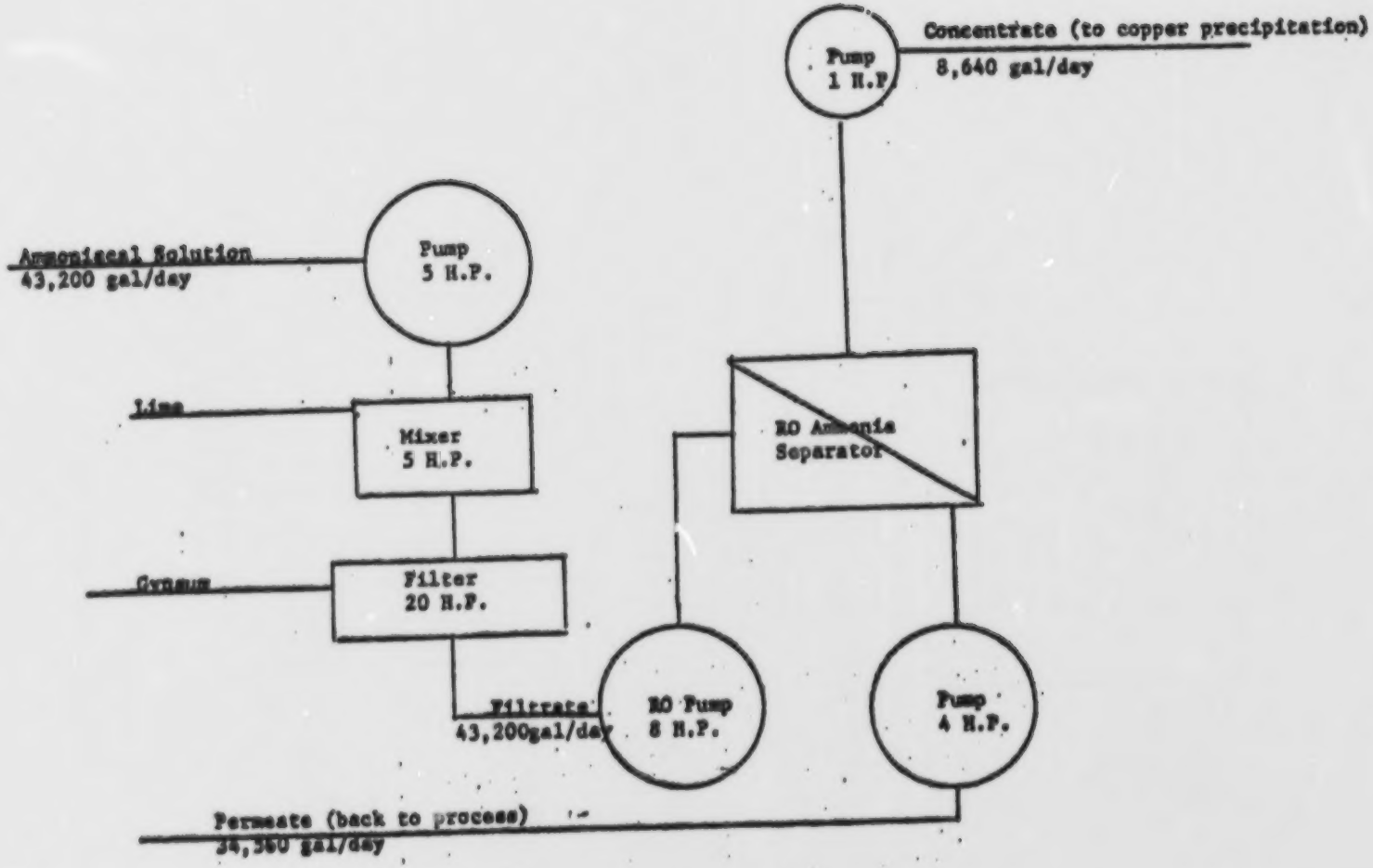


Figure 3. RO Ammonia Recovery and Metal Separation

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3

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WATER MANAGEMENT & TREATMENT

FOR

MINING & METALLURGICAL OPERATIONS

1 JUNE 1985

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WATER MANAGEMENT & TREATMENT

FOR

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.).....	Milligrams per liter.....	17.12
Milligrams per liter.....	Grains per gallon (U.S.).....	0.05841
Milligrams per liter.....	Tons per acre-foot.....	.001360
Tons per acre.....	Metric tons per hectare.....	2.217
Grams.....	Ounces (avoirdupois).....	.03527
Ounces (avoirdupois).....	Grams.....	28.35
Gallons (Imperial).....	Gallons (U.S.).....	1.2009
Acre-feet.....	Gallons.....	325,851
Acre-feet.....	Cubic feet.....	43,560
Cubic feet.....	Cubic meters.....	.028317
Cubic feet.....	Gallons.....	7.481
Cubic meters.....	U.S. Gallons.....	264.2
Cubic meters.....	Imp. Gallons.....	220.0
1,000 m^3/d.....	I gpm.....	152.8
1,000 m^3/d.....	U.S. gpm.....	183.6
U.S. gallon.....	Cubic meter.....	0.3785

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INTRODUCTION

Acid mine drainage (AMD) is the most serious environmental problem of the mining and mineral processing industry. It causes the discharge of toxic contaminants from mines and mineral waste that continues for many centuries after a mine, mill, or colliery has shut down. Acid mine drainage inhibition would get to the root of so many environmental impact problems that there is no more urgent need for further research and development than this.

Acid mine drainage (AMD) refers to water draining or pumped from mines or draining through or from wasterock piles, overburden and tailings, or which has come into contact with sulfide minerals in any possible way that may have affected its quality, usually by a drop in pH and/or an increase in TDS, especially sulfates, iron, and often a variety of base and heavy metals. Frank Carruchio of the West Virginia Acid Mine Drainage Technical Advisory Committee has observed that only one type of pyrite, the framboidal variety, generates AMD along with other more reactive iron sulfide minerals such as pyrrhotite and marcasite. Whether or not this is so in all environments remains to be established.

In some parts of West Virginia, the need to inhibit AMD from spoil in order to operate a coal mine is preventing coal from being mined because no economic way of preventing it has been found.

Not all mine drainage and effluents from tailings are acid. Even neutral or slightly alkaline waters can contain contaminants that require removal, but these problems are often small compared to the more prevalent acid mine drainage.

Acid mine drainage impact on water quality ranges from small scale problems from small coal mines and even small clay pits to the more significant problems associated with the mining of massive sulfide orebodies and large scale mining of Precambrian conglomerate ores, for example, the uranium mines around Elliot Lake in the Canadian Shield and the gold and uranium mining industry in South Africa, each generating huge quantities of wasterock and tailings. The greatest source of AMD is the coal mining industry with the large quantities of sulfide-bearing waste, particularly in Appalachia, but occurring just about everywhere that coal is mined. Massive sulfide base metal mine and mill waste is almost always a potential source of acid mine drainage. What these all have in common is the presence of sulfide minerals in the ore, wasterock, and tailings material.

AMD has been known to be associated with coal mining for many years, but only within the last decade or so has its full extent in the rest of the mining industry started to be appreciated. Recognition of acid mine drainage from base metal mining still is only partially acknowledged, and in the gold and silver mining industry of the Witwatersrand, it has been identified as a phenomenon to be dealt with in water pumped from some of the deep underground mines. The possibility of larger diffuse source impact of AMD from mine wasterock piles and mine tailings dams has yet to be determined. It is likely that

these will become important targets for remedial programs within the next five years. That Witwatersrand gold and uranium mines tailings and wasterock are acid generators is obvious when these sites are inspected from the air. The table from SMITH, et al. (1984) inserted below indicates that although there is evidence of AMD in groundwater below Witwatersrand tailings impoundments, the problem may be partly alleviated by the way tailings are disposed of in that industry center. Note pH, Mn, and SO_4 levels.

OBJECTIVES OF AMD INHIBITION

Acid mine drainage from sulfide-containing tailings and wasterock piles as well as from old mineworkings can continue for centuries, and AMD treatment would be required to meet effluent discharge regulations; this has resulted in the need to maintain and operate treatment plants "in perpetuity." Consequently, the goal of AMD inhibition must be to avoid such needs for perpetual maintenance of tailings and wasterock disposal sites and, above all, to avoid the need for "perpetual" water treatment.

COMPARISON OF TOTAL CYANIDE LEVELS WITH GROUNDWATER COMPOSITION

DESCRIPTION OF DAM	TOTAL CN	TDS	SO_4	Fe	Mn	PH
① OPERATIONAL DAM ± 5 YEARS AGE	<0.01	712	317	0.1	15	6.8
② ABANDONED DAM >20 YEARS AGE	0.04	500	400	34	69	2.9
③ RECENTLY DECOMMISSIONED DAM ± 20 YEARS OLD	0.08	300	70	4	0.8	5.8
④ OPERATIONAL DAM ± 10 YEARS	<0.01	500	—	—	—	7.5
⑤ "BACKGROUND" WATER QUALITY	<0.01	250	50	0.1	0.1	7.8

1. ALL VALUES IN mg/l, EXCEPT PH; UNITS

Groundwater Composition under Selected Witwatersrand Tailings Ponds
Source: SMITH, et al. (1984)

1164

sored by: National Association of Mining Engi-
Superior Council of Institution of Mining Engi-
Spain

CORRESPONDENCE
Please address all communication to: Prof. R. Fernández Rubio - School of Mines - Technical University of Madrid - Ríos Rosas, 21 - Madrid, 3. Spain

Imprenta T. Gráficas ARTE, S.A.

SECOND INTERNATIONAL CONGRESS OF THE INTERNATIONAL MINE WATER ASSOCIATION (IMWA)

GRANADA, SPAIN
17 to 21 September, 1985

Hopefully the day will come when large pyrite and other iron sulfide and AMD resources are sought after as profitable resources of sulfur and hydrogen; additional resource recovery will then provide a profitable solution to what today are some of the most serious potential environmental liabilities of mining.

TEN ASPECTS OF ACID MINE DRAINAGE INHIBITION

Ten aspects of acid mine drainage (AMD) abatement were encountered during the course of the RANDOL study:

1) Climate.

2) Encouraging laboratory scale demonstration of AMD inhibition through special techniques in revegetation of tailings by CANMET, Ottawa.

3) The U.S. Bureau of Mines work by Robert L. P. Kleinmann, et al. in the use of anionic detergents.

4) Brand new research by Dr. Al Stiller at the University of West Virginia in the application of low grade phosphate rock.

5) Successful control of AMD in restoration of the active coal mine waste dump at Burnside Colliery, Natal, South Africa.

6) Experience at the Kromdraai Coal Mine restoration site, Transvaal, South Africa.

7) Results reported by BOSMAN (1982) and WATSON (1982) on removal of water from underground mines.

8) AMD abatement by discouraging bacterial action.

9) Wasterock utilization.

10) Concentrate stockpiles and transportation.

11) Backfill of Tailings and wasterock.

1. Climate

Climate has a major impact on AMD generation and possible ways of inhibiting it.

Dry Climates: In dry climates with net evaporation, as long as AMD can be contained, it will evaporate. For tailings and wasterock piles that contain sulfides, this implies that provided groundwater is protected from seepage where necessary and runoff is collected and impounded, the problem of AMD would be containable.

Volumes of AMD pumped from underground mines on the Witwatersrand, on the other hand, are so large that evaporation would require enormous land areas and, besides, this would be a waste of water in an area that is short of water.

Revegetation as a means of stabilizing tailings is more difficult in very dry climates. Revegetation of large tailings areas would possibly require more water than can be spared. In drier climates, vegetation may not be lush enough to generate an adequate oxygen barrier to inhibit oxidation of sulfides in tailings. Revegetation of tailings on the Witwatersrand has made a major difference in the control of dust which used to be a major problem in Johannesburg. Non-vegetative ways of stabilizing tailings surfaces have also been demonstrated, but these will do little to prevent AMD generation in the tailings. A dry climate makes the use of "semi-dry" or "sub-aerial" tailings deposition more effective. This method of applying tailings in thin layers which are decanted and allowed to dry between applications and can, depending on the nature of the material, result in extremely impermeable tailings that may effectively encapsulate acid generators in some cases. This method of tailings disposal lends itself to further examination to determine whether it can perhaps be further developed with AMD inhibition in mind.

Wet Climates: In wet climates with a net precipitation, runoff and collected seepage water cannot simply be contained in a pond as the volume of water in the impoundment will eventually exceed the size of the pond because of precipitation. In the end, a discharge will be unavoidable.

Revegetation in a wet climate is easier and can be much more prolific. The rate of humus development in a wet climate with prolific seasonal growth of deciduous plants is faster, and there is a hope of generating a surface oxygen barrier of decaying organic matter on the surface.

Rate of evaporation can be enhanced through vegetation due to evapotranspiration of plants which have a large surface area.

To date, most mining company efforts to revegetate tailings have focused on determining how much lime to add and what seeds will grow. There has been considerable success in some cases. However, the focus has been on getting plants to grow in a way that controls dust and hoping that AMD will be inhibited. Understanding of the mechanisms and fundamental aspects of acid mine drainage generation and how to prevent it are largely not understood as yet.

Much more testwork on the effects of revegetation of various kinds on AMD generation is required, particularly under field conditions.

2. Encouraging Lab Scale Demonstration Through Special Revegetation Techniques

CANMET has undertaken several series of laboratory-simulated tailings disposal. They are able to simulate many years of the life of a tailings impoundment in a much shorter space of time for study purposes in "Lysimeter" tests. A three-year test simulating a 25-year period on uranium tailings was described by RITCEY and SILVER (1982), whose paper is inserted in Chapter 58 on Tailings Impoundments.

In one series of lysimeter tests, four different revegetation approaches have been simulated side-by-side over sulfide tailings. Seepage through each has been collected and monitored for AMD, and markedly different results obtained. In all but one case, the seepage was acid, indicative that normal revegetation does not inhibit AMD. Special measures were taken in the lysimeter in which AMD inhibition is demonstrated and, even there, AMD inhibition is not perfect. These lysimeter tests are still ongoing at CANMET and can be inspected in Ottawa.

The comparative lysimeter tests by CANMET are one aspect of their study which have made a good start in first understanding what processes, influencing factors, and end results are involved in disposal of sulfide-bearing tailings. Certainly, they have shown that the various ways in which tailings can be disposed have a major impact on the composition of seepage and runoff and that this problem is much more complicated than is generally realized.

The CANMET studies to date have accumulated more basic data and information than has been gathered on AMD from tailings as well as experimental procedures of immense value than is available anywhere else. This work clearly represents an important and promising beginning in defining fundamental aspects of the problem and in finding useful answers. This crucial program hopefully will receive all the funding it needs to continue in the lab and be extended to field demonstration.

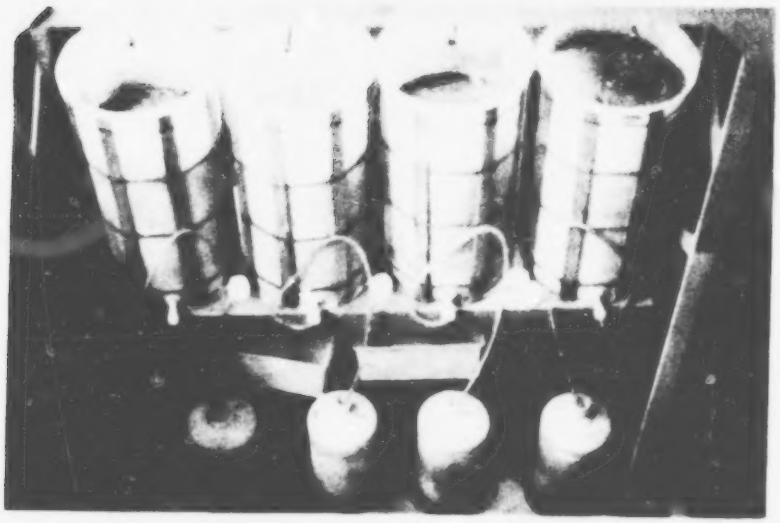
CANMET is a valuable source of assistance and information on basic research to industry and can be contacted as follows:

CANMET
Energy, Minerals, and Resources CANADA
555 Booth Street
Ottawa, Ontario
Canada K1A 0G1
Gordon Ritcey
Maruin Silver

Other useful work in tailings disposal in which several years are simulated in a shorter space of time in the laboratory have demonstrated the "semi-dry" or "sub-aerial" tailings disposal method also for uranium tailings at ONTARIO RESEARCH FOUNDATION and at SHERRITT-GORDON MINES LTD. These, however, looked more at encapsulation and permeability effects rather than at the effects of revegetation methods:

ONTARIO RESEARCH FOUNDATION
Mineral Processing and Hydrometallurgy Mgr.
Sheridan Park Research Community
Mississauga, Ontario L5K 1B3
(416) 822-4111
Dr. V. I. Lakshmanan

SHERITT-GORDON MINES LTD.
Fort Saskatchewan, Alberta
Canada T8L 2P2
(403) 998-6911
Herbert Veltman



Laboratory Arrangement for Lysimeter Tests
of Tailings Generation of AMD at CANMET

3. Anionic Surfactants

Work on the inhibition of acid mine drainage using anionic surfactants has been adequately described by the following publications: KLEINMANN (1982), KLEINMANN and ERICKSON (1982), KLEINMANN and ERICKSON (1983), and FOX (1983).

The mechanism whereby the bacteria are destroyed after coming in contact with the anionic surfactant is of interest. Bacteria such as thiobacillus ferroxidans which enhance the oxidation of sulfides to acid and ferrous/ferric ions are fragile cells which survive in the acid medium by surrounding themselves with a protective coat of polypeptide material.

The surfactant however causes this protective coat to be rendered imperfect to the extent that they are no longer viable in the acid medium and die as soon as acidity starts to develop.

Efforts to spray anionic surfactants into mineworkings to inhibit acid mine drainage underground seem less promising although work is progressing on the use of a volatile fume that could possibly penetrate cracks or fissures more effectively. Two of the reagents being tested are potassium benzoate and sodium sorbate.

Spraying anionic surfactants over surface waste dumps on a regular basis to inhibit AMD generation amounts to a perpetual treatment process requirement which, for that reason, is not likely to be the final answer.

The use of anionic surfactants such as sodium lauryl sulfate mixed into elastomer as slow release agents scattered over the waste dump that has been contoured and restored before adding a layer of topsoil and establishing plant growth is being evaluated. It is hoped that by the time the slow release agent has dispensed all the anionic surfactant, that the soil and organic material from the vegetation will have built up to keep oxygen from reaching the pyritic materials. Work by the Chamber of Mines in South Africa has shown that oxidation of pyrite in gold mine dumps was not prevented by the establishment of grass vegetation on the dumps. However, considering the very different climatic and vegetation conditions that prevail in most of the eastern and central U.S.A. coalfields, it is possible that the result may be different. First, North American winters are so cold as to inhibit AMD generation. Second, because summers are so hot and humid, deciduous growth is prolific and would generate much more organic matter in the soil than on the Witwatersrand. Many U.S. coal mines are currently testing acid mine drainage inhibition following the techniques of KLEINMANN, et al., and within a few years, it will be possible to determine the degree of success achieved. Meanwhile, the results to date indicate a short-term success but are still inconclusive as to a long term result that would allow operators to walk away from the site without further attention.

Several commercial companies manufacture anionic surfactants for AMD inhibition on a trial basis. Manufacturers of sodium lauryl sulfate are:

SODIUM LAURYL SULFATE SUPPLIERS

Company	Trade Name, SLS Purity, Shipping Method, Contact Person
Alcolac, Inc. 3440 Fairfield Road Baltimore, MD (301) 355-2600, Ext. 240	Sipex UB 30% 55 gal. fiber drum, tanker Mary Lisle
E. I. du Pont de Nemours Brandywine Building Wilmington, DE 19898 (800) 441-7515	Duponal WAC 29% Rosalie Gagliardi
Proctor & Gamble 120 West Fifth Street, 5th Floor Cincinnati, OH 45202 (800) 545-1580	Esquex S 29% 55 gal. drum, tanker Mike Hill
Stepan Chemical Northfield, IL 60093 (312) 446-7500, Ext. 300	Stepanol WAC 29% 55 gal. fiber drum Roger Peters
Witco Chemical 400 North Michigan Avenue Chicago, IL 60611 (800) 231-1542	Witcolate A 30% 55 gal. drum, tanker Thomas L. Beveridge

More information on the performance of AMD inhibition technology as applied on a commercial scale and, as it is further developed, can be obtained from the following contacts:

BUREAU OF MINES
U.S. Dept. of the Interior
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Dr. Robert L. P. Kleinmann
Patricia M. Erickson

B. F. GOODRICH
Engineered Products Group
500 South Main Street
Akron, OH 44318
(216) 374-4341
Telex: 986430
Vijay Rastogi
Mine Acid Control Program Manager

GRANGER TECHNOLOGIES
114 Waterside Drive
Medina, OH 44256
(216) 666-5663
R. N. Naranch
President

DEPT. OF ENVIRONMENTAL QUALITY
Frankfurt, KY
Sara Cunningham

DEPT. OF MICROBIOLOGY
Ohio State University
Columbus, OH
Dr. Pat Dugan

A senior coal mining company representative who is following the development of acid mine drainage inhibition is:

BRUCE R. LEAVITT
Consolidation Coal Company
Pittsburgh, PA
(412) 228-3454

Other sources of information may be:

WEST VIRGINIA ACID MINE DRAINAGE
Technical Advisory Committee
Dept. of Geology
University of South Carolina
Columbia, South Carolina
(803) 777-3120
Frank Carruchio

Dr. R. L. P. Kleinmann's group at the U.S. Bureau of Mines provides an interesting technology transfer workshop on acid mine drainage each year which would be well worth attending for those interested in this field, not necessarily restricted to the coal industry.

Another source of expertise on acid mine drainage inhibition and treatment who has experimented with numerous approaches is:

DR. H. L. LOVELL
Dept. of Mineral Sciences
Pennsylvania State University
State College, PA

United States Patent [19]

Kleinmann

[11] **4,314,966**

[45] **Feb. 9, 1982**

[54] **METHOD OF CONTROL OF ACID DRAINAGE FROM EXPOSED PYRITIC MATERIALS**

[76] Inventor: **Robert Kleinmann**, 5774 Smith Dr., Bethel Park, Pa. 15102

[21] Appl. No.: **186,898**

[22] Filed: **Sep. 12, 1980**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 94,426, Nov. 15, 1979, abandoned.

[51] **Int. Cl.**[3] **A61L 2/22**

[52] **U.S. Cl.** **422/28**; 424/19; 424/22; 424/30; 422/32; 422/900

[58] **Field of Search** 424/19, 22, 30; 422/28, 422/32, 900

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,094,846	6/1963	Peeler	422/1
3,306,728	2/1967	Campbell	71/64 F
3,400,011	9/1968	Fox	71/64 F
3,443,882	5/1969	Flynn	422/900
3,590,119	6/1971	Cardarelli	424/78
3,639,583	2/1972	Cardarelli	424/125
3,740,419	6/1973	Campbell	424/38
3,851,053	11/1974	Cardarelli	424/78
3,928,564	12/1975	Cardarelli	424/78
4,012,221	3/1977	Walker	424/22
4,166,111	8/1979	Cardarelli	424/78

OTHER PUBLICATIONS

Dugan, P. et al.: "Acid Production by Ferrobacillus Ferrooxidans and its Relation to Water Pollution", *Developments in Industrial Microbiology*, vol. 5, 1964, pp. 250-257.

Primary Examiner—Dennis L. Albrecht

[57] **ABSTRACT**

Acid drainage from exposed pyritic m[illegible] such as coal mine tailings is reduced through the controlled application of anionic detergents which inhibit the bacterium *Thiobacillus ferrooxidans*. The controlled application of anionic detergent comprises an initial application of anionic detergent in sufficient quantities to satisfy the adsorptive capacity of clay or clay-sized particles overlying the pyritic material coupled with the application of an anionic detergent inhibitor of *Thiobacillus ferrooxidans* from a slow release matrix containing the inhibitor. The two applications are to intercept infiltrating water up-gradient of the pyritic material or strata. The amount of matrix employed is calculated in accordance with a described formula. The method can be used to reduce acidity in drainage from pyritic mine tailings, coal mines, coal refuse piles and construction sites at which acid drainage is a problem.

Acid drainage is also reduced by the mere controlled application of specific anionic detergents which inhibit the bacterium *Thiobacillus ferrooxidans* utilizing a detergent-containing matrix which provides detergent concentrations of greater than 10 ppm and preferably greater than 25 ppm in the infiltrating water.

17 Claims, 1 Drawing Figure

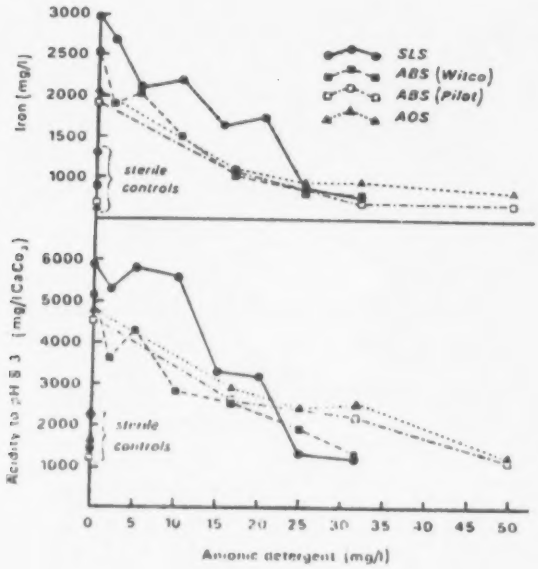
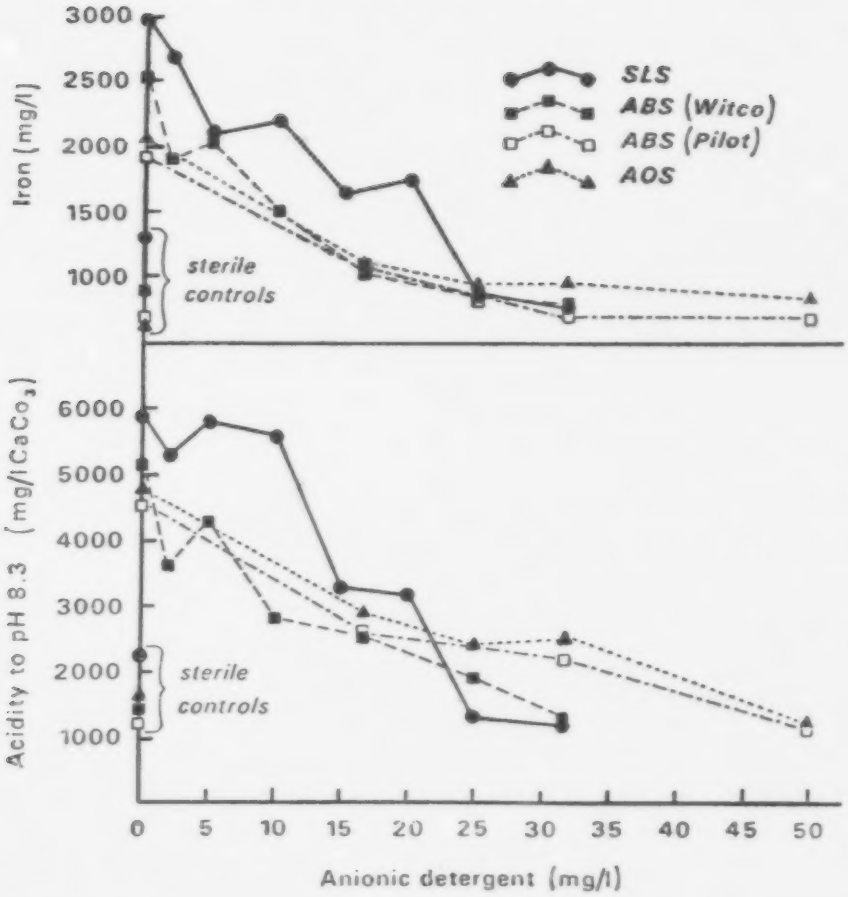


FIG. I


3000
2500
2000
1500
1000
Iron (mg/l)
SLS
ABS (Witco)
ABS (Pilot)
AOS
sterile controls
6000
5000
4000
3000
2000
1000
Acidity to pH 8.3 (mg/l CaCo3)
sterile controls
0
5
10
15
20
25
30
35
40
45
50
Anionic detergent (mg/l)

METHOD OF CONTROL OF ACID DRAINAGE FROM EXPOSED PYRITIC MATERIALS

RELATED APPLICATION

This application is a Continuation-in-Part of my copending application, Ser. No. 94,426, filed Nov. 15, 1979, abandoned on the filing date of this application, all the teachings of which copending application are incorporated herein by specific reference thereto.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for the reduction of acidity in drainage from pyritic mine tailings, coal mines, coal refuse piles and construction sites.

2. Description of the Prior Art

Acid drainage results from the oxidation of iron pyrite (FeS_2) associated with coal, mine tailings and overburden material. The problem of acid formation also may occur during building or road construction due to pyrite present in the disturbed strata. The conventional technique to overcome this problem has been to collect the drainage from the area and then neutralize it with lime and/or limestone.

Previous research by biologists suggests that a bacterium, *Thiobacillus ferrooxidans*, plays a role in the acid formation process. However, geologists have remained sceptical of such research primarily because the laboratory experimental conditions tend to deviate radically from actual field conditions. Hence any correlation between laboratory and field conditions is suspect.

The tolerance of *T. ferrooxidans* to a large range of chemical substances has been examined in the literature. Indeed, two detergents, alkyl benzene sulfonate and sodium lauryl sulfate, were tested by Dugan and Lundgren in 1964 and shown to inhibit *T. ferrooxidans* at concentrations of 2–5 ppm in culture media. Another detergent was also tested and found inhibitory at only extremely high concentrations. The inhibition observed was attributed by Dugan and Lundgren to a coating of the bacteria caused by the detergents' alkyl side chain.

It is of course possible to protect coal from contact with water and thereby prevent formation of acid drainage by coating each individual particle with various oils and waxes. Moreover, coal may be protected as disclosed in U.S. Pat. No. 2,204,781, Wattles, by spraying the outside surface of piles or large masses of coal with a material congealable at atmospheric temperatures whereby a non-tacky weather resistant jacket adherent to the coal at the surface of the pile or mass is formed. However, both of the foregoing procedures require substantial expenditures of coating material, and are not practical where the primary purpose is to avoid acid drainage as opposed to the prevention of water contact.

One prior art approach to prevention of acid drainage relates to treatment with an aqueous alkali metal silicate solution which reacts with acid present to form a sila gel which in turn may coat the pyrite surface. (U.S. Pat. No. 3,094,846). Another prior art method of preventing acid drainage involves use of a mixture of pulverized phosphate and sulfuric acid to precipitate soluble iron as phosphates which in turn may coat the pyrite surface. (U.S. Pat. No. 3,443,882).

In accordance with this invention acid drainage in a pyritic material which is exposed to water is controlled by addition of at least about 10 ppm of an anionic detergent capable of inhibiting *T. ferrooxidans* to the water which contacts the exposed material. The concentration is necessarily higher than that previously reported to be required to inhibit *T. ferrooxidans* in culture media. In order to avoid repopulation, the addition is effected by controlled release from a matrix containing anionic detergent dispersed therein. Controlled addition is accomplished by placement of the matrix to intercept infiltrating water upgradient of the pyritic material. The quantity of anionic-detergent containing matrix required to effect the controlled release is calculated in accordance with the formula set forth in the summary of the invention.

I have developed a method of dealing with acid drainage which, unlike the conventional prior art, does not address the problem by treating the resultant acid, but rather prevents acid formation in a facile and economically viable manner.

SUMMARY OF THE INVENTION

This invention relates to reducing acid drainage in a pyritic material which is exposed to water by controlled addition of at least about 10 ppm of an anionic detergent capable of inhibiting *T. ferrooxidans* to the water which contacts the exposed material by controlled release from a matrix containing anionic detergent dispersed therein. The matrix may be an elastomer and may be comprised of rubber. The matrix may alternatively be a high melting point wax. Controlled addition is accomplished by placement of the matrix to intercept infiltrating water up-gradient of the pyritic material.

The pyritic material which may be treated includes pyritic mine tailings, pyritic coal mines, pyritic coal refuse piles and pyritic construction sites; however, any mass of pyritic material susceptible to acid drainage may be treated in accordance with this invention.

The anionic detergent may be selected from the group consisting of *Thiobacillus ferrooxidans*-inhibiting water soluble salts of (a) alkyl aryl sulfonic acids, (b) alkyl sulfonic acids, (c) alkenyl sulfonic acids, (d) sulfonated alkyls, (e) sulfonated alkenyls, (f) sulfated monoglycerides, (g) sulfated fatter esters. Above a pH of about 2.5, sodium lauryl sulfate is preferable.

This invention relates to a method of reducing acid drainage in a pyritic material which is exposed to water, which method comprises adding at least about 10 mg of an anionic detergent which inhibits the bacterium, *Thiobacillus ferrooxidans* per liter of said water which contacts the exposed material.

Pyritic material at construction sites is predominately associated with clays or shales. Pyritic material is also associated with shale tailings obtained after extraction of hydrocarbonaceous material therefrom. Moreover, coal refuse piles contain substantial quantities of clay and shale fragments. Accordingly the overall treatment to reduce acid drainage should preferably be adapted to provide for saturating adsorption sites or these non-pyritic particles associated with pyritic materials during the initial stage of anionic detergent application. Initial application of anionic detergent to saturate adsorptive sites of adsorbtive compositions associated with the pyritic material can be before, at the time of or after placement of the controlled release matrix. Such initial treatment may precede or follow placement of the matrix by a matter of weeks, although substantially longer periods are also suitable.

The most-preferred embodiment of this invention comprises an initial application of anionic detergent to

saturate the adsorptive capacity of clay particles associated with the pyritic material coupled with addition of anionic detergent by controlled release from a matrix containing said anionic detergent dispersed therein. Specifically, the initial application consists of an anionic detergent applied at concentrations greater than 50 mg per liter of water and typically at least 100 mg per liter of water. Controlled release addition of anionic detergent is effected by controlled release from a matrix containing said anionic detergent dispersed therein. Specifically the addition is effected by placing the matrix containing said anionic detergent dispersed therein to intercept infiltrating water up-gradient of the pyritic material.

The quantity of matrix required to effect controlled release which is placed up-gradient of the pyritic material is represented by Q, determined in accordance with the following formula:

$$Q = \frac{Pa\ I\ A\ C}{Dr\ R} \cdot 10$$

Q = the quantity of detergent-continuing matrix in kg

Pa = the numeral representing the annual average precipitation in area [m]

I = percent infiltration

A = the numeral representing the area to be treated in M^2

Dr = the numeral representing the detergent-release rate for matrix at particle size range to be used, mg detergent/kg matrix year

R = the numeral representing the effective release-life of the matrix in years

C = the numeral representing the optimal average concentration of detergent in mg/l

The percent infiltration, I, is site-specific and generally is estimated at 50% for reclaimed or undisturbed land surfaces and 75% for coal refuse and unreclaimed surface mines.

The annual detergent release rate, Dr, is determined by measuring detergent release under saturated conditions. It is expressed as mg detergent/kg matrix year.

The effective release life of the matrix is dependent on the specific matrix and falls within the range of about 2 to about 5 years.

The optimal average concentration of detergent is generally about 20 to about 25 mg/l for sodium lauryl sulfate and about 20 to about 40 mg/l for the other anionic detergents.

Preferably, the anionic detergent is added in an amount of at least about 25 mg per liter of said water. The matrix is preferably in particulate form with shredded particles of a size of about one inch preferred. Anionic detergents suitable for this invention are (a) alkyl aryl sulfonic acids, (b) alkyl sulfonic acids, (c) alkenyl sulfonic acids, (d) sulfonated alkyls, (e) sulfonated alkenyls, (f) sulfated monoglycerides and (g) sulfated fatty esters. Among the foregoing anionic detergents are the long chain alpha olefin sulfonates; soluble salts of alkenyl sulfonic acid such as the sodium salt of C_{14}–C_{16} alpha olefin sulfonates; water soluble alkenyl aryl sulfonic acid salts; water soluble alkyl aryl sulfonic acid salts such as sodium alkylnaphthalene sulfonate and sodium alkyl benzene sulfonate; water soluble salts of sodium lauryl sulfate; and water soluble salts of sulfated monoglyceride.

The matrix may be an elastomer such as rubber or a high melting point wax or other suitable material capable of slow release of the detergent.

DETAILED DESCRIPTION OF THE INVENTION

One aspect of this invention resides in the discovery that high levels of certain anionic detergents having a long alkyl chain of 6 or more carbon atoms, are effective in reducing or stopping acid drainage from water-exposed pyritic materials. Concentrations of at least about 10 ppm and preferably within the range of from about 10 ppm to about 20 ppm have been found to inhibit bacterial activity of *T. ferrooxidans*, and levels above about 20 ppm kill the bacteria.

An important aspect of this invention relates to the initial application of anionic detergent. The primary purpose of this initial application is to reduce subsequent adsorption of anionic detergent by clay particles up-gradient of the pyritic material by saturating absorptive capacity which would otherwise reduce the effectiveness of the controlled release. A secondary purpose is a rapid reduction in population of *Thiobacillus ferrooxidans* in and up-gradient of the pyritic material.

The amount of anionic detergent required for the initial application depends on the volume of pyritic material, the volume of overlying material and the percent clay content of the overlying material. Preferably, the detergent is applied in a concentration of at least 100 mg/l, in sufficient volume so that each acre-foot of pyritic material is treated with the equivalent of 7 pounds of detergent (ie. 85 gallons of 1% solution, or 1,000 gallons of 850 ppm solution). In practice, the initial application can be estimated in one of two ways:

1. by estimating adsorption from the percent clay and silt present in overlying material. Each foot of silt-clay can be assumed to adsorb approximately 10–15% of the initial application. Strata containing lesser amounts of silt and clay can be assumed to adsorb proportionally lower amounts. Thus, for example, if there was six feet of disturbed strata overlying the pyritic material, of which four feet was primarily fine-grained and two feet was a mixture of fine- and coarse-grained material, an initial application would be calculated by multiplying the required concentration in the pyritic material by the mount adsorbed by the overburden, ie. four feet of fine-grained material will adsorb 40–60%, two feet of mixed material will adsorb 10–15%. Thus a minimum application for the given strata would be approximately three times that required to treat the pyritic material. Thus, for a quarter-acre site containing a foot of potentially acid-forming material and the described overburden, an appropriate initial application estimate would be 5 pounds of detergent (7 pounds of detergent × 0.25 acre-feet × 3) or 1,000 gallons of 600 ppm solution.

2. by application of detergent at concentrations of at least 100 ppm until groundwater samples, taken immediately down-gradient at the pyritic material, foam upon gentle agitation. Monitoring stations should be as near as possible to the pyritic material; it is not desirable nor appropriate to apply detergent until streams in the area are foaming.

Another aspect of this invention resides in the discovery that the potential problem associated with the high solubility of anionic detergents and easy re-establishment of bacteria where anionic detergent is not continuously present, can be overcome by the continuous and controlled release of anionic detergent from a matrix.

Where an elastomeric matrix, e.g. a rubber comprising matrix is employed, preferably the ratio by weight of anionic detergent to elastomer is from about 30 to about 80 parts by weight of anionic detergent per hundred parts by weight matrix.

Examples of suitable controlled release compositions are set forth in the table which follows:

FORMULATIONS CONTROLLED RELEASE ANIONIC SURFACTANT (DIFFUSION - DISSOLUTION) I	
natural rubber	50 parts
thermoplastic styrene butadiene	50 parts
carbon black	10 parts
anionic detergent	10–50 parts
II	III

Still another aspect of my invention resides in my discovery that water soluble alkenyl sulfonates such as alpha olefin sulfonates, and specifically long chain alpha olefin sulfonates, suitably C_{14}–C_{16} admixtures are effective as *Thiobacillus ferrooxidans* inhibitors when dispersed within a slow release matrix. Sodium salts of C_{14}–C_{16} alpha olefin sulfonates are particularly preferred.

I have also discovered that water soluble alkylnaphthalene sulfonates such as "Alkanol" XC, a sodium alkylnaphthalene sulfonate produced by the DuPont Company are very effective as *Thiobacillus ferrooxidans* inhibitors when dispersed within a slow release matrix.

In addition to the foregoing I have further discovered that water soluble sulfated monoglycerides operate in the same manner as the foregoing alkenyl sulfonates and alkylnaphthalene sulfonates.

It is important to add that, although certain groups of anionic detergents have been found to be effective in reducing the acidity of pyritic mine tailings, anionic surfactants such as "Zonyl" fluorosurfactants, sulfated alkyl ethers, and sulfated ethoxylated alkyl phenols are ineffective in the environment associated with mining drainage, the water soluble salts previously related have been found to be effective. Among the suitable anionic detergents are alkyl aryl sulfonates, long chain alcohol sulfates, olefin sulfates and sulfonates, sulfated monoglycerides, sulfated ethers, sulfo-succinates and alkane sulfonates.

The configuration of matrix which has been found most suitable for use in connection with the method of this invention is particulate, of a size generally of about one inch±one half inch with shredded material being most preferred. Such particles because of irregular surface best retain the configuration of the matrix mass and offer maximal surface area.

EXAMPLE

This example illustrates the results of laboratory testing of pyritic overburden materials under simulated field conditions developed for the purpose of laboratory testing.

Sodium lauryl sulfate (SLS), the sodium and calcium salts of linear alkylbenzene sulfonate (ABS) and alpha olefin sulfonate (AOS) were tested as inhibitors. Natural and synthetic rubber formulations and the amide ester of monoethanolamine and stearic acid (a high melting point wax) were tested as release agents.

Pyritic Material Tested

For laboratory testing coal and overburden materials, collected from Clarion, Pa. and averaging 5% total sulfur, were crushed and sieved to a size within the range of from 0.2 to 2.0 cm. The particles were rinsed with deionized, distilled water.

T. ferrooxidans Employed

T. ferrooxidans obtained from the American Type Culture Collection (ATCC #13728), was cultured in 9-K medium.

Composition of Simulated Rainfall

Simulated rainfall infiltration consisted of a synthetic ground water formulation of water containing 50 ppm $CaCO_3$; 25 ppm $MgSO_4$; 2 ppm $(NH_4)_2$ and 0.25 ppm KH_2PO_4.

Apparatus and Procedure

Tubulated desiccators were used to simulate the humid environment of the intermediate belt of the zone of aeration. The experiments were performed in perforated polypropylene beakers, each containing 50 g rinsed crushed sample material. The beakers were positioned so as to drain into slightly larger beakers and the entire double beaker assemblage was autoclaved before being placed on a tray inside the desiccator. Water beneath the tray was heated for about 15 minutes to provide a humid atmosphere. Two 0.5 cm diameter tubes were inserted through the desiccator lid to allow controlled contact with the atmosphere and to simulate rainfall infiltration. To simulate the presence of *T. ferrooxidans* in natural mine infiltration, a 0.1 ml inoculum of the 9-K medium was trickled onto the samples every three days. Immediately following this, 6.0 ml of synthetic groundwater, with varying concentrations of detergent, was applied. Sterile controls received no inoculum.

At the end of each run, the contents of the beakers were filtered and rinsed with 100 ml deionized, distilled water. Approximately 0.5 g of the test material was placed in 9-K culture medium to test for *T. ferrooxidans*. Oxidation of the medium in 3–4 days showed that the bacterium was present and uninhibited. Oxidation which occurred after 6–10 days was interpreted as lowered population density, due to either partial inhibition or bacteriostatic action.

The collected filtrate was analyzed for total dissolved iron by atomic absorption spectrophotometry, and for acidity, by the hot peroxide method (Standard Methods, No. 402 of "Standard Methods for the Examination of Water and Wastewater", 14th ed., A.P.H.A. Washington, D.C. 1976.)

Inhibitory Effects of Anionic Detergents

Referring to FIG. 1, the effect of sodium lauryl sulfate (LSL); linear alkyl benzenesulfonate (ABS), from Witco C-18, 90% active content; linear alkenyl benzene sulfonate (ABS) from Pilot, C_{14}, also 90% active content, and alpha olefin sulfonate (AOS) C_{14}–C_{16}, 88% active content, in reducing acidity and iron concentrations in water contacting pyritic coal particles containing 5% sulfur is shown.

The inhibitory effect was especially marked for sodium lauryl sulfate, which was also the most effective in limiting bacterial population. Samples containing SLS at concentrations increasing from 5 to 20 ppm showed proportionally delayed growth when transferred to 9-K

culture medium. At 25 ppm, SLS was bactericidal, reducing acidity and iron concentrations to about that of sterile controls. The other anionic detergents as will be noted by reference to FIG. 1 required somewhat higher concentrations to obtain the same effects.

The concentration of detergent necessary to inhibit *T. ferrooxidans* in the simulated mine environment was determined to be greater than that required in 9-K culture media. It is possible that the substrate material reduces the vulnerability of the bacteria, that the detergent does not saturate all of the crushed material before draining or that the effectiveness of detergents in synthetic groundwater differs from that in 9-K medium.

TABLE 1

Release of sodium lauryl sulfate from wax (particle size 4–8 mm) under saturated conditions.

Detergent concentration in wax (weight percent)	Length of experiment (days)	Avg. release per g of material (μg/day)
9	1	70
21	1	120
33	1	75
9	30	9
21	30	8
33	30	12

TABLE 2

Composition	Detergent composition in rubber	Particle size (mm)	Avg. release per g of material (μg/day) at pH 4.5
vulcanized natural rubber	14.5% SLS	8–40	4
	14.5% Na-AB	8–40	4
	20% Ca-ABS	8–40	6
	20% SLS	8–40	10
	20% Na-ABS	8–40	12
	26% Ca-ABS	8–40	12
	26% SLS	8–40	30
	31% SLS	8–40	40
	37% SLS	8–40	45
	41% SLS	8–40	40
unvulcanized thermoplastic SBR + natural rubber	27% SLS	8–40	20[a]–50[b]
	27% SLS	4–8	120[a]–150[b]
	27% SLS	42–4	185[c]
sponge rubber	13% SLS	4–8	14

[a]release rates at pH 2.5
[b]release rates at pH 4.5
[c]release rates at pH 2.5 and 4.5 were equal

Inhibitory Effect of Controlled Release of Anionic Detergents in Simulated Field Conditions

Controlled release was investigated in laboratory simulated field conditions as a means of administering anionic detergents with each rainfall over prolonged period to a pyritic coal pile wherein the coal contained 5% sulfur. The rubber-detergent formulations were prepared in a Brabender plasticorder by premixing the non-curing ingredients and adding them with the rubber, followed by the curing ingredients after a minute and a half. The wax matrices were prepared by mixing the detergent into the melted wax with a magnetic stirrer and hot plate. All release materials were rinsed before testing.

The rate of release from 5.0 g each of the below-described wax and rubber formulations was ascertained by measuring detergent concentration when the material was rinsed each week, and alternatively, when it was continuously submerged in distilled, deionized water, adjusted to pH 4.5, and in some cases pH 2.5, with H_2SO_4. Also examined was the effect of particle size on detergent release, using duplicate runs of sieved size fractions of 0.42–4 mm, 4–8 mm and 8–40 mm. In all cases, detergent concentration was determined by the methylene blue method. "Standard Methods for the Examination of Water and Wastewater", 14th ed., A.P.H.A., Washington, D.C. 1976.

The results of anionic detergent release from wax and rubber matrices is indicated below in Tables 1 and 2 respectively.

As will be noted by reference to Table 1, release of the detergents from the wax formulations was initially fast, but decreased rapidly with time. However, formulations containing 33% detergent showed a second rapid-release period after about two months as porosity caused by detergent dissolution led eventually to complete disaggregation. Accordingly, high molecular weight formulations which are formulated for long term utilization should comprise at least about ⅓ anionic detergent.

The diffusion-dissolution of detergent from rubber matrix proceeds at a release rate proportional to the square root of time, until approximately 60% of the active agent has been released, after which the release rate drops off exponentially. Thus, the ideal release rate for a rubber matrix would be one in which 60% depletion coincides approximately with the stability lifespan of the matrix.

The daily average release rate for the vulcanized natural rubber formulations set forth in Table 2 would require in excess of twelve years for 60% release of anionic agent release before breakdown of the rubber.

Assuming as the lifespan of the rubber 2–5 years, in order to obtain an ideal coincidence of depletion and matrix lifespan, the mixture of 50 parts natural rubber to 50 parts thermoplastic styrene butadiene rubber, which can be handled without vulcanization, best approximated the ideal formulation. An average release rate of 50 mg/day per g of matrix was observed in the foregoing formulations.

Inhibitory Effect of Controlled Release of Anionic Detergent Under Field Conditions

The detergent-matrix combination which optimized rate of release and inhibition of *T. ferrooxidans* compris-

ing a matrix of an unvulcanized admixture of SBR and rubber was applied to one of two 25 ton coal refuse piles in central Pennsylvania made available by Barnes and Tucker Coal Co. Each pile sat on a plastic sheet and was graded so as to drain in one direction. A perforated pipe ran through each pile and drained into a collecting bucket, which was emptied after sampling. Seven slabs of unvulcanized admixture, each approximately 0.3 m^2 in areas and totalling 27 kg (of which about 27% was an anionic detergent, sodium lauryl sulfate), were placed beneath the surface of one of the piles in such a manner as to minimize interference with natural infiltration. Samples of the drainage from each pile were analyzed for acidity, total dissolved iron, ferrous iron, detergent concentration and population of *T. ferrooxidans* by most probable number ("Standard Methods for the Examination of Water and Wastewater", 14th ed., A.P.H.A., Washington, D.C. 1976.)

The amount of anionic detergent containing matrix necessary for the coal refuse pile was determined from the average laboratory release rate, the horizontal area of the pile (16 m^2) and the average annual rainfall for the area (approximately 100 cm), as heretofor more fully explained. The actual concentration of dissolved detergent dependant on the time interval between rainstorms and the quantity of rainfall and is, therefore, not precisely calculable. It is generally necessary that detergent concentration exceed 10 ppm, preferably 15 ppm and occasionally 25 ppm to prevent bacterial repopulation; therefore, it is preferable to exceed rather than fail to reach the minimal detergent concentration required.

After about 100 days acidity and iron values for the treated pile were less than 1/80 times those observed in the drainage from the control pile. However, detergent concentration was lower than anticipated (approximately 10 ppm) due to the low surface area of the rubber, causing a second rise in acidity, which eventually resulted in acidity ½ the level of the control pile.

The same detergent-rubber combination was field tested on acid-producing overburden material using a pair of leaching tubs at a site in northern West Virginia. The tubs were buried to ground level in pyritic shale and enclosed approximately 0.3 m^2 of the material. One tub was treated with approximately 1.5 kg of the unvulcanized SLS-rubber in pieces approximately 30 cm^2 in area; the other was left untreated as a control. Drainage was collected via tubing leading from the bottom of each, and was analyzed for acidity, total dissolved iron, ferrous iron, detergent concentration and presence or absence of *T. ferrooxidans*.

The West Virginia field test tested the effect of controlled release of anionic detergent on acid production in an abandoned surface mine. Abandoned coal mines produce over three-fourths of the acid drainage of Appalachia. Sufficient rubber was applied to generate an anticipated detergent concentration of at least 25 ppm, assuming a release rate under acid conditions of 20 mg/day per g of matrix. Two weeks after application of the rubber, approximately 250 milliliters of 30% detergent solution was mixed with 1,000 milliliters of water and added to the section treated with the detergent releasing rubber matrix. This application was adopted to saturate the adsorptive sites which were present in the oberburden clays associated with the residual pyritic materials of the abandoned surface mine area where the rubber matrix was applied. The rubber was added to the more acid-producing section and generated a detergent concentration which ranged from 10 to 60 ppm in the drainage (the latter after the winter freeze). *T. ferrooxidans* was observed in the drainage from the untreated control throughout the duration of the experiment. However, it was only present in drainage for three weeks after treatment with the controlled release material and the aqueous diluted detergent solution.

Acidity before treatment averaged approximately 30,000 mg/l (as $CaCO_3$) with a pH of 2.1. Two months after treatment, significant decrease in acidity was observed with 95% reduction after six months. Nine months after treatment, pH of the drainage from the treated section was 6.86 with only 25 mg/l acidity as compared to pH in the control section of 2.0 and acidity of 28,250 mg/l.

It should be pointed out that the effect of particle size on the rate of detergent release has been discovered to be a viable method of obtaining optimal release rate. Table 2 includes release rates for unvulcanized rubber of various size ranges, the finest-grained of which was a coarse powder (between sieve sizes 5 and 40) that gave an average release of 185 mg/day per g of rubber. This would give an expected release life of 2.5 years before 60% depletion, which is a reasonable estimate of the stable lifespan of the buried rubber. At this rate, again assuming an average annual rainfall of 100 cm and a desired detergent concentration of 25 ppm, 37 kilograms would treat a hectare of coal refuse at a cost of $50–75 ($20–30/acre) per year.

It will be obvious that modifications to this process may be made and it is intended to cover such modifications and changes as would occur to one skilled in the art, as the following claims permit and consistent with the prior art.

What I claim is:

1. A method of reducing acid drainage in a pyritic material which is exposed to water, which method comprises:

(1) treating each acre-foot of pyritic material with at least seven pounds of a first anionic detergent which inhibits the bacterium *Thiobacillus ferrooxidans*; and

(2) adding at least 10 mg of a second anionic detergent which inhibits the bacterium *Thiobacillus ferrooxidans* per liter of said water which contacts the exposed material, said addition being effected by controlled release from a matrix containing said second anionic detergent dispersed therein; said first and second anionic detergent being selected from the group consisting of *Thiobacillus ferrooxidans*-inhibiting water soluble salts of (a) alkyl aryl sulfonic acids, (b) alkyl sulfonic acids, (c) alkenyl sulfonic acids, (d) sulfated fatty esters.

2. The method of claim 1 wherein the first and second anionic agents are the same.

3. The method of claim 1 wherein said addition is effected by placing the matrix containing said second anionic detergent dispersed therein to intercept infiltrating water up-gradient of the pyritic material.

4. The method of claim 3 wherein the quantity of matrix placed up-gradient of the pyritic material is represented by Q, determined in accordance with the following formula:

$$Q = \frac{P_s I_a C}{D_r R} \times 10$$

Where:

A = the quantity of detergent-continuing matrix in kg

Pa = the numeral representing the annual average precipitation in area in m

I = percent infiltration

A = the numeral representing the area to be treated in m^2

Dr = the numeral representing the detergent-release rate for matrix at particle size range to be used, mg detergent/kg matrix year

R = the numeral representing the effective release-life of the matrix in years

C = the numeral representing the optimal average concentration of detergent in mg/l.

5. The method of claims 1 or 3 wherein the anionic detergent is added in an amount of at least about 25 mg per liter of said water.

6. The method of claim 4 wherein said matrix is in particulate form.

7. The method of claim 6 wherein said particles are shredded particles.

8. The method of claim 4 wherein the anionic detergent is a long chain alpha olefin sulfonate.

9. The method of claim 4 wherein the water-soluble salt of alkenyl sulfonic acid is a sodium salt of C_{14}-C_{16} alpha olefin sulfonates.

10. The method of claim 4 wherein the anionic detergent is a water soluble alkyl aryl sulfonic acid salt.

11. The method of claim 4 wherein the water soluble alkyl aryl sulfonic acid salt is a sodium alkylnaphthalene sulfonate.

12. The method of claim 4 wherein the water soluble alkyl aryl sulfonic acid is sodium alkyl benzene sulfonate.

13. The method of claims 4 wherein the water soluble salt is sodium lauryl sulfate.

14. The method of claim 4 wherein the water soluble salt is a sulfated monoglyceride.

15. The method of claims 1, 3 or 4 wherein the matrix is an elastomer.

16. The method of claim 15 wherein the elastomer comprises rubber.

17. The method of claim 16 wherein the matrix is a high melting point wax.

* * * * *

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Full-Scale Field Trials of a Bactericidal Treatment to Control Acid Mine Drainage

by

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Abstract. Sodium lauryl sulfate (SLS) is one of several anionic detergents known to be effective in inhibiting the iron-oxidizing bacterium, Thiobacillus ferrooxidans. Since T. ferrooxidans plays a critical role in determining the rate of pyrite oxidation, the Bureau of Mines has investigated the use of SLS as a method to control the formation of acid mine drainage. In previously reported pilot-scale tests, the detergent successfully controlled T. ferrooxidans and thereby reduced acid production 60-90 pct. During the past year, the Bureau of Mines has conducted five full-scale field trials at active and abandoned surface mines and coal refuse piles.

The first of these field tests was at a ten acre inactive refuse pile near Beckley, West Virginia. After a three month lag period, average acidity decreased from 900 mg/l to 350 mg/l and iron decreased from over 100 mg/l to 2 mg/l. An eight acre active section of a large refuse pile was treated similarly; acidity and sulfate decreased from over 4,000 mg/l to less than 100 mg/l and iron decreased from 1,000 mg/l to 2 mg/l or less. At both sites, a single application was effective for about 4 months.

Our other field tests have been at active and abandoned surface mines in Ohio and West Virginia. At two of the sites, SLS was applied both as a solution and in slow release rubber pellets; the latter are an attempt to provide long term control of acid drainage from inactive sites where periodic reapplication would not be feasible.

Introduction

The exposure and subsequent oxidation of sulfide minerals, causes the acidic drainage associated with many coal mines and refuse piles. To meet state and federal discharge regulations, mining companies spend millions of dollars annually to treat acid water. The Bureau of Mines has investigated possible methods of reducing these costs by controlling the rate of oxidation of pyrite, thereby eliminating the acid at its source.

The kinetics of acid formation are dependent on the availability of oxygen, the surface area of pyrite exposed, the activity of iron-oxidizing bacteria and the chemical characteristics of the influent water. Thiobacillus ferrooxidans is the principal iron-oxidizing bacterium involved in determining the rate of pyrite oxidation[1-2]. Acidification progresses in a three-stage sequence dependent upon the activity of T. ferrooxidans and solution Eh and pH[3]. One potential method of slowing pyrite oxidation is by inhibition of T. ferrooxidans. Certain anionic surfactants (cleansing detergents) can be used to kill T. ferrooxidans at low pH in an economical and environmentally safe manner, thus reducing acid formation[4-6].

Background Information

T. ferrooxidans actually accelerates pyrite oxidation by two mechanisms: by direct oxidation and by oxidizing Fe^{2+} to Fe^{3+}, which in turn oxidizes the sulfide minerals[5-10]. Direct oxidation is probably most important during initial acidification, when hydrolysis of Fe^{3+} is too rapid to allow significant ferric oxidation of pyrite.

During the initial stage of this process, fine-grained pyrite is oxidized either by T. ferrooxidans or by air with equal amounts of acidity produced by the oxidation of sulfide to sulfate (reaction 1) and by the oxidation and hydrolysis of Fe^{2+} (reaction 2). The ability of T. ferrooxidans to accelerate the rate of pH decline is important, for each rainfall potentially interferes with the initial buildup of acid. During this stage, it is possible to forestall acidification by adding alkalinity to the reaction system[3]; if alkalinity exceeds acidity, the only major downstream effect is an increase in sulfate concentration. Thus, the addition of lime, soda ash or other sources of alkalinity to freshly exposed pyritic material can stop or postpone acidification. Once acidity significantly exceeds alkalinity, it

becomes much more difficult to return the acid-producing system to stage 1.

$$FeS_2 + \frac{7}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + \frac{5}{2} H_2O + \frac{1}{4} O_2 \longrightarrow Fe(OH)_3(s) + 2H^+ \quad (2)$$

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ \longrightarrow Fe^{3+} + \frac{1}{2} H_2O \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{3+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

As decreasing pH causes abiotic oxidation of Fe^{2+} to proceed slowly, T. ferrooxidans takes on its primary role of oxidizing Fe^{2+}, thereby allowing reaction 2 to continue producing acidity and ferric hydroxide. This initiates the second stage of the reaction process. Once again it is possible for the pH to stabilize in this stage, though this will usually occur only when permeability of the spoil is low or the amount of exposed pyrite surface area is small. Otherwise, the pH decline continues to the third stage, where acid is produced in a biologically mediated cycle of reactions 3 and 4[3].

As acidification proceeds and the pH in the immediate vicinity of the pyrite falls to less than 3, the increased solubility of iron results in increased Fe^{3+} activity[11]. At an interstitial pH of approximately 2.5 (corresponding to a drainage pH of 3.5 to 4.0), bacterial oxidation of Fe^{2+} and reduction of Fe^{3+} by the pyrite (reactions 3 and 4) combine to cause an exponential increase in acidity and iron concentrations, as can be seen in figure 1. Eliminating the bacteria halts this third stage and thus reduces acid production by at least 75 pct[3].

The biological literature contains numerous laboratory inhibition studies of T. ferrooxidans conducted in an attempt to understand the unusual

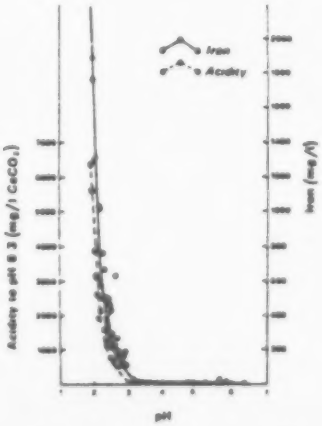

Figure 1. Acidity and total dissolved iron vs. pH for a series of experiments conducted in laboratory simulations of a coal refuse pile.

biochemistry of its metabolism. These demonstrated the vulnerability of T. ferrooxidans to certain metals, organic acids and anionic surfactants[4, 12-15]. After eliminating substances that were environmentally unsafe or too expensive for large-scale use, we decided to test anionic surfactants.

Although T. ferrooxidans lives in acid water, its internal pH is approximately neutral. The anionic surfactants alter the semipermeable properties of the cytoplasmic membrane, allowing seepage of the acid water into the cell[16-24]. These surfactants, used as cleansers in laundry detergent and shampoos, kill T. ferrooxidans in culture medium at concentrations as low as 2-5 mg/l, and in coal refuse at concentrations of 25-50 mg/l[4, 25-26].

To avoid substituting one environmental problem for another, the consequences of using anionic detergents to reduce acid formation must be considered. The chronic and acute effects of anionic detergents on fish[27-28] and aquatic invertebrates[29] have been examined, with kidney damage observed after long exposure to low levels (2-15 mg/l) of detergent, and acute toxicity observed in some species at concentrations as varied as 0.6 - 40 mg/l. The World Health Organization recommends that stream concentrations not exceed 1.0 mg/l; other regulatory groups have recommended even lower values (e.g., Pennsylvania's Department of Environmental Resources, 0.25 mg/l).

Application Rates

To be effective in the field, surfactant must reach the reactive pyritic material. At a surface mine, excess surfactant must be applied to compensate for that which will be absorbed by non-pyritic overburden material. A refuse pile is somewhat to treat because surfactant can be applied directly to the pyritic material and because most acid production occurs near the surface of the pile, due to the presence of a fine-grained oxygen diffusion barrier[30]. Sufficient surfactant must be applied to treat this near-surface layer.

A simple laboratory procedure has been developed to provide an estimate of adsorption potential for overburden and coal refuse. A representative sample of the material to be treated is placed in a large, tared Buchner funnel, tamped to a uniform depth of two inches, and weighed. A surfactant, such as sodium lauryl sulfate (SLS), is applied evenly over the material at approximate loads of 60 mg of SLS per kg of coal refuse or 30 mg of SLS per kg of overburden and subsoil. Typical solution concentrations range from 300 to 30,000 mg SLS/l, depending on the anticipated infiltration rate at the site.

After SLS application, the top section of a second funnel is fitted onto the packed funnel to allow even distribution of a distilled water rinse. The rinse solution is continuously applied through plastic tubing from a distilled water reservoir. The height of the reservoir is adjusted to balance influent and effluent volumes; in relatively impermeable samples inundation is unavoidable and effluent flow rates can be as slow as 100 ml/hr. Rinse solution is collected in 100 ml fractions until no sudsing is observed on shaking.

The stock SLS solution and rinse fractions are analyzed for anionic surfactants by the methylene blue technique or a comparable standard method[31]. Adsorption is calculated as the difference between the mass of SLS applied and that eluted, and is recorded as mg of SLS adsorbed per kg sample. Alter-

natively, adsorption can be reported as lb SLS/acre-inch, calculated from the known funnel area and sample thickness.

The laboratory test provides a relative measure of adsorption capacity, since field conditions are not duplicated. On coal refuse, we base our application rate on the adsorptive capacity of the top 1 foot, knowing that the most active zone of oxidation is typically shallow and that surfactant, at reduced concentrations, will penetrate beyond this surface layer. We have been admittedly conservative rather than risk significant surfactant concentrations in the effluent; we will, in the future, be testing the effect of higher dosage rates.

If pyritic overburden is treated while exposed, application rates can be based on the adsorptive capacity of the material. However, if inert material has already been placed over the pyritic material, higher dosage rates must be applied to ensure that sufficient surfactant penetrates to the pyrite. To avoid surfactant runoff, areal application should not be attempted at sites where a clay blanket or compaction severely limit permeability; in addition, surfactants should only be applied during dry weather.

Field Tests

Based on laboratory results, it was apparent that anionic surfactants had the potential to slow down pyrite oxidation by inhibition of T. ferrooxidans. However, the possibility of repopulation remained. The required frequency of reapplication and the extent to which water treatment costs could be lowered would be the key factors in determining cost-effectiveness. Full-scale field tests were started in Fall, 1981 to answer these questions.

The first site chosen was a ten-acre inactive coal refuse pile in Raleigh County, WV. The pile was formed of Beckley seam refuse during the late nineteenth century by dumping from an aerial tramway. It is long and narrow and approximately 130 ft high at its crest. Drainage from the pile is currently being treated, at a cost of about $7,500 a month by Westmoreland Coal Company, which operates the nearby mine and preparation plant. Quality of the drainage from the pile has been monitored by Westmoreland for over a decade, thus providing a good baseline against which the effectiveness of the method could be judged.

The second field site selected was an active coal refuse pile in Preston County, WV. The pile consists primarily of Freeport seam refuse, from a preparation plant operated by Kingwood Mining Company. Inactive sections of the refuse pile are downgradient of the 8-acre active section and are revegetated; treatment of the drainage from the entire refuse area costs Kingwood Mining about $1,000 a month.

One problem with the Kingwood refuse site was the lack of background data for just the active section being treated. A channel was therefore constructed by Kingwood Mining to collect surface runoff from much of the treated area, thus providing some indication of whether the application of the surfactant improved water quality.

Coal refuse from both sites had an adsorption capacity of about 45 mg SLS/kg of material. This is equivalent to 154 lbs of SLS/acre-ft, or 1 drum (55 gallons) of 30% SLS solution per acre; a drum costs about $200. Both sites were treated by hydroseeder. At Westmoreland, the SLS was diluted approximately 500:1; at Kingwood, a shortage of good quality water resulted in using a dilution ratio of only 50:1. The Westmoreland site was treated in late September; the Kingwood site in early October. Water samples were collected at least once a week thereafter and routinely analyzed for sulfate, acidity, pH, iron and anionic surfactants.

At the active (Preston County) site, water quality improved dramatically within a month of the SLS application. Acidity, sulfate and iron were reduced by more than 95 pct and remained low for about four months after treatment (figure 2). A

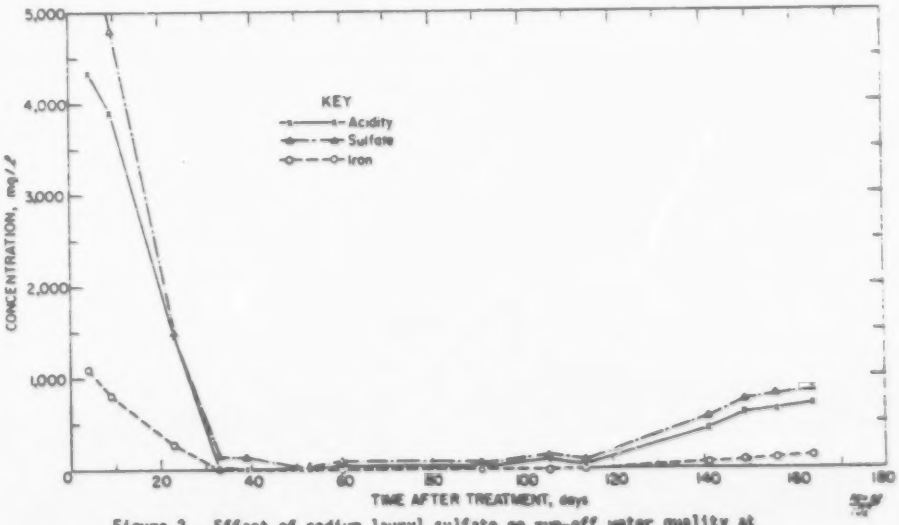

Figure 2. Effect of sodium lauryl sulfate on run-off water quality at an 8-acre active coal refuse pile in northern West Virginia.

complicating factor at the site is untreated material which was added during that interval; it is impossible to separate out the effects of the acidification of the new refuse from the diminishing effects of the SLS.

Water quality at the inactive (Raleigh County) site improved after a three month lag period, with a 60% decrease in acidity, sulfate and manganese and a 90% decrease in iron (figures 3-6). The lag period was presumably caused by the time required for infiltration to flow through the old pile, but stored acidity (sulfate salts) in the system may also have been a factor. The obvious correlation between sulfate, acidity and manganese indicates that as acid production was reduced, leaching of trace metals such as manganese also decreased. The disproportionately greater decrease in iron appears to indicate that at least some of the refuse reached a pH high enough to precipitate ferric hydroxide within the pile.

Effluent concentrations of surfactant have been extremely low at both sites. Except for one measurement of 0.6 mg/l shortly after application of the SLS to the inactive pile, SLS concentrations have been consistently less than 0.1 mg/l; no SLS has been detected in the stream at the discharge point of either treatment plant.

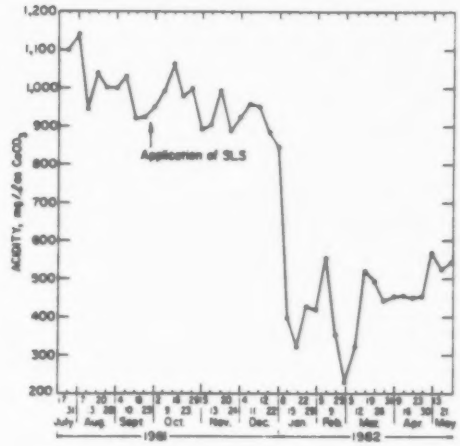

Figure 3. Effect of sodium lauryl sulfate on acidity of drainage from a 10-acre inactive coal refuse pile in southern West Virginia.

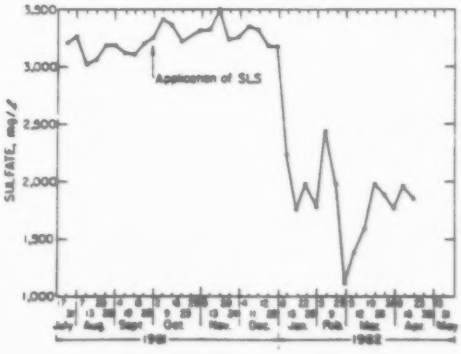

Figure 4. Effect of sodium lauryl sulfate on sulfate concentrations at the southern West Virginia site.

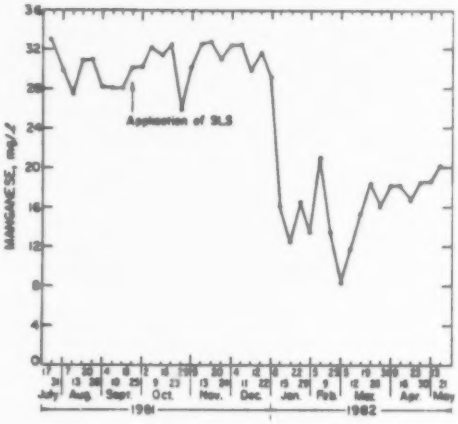

Figure 5. Effect of sodium lauryl sulfate on manganese concentrations at the southern West Virginia site.

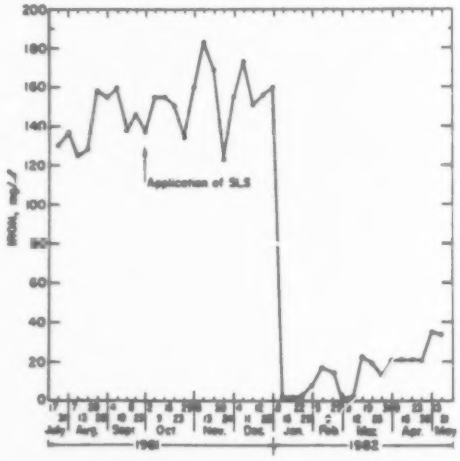

Figure 6. Effect of sodium lauryl sulfate on iron concentrations at the southern West Virginia site.

The surfactant treatment can also be used as a preventive measure. For the past three years, Barnes and Tucker Coal Co. has been applying SLS to an active refuse area using a road watering truck three times a year. The drainage from the area still shows a net alkalinity although their refuse piles generally become acid-producing within six months. Another company in central West Virginia is applying an anionic surfactant to their coal refuse as it leaves the preparation plant. A soil and vegetative cover will be placed on the refuse as soon as the pile is complete, and will, they hope, eliminate the necessity of retreatment.

However dramatic the results, field tests such as those described above are subject to external influence. We have therefore recently initiated several full-scale field tests in which experimental control is provided by a nearby hydrologically isolated, untreated area.

We have treated: one of two adjoining 30-acre surface mines in Preston County, WV; one of two adjoining coal refuse areas, containing refuse from the same preparation plant, in Monongalia County, WV; and one of two piles in a single refuse area in Marion County, WV. The results from some or all of these tests will be available for presentation at the conference.

Although active operations can be easily retreated as necessary, abandoned mined lands require a long-term solution. We have developed SLS-natural rubber compositions which slowly release SLS over time. The SLS is washed from the surface of the rubber whenever it is wet, with internal solution pressure causing migration of the surfactant through the elastic medium to the surface[32]. Ideally, surfactant release should last at least five years, to provide sufficient time for re-establishment of normal soil biota.

We have previously reported the results of pilot-scale tests in Pennsylvania and West Virginia[33]. A full-scale field test was initiated in July 1981 in eastern Ohio on a well-studied inactive surface mine. The area was mined between 1968 and 1970, exposing a pyritiferous sandstone overburden in a series of ridges and valleys. One 12 acre section, with a known flow-through time of 15-18 months[34] was treated by seeder with approximately 18 gallons of 30% SLS solution per acre and 1,500 lbs of SLS-impregnated rubber pellets. The effect of the treatment should be observed during Fall, 1982 and will be reported at the conference.

A second field test is currently underway at an active mine site in Upshur County, WV. An isolated 15-acre ridge has been divided into three sections in such a way that the drainage from each area can be monitored. The operator is using state-of-the-art reclamation practices, including the use of an inert pad, application of alkaline material to the pyritic overburden and the covering of the pyritic material with clayey soil, more inert material and topsoil. One section will be treated with the SLS-impregnated rubber pellets, at a rate of about 400 lbs/acre, and SLS solution at a rate of 55 gallons/acre. A second section will be treated with just the SLS solution, the third section will provide experimental control.

As mentioned in an earlier paper[32], we are attempting to optimize release characteristics of the rubber to provide low-cost long-term treatment. We are currently testing a new formulation developed by B. F. Goodrich which contains over twice as much SLS as rubber; if release lifetime is not adversely affected by the loading, a product may be commercially available by early 1983.

Summary

Application of an anionic surfactant to active and abandoned coal refuse areas reduced acid drainage 60-95 pct by inhibiting the bacterium, Thiobacillus ferrooxidans. Parallel decreases in sulfate and acidity confirmed that the actual acid formation mechanism was affected. Due to reduced acid dissolution, trace metal concentrations also fell concordantly. Iron concentrations decreased disproportionally, indicating that precipitation of iron hydroxide is probably occurring with the refuse piles.

Additional field tests are in progress to evaluate the applicability of the method to active and abandoned surface mines and the possibility of long-term control of acid production by slow release of the anionic surfactant from an elastomer.

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Report of Investigations 8847

Control of Acid Drainage From Coal Refuse Using Anionic Surfactants

By Robert L. P. Kleinmann and Patricia M. Erickson

ABSTRACT

To control the formation of acid drainage at its source, the Bureau of Mines has investigated the role of iron-oxidizing bacteria in the oxidation of pyrite. In laboratory tests, it was determined that Thiobacillus ferrooxidans could be controlled in coal refuse using anionic surfactants, with an associated decrease in acid production of about 75 pct. Based on these results, large-scale tests were conducted at an 8-acre active coal refuse area in northern West Virginia and an 11-acre inactive refuse pile in southern West Virginia. Acid production was decreased 60 to 95 pct for 4 to 5 months after application of 55 gal/acre of 30-pct sodium lauryl sulfate solution. To date, effluent surfactant concentrations have been extremely low.

Either a hydroseeder or a road-watering truck can be used to apply the surfactant. Since the surfactant solution must reach the pyritic material to be effective, sites that have been reclaimed are generally not amenable to these procedures. A simple laboratory test is described that provides an estimate of adsorption potential; this can be used to calculate a safe application rate.

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INTRODUCTION

The exposure and subsequent oxidation of iron sulfide minerals causes the acidic drainage associated with many coal mines and refuse piles. To meet State and Federal discharge regulations, mining companies spend millions of dollars annually to treat acid water. The Bureau of Mines has investigated possible methods of lowering these costs by slowing the rate of pyrite oxidation, thereby controlling the problem at its source.

The kinetics of acid formation are dependent on the availability of oxygen, the surface area of pyrite exposed, the activity of iron-oxidizing bacteria, and the chemical characteristics of the influent water. Thiobacillus ferrooxidans is the principal iron-oxidizing bacterium involved in pyrite oxidation (29, 35).[3] Acidification progresses in a three-stage sequence dependent upon the activity of T. ferrooxidans and solution Eh and pH (30).

One potential method of slowing pyrite oxidation is by inhibition of T. ferrooxidans. Certain anionic surfactants (cleansing detergents) can be used to kill T. ferrooxidans at low pH (13, 30) in an economical and environmentally safe manner, thus reducing acid formation. This report presents the results of treating coal refuse with an anionic surfactant. It also includes a procedural guide for determining if the surfactant treatment is appropriate for a specific site and a method of calculating application rates. Future reports will discuss the treatment of pyritic mine spoil and incorporation of the surfactant into slow-release formulations for long-term control of the problem.

ACKNOWLEDGMENT

The laboratory work described on pages 4-5 was conducted by R. Kleinmann as part of his graduate studies at Princeton University. The financial support contributed by Princeton University, technical assistance provided by E. Mohring, graduate student, University of Minnesota, and geochemical advice provided by D. Crerar, associate professor, during that period are gratefully acknowledged. We also thank Westmoreland Coal Co., Raleigh County, WV, and Kingwood Mining Co., Preston County, WV, for their cooperation.

BACKGROUND INFORMATION

THE PYRITE OXIDATION SYSTEM

The possible involvement of bacteria in the formation of acid drainage was first reported in 1919 by Parr and Powell, who determined that coal inoculated with an unsterilized ferrous sulfate solution produced drainage with higher concentrations of sulfate than did sterile controls (37). The isolation of the bacteria responsible did not take place until 1947 (10-11), at which time it was proposed that Thiobacillus thiooxidans accelerated pyrite oxidation, whereas T. ferrooxidans (47) merely accelerated iron oxidation. Later studies revealed that T. ferrooxidans could also significantly accelerate pyrite oxidation (48) and that in fact T. thiooxidans could not (35). Other bacteria similar to T. ferrooxidans and capable of accelerating pyrite oxidations were isolated and named Ferrobacillus ferrooxidans (36) and Ferrobacillus sulfooxidans (26). However, these were later judged to be strains of T. ferrooxidans (9, 51).

T. ferrooxidans actually accelerates pyrite oxidation by two mechanisms: by direct oxidation and by oxidizing Fe^{2+} to Fe^{3+}, which in turn oxidizes the sulfide minerals (6, 15, 21, 43). Direct

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

bacterial oxidation of pyrite is generally slower than the indirect process (52), although some strains and adapted cultures display the opposite tendency (18). Direct oxidation is probably most important during initial acidification, when complete hydrolysis of Fe^{3+} and the resultant precipitation of $Fe(OH)_3$ are too rapid to allow ferric iron to act as an important oxidant.

During the first stage of this process, fine-grained pyrite is oxidized either by T. ferrooxidans or by air with equal amounts of acidity produced by the oxidation of sulfide to sulfate (reaction A) and by the oxidation and hydrolysis of iron (reaction B) (5):

$$FeS_2 + \frac{7}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+; \quad (A)$$

$$Fe^{2+} + \frac{5}{2} H_2O + \frac{1}{4} O_2 \longrightarrow Fe(OH)_3(s) + 2H^+. \quad (B)$$

The ability of T. ferrooxidans to accelerate the rate of pH decline is important, for each rainfall potentially interferes with the initial buildup of acid. As long as alkalinity exceeds acidity, the only major downstream effect is an increase in sulfate concentration. Once acidity significantly exceeds alkalinity, it becomes difficult to return the acid-producing system to stage 1.

As the pH decreases, abiotic oxidation of Fe^{2+} slows down dramatically, according to the rate law:

$$\frac{-d\,(Fe^{2+})}{dt} = k\,\frac{(O_2\,(aq))\,(Fe^{2+})}{(H^+)^2}, \quad (1)$$

where (Fe^{2+}), $(O_2\,(aq))$, and (H^+) are activities, k is the rate constant, and t is time (46).

As the abiotic rate decreases, T. ferrooxidans assumes its primary role of oxidizing Fe^{2+}, thereby allowing reaction B to continue producing acidity and ferric hydroxide. Although the reaction stoichiometry remains the same, this step is defined herein as a transition point from the primarily abiotic stage 1 to the bacterial catalysis-controlled stage 2. Eliminate T. ferrooxidans and the pyritic system will stabilize. Otherwise, the pH decline typically continues to stage 3, where the reaction chemistry changes to a biologically mediated cycle of reactions C and D (30, 48):

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ \longrightarrow Fe^{3+} + \frac{1}{2} H_2O; \quad (C)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+. \quad (D)$$

As acidification proceeds and the pH in the immediate vicinity of the pyrite falls to less than 3, the increased solubility of iron and the decreased rate of $Fe(OH)_3$ precipitation result in increased Fe^{3+} activity (43). At an interstitial pH of approximately 2.5 (corresponding to a drainage pH of 3.5 to 4.0), bacterial oxidation of Fe^{2+} and reduction of Fe^{3+} by the pyrite (reactions C and D) combine to cause a dramatic increase in acidity and iron concentrations, as can be seen in figure 1. Eliminating the bacteria halts this third stage and thus reduces acid production.

The possibility of reducing acid drainage by bacterial inhibition was first considered in 1953 but was rejected as impractical due to probable rapid repopulation (34). Later attempts to inhibit T. ferrooxidans in the field or in large-scale laboratory experiments were unsuccessful (5, 42), which supported this viewpoint. Despite the results of these early attempts, it was felt that the crucial role played by T. ferrooxidans in pyrite oxidation warranted a reexamination of the potential use of bactericidal methods in mining environments.

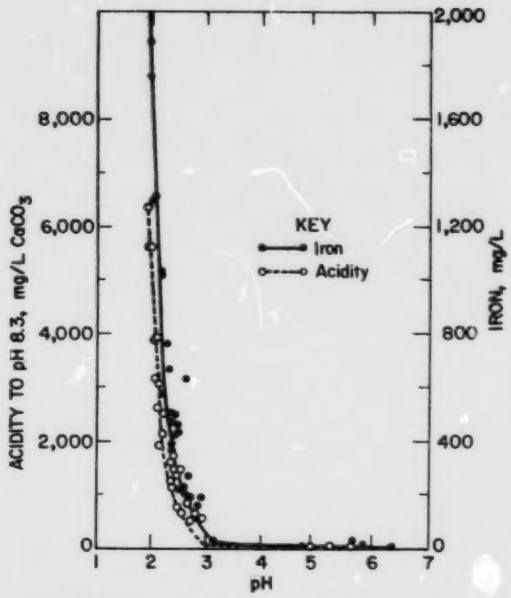

FIGURE 1. - Acidity and total dissolved iron versus pH for a series of experiments conducted in laboratory simulations of a coal refuse pile (28).

The biological literature contains numerous laboratory inhibition studies of T. ferrooxidans conducted in attempts to understand the unusual biochemistry of its metabolism. These studies demonstrated the vulnerability of T. ferrooxidans to certain metals (such as mercury, tellurium, and molybdenum), organic acids, and some anionic surfactants (13, 25, 41, 49-50). After eliminating substances that were environmentally unsafe or too expensive for large-scale use, it was decided to test anionic surfactants. These surfactants, used as cleansers in laundry detergent and shampoos, fill T. ferrooxidans in culture medium at concentrations as low as 2 to 5 mg/L (13-14, 28).

INHIBITORY EFFECTS OF ANIONIC SURFACTANTS

Anionic surfactants are generally regarded as good cleansers but poor bactericides (54). However, it has been shown that their ability to inhibit bacterial activity increases markedly at low pH (16). The various means by which surfactants affect microorganisms have been summarized by Hugo (24), who concluded that alteration of the semipermeable properties of the cytoplasmic membrane is the most typical mode of inhibitory action. This view is supported by demonstrated disaggregation of cell walls of other bacteria by the interaction of sodium lauryl sulfate (SLS) with the lipid, lipoprotein, and lipopolysaccharide fractions of the cell wall (40). T. ferrooxidans possesses a multilayered cell wall, which allows it to maintain an approximately neutral internal pH despite the extremely acid environment in which it lives (3, 7, 12, 23, 33). At low concentrations, it appears that anionic surfactants induce seepage of H^+ into the cell, which slows Fe^{2+} oxidation by decreasing the activity of pH-sensitive enzymes. Higher concentrations of the surfactant kill the bacteria, presumably by causing permanent damage to these enzymes and the membrane material (13, 22, 28, 38).

LABORATORY TESTS

Inhibitory effects of anionic surfactants were monitored in the laboratory under humid conditions simulating the intermediate belt of the zone of aeration as described in Kleinmann and Crerar (29), using 50-g samples of crushed, rinsed, and sterilized high-sulfur coal. To simulate the presence of T. ferrooxidans in natural mine infiltration, a 0.1-mL inoculum of a pure culture of the bacteria, in 9K medium (44), was trickled onto the samples every 3 days. Immediately following this, 0.6 mL of water with varying concentrations of surfactant was applied. Sterile controls received no inoculum.

Figure 2 shows the effect of four of the anionic detergents on acidity and dissolved iron. The inhibitory effect was especially marked for SLS, which was also the most effective in limiting bacterial population. Samples containing SLS at concentrations from 5 to 20 ppm showed proportionally delayed growth when transferred to 9K culture medium; at 25 ppm SLS was bactericidal, with acidity and iron concentrations reduced to about those of sterile controls. Other anionic detergents required somewhat higher concentrations to obtain the same effects (fig. 2). Generally, about 10 times more surfactant was required to kill T. ferrooxidans in coal refuse than in 9K culture media (28).

Possible inhibition of inorganic pyrite oxidation by anionic detergents was also investigated (28). Table 1 presents the results of a 22-day experiment using the crushed, sterilized pyritic coal refuse and SLS concentrations up to 50 mg/L applied at 5-day intervals. In addition, one experimental pair received 50 mg/L $FeCl_3$ with each application, as a test for inhibition of ferric oxidation of pyrite. At the end of the experiment, the coal was filtered and rinsed with 100 mL of deionized, distilled water. Acidity and iron analysis of the filtrate and the drainage collected during the experiment indicated that the SLS did not significantly affect direct (air) oxidation or abiotic ferric oxidation of pyrite.

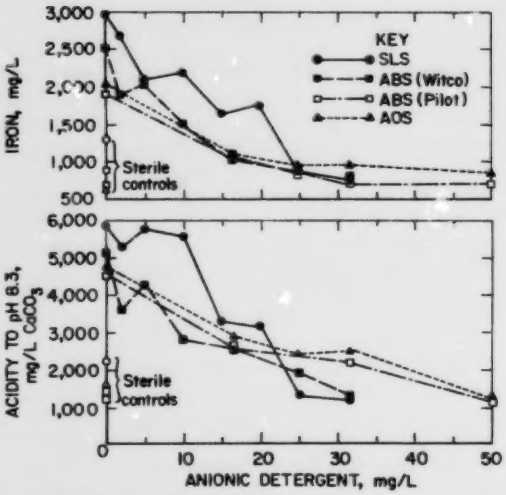

FIGURE 2. - Effect of anionic detergents on acid production from pyritic coal. SLS = sodium lauryl sulfate, ABS = alkyl benzene sulfonate, AOS = alpha olefin sulfonate (28).

TABLE 1. - Effects of sodium lauryl sulfate on crushed sterilized pyritic coal in a laboratory simulation of the intermediate belt of the zone of aeration

Composition of each rainfall infiltration, mL			SLS concentration, mg/L	Acidity to pH 8.3, $CaCO_3$ as mg/L	Total iron, mg/L
GW[1]	SLS[2]	$FeCl_3$[2]			
6	0	0	0	2,380	695
6	0	0	0	2,280	800
3	0	3	0	3,375	765
5	1	0	16.7	2,280	741
4.5	1.5	0	25	2,630	604
4	2	0	33	2,000	645
3	3	0	50	2,875	820
0	3	3	50	3,420	735

[1]Synthetic groundwater (53).
[2]Concentration = 100 mg/L.

FIELD TESTS

INITIAL CONSIDERATIONS

Laboratory and pilot-scale tests (28-30) indicated that anionic surfactants had the potential to slow down pyrite oxidation by inhibiting T. ferrooxidans. Full-scale tests were needed to determine the effectiveness of the method under field conditions. Of particular interest were the degree to which water quality could be improved and the application frequency needed to control pyrite oxidation.

An immediate problem was determining an application rate for the field sites. Application at the inhibitory concentration determined in the laboratory (25 mg/L SLS) was clearly too low: Infiltration from the next rainfall would dilute the surfactant and allow repopulation. Adsorption of SLS on the spoil or refuse also had to be considered since relative adsorption and desorption rates would control pore water SLS concentration and the rate of SLS migration. The application frequency would also depend on the rate of SLS loss by hydrolysis in the acid environment and by biodegradation.

It was decided that initial application rates would be based on the amount of SLS that could be adsorbed within the top 1 ft of refuse. A procedure for estimating this adsorption capacity is described on pages 10-11. The 1-ft-thick treatment zone was selected for several reasons: (1) Oxidation was assumed to occur largely in a near-surface oxygenated zone (17, 20), (2) desorption would subsequently allow downward migration, and (3) it was preferred to undertreat rather than overtreat, to prevent significant SLS concentration off the site. Although SLS is generally regarded as safe for household use, it can have deleterious effects on aquatic life at relatively low concentrations (1-2, 8).

The surfactant is generally shipped as a 30-pct solution and must be diluted on-site. Site-specific factors, such as availability of water and infiltration-runoff characteristics, determine how much the surfactant is diluted.

INACTIVE REFUSE AREA TEST

The first site chosen was an 11-acre inactive coal refuse pile in Raleigh County, WV. The pile was formed of Beckley Seam refuse during the late 19th century by dumping from an aerial tramway. It is 1,500 ft long, 450 ft wide, and approximately 130 ft high at its crest. Quality of the drainage from the pile has been monitored by Westmoreland Coal Co. for over a decade, thus providing a good baseline against which the effectiveness of the method could be judged.

The adsorptive capacity of the coal refuse was determined to be about 45 mg SLS/kg of material, using the procedure described on pages 10-11. This is approximately equivalent to 150 lb SLS/acre ft, or 1 drum (55 gal) of 30-pct SLS per acre. The site was treated during late September 1981 with 10 drums of 30-pct SLS, diluted 175:1 (fig. 3). Water samples were collected at least once a week thereafter and routinely analyzed for sulfate, acidity, pH, iron, and anionic surfactants (4).

Water quality improved after a 3-month lag period, with a 60-pct decrease in acidity, sulfate, and manganese and a 90-pct decrease in iron (figs. 4-7). The lag period was presumably caused by the time required for infiltration to flow through the old pile, but stored acidity in the form of sulfate salts may also have been a factor. Seasonal effects can be discounted since in previous years the contaminant concentrations peaked in winter. The magnitude of the improvement was greater than any change observed over the past 10 years. The obvious correlation between sulfate, acidity, and manganese indicates that as acid production was reduced, leaching of trace metals such as manganese also decreased. The disproportionately greater decrease in

FIGURE 3. - Hydroseeder being used to spray sodium lauryl sulfate on 11-acre refuse area in southern West Virginia. Application rate: 55 gal/acre of 30-pct solution, diluted 175:1.

iron appears to indicate that at least some of the refuse reached a pH high enough to precipitate ferric hydroxide within the pile.

Before application of the SLS, Westmoreland Coal Co. was spending about $7,500 per month to treat the drainage from this pile. Based on the observed improvement in water quality and the costs of the SLS application, reduced water treatment costs paid for the SLS application in about 3 weeks.

ACTIVE REFUSE AREA TEST

The second field test was at an active coal refuse area in Preston County, WV. The pile is primarily Freeport Seam refuse from a preparation plant operated by Kingwood Mining Co. Inactive sections of the refuse pile are down gradient of the 8-acre active section and are revegetated; treatment of the drainage from the entire refuse area costs Kingwood Mining about $1,000 per month.

One problem with the Kingwood refuse site was the lack of background data for the active section being treated. A pond was therefore constructed by Kingwood Mining Co. to collect surface runoff from much of the treated area, thus providing some indication of whether the application of the surfactant improved water quality.

Adsorption tests indicated that an application rate of 1 drum per acre was again appropriate. The area was treated in early November 1981, using a hydroseeder, with a dilution factor of 50:1 (due to a shortage of good-quality water).

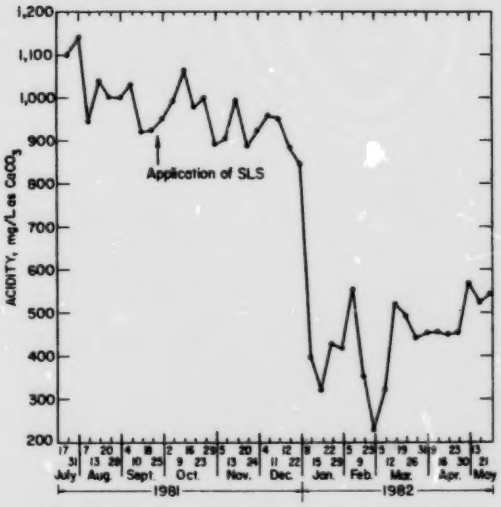

FIGURE 4. - Effect of sodium lauryl sulfate on acidity of drainage from 11-acre inactive coal refuse pile in southern West Virginia.

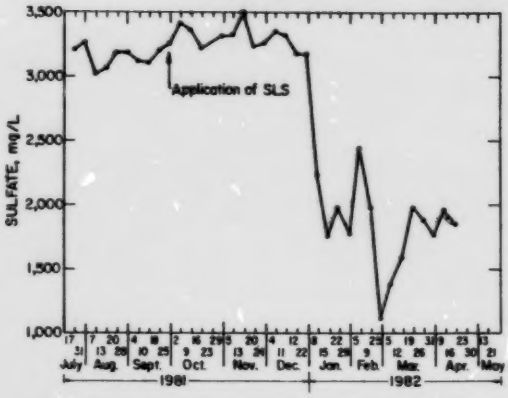

FIGURE 5. - Effect of sodium lauryl sulfate on sulfate concentrations at the southern West Virginia site. Lowered sulfate concentrations demonstrate that the acid production is being controlled at the source.

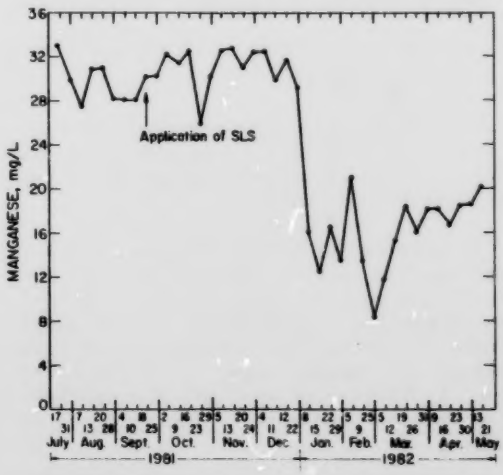

FIGURE 6. - Effect of sodium lauryl sulfate on manganese concentrations at the southern West Virginia site. By reducing acid production, dissolution of trace metals is decreased.

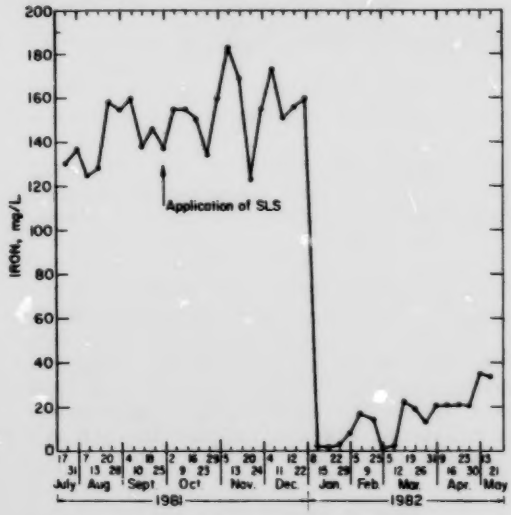

FIGURE 7. - Effect of sodium lauryl sulfate on iron concentrations at the southern West Virginia site. The disproportionate decrease in iron probably indicates that areas of the refuse pile are alkaline enough to result in iron hydrolysis and precipitation.

Water quality improved dramatically within a month of the SLS application. Acidity, sulfate, and iron were reduced by more than 95 pct and remained low for about 4 months after treatment (fig. 8). A complicating factor at the site is untreated material which was added during that interval; it is impossible to separate out the effects of the acidification of the new untreated refuse from the diminishing effects of SLS.

Effluent concentrations of surfactant have been extremely low at both sites. Except for one measurement of 0.6 mg/L shortly after application of the SLS to the inactive pile, SLS concentrations have been consistently less than 0.1 mg/L; no SLS has been detected in the stream at the discharge point of either treatment plant.

PROCEDURAL RECOMMENDATIONS

As a result of previously published articles by the authors (27, 31-32), the mining industry has started using anionic surfactants on coal refuse, coal stockpile areas, unreclaimed mine spoil, and waste sulfide rock. At present, more than 50 mining companies are using the technique with varied success. One coal company has applied an anionic surfactant two or three times a year to a developing coal refuse area for 4 years. The drainage is still showing net alkalinity, despite the fact that the coal refuse typically produces acidic drainage within 6 months. At the other extreme are sites where the technique produced no apparent effect or only a short-term improvement in water quality. Some of these failures can be explained simply, such as when the dosage rate or site conditions were obviously inappropriate. At other sites it may never be known why the technique failed to reduce acid production, although possible reasons are discussed

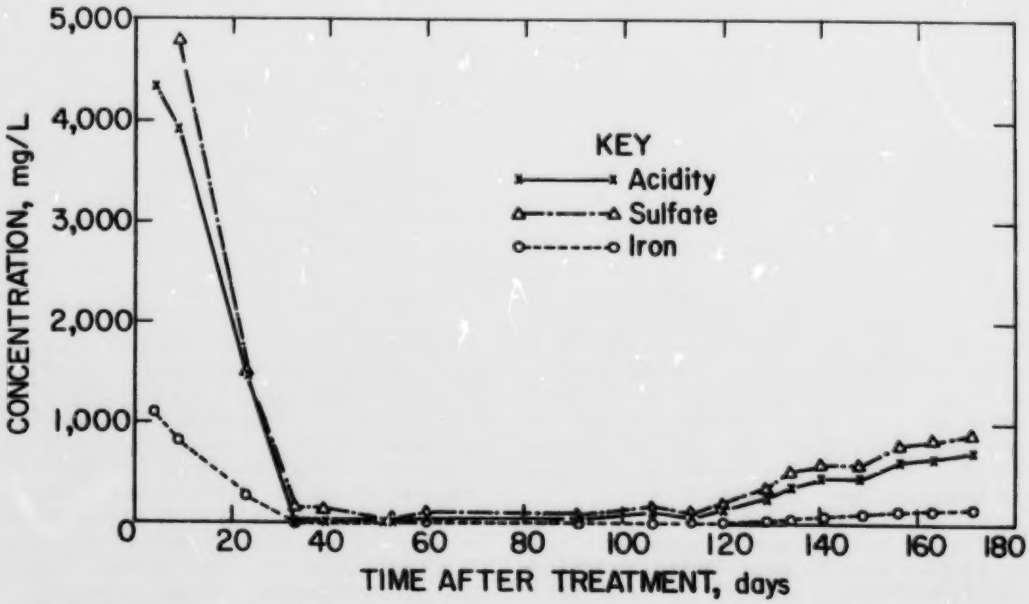

FIGURE 8. - Effect of sodium lauryl sulfate on runoff water quality at 8-acre active coal refuse pile in northern West Virginia. Application rate: 55 gal/acre of 30-pct solution, diluted 50:1.

below. Generally however, the technique has been successful. To improve the success rate, the following procedure is recommended.

PRELIMINARY CONSIDERATIONS

The first step in deciding if the surfactant technique is appropriate for a specific site is determining if it is potentially cost effective. Assume for the moment an approximate annual material cost for surfactant of $600 per acre. Add to that the cost of three applications, the expense of which will vary from site to site. One should consider, for example, whether the surfactant will be applied with equipment already on-site and using available personnel time or with contracted equipment and manpower. For potential savings, assume a 60-pct decrease in acidity; this will reduce neutralization costs by about the same amount. If a 90-pct decrease in sludge accumulation is further assumed, one can estimate an associated annual savings based on the frequency with which the pond is normally cleaned. Other treatment costs, such as equipment and operator expenses, will generally not decrease significantly since the volume of water to be treated stays the same.

Since the surfactant must reach the pyritic material to be effective, the presence of intervening overburden or topsoil will clearly reduce the effectiveness of the treatment. If the cover is highly permeable, treating with somewhat higher levels of surfactant will compensate; if not, the surfactant will probably all be adsorbed by the nonpyritic material or will be washed away in surface runoff. Several mine operators have recently tried to solve this problem by applying the anionic surfactant solution through shallow wells; it is too early to judge if they have been successful.

If quick results are required, two other factors must be considered: hydrologic flow-through time and ground water pools. Flow-through time is the time it takes for rainwater to infiltrate through the mine material and emerge in a spring or seep. In mine spoil, flow-through times of over a year have been measured (19). In such a case, improvement in water quality at the discharge point cannot occur faster than water flows through the material.

Ponding of acid water on the old mine floor or in a refuse area also retards or masks the effect of reduced acid production. The presence of such a pool can sometimes be surmised by a steady acid load in the base flow during dry periods and only slight changes in the acid load during higher flows. If the pool volume is significant, it could be years before a decrease in acid production is reflected by more than a gradual improvement in water quality. If faster results are desired, alkalinity must be added to the pool in sufficient quantities to neutralize all of the acidity present.

APPLICATION PROCEDURES

If, based on the above considerations, the site appears appropriate for the surfactant treatment, the obvious question is how much surfactant is required. As described earlier, the concentrations needed to kill T. ferrooxidans in small volumes of coal refuse are quite low (25 to 40 mg/L). Such an application would be ineffective at an actual mine site because it would fail to reach most of the oxidizing pyrite. It is necessary to determine the adsorption capacity of the material being treated and to compensate for that adsorption with extra surfactant.

A simple laboratory procedure has been developed to provide an estimate of adsorption potential for overburden and coal refuse. A representative sample of the material to be treated is placed in a large, tared Buchner funnel, tamped to a uniform depth of 2 in, and weighed. A surfactant, such as SLS, is applied evenly over the material at approximate loads of 60 mg SLS/kg of coal refuse. Typical SLS concentrations range from 300 to 30,000 mg/L and are selected on the basis of the anticipated infiltration rate.

After the surfactant application, the top section of a second funnel or a perforated plate is fitted onto the packed funnel to allow even distribution of a distilled water rinse. The rinse solution is continuously applied through plastic tubing from a distilled water reservoir. The height of the reservoir is adjusted to balance influent and effluent flow rates; in relatively impermeable samples inundation is unavoidable and effluent flow rates can be as slow as 100 mL/h. Rinse effluent is collected in 100-mL fractions until no sudsing is observed on shaking.

The stock SLS solution and rinse fractions are analyzed for anionic surfactants by the methylene blue technique or a comparable standard method (4). Adsorption is calculated as the difference between the mass of SLS applied and that eluted and is recorded as milligrams of SLS adsorbed per kilogram of sample. Alternatively, adsorption can be reported as pounds SLS per acre inch, calculated from the known funnel area and sample thickness.

The laboratory test provides only a relative measure of adsorption capacity, since field conditions are not duplicated. On coal refuse, we base our application rate on the adsorptive capacity of the top 1 ft, since the most active zone of oxidation is typically shallow, and since surfactant, at reduced concentrations, will penetrate beyond this surface layer. We have been deliberately conservative to avoid the risk of significant surfactant concentrations in the effluent; we will test the effect of higher dosage rates in the future.

At sites where the pyritic material is not exposed, excess surfactant must be applied to compensate for that which will be adsorbed by the overburden. The adsorption rate can be determined using the procedures described and by assuming that the adsorptive capacity of the entire column must be accounted for. The extent of oxidation in buried pyritic spoil and refuse has not been determined, making it difficult to determine how much surfactant should be allotted for the actual acid source. Research is underway to determine oxygen concentrations at depth in coal refuse and mine spoil, which should help answer this question.

Based on adsorption tests conducted to date, application rates generally range from 1/4 to 1 drum of 30-pct SLS per acre. It is necessary to dilute the surfactant solution both to provide sufficient coverage and to allow for infiltration; the optimal dilution ratio is site specific. At low dilution rates (less than 125:1), application rates should be increased slightly to compensate for higher adsorption rates; also, excessive foaming can be a problem. Ideally, a dilution of 500:1 or even greater would be best, but in practice this would result in surfactant solution flowing over land as runoff, and in significantly higher labor costs.

Both hydroseeder and road watering trucks have been used by mine operators for application of the surfactant solution. With either machine, it is important to add the water to the tank at the bottom (using a hose) to avoid excessive foaming. For the same reason, agitation should be avoided as much as possible. Care should be taken when dealing with the concentrated surfactant; gloves should be worn to avoid "dishpan hands," and contact with the skin and eyes should be avoided. Finally, it is recommended that the tank and hoses be thoroughly rinsed of all surfactant after the application is completed, as the concentrated solution can cause pitting if allowed to remain.

OTHER CONSIDERATIONS

In the field tests and laboratory work, SLS was used rather than other anionic surfactants. There were two reasons for the initial choice: SLS inhibited *T. ferrooxidans* at lower concentrations than other generally available surfactants tested, and it hydrolyzes and breaks down in an acid environment. It was felt that these two factors would reduce the likelihood of significant contamination in

the receiving stream. High adsorption, which was not initially considered, has probably contributed to the fact that effluent surfactant concentrations have been extremely low. We have, however, continued to use SLS in our field tests rather than introduce other variables. Some may wish to test other anionic surfactants, such as linear alkyl benzene sulfonate and alpha olefin sulfonate, which require somewhat higher concentrations to effectively inhibit T. ferrooxidans but which are less expensive and less acid sensitive than SLS. The latter factor may be especially important on refuse areas where the surface pH is very low; it is possible that in such a case SLS may lose its effectiveness by hydrolyzing before it contacts most of the oxidizing pyrite. Experiments are in progress to find acid-resistant surfactants that are equal to or more effective than SLS in inhibiting T. ferrooxidans (39, 45).

Reapplication of the surfactant is normally required to replace what is desorbed or degraded. When material from an exposed refuse area was tested 2 months after treatment, virtually no surfactant was found in the top 1 ft, although some surfactant remained below that level. In contrast, at another site that had been topsoiled and revegetated immediately after application of the surfactant, and from which there was virtually no subsurface drainage for about 18 months, enough surfactant remained to cause visible sudsing when, after 2 months of heavy rainfall, ground water reached the surface.

Potential consequences of using anionic detergents to reduce acid formation must be considered so as to avoid substituting one environmental problem for another. Studies of the chronic and acute effects of anionic detergents on fish and aquatic invertebrates indicate that kidney damage occurs in fish after long exposure to low levels (2 to 15 mg/L) of detergent, and that acute toxicity occurs in some species at concentrations as varied as 0.6 to 40 mg/L (1-2, 8). The World Health Organization recommends that stream concentrations not exceed 1.0 mg/L; other regulatory groups have recommended even lower values (e.g., Pennsylvania's Department of Environmental Resources, 0.25 mg/L). As stated earlier, effluent concentrations of SLS at the Bureau's field sites have been very low, typically below 0.1 mg/L in the effluent and below detectable limits in the receiving stream. The laboratory procedure to determine the application rate is apparently effective in preventing overtreatment; the only remaining concern is surfactant concentrations in the runoff. To minimize this risk, it is recommended that the surfactant be applied only when the ground is unsaturated and when no major rainstorms are expected for several days.

The surfactant solution has been sprayed onto revegetated sites with no apparent adverse effects on vegetation. It is recommended that treatment predate seeding by several weeks. It should similarly be in advance of any lime applications, as that might diminish the effectiveness of the surfactant.

CONCLUSIONS

1. Thiobacillus ferrooxidans plays an important role in determining the rate of pyrite oxidation. Anionic surfactants, applied at concentrations greater than 25 mg/L, reduce this bacterial activity and thereby slow acid production.

2. A laboratory procedure has been developed to determine suitable application rates for a specific site. Based on existing field data, the procedure appears to be effective in preventing overtreatment. Surfactant concentrations have generally been less than 0.1 mg/L in the effluent from the treated areas.

3. Sodium lauryl sulfate was applied to an 11-acre inactive coal refuse pile in southern West Virginia at a material cost of about $200 per acre. Acid

production fell approximately 60 pct, with an associated 90-pct decrease in iron concentration.

4. An 8-acre active coal refuse area in northern West Virginia was similarly treated. Acid production fell approximately 95 pct, with an associated 95-pct decrease in iron concentration.

5. At sites where water treatment costs are high, application of an anionic surfactant should be considered. Surfactant application should be repeated three times a year for maximum benefit.

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Developments in Controlled Release Technology and Its Application in Acid Mine Drainage

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Abstract. It has been previously demonstrated that anionic detergents inhibit the bacteria T. ferrooxidans which otherwise catalyze the formation of acid drainage from pyritic material. Liquid sprays of these detergents are effective for short periods of time and are useful in satisfying overburden adsorption capacity and in initial rapid inhibition of bacteria. For a permanent solution, controlled release systems are needed to provide the required concentration of detergent over prolonged periods of time sufficient to permit healthy growth of vegetation on the reclaimed overburden. A good ground cover, when sustained over a period of years, will eventually deprive the spoil of oxygen and water needed to generate acidity. Different materials and configurations for obtaining desired rates of release of anionic detergents are described. Laboratory tests have been developed to analyze the release rates of the controlled release materials. These tests are used to determine application rates. Field trials have been conceived to verify application theories and to demonstrate long term effectiveness of these materials together with their biodegradability to insure that one environmental problem is not replaced by another. Laboratory and field tests are described and discussed.

Introduction

Acid mine drainage occurs as a result of the oxidation of ferrous sulfides such as pyrite and marcasite and is catalyzed by the bacteria Thiobacillus ferrooxidans. A pH dependent three stage mechanism of acid generation has been proposed.[1] Numerous substances have been tested and found to be inhibitory or toxic to T. ferrooxidans.[2-10] Of the compounds tested, anionic detergents, particularly sodium lauryl sulfate (SLS), have been shown to be inhibitory at concentrations on the order of 10^{-6} M in culture media[8] and in mine spoils at somewhat higher concentration.[11] Sodium lauryl sulfate has the additional benefits of being low in mammalian toxicity[12] and quite biodegradable[13] so subsequent environmental problems are unlikely.

Spray application of SLS solution inhibits acid production of refuse piles for approximately four months.[14] Sulfate and iron levels are also reduced. As the SLS degrades or is lost due to runoff, the bacteria repopulate and acidification and resultant high iron and sulfate levels again occur. To bypass the inherent short effectiveness period of spray applications, Kleinmann[15] proposed and evaluated a controlled release form of SLS contained within the rubber matrix. He found that a combination of SLS solution spray and controlled release solid SLS resulted in major reductions of acidity, iron, and sulfate levels in drainage from a refuse pile (compared to a control) for a period of about one year.

To insure successful reclamation, that is, returning water quality to its premining condition for pH, total sulfate and total iron concentrations, bacterial inhibition longer than one year is desired. Acid generated in the early phases of reclamation can cause acid percolation to the surface resulting in the destruction of vegetation. If a lush vegetative cover can be maintained for about five years the acid production cycle might be permanently broken due to three natural biological processes. (1) As a healthy root system is established it competes for both oxygen and moisture with potentially acid-producing bacteria. (2) Populations of beneficial heterotrophic soil bacteria and fungi are reestablished resulting in the formation of organic acids which are inhibitory to T. ferrooxidans.[10] (3) The action of these heterotropic bacteria increases CO_2 levels in the groundwater resulting in increased solubilities of neutralizing calcareous materials. Reclamation has been shown to return pH and iron levels to near premining levels.[16]

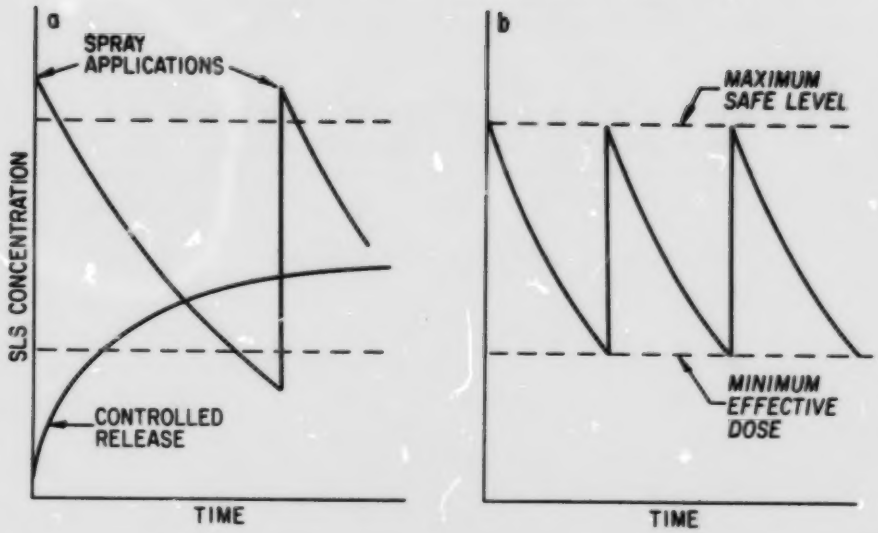

Figure 1. a. Hypothetical application of sodium lauryl sulfate as a spray and in controlled release form. Spray applications provide an effective dosage quickly but the concentration falls rapidly. To maximize the effective lifetime of a spray application it is necessary to overdose the system initially. Controlled release systems maintain the dosage in the proper range but there is a significant delay between application and attainment of an effective dose. b. To prevent initial overdosing and inadequate concentrations just prior to reapplications it is necessary to respray smaller doses more frequently.

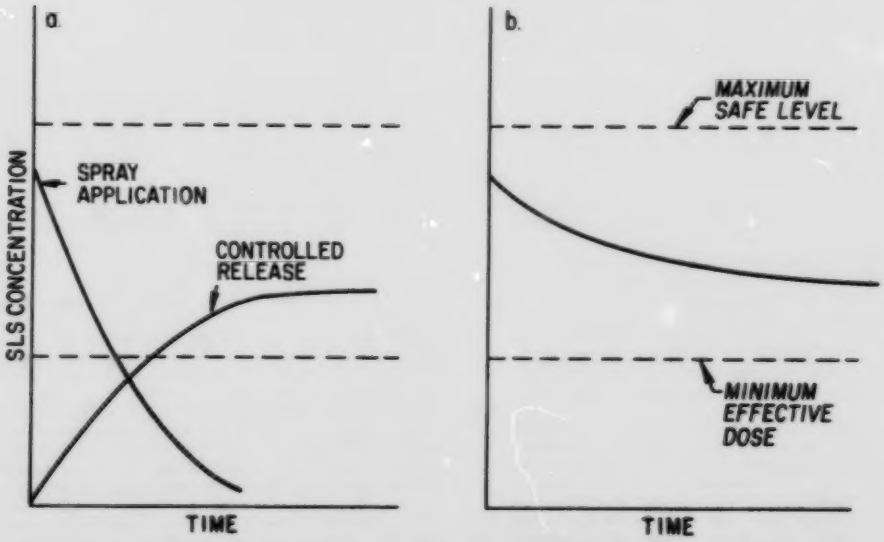

Figure 2. a. Level of SLS due to an initial spray application and due to a controlled release application. b. By carefully tailering the initial spray applications and controlled release system the level of SLS can be maintained nearly constant from the initial application onward.

Controlled Release Technology

It has already been noted that spray applications of SLS effectively inhibit mine acid formation for three or four months and simple controlled release systems for up to about one year. Figure 1 shows a hypothetical scenario relating spray applications to ideal controlled release application of detergent.

Spray applications have the advantage of delivering an effective dose of the active agent quickly, but the level falls rapidly due to runoff and biodegradation. To maximize the duration of effectiveness using a spray application it is necessary to use large amounts of the agent resulting in potential environmental problems (Figure 1a). Decreasing the dosage minimizes the potential environmental problems but increases the application frequency required (Figure 1b). A potential disadvantage of controlled release is the long time interval between application and attainment of the minimum effective concentration. The primary advantage however is that once an effective concentration is attained it can be maintained for extended periods using less total active agent. The removal processes (biodegradation, degradation, hydrolysis, photolysis, leaching etc.) following spray application follow first order kinetics;[17]

$$t_e = \frac{1}{k_r} \ln \frac{M_\infty}{M_e} \qquad (1)$$

where t_e is the time an effective level is maintained, k_r is the rate constant for removal, M_∞ is the initial amount of agent applied and M_e is the minimum effective amount. Thus, increasing the duration of effectiveness requires an exponential increase in the initial application. Maintaining an effective concentration using a controlled release system results in a greatly enhanced duration of effectiveness as follows:[17]

$$t_e = \frac{M_\infty - M_e}{k_D M_e} \qquad (2)$$

where k_D is the rate constant for delivery from the controlled release device.

Figure 2 shows how a combined initial SLS spray application and controlled release system can be utilized to get an immediate effective dose and long term effectiveness without the danger of overapplication nor the need for frequent reapplication. The initial spray application required is dependent not only on the concentration required to kill acid producing bacteria, but on the capacity of the overburden to adsorb SLS. This aspect has been dealt with elsewhere.[14]

Among the various factors which must be considered in the design of a controlled release system for sodium lauryl sulfate are the choice of the polymer system and its interaction with the active agent. The polymer must be capable of incorporating the agent either by solution or as a heterogeneous blend in which particles of the SLS are contained within the polymer matrix. Furthermore, the polymer - SLS - system should not chemically alter the SLS, but rather should act as safe harbor for the active agent until release occurs. The polymer system and any additives present must be harmless to the environment and preferably be themselves biodegradable after the useful lifetime of the product is complete. The chemical and physical environment must be considered when developing controlled release systems. The system must be functional in the environment for which its use was intended, conditions which frequently vary from idealized conditions generally employed in the laboratory. The controlled release system must be designed in such a way as to be applicable in the field providing uniform coverage over infected areas with the ability to remain active at the site for the desired lifetime of the product. Some specific factors which should be taken into account in the development of a controlled release product are reviewed in Table I.

Table I. Some specific factors which must be taken into account in developing a controlled release system.

- Chemical environment
  - pH, acidity, sulfates, iron
  - Moisture content
  - Pyrite content
- Physical Environment
  - Particle size distribution
  - Soil cover
  - Slope
  - Accessability (application)
  - Degree of vegetation
  - Type of overburden material
  - Spoil age - stage of acid production
- Climatological
  - Precipitation (average, events)
  - Temperature - (average and extremes)
- Hydrologic
  - Percolation rates
  - Runoff rates
  - Transpiration rate

The Process of Diffusion

A controlled release device basically consists of a reservoir of active agent which is systematically metered into the environment of intended use over a prolonged period of time. For mine acid control applications the system must consist of small, self contained units which can be easily distributed over the treatment area. The reservoir system can conveniently consist of a membrane coating over the active agent or a membrane coating over a polymer core containing dispersed or dissolved agent or a combination of these. Diffusion, osmotic pressure or bioerosion can be utilized to release the active substance from the reservoir system.

The process of diffusion is perhaps the simplest means of regulating release. Diffusion in polymer systems has been recognized as an important process since Graham[18] first observed the diffusion of a gas through a rubber membrane in 1829. Diffusion is the net transport of matter by means of random molecular motion, resulting in the removal of a chemical potential difference in a system leading eventually to equilibrium. The ability for a substance to diffuse through a polymer layer is related to the solubility and molecular mobility of the substances and follows Ficks laws for rubbery materials.[19,20]

Basic Concepts of Controlled Release

A number of concepts have been employed for controlled release and have been extensively discussed.[21] For the purpose of this paper we will briefly discuss the release characteristics of two major options available for controlled release treatment of acid mine drainage. These are the membrane bound reservoir system and the monolithic system.

For rate controlling membrane bound reservoir systems, where the concentration of release agent at the membrane reservoir interface is constant, Ficks law predicts that the release rate will be constant and independent of time and geometry. Thus

$$M_t = kt \qquad (3)$$

where M_t is the amount of agent released, t is time and k is the release rate. In treating mine spoils, ideal release kinetics may not be realized due to changing boundary conditions resulting from various climatic factors such as variable rates of precipitation.

Reservoir systems without rate controlling membranes follow $t^{1/2}$ order release kinetics such that

$$M_t = kt^{1/2} \qquad (4)$$

Such systems give initially large release rates followed by much slower rates during the last part of the product life.

Non-erodible monolithic systems consist of a physical blend of active substance in a polymer matrix with the polymer acting to control the release of the substance. The active agent may be either in solution within the polymer or dispersed within it. Where the control release substance is dissolved within a rubbery matrix extraction of the substance is usually due to Fickian diffusion of the solute to the surface where the substance is desorbed and enters the water phase. If the matrix material is water swellable, such swelling enhances extraction by increasing free volume and molecular mobility. Release rate characteristics for dissovled substance monolithic systems generally obey $t^{1/2}$ kinetics until about 60% of the substance is released after which the rate is exponentially related to time:[17]

$$\frac{dMt}{dt} = k_1 e^{-k_2 t} \qquad (5)$$

where k_1 and k_2 are constants. This type of release is called "first order" and is also observed in reservoir systems in which the solution of active substance is less than saturated.

For dispersed substance monolithic systems, where the soluble and the dispersed component are in equilibrium within the polymer matrix and the concentration of dispersed particles is sufficiently low so they are not interconnected, release is proportional to $t^{1/2}$. This type of release kinetics holds for almost the entire release curve. Where the solubility of the active agent is sufficiently low, and where the concentration is high, a porous network of interconnecting capillaries or pores exists. Release from such systems is not due to diffusion of the active substance through the polymer matrix but through the elution media.[22] These systems also follow $t^{1/2}$ kinetics. The release rate is directly proportional to the porosity ε and the tortuosity τ of the matrix such that

$$Q_t = [SD \frac{\varepsilon}{\tau} (2A-\varepsilon \cdot S)t]^{1/2} \qquad (6)$$

where Q_t is the amount extracted at time t per unit surface area, S and D are solubility and diffusion coefficients and A is the total concentration of dispersed agent within the polymer matrix.

The Effect of Surface Area

The release of active substance is related not only to the type of system employed but also to the geometry of the controlled release device. Many shapes and sizes are available ranging from large slabs or sheets to microcapsules measured in microns. It is intuitively obvious that given a fixed total volume of material, the release rate will be greater where the surface to volume ratio is large. The release kinetics will be profoundly affected by geometry where the active surface area from which diffusion occurs changes with time due to extraction of material from the outer layers. Certain shapes such as spheres and cylinders favor rapid extraction rates at early times and lower rates later as the effective surface area decreases.[22]

One way to counter diminishing extraction rates with time is to design novel geometries in which the effective area of release increases rather than decreases as a function of time. A right cylinder for example has surface area of:

$$A = 2\pi r(h+r) \qquad (7)$$

If h becomes sufficiently large or r sufficiently small, the area of the end becomes insignificant and

$$A \cong 2\pi rh. \qquad (8)$$

The effective release area as successive shells of SLS are depleted becomes:

$$A_{eff} \cong 2\pi h(r-\tau) \qquad (9)$$

where τ is the thickness of the depleted shell and

$$\frac{\partial A_{eff}}{\partial t} \cong -2\pi h \frac{\partial \tau}{\partial t} \qquad (10)$$

which gives a decreasing area with time. Now consider a hollow tube in which release is through the interior surface into the lumen of the tube. This can be accomplished by coating the outer surface with an impermeable barrier (see Figure 3). The initial area from which release occurs now becomes:

$$A \cong 2\pi r_1 h \qquad (11)$$

where h is large compared to the radius and r_1 is the radius of the lumen. As active agent is depleted from the matrix in shells of thickness τ,

$$A_{eff} \cong 2\pi h\ (r_1+\tau) \qquad (12)$$

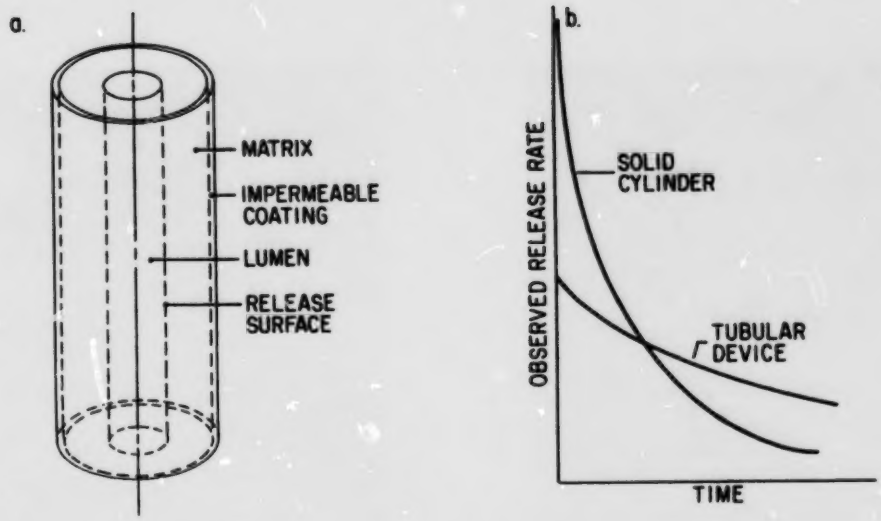

Figure 3. a. Tubular shaped release device. Release is through the interior surface into the lumen. The impermeable coating prevents release from cylinder exterior. b. Comparison of release characteristics for tubular device compared to a solid cylinder.

and

$$\frac{\partial A_{eff}}{\partial t} \cong 2\pi h \frac{\partial r}{\partial t} \qquad (13)$$

which gives an increasing area with time. The system can be designed to therefore offset the effect of depletion of the active agent. This concept has already been used by Langer[23] to design hemispherical release devices in which the increase in area exactly offsets the increasing diffusion distance and linear release is obtained over the entire lifetime.

Controlled Release of Sodium Lauryl Sulfate

For acid mine drainage treatment, we have so far tested monolithic polymer systems in right circular cylindrical form. The development and testing of these controlled release devices is described below.

Materials and Methods

All polymer sodium lauryl sulfate (SLS) compounds were prepared either using a standard rubber mill or a Banbury rubber mixer using standard rubber processing industry practice. Cylindrical pellets 1/4 inch in diameter by 1/2 inch high were prepared using a Haake Rheleox 530 extruder to give a smooth uniform output which was subsequently chopped.

The US Bureau of Mines[15] has developed an extraction test which can be used to evaluate the release characteristics of SLS from a polymer matrix under simulated field conditions and have presented release data on SLS rubber systems. The test is time consuming and therefore inconvenient for screening materials. To rapidly screen materials for relative release characteristics a quick extraction procedure was developed.

Fourteen cylindrical controlled release pellets of nominal dimensions 1/4 inch dia. x 1/2 inch and having a surface to volume ratio S/V = 20.0 in^{-1} were placed into a wide mouth quart jar. This number was chosen because it gave a total amount of available SLS for extraction that is easily detectable by X-ray fluorescence analysis for sulfur. A large volume of water was added to the container such that the extractable SLS within the pellets was removed rapidly.

Since total surface area is important the same pellet size and shape were maintained for all tests in which polymer/SLS systems were being evaluated.

Time zero was taken to be the time at which the water was first added to the jars. Five ml of the aqueous phase were removed at 5, 10, 20, 60, 300 and 1440 minutes (24 hours). The containers were constantly agitated except during sampling. Each five ml sample was analyzed for sulfur and the amount of SLS extracted from the pellets calculated.

Results and Discussion

Uncrosslinked natural rubber was found to be an ideal polymer for uptake of SLS. The solubility of SLS in natural rubber was determined to be extremely high using electron microscopy. Further evidence that the SLS was highly soluble in uncured natural rubber was the high modulus of the material due apparently to strain crystallization of the SLS molecules. The release characteristics of numerous rubber compounds are now in the process of investigation to develop formulation

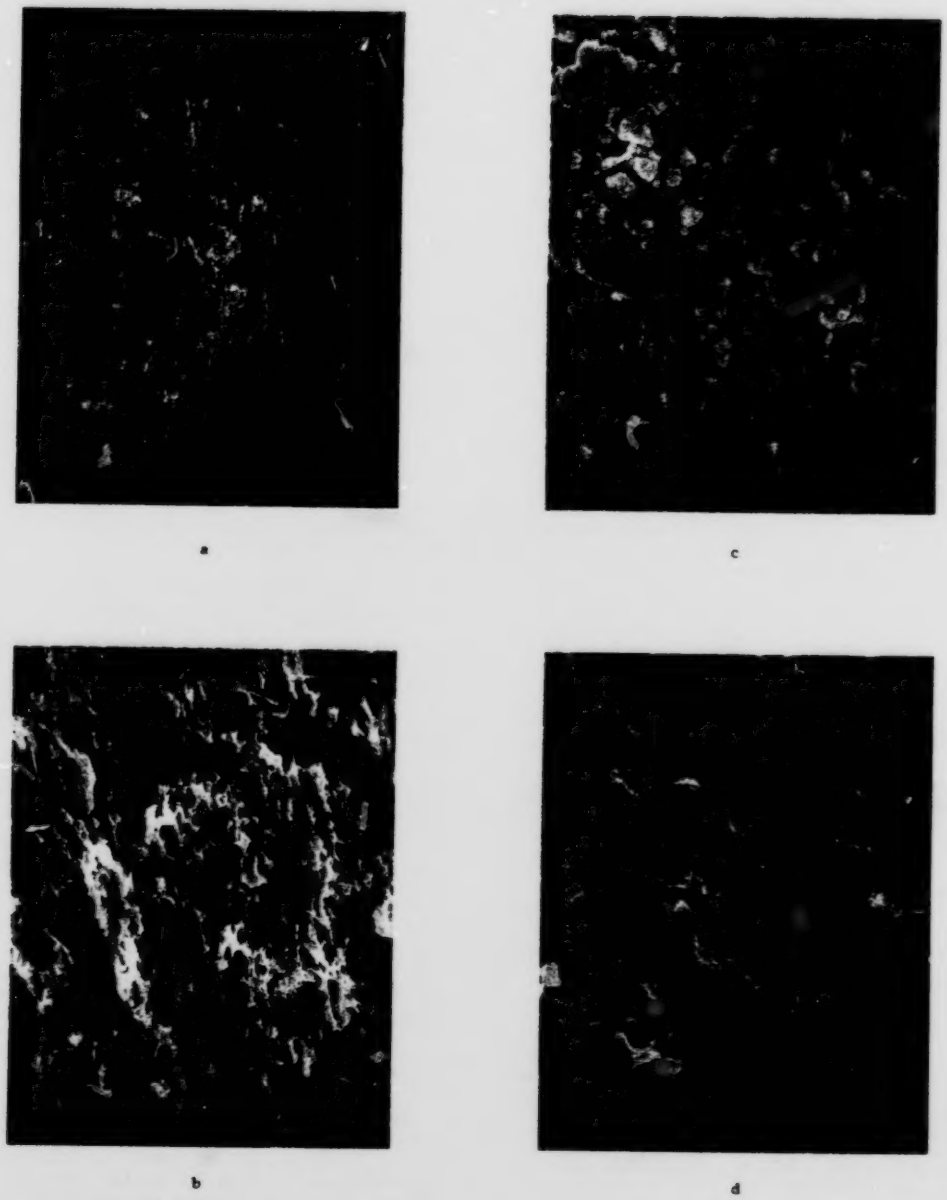

Figure 4. Electron micrographs showing partial cross-sections of a partially extracted 1/4" dia. polyethylene pellet containing SLS. a. View showing extracted zone (top), active leaching zone and an unextracted zone (40X). b. Enlargement of extracted zone showing depleted porous network (500X). c. Active extraction zone showing recrystallized SLS (500X). d. Interior region of pellet containing unextracted SLS (500X).

with more favorable release characteristics. Original formulations were found to be effective for approximately one year.[15] Rubber modifications currently under investigation include higher loadings of SLS, addition of additives to modulate release characteristics and the investigation of crosslinking. Crosslinked systems like uncrosslinked systems accept very high SLS loadings but have different release characteristics due to restricted molecular segment mobility of the polymer cage network.

In addition to natural rubber, thermoplastic matrix materials such as polyethylene (PE) and Ethylene Vinyl Acetate (EVA) were investigated as carriers for SLS. Unlike natural rubber SLS does not appear to be highly soluble in these materials, nevertheless, high loadings were possible. Fickian diffusion through PE and EVA is very slow, due in part to crystalline domains within the polymer matrix. Such domains will not uptake solutions nor allow their passage. Therefore, release of SLS from such a matrix is due to the porous nature of the system. Figure 4 shows cross-sectional electron micrograph views of a partially extracted PE pellet which was freeze fractured to reveal the interior of the pellet. Three distinct zones were observed as revealed in Figure 4a. The edge of the pellet seen in the righthand region of Figure 4a contained a porous network depleted of SLS as shown enlarged in Figure 4b. An intermediate zone (the light colored region in the center of 4a) represents the active front from which SLS was being extracted and contained highly visible recrystallized SLS (Figure 4c) due to removal of the pellet from the extraction medium. The interior portion of the pellet seen at the left on Figures 4a and 4d contained unextracted SLS within the porous matrix. The active extraction front moves progressively from the surface to the interior of the pellet. In such a system both loading level and particle size of the active substance are important determinants in release characteristics of the system.

Figure 5 shows extraction data for three systems. The natural rubber system was similar to previously field tested materials[15] but with more than twice the initial SLS loading. These pellets were completely extracted in less than one day when totally immersed. The polyethylene and EVA systems exhibited much slower release characteristics.

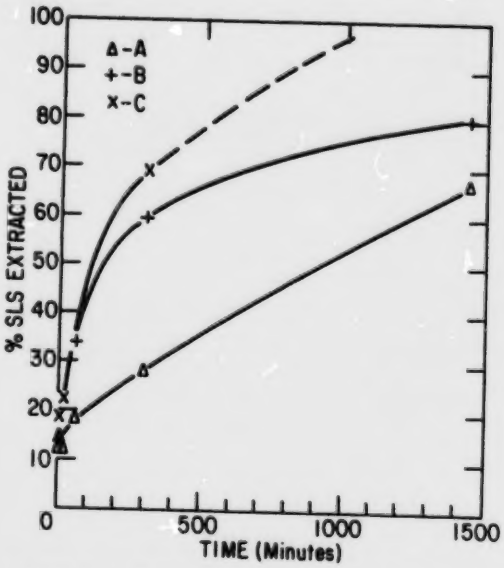

Figure 5. Extraction data for three SLS containing monolithic systems. A. Low density polyethylene. B. Ethylene vinyl acetate. C. Uncured natural rubber.

Effect of Shape, Size, and Other Factors

As discussed in the section on "The Effect of Surface Area", particle size and shape play an important role in governing the effective release rate from pellets. For the purpose of the tests and developments reported here, we chose the right cylinder as the geometry because (1) it was simple to manufacture, (2) the release rate could be readily tailored by changing height or radius, and (3) the pellets could be easily applied in reclamation.

For cylinders in which r>>h, the ends dominate the total surface area and surface to volume ratios are large, while in the case in which h>>r the walls dominate the area and S/V ratios are smaller at equivalent volume. Thus for a cylinder of large r release through the ends is favored while for a cylinder of small r, release through the walls is dominant. Reducing particle size favors rapid extraction as S/V increases rapidly as particle size approaches zero. One additional point should be made. When particle volume is very small, small changes in particle volume result in major changes in S/V. At large particle volume very large volume changes are required to observe significant S/V changes. Thus, if slow release is desired, there is a practical limit of volume beyond which little is to be gained by additional increases in size.

Many factors influence the extraction of SLS from a controlled release system under natural conditions. These include the nature of the controlled release systems, climatological variables, hydrologic factors and the chemical/biochemical environment in which the system exists. Precipitation is probably the dominant climatological factor which effects the rate of SLS release. Rainfall extremes may be as significant as average annual rainfall. Certainly the form of precipitation, be it rainfall or snow, is important as is the state of the ground. Frozen ground is less permeable then non-frozen ground resulting in increased runoff. Snowmelt can saturate the ground and enhance pellet extraction. Refuse piles tend to be less permeable than spoil which effects the percolation rate. Slope and contour elevation relative to the groundwater table are also important parameters in regulating release rates. Pellets which lie in a wet depression will be depleted more rapidly than pellets in a less saturated environment.

Field Demonstration Projects

We are beginning an extensive program of field testing in an effort to better understand

how these variables interact to effect SLS release and to demonstrate the effectiveness of controlled release sodium lauryl sulfate. Two trials are scheduled to begin in the summer of 1983.

The first of these is a demonstration project in conjunction with the Ohio Department of Natural Resources on a site near Wintersville, Ohio in Jefferson County. The site is approximately a 3.5 acre refuse area which will be divided into two tracts. One of the two tracts is to be treated with both spray sodium lauryl sulfate and controlled release pellets while the other tract will serve as a control. Some regrading of the site will be required to provide positive drainage and reduce excessive slopes.

Immediately following controlled release pellet application to the treated tract, both tracts will be reclaimed by applying topsoil and establishing a cover of grass. In order to monitor the sites, lysimeters will be installed in both tracts as will a groundwater drainage collection system near the toe of the slope in each tract.

A second field demonstration project is being conducted in conjunction with the Pennsylvania Department of Environmental Resources at a site in Indiana County, Pennsylvania. The site consists of a refuse pile approximately five acres in size and 10-15 feet in height. The pile is relatively flat and will require minimal grading to insure positive drainage. The pile also contains actively flowing acidic seeps. Unlike the Ohio site this site will not be reclaimed, nor will a control tract be employed. The pile will be treated in the summer of 1983 with both solution SLS and controlled release SLS pellets which will be disked into the surface. Monitoring will be through active seeps and lysimeters which will be strategically located throughout the pile.

These trials will provide large natural laboratories to study not only the effect of SLS on acid generation but on the controlled release process itself. Monitoring will include the traditional water quality parameters such as pH, acidity, alkalinity, total and ferrous iron, manganese, sulfate, conductivity and Eh as well as biological parameters and the fate of SLS and the pellets in the refuse environment. Controlled release pellets will periodically be removed and analyzed for SLS content and evidence of biodegradation. Groundwater will be analzyed for sodium lauryl sulfate content to insure that an effective dosage is being administered and to demonstrate that SLS is not contaminating the environment. This information should provide a far more detailed picture of the controlled release process which will be used in the design of more advanced controlled release systems to eliminate or reduce acid mine drainage.

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Bureau of Mines
Technology Transfer

Seminar on
Acid Mine Drainage Control

Bureau of Mines
Technology Transfer
Seminar on Acid
Mine Drainage Control

April 3-4, 1985
Pittsburgh, PA

A special one and a half day meeting updating new research breakthroughs in controlling acid mine drainage from coal mines has been planned by the Bureau of Mines. This seminar will feature technical discussions describing test results in areas such as the prediction of acid mine drainage before mining; how hydrology affects acid mine drainage; the use of alkaline materials for controlling acid mine drainage; and in-line aeration and treatment of acid mine drainage.

Technical personnel will be available at this meeting to answer any questions, and literature packages filled with additional information will be available to the attendees.

A field trip to demonstrate the in-line aeration and treatment system in operation at a local mine has been arranged for interested persons after the seminar. Transportation will be provided between the meeting site and the mine.

Please take a moment to read over the agenda, and if you would like to attend this seminar, simply fill out the attached reply card and return it to the Bureau of Mines at your earliest convenience or give us a call and we will register you over the telephone. If you have any questions or would like further details about this meeting, please contact:

Sheri L. Harris
Branch of Technology Transfer
2401 E Street, NW, MS 1041
Washington, DC 20241
Telephone: (202) 634-1224

Agenda

Wednesday, April 3

9:05- 9:15 a.m. **Introduction and Welcome** by *John Murphy*, Research Director, Pittsburgh Research Center, Bureau of Mines

9:15- 9:35 a.m. **Technical Overview** by *Robert Kleinman*, Pittsburgh Research Center

9:35-10:40 a.m. **Pre-mine Prediction of Acid Mine Drainage:**
- **Field evaluation of current technology** by *Patricia Erickson*, Pittsburgh Research Center and *Andrew Sobek*, Engineers International
- **Pyrite reactivity and relationship to thermal activity** by *Richard Hammack*, Pittsburgh Research Center

10:40-11:00 a.m. **BREAK**

11:00-11:45 a.m. **Hydrological Aspects of Acid Mine Drainage Control** by *Kenneth Ladwig*, Pittsburgh Research Center

11:45 a.m.-1:00 p.m. **LUNCH**

1:00- 1:20 p.m. **Gas composition of Coal Spoil and Refuse** by *Patricia Erickson*, Pittsburgh Research Center

1:20- 2:20 p.m. **Bactericidal Control of Acid Mine Drainage:**
- **Review of previous work with anionic surfactants** by *Robert Kleinmann* and *Patricia Erickson*, Pittsburgh Research Center
- **Use of alternative materials such as benzoate and sorbate** by *Robert Kleinmann*, Pittsburgh Research Center
- **Slow release by bactericidal agents** by *Vijal Rastogi*, B. F. Goodrich

2:20- 2:40 p.m. **BREAK**

2:40- 3:30 p.m. **Injection of Alkaline Materials for Control of Acid Mine Drainage** by *Kenneth Ladwig*, Pittsburgh Research Center

3:30- 4:10 p.m. **Alternative Methods to Remove Manganese from Acid Mine Drainage** by *George Watzlaf*, Pittsburgh

Questions, Answers and Discussion

Use of Sphagnum Moss/Limestone for Treatment of Acid Mine Drainage by *Robert Kleinmann*, Pittsburgh Research Center, *Brent Huntsman*, Wright State University, and *Benjamin Pesavento*, Environment Analytic

BREAK

In-Line Aeration and Treatment of Acid Mine Drainage by *Terry Ackman*, Pittsburgh Research Center

Questions, Answers, Discussion

Closing Remarks by *Robert Kleinmann*, Pittsburgh Research Center

LUNCH

Optional field trip to see in-line system in operation at a local mine led by *Terry Ackman*, Pittsburgh Research Center

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2401 E Street, N.W.
Washington, D.C. 20241

In South Africa, methods for the inhibition of acid mine drainage using different chemicals along similar lines is a topic of research at the University of Stellenbosch. This is a joint project between the Institute for Polymer Science and the Dept. of Microbiology, funded by the South African Water Research Commission. Confidentiality seems to be one of the stipulations of Water Research Commission research, but whatever information can be released could be requested from:

INSTITUTE FOR POLYMER SCIENCE
University of Stellenbosch
Stellenbosch 7600
South Africa
(02231) 71054
Telex: 52720383
Dr. R. D. Sanderson
Director

4. Low Grade Phosphate Rock Addition - Experimental Process

Dr. Al Stiller has demonstrated a remarkable application of basic chemistry which offers a potential solution to AMD from finely disseminated tailings containing oxidizable sulfides such as, for example, coal flotation refuse and base metal sulfide flotation tailings.

Examining the sequence of reactions that result in AMD generation, it becomes clear that two initial reactions pay a role: 1) bacterial oxidation of ferrous ions to ferric ions; 2) reaction between ferric ions with pyrite and other sulfide minerals as shown in equation 4. The second reaction causes by far the greatest generation of acid.

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{=} + 4H^+ \quad (1)$$

$$4Fe^{2+} + 10H_2O + O_2 = [4Fe(OH)_3]^{+5} + 2H^+ \quad (2)$$

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

By adding an intimate mixture of low grade phosphate rock with the tailings, the AMD generation can be inhibited by the following surface reactions.

$$3H_2SO_4 + Ca_3(PO_4)_2 = 3CaSO_4 + 2H_3PO_4$$

$$H_3PO_4 + 3OH^- = PO_4^{3-} + 2OH^-$$

$$3Fe^{2+} + 2PO_4^{=} = \underline{Fe_3(PO_4)_2}$$

$$Fe^{3+} + PO_4^{=} = \underline{FePO_4}$$

Ferrous phosphate has a solubility coefficient of 10^{-22}, and ferric phosphate is also almost insoluble.

At very low pH levels around pH 3.0-3.25, phosphate rock dissolves readily. In an oxidizing tailings pile, the pH of seepage may be around 2-5, but at the actual oxidation site on the mineral surface where reaction is occurring, the localized pH is about pH 1. Consequently, if phosphate rock can be brought in close contact with the tailings particle, the phosrock will be locally dissolved where needed. When this happens, ferrous and ferric phosphate immediately coat the particles and inhibit further reaction. It is claimed that acid generating bacteria that normally play such an important role in AMD generation are unable to oxidize ferrous ions once they have been precipitated in this way so the energy source vital to their growth is made unavailable.

This method for inhibition of AMD has been demonstrated on bench scale and also in barrel quantities. It is now being demonstrated on 350 ton test piles at:

ENOXY COAL, INC.
Post Office Box 710
Buckhannon, WV 26201
(304) 472-9272
Allan Meek

The development and testwork is being funded by the West Virginia Dept. of Natural Resources.

Tests have indicated that low grade phosphate rock slimes, an environmental disposal problem in Florida, are suitable for use. The schmectite clay content of the slimes is also useful for its soilmaking properties for the restoration of the tailings, however, these slimes are very bulky and may not justify the cost of shipment.

Importantly, the amount of phosphate rock needed is not stoichiometric because this is a surface reaction, and it is therefore not necessary to react the full mass of iron sulfides. Phosphate rock slimes are available delivered to Morgantown, West Virginia, at a cost of $50/t.

This innovative emerging technology deserves attention and support for more testwork and development. It is particularly appropriate where tailings are disposed of in slurry form, and the finely divided phosphate rock can be readily added and mixed into the pulp without great cost. If it proves practicable for commercial use, then it may lend itself to mixing with a high pyrite fraction that can be separated from base metal tailings to yield a more easily disposable low sulfide tailing and a smaller volume of high sulfide tailings to be mixed with the phosrock for disposal in a way that inhibits AMD generation.

More information on the concept and progress to date is available from:

DR. AL STILLER
Dept. of Chemical Engineering
University of West Virginia
Morgantown, WV
(304) 293-5398

An immediate offshoot from this concept would be the possibility of applying phosphate in liquid form to wasterock and tailings; however, here the risk of complicating the issue through phosphate pollution effects and the possibility of introducing phosphate in such a way that bacterial growth would be enhanced rather than inhibited must be considered.

5. Burnside Colliery, Glencoe, Natal

Gencor Ltd. spent a considerable amount of money and effort to restore the old worked out Burnside Colliery at Glencoe, Natal, South Africa. Several physical methods have been employed with remarkable success to control and inhibit acid mine drainage from the old minesite including old waste piles that were active. Whether or not these measures would be adequate to meet all requirements of a U.S. permit, which requires groundwater protection to be taken into account, is debatable. The measures, however, certainly made a big impact on the aesthetics of the site and the usability of the land and local streamwater. These measures were:

- Diversion of a drainage stream around the coal waste dump that had been located on the stream channel.

- Construction of a 80,000 m^3 capacity dam to collect and retain runoff water above the waste pile. Water is released at a controlled uniform rate so as not to erode the dump. Cost - R100,000.
- The coal waste dump was recontoured so precipitation will drain off the dump with no standing pools and a minimum of seepage into the dump.

- The coal waste dump surface was compacted to further reduce air and water penetration.

- The sides and top of the dump were planted with Kikuyu grass. Normal Kikuyu grass died, but grass taken from the immediate vicinity was acclimated to the lower pH and survived well.

- Collection dams were constructed to retain any surface drainages from the waste dump for evaporation.

- The shaft opening was sealed by a 2 m thick concrete plug and provided with a collar to prevent water from draining into the shaft. A valved pipeline was embedded through the plug to allow excess water to be bled at times when the

nearby river is in flood during which time released water would drain to the sea without causing damage.

The results of the R3 million site restoration program are highly successful. Water flowing into the nearby creek now meets effluent limits, and the creek water is once again usable for livestock watering and crop irrigation.

Clearly, coal mine waste reclamation in South Africa is possible without necessarily resorting to chemical AMD inhibition. Gencor Ltd. kept the manager of the mine at the site for three years after its closure to supervise the restoration program. This manager at first may have resented the task; however, he is now in charge of developing the latest Gencor Colliery where he can apply his restoration experience to the design and layout of the new operation. This is certainly an astute and innovative management move, considering the extent to which restoration costs can be reduced if properly planned in advance.

More information can be requested from the man responsible for the program:

P. J. BUYS
Blinkpan Collieries
Glencor Ltd.
Post Office Box
Blinkpan, Transvaal
(0132252) No. 7

6. Kromdraai Coal Mine

The Old Coronation Coal Mining Division of the Kromdraai Coal Mine is located near Witbank in the Transvaal, and belongs to the Anglo American Corporation. This site has been beautifully restored to the extent that, apart from the water treatment plant, there are now virtually no signs of the old mining operation.

When the mine was closed down in 1970 and the site restored, a flow of acid mine drainage amounting to 14,000 m^3/d with 1750 mg/l TDS and pH 2.2-2.4 had to be treated for discharge. The initial lime neutralization plant resulted in a sludge volume equal to 10% of the original flow, and it was possible to achieve a 4% solids density. The prospect of having to dispose of an estimated 1,400 m^3/d of sludge required a costly surface impoundment. This led to the highly successful installation of a high density sludge process plant yielding a sludge with a density of about 30-34% solids and which could have been increased had there been a need to do so.

Initially, the plant operated at 14,000 m^3/d working 24 hours/day, but after three years, the mine was successfully dewatered and today the plant is operated only eight hours per week.

At the full rate of operation, lime consumption amounted to R0.05/m^3 treated at a lime cost of R18-R20/t.

The high density sludge is disposed of to a surface impoundment where it soon dries to a low density dry material that is stable enough to be walked on.

Apart from the fine performance of the Kromdraai HDS plant which is described in Appendix I, the main point in referring to it here is that, were it known that the flow into the mine would decline, a smaller plant could have been designed. The Kromdraai HDS plant was one of the first HDS installations in the world. Since the owners had no prior experience in the HDS plant performance at that time, they may have felt it was necessary to overdesign the plant to be on the safe side. The Kromdraai experience has led to identification of the benefits of finding ways to prevent water from getting into a mine as a way of reducing the need for AMD treatment.

By installing an oversize plant, it was also possible to dewater the mine faster, thereby reducing the rate at which acid is generated underground and cutting back on the overall lime consumption, which would be an example of adopting a systems approach. This method of reducing AMD generation is described by WATSON (1982).

More information on the Kromdraai HDS plant could be obtained from:

ANGLO AMERICAN RESEARCH
LABORATORIES
Post Office Box 106
Crown Mines 2025
(011) 835-3251
Danie J. Bosman

It has also been described by BOSMAN (1974).

7. Rapid Dewatering of Coal Seams

WATSON (1982) and BOSMAN (1982) report that significant reductions in the rate of acid formation have been obtained where it is possible to prevent water collecting in underground pools in mines.

6. AMD Abatement by Discouraging Oxidation

The chemical requirements for unrestricted oxidation of iron sulfide minerals include an adequate supply of water, oxygen, carbon dioxide, ammonia, phosphorous, and various micronutrients. The restriction or elimination of the supply of one of these will influence acid generation. In the extreme case, the process can be completely inhibited by providing a hostile environment for the bacteria. It is not considered feasible to inhibit the oxidation process by the conscious control of micronutrients as these are

generally available in the water. However, considerable effort has been directed toward the conscious creation of a hostile environment for the bacteria with the objective of eliminating or substantially reducing the problem at the source.

These have included:

- Restricting the supply of oxygen.
- Restricting the supply of water.
- Isolating the sulfide components.
- Reducing the ferric iron levels.
- Controlling pH.
- Use of bactericides.
- Limiting the area of reactive surfaces.
- Controlling temperature.

Restricting the Supply of Oxygen

Oxygen enters a mine or tailings area both as a gas phase and as a dissolved component in the water. Water can supply only a limited amount of oxygen since 8-9 ppm of oxygen in water is the saturation level which corresponds to a maximum of 15 ppm acid according to equation 1.

Oxygen in an operating mine cannot be restricted on a practical basis at this time. Experiments performed in the USA, using an inert mine atmosphere and providing the work force with a separate life support system not surprisingly did not prove practical.

After abandonment, seals can be used to restrict both oxygen and water entry, and this approach as been used successfully in some old coal mines in the U.S.A. The sealing of surfaces of open pit mines is still not fully developed, and those pits which generate acid are a major unsolved problem in the future development of control technology.

Restricting oxygen access to stored tailings and sulfidic wastes has a greater chance of being viable. Techniques available for control of long term acid seepage from waste embankments are:

(i) Revegetation

An active soil layer consumes oxygen in its uppermost layers and may gradually become anaerobic if enough organic soil is available. The addition of sewage sludge or other decaying organic matter not only helps consume oxygen but also aids in the rapid establishment of a self-sustaining soil cover.

This approach is site specific. For example, on the Witwatersrand it was found that established grass vegetation on the dumps failed to prevent oxidation of tailings although it prevented windblown distribution of sulfide-bearing silica tailings to the environment.

More information on the oxidation within Witwatersrand gold and uranium mill tailings and the effect of grass cover can be requested from the Chamber of Mines of South Africa, although requests on behalf of this investigation were not very rewarding.

MR. D. MARSDEN
Chamber of Mines of South Africa
No. 4 Shaft, City Deep Mine
Alberton, Transvaal
South Africa
(011) 86-7358

Climatic constraints may have something to do with the failure of grass cover to prevent pyrite oxidation in Witwatersrand tailings in that during winter the grass effectively dies, and there may not be adequate organic humus generated to yield the anaerobic soils. Also, air may penetrate from the base or sides of the dumps. Appalachia has an ideal climate for dense vegetation and seasonal variations, such that most of the vegetation is deciduous so generation of anaerobic soil layers may possibly be more effective.

Revegetation - Canada

The high pyrite-pyrrhotite tailings observed at several operations including Noranda's Waite-Amulet and Horne Division in Quebec, Inco and Falconbridge at Sudbury and Onaping, Ontario, and the major uranium mill tailings near Elliot Lake supported vegetation in a widely varying degree ranging form negligible to lush. At Waite-Amulet, a way was developed to grow a prolific stand of birdsfoot trefoil (a legume) and creeping red fescue (a grass) directly in a limestone pH modified pyritic tailings surface. Several stands of spruce have also volunteered on the tailings. Noranda Mines Ltd., in conjunction with consultants at the University of Guelph, have developed a bio-assay method to select viable species and appropriate conditions for planting.

More information on the prominant success in revegetating the Waite-Amulet tailings can be obtained from:

NORANDA MINES LTD.
Horne Division
BP 4000
Noranda, Quebec J9X 5B6
(819) 762-7764
Bernard W. Brooks

BILL MARSHALL
Consultant and Retired
Vice President of Noranda Mines, Ltd.
Oakville, Ontario
(416) 844-1326

MINE WASTE RECLAMATION LTD.
565 Massey Road
Guelph, Ontario
Canada
Dr. Edward M. Watkin
Jo Ann Watkin

The question now remains as to whether the vegetation method developed is successful in inhibiting AMD generation as well as preventing windblown distribution of AMD-generating dust to a wider area and looking good.

On several pyrite-rich tailings observed at Elliot Lake, the oxidized cap supports a moss growth which forms a new surface layer every year. There were signs of capillary action transport of salts to the surface with evaporites forming at the surface. As shrinkage cracks develop in the mass surface, spruce seedlings were germinating and growing. Some small trees had taken hold, but their root system was limited to the moss layer which did not appear able to support mature trees. A capillary barrier would undoubtably have helped provided there is enough soil covering it to store moisture to support the vegetation.

At Falconbridge's Onaping operations in Ontario, experiments are being undertaken to place a layer of crushed wasterock and municipal garbage over the segregated high sulfide tailings to act as a capillary barrier. Then the layer is sprayed with sewage sludge, and finally, it is planned to place a layer of sterile low sulfide tailings over the top which can be fertilized and seeded. The program is in a developement stage and at the time of the RANDOL summer of 1984 visit, there was not much vegetation to observe, but the results of these experiments will be very well worth following as they develop.

More information about this innovative systems approach can be obtained from:

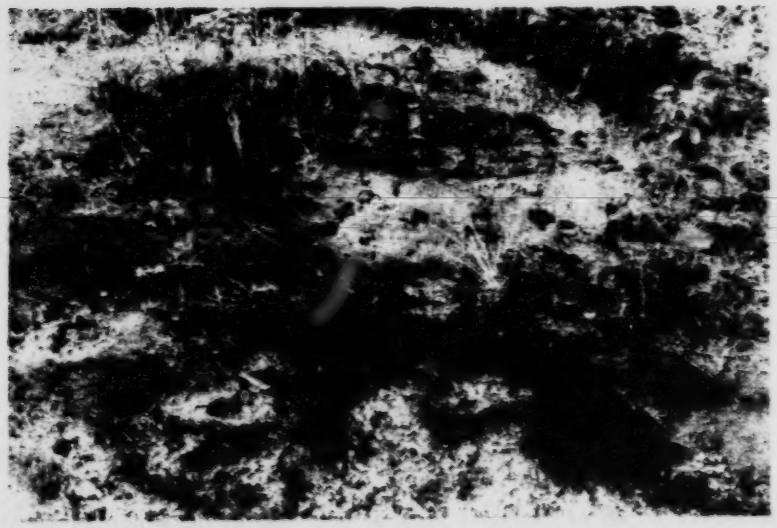
FALCONBRIDGE ONAPING OPERATIONS
Falconbridge Ltd.
Onaping, Ontario POM 2R0
(705) 966-3411
Mark Wiseman

FALCONBRIDGE NICKEL MINES LTD.
Sudbury Operations
Falconbridge, Ontario POM150
(705) 693-2761
John K. Weglo,
Director of Environmental Control
Robert E. Michelutti

INCO Ltd. has 2700 acres of disposal area at one site alone which is fertilized and seeded with rye and harvested annually. This seems expensive and less attractive from a long-term restoration point of view for abandonment than Noranda's vegetation program using birdsfoot trefoil which is adaptable, winter hardy and maintenance-free once established. On the other hand, in some parts of the world, perhaps tailings could support an ongoing profitable agricultural industry.

SOURCES OF ACID MINE DRAINAGE

INDISCRIMINATE USE OF WASTEROCK FILL



CAPILLARY AND RUNOFF TRANSPORT OF SALTS FROM HIGH-SULPHUR TAILINGS

CONCENTRATE SPILLS AROUND TRACKS AND CAR LOADING AND OFFLOADING AREAS

WASTEROCK COVER OVER HIGH SULFUR TAILINGS
FALCONBRIDGE ONAPING OPERATIONS

(ii) Flooding

Water is an excellent diffusion barrier for oxygen. The depth of water needed in a given case is a function of the size of the pond and the wave or mixing action taking place. This technique does, however, require an impervious embankment. It is also not applicable as long-term control in areas where evaporation exceeds precipitation.

(iii) Sealants

Chemical sealants have been used with some success. Typically an aqueous solution of the sealant is sprayed onto the surface of the tailings which, when cured, forms a semi-flexible impermeable mat. The sealant is often mixed with fibrous material to improve its strength and binding properties. Unfortunately, the sealant has a finite life and must be renewed generally every two to three years.

On certain high sulfide tailings with up to 90% pyrite and pyrrhotite, as observed at several mine-mill complexes in Canada, the sulfides formed their own almost impermeable skin on the surface exposed to the air. At Waite-Amulet, for example, a two to three foot layer of the iron sulfide-rich tailings pile was oxidized to yield a strong cemented crust. Below that, the sulfide concentrate was still grey (unoxidized) in color and had a soupy consistency. In this case the pile had formed its own sealant shell. It was strong enough to support a pickup truck, but not for heavy equipment operation on top of these ponds.

At Noranda's Waite-Amulet tailings, prior to their very successful revegetation program, the surface would occasionally dry out to yield undesirable dust problems resembling dust storms. Chemical sealants suffered wind damage, and after 2-3 years, 25-30% of the sealant had blown away according to informal information provided by employees.

Cotter Corporation's old millsite is a cause of acid drainage contamination of groundwater due to leaching from an unlined former ore storage area. This may be overcome by placing an impermeable clay capping over the area to prevent water from reaching the source of contaminants. A similar effect, although expensive, may prove useful in preventing AMD from generating in sulfidic tailings or waste impoundments when the site has to be restored.

9. Wasterock Utilization

Another important way to inhibit AMD is through careful use of wasterock. Many mines in Ontario, Quebec, and elsewhere use wasterock to build road and railbeds, as fill for storage areas and workshop yards, as tailings dam walls, or inside and outside riprap. One mine in Ontario discharges neutralized decant water containing 0.9 ppm Ni, and by the time it reaches the receiving waters and discharge sampling point, the level has increased to 1.0 ppm Ni in the course of about half a mile of stream alongside the road.

The roadbed was built of wasterock, and AMD from this small stretch of road is enough to contribute 10% to the nickel value in the final effluent.

Very careful use of wasterock both above ground and underground is required to control AMD.

Many Canadian massive sulfide orebodies lend themselves to cut and fill mining techniques. Wasterock is crushed and used as backfill underground where it is mixed with coarse sand from the tailings and cement. It is usually found that cement addition inhibits AMD generation underground from the backfill material.

In some cases where tailings and wasterock are very high in pyrrhotite, they cannot be used as backfill because they can be so reactive as to catch fire. This material is usually disposed of in the tailings pond or wasterock pile where it is a likely acid generator.

10. Concentrate Stockpiles and Transportation

Concentrate left in the open will also generate AMD in surface runoff and seepages. Careless handling of concentrate stockpiles and spillages must be avoided for this reason. These are likely to occur in areas where concentrate is loaded and unloaded onto trucks and railcars and along roadways and rail lines along which concentrate is hauled. Railcars and trucks must be kept in good repair to prevent leaks of material.

At Falconbridge Onaping works, the surface of a railcar loading site was ripped up and processed through the mill to prevent AMD contamination of a potable water well. Undoubtedly this also occurs at other millsites. Outdoor handling and open stockpiles of concentrate can also result in windblown distribution of concentrate which can result in AMD too.

11. Backfill of Tailings and Wasterock

Sulfide-rich wasterock and tailings can be disposed of as cemented backfill as a means of inhibiting acid mine drainage. This serves two purposes. First, the material once stored underground in this way is much less likely to generate AMD that can impact the environment. First the material is encapsulated and mixed with cement which has a high pH and, therefore, inhibits oxidation of sulfides. Second, by filling the stopes underground, there is less room for water to accumulate or to circulate and, therefore, two sources of AMD are inhibited at the same time.

There are limitations, however. 1) Not all the mined tailings and wasterock will fit into the cavity because of the expansion factor when it was crushed. At least 40% will have to be disposed of elsewhere. 2) Some of the material that is richest in sulfides from

massive sulfide mines cannot be used as backfill because it is pyrophoric and may generate heat or even catch fire underground. 3) Once tailings and waste has been disposed of in this way, it is not that easy to reclaim them if, at a future date, they would represent valuable resources had they been stored on the surface.

12. Deep Lake and Submarine Disposal of Tailings

The disposal of tailings in deep lakes may represent one of the best disposal alternatives from the AMD point of view where such lakes exist, and this is done in several cases. The full ramifications of the effects of deep lake disposal need to be considered, however.

In shallow lake tailings disposal, wind and wave action may regenerate the oxygen supply, and some degree of oxidation may be experienced. Here, the idea of KALIN (1984, personal communication) of establishing an underwater plant cover which would serve to generate an anaerobic zone on the water-tailings interface and simultaneously also potentially remove some undesirable dissolved metals and suspended solids from the water above.

HAWLEY (1975) cited the following advantages of underwater (deep) tailings disposal:

(1) Low operating and maintenance costs.

(2) Large capacity.

(3) Tailings deposits in deep water sites are not in direct contact with the atmosphere. It is logical to assume, therefore, that chemical reactions at land tailings sites such as between reactive tailings particles such as iron sulfides and atmospheric oxygen, etc., are either subdued or absent in many deepwater sites. To be more specific, it is extremely probable that acid generation problems due to the reactions involving sulfide gangue minerals in situ in tailings masses would be completely or largely eliminated by using proper deepwater tailings disposal procedures (in either salt water, which would be preferable because of its alkaline nature, or in fresh water).

(4) Less chance of mechanical failure.

(5) On completion of the project, the deepwater disposal site can be completely hidden with no revegetation needs.

The disadvantages cited were:

(1) No opportunity to recover a decanted solution.

(2) Migration of fine particles of solids which can't be confirmed underwater.

(3) Underwater disposal may have a large number of direct impacts on fishery resources.

(4) No chance to control environmental impacts that develop after the fact.

(5) Not nearly enough is known about the effects of this practice on the environment.

Despite the potential advantages of deep lake disposal of tailings for several Canadian operations, including the uranium operations at Elliot Lake, this practice is not currently employed on the Canadian Shield. The reasons are not clear.

There have been cases where settling ponds have been used to trap concentrate particles from water runoff draining from base metal mills. Many years later these ponds were dredged and found to yield a sulfide concentrate that could be used either as an incremental metal source in the smelter (as at Falconbridge, Ontario), or as feed to the flotation circuit (as at St. Joe, Balmat, New York). In the case of the ponds at Falconbridge, although the concentrate could be recovered, the quality of the water in contact with it in the shallow pond had a high metal content which had to be precipitated prior to discharge. The significance of this is that shallow water impoundments of sulfide wastes will not solve the problem.

HAWLEY (1975) referred to the fact that, in mountainous terrain near the sea, several mining companies use the sea as a tailings disposal area, e.g.:

Bouganville Copper,	78,000 tpd
Utah Mines Ltd., Vancouver Island	15,000 tpd
Atlas Consolidated, Cebu, Phillipines	63,000 tpd
Greenex Mines Ltd. (Cominco), Greenland	

Deep water lake disposal of sulfide tailings is already practiced by Western Mines Ltd. at their Myra Falls copper-zinc flotation plant in British Columbia which could be a good site at which to test the degree of oxidation of the sulfides and the effect on water in contact with the tailings.

AMD Inhibition - Systems Approach and Summary

In order to inhibit AMD, a systems approach can be a big help even though the final answers as to the best way to completely prevent it are not yet known.

In open pit mines, to date, there do not seem to be any answers other than to keep water out of the pit and to cut off seepages and drainage into the pit. COMINCO solved the acid mine drainage problem at their Wedge Mine in New Brunswick by filling the pit back up again with wasterock and revegetating the site after sealing and contouring the surface.

In underground mines, it appears that AMD can be reduced by sealing the mine, keeping the mine dry, and possibly by using volatile bacteria inhibiting chemicals to penetrate the fractures.

With selective use of wasterock above ground and appropriate disposal of wasterock and tailings in such a manner, AMD is minimized. Where AMD generation is unavoidable, it can be neutralized by placing potential acid generating wasterock over basic calcerous waste in the impoundment or storage area as has been designed in HOMESTAKE MINING CO.'s new McLaughlin gold operation.

Several disposal methods which incorporate synergistic use of urban garbage and sewage sludges were mentioned above as well as ways to revegetate waste and tailings to reduce oxygen and water incursions.

Good housekeeping of ore and concentrate stockpiles is essential.

In some cases, pyrite is now floated from gold-uranium tailings for use in making sulfuric acid, and this leaves the tailings with a much lower sulfide mineral content. Such tailings have a correspondingly reduced acid generating capacity.

In some more recent uranium extraction developments, pressure oxidation and leaching is employed which consumes the acid generating sulfide in the ore leaving tailings inert and more easily stabilized for disposal.

Where water is to be treated, the capital and operating costs depend on the volume of water to be treated. Therefore, appropriate diversion of runoff from outside the area makes it possible to reduce the effective watershed and hence the volume of water to be treated and thereby also reduce operating and capital costs.

The magnitude of the acid mine drainage problem is so great, and the costs of meeting regulatory requirements for operating and abandoned mine, mill, and tailings sites are so huge, that this area deserves urgent and special attention. A concerted effort is required to fully understand and characterize acid mine drainage and to develop ways to inhibit or prevent it. No effort or expense should be spared in these endeavors.

CHAPTER 24

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ACID MINE DRAINGAGE

INTRODUCTION

A very wide range in approach was found in the treatment of AMD. In this discussion, AMD is used in the sense of all water and effluents that have undergone a change in composition through contact with sulfide ore, gangue, wasterock, tailings, etc. Usually, this results in a reduced pH and elevated levels of sulfate, iron, and many metals such as Cu, Zn, Cd, Hg, Su, Ni, Co, Mn, etc. In the context used here, the water may never have been in a mine nor need it be acid--just impacted by a mining activity past or present.

Treatment of AMD ranges from simple addition of lime or limestone for pH adjustment in a passive system to an elaborate sequence of settling, oil removal, pH adjustment for precipitation, coagulation, solid-liquid separation to remove precipitates, clarification, and acid addition for final pH adjustment before discharge. Some of these applications are listed in the table overleaf.

The selection of an appropriate treatment plant depends on many factors including flowrate, composition, topography and the environmental sensitivity and permit regulations for discharge. The treatment methods to choose from include:

1) Lime addition and pond settling.
2) Limestone addition and pond settling.
3) Lime addition, thickener-clarifier, filtration.
4) Lime addition, thickener-clarifier, polishing pond.
5) High density sludge process (HDS).
6) High density sludge process plus desalination.
7) NaOH addition, static mixer, settling pond.
8) NaOH addition, continuous filtration.
9) Limestone passive system, biological polishing pond.
10) Polishing pond alone.
11) Alumina-lime-soda process.
12) Seeded slurry reverse osmosis/evaporation.
13) Low pressure ultrafiltration with charged membranes.

Several of these systems are still in the experimental stages, and although there has already been significant innovation, there is room for much more. Several useful, innovative, and interesting approaches were found during this investigation. Here some of the highlights are discussed.

ACID MINE DRAINAGE TREATMENT

Company	Location	Type of Mine-Mill	Precipitating Reagent	Process	Capacity m^3/d	Effluent Treated	Comments
Bethlehem Mines Corp.	Mine 77, Cambria Division	Bituminous Coal	Lime	HDS	2,195	AMD	Conventional thickener-clarifier.
Bethlehem Mines Corp.	Mine 31, Cambria Division	Bituminous Coal	Lime	HDS	18,550	AMD	Conventional thickener-clarifier.
Bethlehem Mines Corp.	Mine 32-33, Cambria Division	Bituminous Coal	Lime	HDS	39,225	AMD	Conventional thickener-clarifier.
Bethlehem Mines Corp.	Mine 78, Cambria Division	Bituminous Coal	Lime	HDS	2,725	AMD	Conventional thickener-clarifier.
Bethlehem Mines Corp.	Mine 38, Cambria Division	Bituminous Coal	Lime	HDS	1,630	AMD	Conventional thickener-clarifier.
Rand Mines Ltd.	ERPM, Springs, South Africa	Gold and Uranium Mine	Lime	HDS	46,335	AMD	Conventional thickener-clarifier.
Bethlehem Mines Corp.	Panther Valley Division	Anthracite Coal	Lime	HDS	65,410	AMD	Conventional thickener clarifier, CO_2 removed by aeration ahead of lime addition, 30-40% solids in sludge.
Noranda Mines Ltd.	Waite Amulet, Quebec	Cu-Zn Mine Runoff and Tailings	Lime	HDS	4,320	AMD	Lamella platepack inside conventional clarifier.

ACID MINE DRAINAGE TREATMENT (Continued)

Company	Location	Type of Mine-Mill	Precipitating Reagent	Process	Capacity m^3/d	Effluent Treated	Comments
Noranda Mines Ltd.	GECO Division, Ontario	Sulfide Tailings Cu-Pb-Zn Mine	Lime	Conventional Settling	4,100	AMD	Scaling effluent. Conventional clarifier.
Noranda Mines Ltd.	Les Mines Gallen	Zn-Au-Ag	Lime	HDS	2,600	AMD	Lamella thickener.
Noranda Mines Ltd.	Mattabi Division Ontario	Sulfide Tailings Cu-Pb-Zn Mine	Lime	HDS	3,900	AMD	Lamella clarifier, zinc-rich precipitate to smelter. At over pH 10, precipitate flocs are light.
Noranda Mines Ltd.	Brunswick Mining and Smelting, Bathurst, N.B.	Sulfide Mine Cu-Pb-Zn	Lime	Formerly HDS, Now Lime Settled	1,800	AMD	High scaling interfered with Lamella clarifier.
Anglo American Corp.	Kromdraai Coal Mine	Restored Coal Mine Drainage	Lime	HDS	10,000	AMD	Conventional thickener-clarifier. 30-34% solids in sludge without optimization.
Cominco Ltd.	Kimberly, B.C.	Copper Moly	Lime	HDS	13,000	AMD	Conventional thickener-clarifier.
Cominco Ltd.	Trail, B.C.	Cu-Pb-Zn Refinery	Lime	HDS	6,500	Refinery Effluent	Conventional thickener. Recycle of sludges to smelter.

ACID MINE DRAINAGE TREATMENT (Continued)

Company	Location	Type of Mine-Mill	Precipitating Reagent	Process	Capacity m^3/d	Effluent Treated	Comments
INCO Ltd.	Sudbury, Ontario Copper Cliff Creek	Nickel-Copper	Lime and Air	Precipitation Settle in Thickener Filter	272,000	AMD and Surface Drainage	2% sludge density discarded to tailings pond.
Falconbridge Ltd.	Sudbury, Ontario	Nickel-Copper Mines-Mill-Smelter	Lime and Air	Precipitation, Settle in Pond, Polish with Plants	16,000	AMD and Tailings Recycle	Excellent example of biological polishing and systems approach to water management.
Falconbridge Ltd.	Onaping, Ontario	Nickel-Copper	Limestone	pH Adjustment Only	44,000	AMD and Tailings Recycle	
Kidd Creek Mines Ltd.	Timmins, Ontario	Mine Zn-Cu-Ag	Lime	Precipitation, Settle in Pond	16,000	AMD from Mine	Sludge dredged from pond periodically.
Kidd Creek Mines Ltd.	Timmins, Ontario	Mill-Smelter Zn-Cu-Ag	Lime	Precipitation, Settle in Pond	44,000	AMD from Mill Tailings	

ACID MINE DRAINAGE TREATMENT (Continued)

Company	Location	Type of Mine-Mill	Precipitating Reagent	Process	Capacity m^3/d	Effluent Treated	Comments
Noranda Mines Ltd.	Brunswick Mining Bathurst, N. B.	Cu-Pb-Zn Minewater	Lime	Lime Precipitation Settle and Age in Pond		Mine and Mill Water	Serious thiosulfate problem.
Rio Algom Ltd.	Elliott Lake	Uranium	Lime	Lime Addition to Pond		AMD from Tailings Oxidation	$BaCl_2$ precipitates radium.
AMAX, Inc.	Climax, Colorado	Molybdenum	Lime Plus	Lime Plus Oxidant Precipitates Metals Decomposes Cyanide Electro Coagulation Lectroclear Flotation		AMD From Molybdenum Flotation Tailings	CIX installed for Mo removal.
AMAX, Inc.	Mount Emmons, Colorado	Zinc Mine AMD and Tailings	Lime and Air	Precipitation of Metals Electrocoagulation Lectroclear Flotation Sand Filtration	9,500	AMD From Old Zinc Mine and Tailings	Perpetual treatment for AMD from a site from which owners never mined a product. Cost $12 million and $700,000 per year.

ACID MINE DRAINAGE TREATMENT (Continued)

Company	Location	Type of Mine-Mill	Precipitating Reagent	Process	Capacity m^3/d	Effluent Treated	Comments
Falconbridge	Sudbury, Ontario	Ni-Cu	Lime and Air	Plants in Bog for Polishing S/S & Metals	16,000	AMD From Tailings	Water is macro recycled. Marsh helps remove precipitated metal.
St. Joe Minerals	Balmat, New York	Pb	Lime for pH Adjustment	Plants in Marsh Polish S/S & Metals		AMD From Mine and Wasterock	Difficulty meeting temperature criteria for discharge in summer due to shallow pond. Water depth in polishing pond critical for cattails.
AMAX Lead Tollers, Inc.	Buick Mine-Mill Missouri	Pb-Zn			20,800	Mine and Mill Waters	Large tailings lagoon and artificial meanders, polishing ponds, algae and plants with final polishing lagoon.

Water Recovery from Acid Mine Drainage

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Acid mine drainage (AMD) is a major deleterious pollutant associated with the coal extraction industry. The AMD is formed by the oxidation and subsequent hydrolysis of pyrite (FeS_2) yielding sulfuric acid and water. The sulfuric acid, in turn, dissolves metallic and other elements from the surrounding strata or material. An AMD stream with a *p*H below 3 is common in regions where this problem is most intense. Acidities between 20,000 to 30,000 mg/liter as $CaCO_3$ can be found in some seeps from the refuse piles of West Virginia and Pennsylvania and in some strip mine ponds in Illinois.

The problems of AMD are most significant in the eastern coal mining regions where enormous quantities of pyritic shales are exposed during the extensive surface and underground mining operations found there. This is not to imply that AMD is found only in the East; for example, significant AMD pollution is associated with the gold-mining operations in Colorado as well as the lead-silver mines in Montana. In general, AMD is a problem associated with the extraction of all the sulfide-associated minerals (e.g., lead, zinc, copper, etc.) where their occurrence is in nonarid areas. With the increased emphasis on energy and the simultaneous expansion of western mining operations, the problem of AMD must receive increased attention.

The U. S. Environmental Protection Agency (EPA) is currently conducting and/or sponsoring research in the field of AMD treatment. Several of these current projects are sufficiently advanced to report the major conclusions. Seven major treatment processes will be briefly discussed in this report (i.e., limestone neutralization, lime neutralization, combination limestone-lime neutralization, lime-soda treatment, alumina-lime-soda treatment, reverse osmosis treatment, and ion exchange treatment). The emphasis will be placed on effluent quality, operational limitations, cost, and overall applicability.

Neutralization of AMD is accomplished by the addition of an alkaline reagent to elevate the *p*H to a level (generally 7 to 8) where statisfactory precipitation of such metals as iron and aluminum is effected. The trade-off for iron and aluminum removal is an increase in the calcium level where calcium neutralizers are used. Neutralization has very little effect upon total dissolved solids levels.

LIMESTONE NEUTRALIZATION

Considerable energy input and process complexity are involved in transforming (calcining) limestone ($CaCO_3$) into lime [CaO or more commonly

Table 1.
Neutralization Data Summaries for Limestone at One Liter/Sec Where Hydrogen Peroxide Was Injected into Process B to Oxidize the Ferrous Iron

		Mean	*Std. Dev.*
Effluent *p*H	A	6.49	0.09
	B	6.58	0.09
Neutralizer usage, kg/cu m	A	2.72	1.0
	B	1.06	0.2
Neutralizer usage, lb./1,000 gal.	A	22.7	8.4
	B	8.8	1.6
Neutralizer usage, g/cu m/ppm influent acidity	A	4.52	1.8
	B	1.74	0.3
Cost, cents/1,000 gal.	A	12.48	4.6
	B	4.87	0.9
Cost, cents cu m	A	3.30	1.2
	B	1.29	0.2
Cost, cents/10^3 cu m/ppm influent acidity	A	5.48	2.2
	B	2.11	0.4
Utilization efficiency, %	A	19.	5.9
	B	62.	11.
Stoichiometric factor (influent acidity)	A	4.5	1.8
	B	1.8	0.3
Sludge to waste, % of influent AMD	A	3.1	0.3
	B	2.6	0.3
Dry solids to waste, lb./1,000 gal.	A	21.4	10.4
	B	11.2	4.2
Dry solids to waste, kg/cu m	A	2.56	1.3
	B	1.35	0.5
Underflow solids, %	A	7.9	4.0
	B	4.9	1.9
Effluent turbidity, JTU	A	60.	19.
	B	46.	5.
Effluent suspended solids, mg/liter	A	82.	16.
	B	34.	3.6
Difference in reagent usage between Process A and B, %		156.	

Table 2.
Chemistry Analyses Illustrating Effluents from Various Processes to Treat AMD

Sample	*Cond*	*Acid*	*pH*	*Ca*	*Mg*	*Total iron*	*Fe^{2+}*	*Na*	*Al*	*Mn*	*SO_4*	*Alk*	*TDS*
Example One—Limestone Neutralization: Ferrous(A) versus Ferric(B) Using No Coagulants													
Raw feed A	4,000	610	5.2	360.	110.	270.	260.	480.	5.4	5.9	3,000	12.	4,200
Feed B (H_2O_2)	4,000	590	3.1	340.	95.	270.	0.	440.	8.2	5.9	2,500	0.	3,500
Effluent A	4,000	230	6.5	420.	90.	150.	150.	380.	1.0	5.8	2,400	88.	3,500
Effluent B	4,000	13	6.5	380.	70.	6.2	0.	370.	1.2	5.0	2,000	50.	2,900
Example Two—Limestone Neutralization with Extended Aeration, Sludge Recycle, and Coagulant Addition													
Raw feed	3,650	460	5.5	370.	110.	230.	220.	470.	12.	5.4	2,800	8.	4,000
Effluent	3,650	0	7.4	520.	110.	0.9	0.	440.	0.4	3.9	2,700	47.	3,700
Example Three—Lime Neutralization Comparing *p*H 8(A) versus *p*H 7(B) Using Coagulant Addition													
Raw feed	4,000	520	5.7	400.	130.	280.	260.	510.	9.8	6.4	3,200	23.	4,500
Effluent A	4,100	0	7.9	600.	120.	2.1	0.	500.	0.4	1.6	3,300	88.	4,700
Effluent B	4,100	0	7.0	620.	120.	10.	0.7	490.	0.6	4.9	3,300	50.	4,400
Example Four—Combination Limestone-Lime Treatment(A) versus Lime Treatment(B) Using Coagulants													
Raw feed	3,600	630	5.2	340.	100.	290.	270.	380.	15.	5.4	2,700	4.4	3,800
Effluent A	3,500	0	8.0	560.	83.	2.3	0.	370.	0.5	2.2	2,500	100.	3,500
Effluent B	3,500	0	8.0	560.	95.	1.4	0.	360.	0.2	1.2	2,500	110.	3,500
Example Five—Lime-Soda Treatment Where Effluent Hardness Is Less Than 100 mg/liter													
Raw feed	820	170	3.0	28.	18.	17.	—	1.8	13.	4.5	270	0.	350
Sed. eff.	930	0	11.	140.	1.1	0.8	—	1.8	2.7	0.2	240	100.	500
Softener eff.	1,000	0	10.8	41.	0.4	0.3	—	140.	2.5	0.05	220	110.	510
Recarb. eff.	790	0	9.2	33.	0.4	0.3	—	140.	2.4	0.06	220	74.	470
Example Six - Alumina-Lime-Soda Treatment													
Raw feed	—	700	2.8	8.	25.	100.	—	2.	40.	4.0	750	0.	950
Effluent	—	0	7.5	20.	10.	0.3	—	150.	0.2	0.04	250	—	450
Example Seven—Reverse Osmosis Treatment													
Raw feed	1,000	240	3.4	130.	90.	77.	64.	—	12.	12.	750.	0.	1,300
Waste brine	3,600	810	2.9	490.	310.	330.	250.	—	44.	24.	2,800.	0.	4,500
Effluent	17	32	4.5	0.5	0.6	0.5	0.5	—	0.2	0.08	2.2	0.	5
Example Eight Ion Exchange Treatment (Design Values)													
Raw feed	—	240	3.4	130.	90.	77.	64.	1.0	12.	12.	750	0.	1,300
Cation eff.	·	800	1.9	13.	5.	6.	5.	3.	0.2	0.6	750	0.	800
Anion eff.		0	8.0	13.	1.5	1.2	1.0	20.	0.2	0.3	40	20.	110
Neu. eff.	—	0	7.5	20.	1.5	0.1	0.1	20.	0.2	0.04	50	30.	120

Note: All units are mg/liter except for conductivity (micromhos/cm) and *p*H. Alkalinity and acidity are expressed as $CaCO_3$.

$Ca(OH)_2$]; therefore, limestone is a considerably cheaper reagent than lime.

Unfortunately, limestone does not react efficiently with AMD. The reaction is especially inefficient in AMD situations where the iron is in the ferrous state. Because of this and the fact that it is difficult for limestone to elevate the *p*H beyond 7 (therefore the iron oxidation rate is very slow), the use of limestone is generally considered unfeasible for ferrous iron situations. Chemical cost reductions as great as 30% have been noted in ferric iron situations when limestone has been used as the neutralizing agent in place of lime. An example of the relative effectiveness of limestone in neutralizing ferrous versus ferric iron AMD is presented in Table 1. Chemical analyses of influent and product water from that study are presented in Table 2. Use of coagulants can significantly improve effluent quality but can add as much as $.10/1,000 gal. to the treatment cost. The effectiveness of coagulant addition during limestone

treatment of ferrous AMD is shown in Table 2 Example Two.

The effluent water from limestone (and lime) neutralization processes are typically hard because of the high calcium and magnesium concentrations.

As much as 5% of the influent AMD volume exits as a dense, difficult-to-handle sludge. Adequate sludge disposal technologies are not available.

LIME NEUTRALIZATION

Calcium hydroxide (hydrated lime) is the most frequently used reagent for AMD treatment. Lime is readily available, moderately expensive, highly reactive, and versatile in its application to AMD treatment. It is almost always used for ferrous iron treatment situations because it can readily elevate *p*H to enable rapid iron oxidation.

Typical data for lime neutralization of AMD are presented in Table 3 to illustrate operating parameters. Water analyses are tabulated in Table 2—Example Three for comparison with other treatment techniques. As in the case of limestone, the high calcium and magnesium levels render the water quite hard. Chemical costs during these studies were between $.10 and $.20/1,000 gal. including coagulant costs. Sludge from lime neutralization occupies a much larger volume than limestone sludge but is easier to handle.

Table 3.
Neutralization Data Summaries for Lime at 0.8 Liter/Sec (12 GPM) Using Coagulant and Comparing *p*H 8 (Process A) versus *p*H 7 (Process B)

		Mean	*Std. Dev.*
Effluent *p*H	A	7.93	0.1
	B	6.91	0.1
Neutralizer usage, kg/cu m	A	0.739	0.1
	B	0.362	0.1
Neutralizer usage, lb/1,000 gal.	A	6.2	0.6
	B	3.0	0.5
Cost, cents/1,000 gal.	A	10.8	1.0
	B	5.3	0.8
Cost, cents/cu m	A	2.85	0.3
	B	1.40	0.2
Cost, cents/10^3 cu m/ppm influent acidity	A	5.84	0.7
	B	2.83	0.2
Utilization efficiency, %	A	55.	7.
	B	108.	9.
Stoichiometric factor (influent acidity)	A	2.03	0.2
	B	0.99	0.1
Sludge to waste, % of influent AMD	A	2.6	0.2
	B	2.5	0.1
Sludge recycled, % of influent AMD	A	29.4	2.7
	B	26.8	2.4
Dry solids to waste, kg/cu m	A	0.92	0.5
	B	1.02	0.4
Underflow solids, %	A	3.5	2.1
	B	4.1	1.6
Effluent turbidity, JTU	A	7.	2.3
	B	27.	11.
Effluent suspended solids, mg/liter	A	9.3	6.4
	B	13.3	8.1
Difference in reagent usage between Process A and B, %		104.	

COMBINATION LIMESTONE-LIME NEUTRALIZATION

Two-stage treatment composed of first-stage limestone addition to approximately *p*H 6 followed by second-stage lime treatment to *p*H 8 has been shown to offer reagent cost reductions as high as 30% as illustrated in Table 4. No improvements in effluent water quality were obtained (Table 2—Example Four) as compared to lime treatment. Likewise, there is no reduction in TDS from any of the neutralization

Table 4.
Neutralization Data Summaries for Combination Treatment with Reduced First-Stage Limestone Addition (Process A) versus Lime (Process B) Using Coagulants

		Mean	*Std. Dev.*
First-stage effluent *p*H	A	6.8	0.2
	B	—	—
Final effluent *p*H	A	8.0	0.
	B	8.0	0.
Limestone usage, kg/cu m	A	0.21	0.04
	B	0.	0.
Lime usage, kg/cu m	A	0.53	0.07
	B	0.79	0.1
Cost, cents/1,000 gal.	A	8.67	0.9
	B	11.60	1.5
Cost, cents/cu m	A	2.29	0.3
	B	3.06	0.4
Cost, cents/10^3 cu m/ppm influent acidity	A	4.15	0.5
	B	5.57	0.9
Utilization efficiency, %	A	71.	8.0
	B	63.	9.1
Stoichiometric factor (influent acidity)	A	1.69	0.2
	B	1.95	0.3
Sludge to waste, % of influent AMD	A	1.98	0.1
	B	1.88	0.1
Sludge recycled, % of influent AMD	A	21.7	1.0
	B	17.6	1.0
Dry solids to waste, kg/cu m	A	0.51	0.2
	B	0.66	0.2
Underflow solids, %	A	2.6	0.9
	B	3.5	1.1
Effluent turbidity, JTU	A	4.	1.2
	B	4.	1.4
Effluent suspended solids, mg/liter	A	5.5	2.4
	B	5.4	1.3
Difference in reagent usage cost between Process A and B, %		34.	

processes. Sludges from combination treatment are similar to those from lime treatment. Quantification of operating parameters for limestone, lime, and combination treatment were made at the EPA Crown Mine Drainage Control Field Site, Rivesville, West Virginia.

LIME-SODA TREATMENT[1]

This process involves lime neutralization to *p*H 11 for magnesium removal, addition of soda ash (sodium carbonate) to precipitate calcium as calcium carbonate, and final *p*H adjustment to neutrality by the addition of carbon dioxide. The removal of calcium and magnesium significantly decreases the hardness of the effluent. Typical operating parameters are given in Table 5 and chemical data are presented in Table 2—Example Five. These data were generated from an operational full-scale (7 mgd) treatment plant in Altoona, Pennsylvania. The AMD in this situation is extremely dilute. Total treatment costs (including capital, amortization, and operating) were estimated near $.40/1,000 gal. Sludge disposal was not considered in the cost estimates.

In this particular set of data quoted on this process, the effluent quality is almost potable. The influent AMD, however, is unusually mild as previously emphasized, and it is important to note that this process will not normally produce potable-quality water because the TDS levels are not reduced during treatment and the great majority of AMD waters contain greater than 500 mg/liter TDS (the potable limit), including sulfate levels much higher than 250 mg/liter (the potable limit).

Table 5.
Typical Operational Data for Lime-Soda Treatment of Mild-Quality Acid Mine Drainage

	Mean
Flow, mgd	3.5
Flow, cu m/sec	0.15
Lime usage (neutralization), lb./1,000 gal.	1.53
Lime usage (neutralization), kg/cu m	0.18
Soda ash usage (softening), lb./1,000 gal.	2.63
Soda ash usage (softening), kg/cu m	0.32
Carbon dioxide usage (recarbonation), lb./1,000 gal.	0.43
Carbon dioxide usage (recarbonation), kg/cu m	0.05
Chemical cost (neutralization), cents/1,000 gal.	2.68
Chemical cost (softening), cents/1,000 gal.	8.68
Chemical cost (recarbonation), cents/1,000 gal.	1.85
Total chemical cost, cents/1,000 gal.	13.21
Total chemical cost, cents/cu m	3.49

The near-potable capability of the process enables the potential blending of the effluent with insufficient quantities of high-quality water to augment the potable supply. In fact, this is the current use of the 7.0 mgd plant presently operating at Altoona.

ALUMINA-LIME-SODA TREATMENT[2]

A close relative to the lime-soda process, the alumina-lime-soda scheme utilizes the addition of sodium aluminate rather than soda ash. Lime neutralization is taken to *p*H 12 where the sodium aluminate combines with the sulfate and calcium to precipitate as calcium sulfoaluminate. Magnesium precipitates as magnesium hydroxide as in the lime-soda process. In the second stage, carbon dioxide is added to precipitate the excess calcium as calcium carbonate and to reduce *p*H as in the lime-soda process. In contrast to the lime-soda process, the alumina process will reduce the sulfate and TDS levels; therefore, the process will produce a potable effluent.

This process was demonstrated on a bench-scale basis at an AMD source near DuBois, Pennsylvania (Hollywood Treatment Plant). To decrease costs, only 80% of the total AMD was treated by the process and the high-quality effluent was blended with the remaining 20% to degrade the product to the upper limit of potable levels (250 mg/liter of sulfate was the controlling parameter). Typical operating data are given in Table 6 and chemical data are presented in Table 2—Example Six. Chemical costs for the reported study were around $.90/1,000 gal. Some improvement in costs can be obtained as the process is not optimized and bulk prices of sodium aluminate could be reduced by increased demand. Again, no considerations were made of sludge disposal.

Table 6.
Typical Operational Data for Alumina-Lime-Soda Treatment of Acid Mine Drainage

	Mean
Flow, mliter/min	170
Lime usage, lb./1,000 gal.	13.17
Lime usage, kg/cu m	1.58
Sodium aluminate usage, lb./1,000 gal.	4.26
Sodium aluminate usage, kg/cu m	0.51
Carbon dioxide usage, lb./1,000 gal.	1.48
Carbon dioxide usage, kg/cu m	0.18
Chemical cost (lime), cents/1,000 gal.	23.1
Chemical cost (sodium aluminate), cents/1,000 gal.	57.5
Chemical cost (carbon dioxide), cents/1,000 gal.	6.4
Total chemical cost, cents/1,000 gal.	87.
Total chemical cost, cents/cu m	23.

REVERSE OSMOSIS TREATMENT[3]

Reverse osmosis involves the passage of water molecules from the side of a semipermeable membrane containing a higher concentration of pollutants to the side containing the lesser concentration. This transport is accomplished by the application of

Table 7.
Operating Parameters for Spiral-Wound Reverse Osmosis Study at 75% Recovery at Mocanaqua, Pennsylvania

Parameter	*Value*
Raw water feed flow, gpm	6.02
Product water flow, gpm	4.50
Brine water discharged, gpm	1.52
Brine water recycled, gpm	4.26
Minimum brine product flow ratio (Tubes 1 and 2), ratio module	5:1
Maximum brine product flow ratio (Tube 3), ratio module	12:1
Water recovery, %	74.8
Recovery of blended feed, %	43.8
Feed pressure, psig	602.
Feed water temperature, °F	62.6
Tube one flux, gal./ft.^{2}/day at 600 psi net and 77°F	19.56
Tube two flux, gal. ft.^{2}/day at 600 psi net and 77°F	19.52
Tube three flux, gal. ft.^{2}, day at 600 psi net and 77°F	18.77
Length of run, hours	1,672.

All values are means from 73 data sets.
Note: To convert flux (gal./ft.^{2}/day at 600 psi and 77°F) to liters/m^2 day at 4,138 kN/m^2 and 25°C, multiply by 40.67; to convert gal. min. to liters/sec., multiply by 0.063; and to convert psi to kN/m^2, divide by 0.145.

pressure to the concentrated solution. The semi-permeable membrane selectively refuses to allow the majority of pollutants in AMD to permeate to the product side of the membrane. Of course, this explanation is a gross simplification but is sufficient to allow visualization of the process by those who are unfamiliar with it.

A great deal of study has been devoted to reverse osmosis (RO) treatment of AMD because of its ability to demineralize the water and produce a high-quality effluent. The versatility of reverse osmosis technology allows modification of the operating parameters to enable "tailoring" the product to the desired quality level. By such techniques, reverse osmosis can generally produce potable (with the exception of *p*H) water from AMD. Very minimal lime addition is sufficient to increase the product *p*H to acceptable values.

Results of an application of RO treatment to a ferrous-iron AMD in Mocanaqua, Pennsylvania, are given in Table 7. Chemical data are presented in Table 2—Example Seven. Current estimates of RO treatment costs for AMD range from $0.75 to $2.00/1,000 gal. depending upon a wide variety of factors. These costs do not include treatment and disposal of the highly-polluting waste-brine stream resulting from RO treatment.

ION EXCHANGE TREATMENT

Ion exchange is "a reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid. In this definition, the solid is the ion-exchange material (resin)."[4]

Several ion exchange applications to AMD treatment are currently in operation in Pennsylvania. EPA is presently expanding the results of bench-scale research[3] to pilot-scale to evaluate potable water production by a different process than is currently in use.

The ion exchange process involves the use of a 2-resin system; the first resin being an H^+-form, strong-acid cation exchanger and the second resin being a weak-base anion exchanger in the free-base (OH^-) form.

In the cation column, H^+ ions are exchanged for the metal ions (iron, aluminum, magnesium, calcium,

Table 8.
Design Parameters for EPA Ion Exchange Treatment of Acid Mine Drainage

	Cation	*Anion*
Regenerant	HCl	NaOH
Bulk solution concentration, weight %	31.5	20.0
Bulk solution weight, lb./gal.	9.67	9.68
Bulk solution cost, dollars/ton	35.00	40.00*
Desired regenerant concentration, weight %	9.2	4.0
Regenerant dosage, lb./ft.^{3} of resin	2.0	3.5
Resin volume, ft.^{3}	33.	19.
Resin capacity, kilograins/ft.^{3}	14.8	30.0
Influent load, grains/gal.	46.	46.
Flow rate, gal./min.	10.	10.
Equivalence factor, regenerant as $CaCO_3$	9.611	8.778
Regenerant weight, lb./gal. of bulk	3.05	1.94
Regenerant volume, gal. of bulk/ton of bulk	207.	207.
Regenerant cost, cents/lb. of 100% regenerant	5.6	10.
Regenerant usage, lb. of 100%/regeneration	66.	67.
Regenerant usage, gal. of bulk/regeneration	22.	34.
Diluent required to reach desired conc., gal./regen.	61.	160.
Total volume to waste, gal./regeneration	83.	194.
Regenerant cost, cents/regeneration	367.	665.
Exchanger capacity, kilograins	488.	570.
Exchanger capacity, gal. of influent	10,620.	12,390.
Duty cycle, minutes	1,062.	1,239.
Duty cycle, hours	17.7	20.7
Regenerant cost, cents/1,000 gal.	35.	54.
Regenerant utilization efficiency, %	77.	98.

*Based upon $100/ton cost of 50/50 NaOH and diluting on-site to 20% by weight.

manganese, etc.) in the AMD. Since the only anion in AMD is typically sulfate, the cation effluent becomes predominately H_2SO_4 with residual concentrations of metals.

The sulfuric acid solution enters the weak base anion exchanger when the acid is sorbed by the resin and hydroxyl ions are substituted. A weak-base anion exchanger cannot split neutral salts, however, and some carry-over exists of metal salts that were not removed by the cation exchanger and pass unaffected through the anion column.

As the anion effluent contains residual levels of iron and manganese, it must be further treated to meet potability requirements. This is accomplished by lime neutralization to *p*H 9 or 10, followed by filtration, followed by *p*H readjustment back to neutral levels. A small portion of the cation effluent is added to the filtered effluent to reduce the *p*H to acceptable values.

Either hydrochloric acid or sulfuric acid may be used for regenerating the cation column; sodium hydroxide is used for the anion column.

This ion exchange process produces a potable effluent. It is a process similar in application and effectiveness to reverse osmosis treatment coupled with postneutralization. The problems with the process are similar to reverse osmosis and are, namely, cost, residue treatment, and disposal.

A theoretical example of the expected capability of this ion exchange system is given in Table 8 (operating parameters) and Table 2—Example 8 (chemical data) where the RO raw feed quality was chosen as an example. Chemical cost in this illustration was around $1.00/1,000 gal. As in the case of RO treatment, the waste streams will be difficult to treat.

SUMMARY

Lime and limestone neutralization processes are the most economical methods for AMD treatment. The effluent waters are suitable for aquatic life but not for domestic or industrial use. Lime-soda softening produces an effluent suitable for selected industrial uses and for augmenting a high-quality drinking water supply, but not suitable for potable use, per se. Alumina-lime-soda is capable of producing a potable effluent. Reverse osmosis is also capable of producing a potable effluent. The costs for the respective processes increase with improving effluent quality. Ion exchange is generally comparable to reverse osmosis in effectiveness, cost, and application to AMD treatment.

The problems associated with each of these processes were not strongly emphasized in these discussions. In each instance, the major concern is the treatment and/or disposal of the reject stream whether it be in the form of sludge from the neutralization processes, waste brine from reverse osmosis treatment, or waste regenerant from ion exchange treatment. The term "potable" as used in this report assumes postchlorination.

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CONCERN ABOUT TDS LEVELS

Sponsors are cautioned that some of the observations made for cases discussed below may reflect dated material, and in not every case was the information checked by the company concerned. There may be erroneous information and mis-interpretation, and this text should not by any means be followed blindly.

Although precipitation of metals by lime, limestone, NaOH, etc. followed by solid/liquid separation and clarification removes most metals, there is an increasing concern in some parts of the world as to the levels of TDS in the treated effluent, i.e., levels of $SO_4^=$, alkali metals, Cl^-, etc. In South Africa on the Witwatersrand, TDS in the regional water supply, the Vaal Dam, even after conventional treatment by the Rand Water Board, is rising steadily. TDS in minewater and possible drainage/seepage from mill tailings and wasterock dumps is of concern. This investigation found two items of interest in this respect; first is an innovative application of reverse osmosis which avoids membrane fouling problems through the use of a seeded slurry recycle; the second is an alumina-lime-soda process which appears able to reduce sulfate levels in AMD to around 250 ppm.

HIGH DENSITY SLUDGE PROCESS

For large flows of AMD with high precipitable salt loads, particularly those with high iron levels, by far the most effective and practical approach is the high density sludge process which was first developed by P. D. Kostenbader and G. F. Haines of the Bethlehem Steel Corporation.

What is the HDS Process?

HDS is lime neutralization of acid mine drainage to precipitate metals with two added features:

- Recycle of a controlled amount of precipitate sludge.
- Premixing of lime with recycled precipitate sludge to yield a high density sludge seed which is then added to the stream to be treated, as opposed to direct lime addition.

Sludge recycle to the reaction tanks where lime and effluent are added does not constitute the HDS process.

The HDS process has several advantages, the most important of which are:

1) The HDS process yields a compact high density sludge compared with conventional lime precipitation. HDS can achieve sludge densities of 20-50% solids compared with conventional precipitation which achieves only 1-3% solids.

2) HDS sludge, when disposed of, yields a stable, dry residue.

3) HDS sludge, when mixed with power plant fly ash or other pozzolans and lime, yields a dry residue which passes the EP leach test for disposal as a non-hazardous waste on a sanitary landfill.

4) Iron and the most common base metals can all be precipitated at the same pH, as described by HERMAN (?).

5) HDS results in enhanced manganese removal from effluent streams at a lower pH than conventional lime precipitation, which also yields a high density sludge, even in the absence of iron. Conventional lime precipitation of manganese works best when iron is present.

6) HDS has been demonstrated in the laboratory to achieve lower concentrations of base and heavy metals than would be predicted by solubility data, even in the absence of iron, although coprecipitation with iron allows precipitation at a lower pH and eliminates the amphoteric properties of the precipitated base metal hydroxides.

The Bethlehem Steel Corp. points out that conventionally neutralized minewater yields small precipitate particles of less than three microns with a very high surface area and energy. These attract hydrated water, and so a high energy process is needed to dewater the precipitate, e.g., a filter press or the use of a lot of polymer and a belt press. The same is said to apply to the Lectroclear flotation sludges.

HDS, on the other hand, builds up layers like an onion, and it is possible to use a vacuum filter without a flocculant to make a friable filter cake.

HDS sludge filters well on an ultra high-rate sand filter, and HERMAN (1984, personal communication) pointed out that a filtration rate in excess of 4 gpm/ft^2 can be achieved.

Since the Bethlehem Steel Corp. offers knowhow and HDS treatment design services, they do not reveal all aspects of their knowledge about the process and how to scale a plant. More details on the availability of HDS technology and services is available from:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18016
(215) 694-7597
Telex: 847-417 MESBETH
Jim Forand, Vice President

NORANDA, COMINCO, and ANGLO AMERICAN CORP. successfully operate HDS plants that were designed without the help of the Bethlehem Steel Corp.

The HDS process principles and operating parameters and their significance are described in the following publications, the first four of which are inserted below:

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HIGH DENSITY SLUDGE TREATMENT PLANTS

Company	Operation	Location	Solution Treated	Treatment Process	Treatment pH	Influent Water Quality	Treated Water Quality	Sludge Density	Sludge Recycled Disposal	Year Installed	Treatment Plant Capacity	Capital Cost	Operating Cost	Lime Consumption	Environment Effluent Guideline/ Regulation
Anglo American Corp.	Coronation Colliery Kroondrai	Witbank, Transvaal	Underground Coal Mine AMD	Lime Neutralization HDS Thickener designed for 250 Kg/M²/d although pilot plant showed 500/Kg/m²/d probably would be adequate. Large ponds for final polishing.		1976 pH 2.7 Acidity $CaCO_3$: 1000 TDS mg/l 1750 Fe^{2+} mg/l 0-140 Fe^{3+} mg/l 30 200 Fe_T mg/l 175 Al mg/l 50 Ca mg/l 30 Mg mg/l 10 Na mg/l 5 K mg/l 3 $SO_4^{=}$ 1150 Cl^- 5			To disposal pond 66m Mayno pump	1975	14,000 m³/d				750 tpm Lime for 14,000 m³/d = 2.516 Lime/m³	
Bethlehem Mines Corp.	Panther Valley Division	Tamaqua, PA	Acid Minewater	De-carbonation HDS with conventional thickener. 250°D thickener. Aeration to remove H_2CO_3 by Lobb blowers. A reactor 7.5 HP B reactor 2 @ 25 Hp with baffles. Aerator 2 @ 25 HP with baffles. Blowers for CO_2 removal 2 @ 50 HP (includes standby). Reaction vessel blower 30 cfm 25 HP.	Reactor B at pH 8.9 Thickener Well pH 6.6-8.7	14°F yearround pH_{in} 6.3 Fe 30 ppm Mn 13 ppm TDS 1000 ppm	TDS 1,600 ppm	Normally maintained 15-25% solids although 38% solids were achieved in the plant and 40-50% in the lab.	To Minemorking	1982	40,000 m³/d	$1.0 million		No polymer used 68t/wk for 8500 tpm 0.16 Kg Lime per m³ water	Fe 3.5 ppm tot Mn 7.0 ppm to
Cominco Ltd.	Sullivan Mine and Concentrator	Kimberley B.C.	Minewater and Mill Tailings Effluent	Flow regulation through storage. HDS Max. 850 l gpm Recycle	9.5	Fe 250 ppm Zn 22 ppm Pb 5 ppm Cu 0.15 ppm As 0.03 ppm S/S 75 ppm pH 4.5	LT 1.0 LT 0.2 LT 0.1 LT 0.05 LT 0.01 LT 15 9.5	20-25%	15/1 Recycle, 1.3 m³/min 26 tpd sludge disposed of in 10% solid Sludge disposed to separate impoundment area with under-drainage. Two AC 5HL centrifugal pumps for sludge recycle each with 850 tpm capacity. DC variable speed motors adjusted automatically to give a constant amperage.	1970	20,000 m³/d max. to 30,000 m³/d for spring runoff	C$10 million	C$800,000/Year (1980)	20 tpd varies depending on feedwater quality	(Federal) Zn 0.5 ppm Pb 0.3 ppm Cu 0.3 ppm As 0.5 ppm S/S 25 ppm pH min. 6.0

7) 45' Wide x 100' Long x 20' High Building Plus Garage

8) 56' High Butter Ball a Tank, Lime Storage with Vibrating Screw Feeder and Bin Activator

6 ppm Percol

HIGH DENSITY SLUDGE TREATMENT EXAMPLES

Company	Operation	Location	Solution Treated	Treatment Process	Treatment pH	Influent Water Quality	Treated Water Quality	Sludge Density	Sludge Removal Disposal	Year Installed	Treatment Plant Capacity	Capital Cost	Operating Cost	Lime Consumption	Environment Effluent Guideline/ Regulation
Cominco Ltd.	Trail Pb-Zn Refinery	B.C.	Waste Water	HDS Two reactors in series, 30 minute retention time each. Uses 6 kg/d flocculant to assist settling in clarifier. 25 m^3 clarifier with 1,700 m^3 capacity. Yields 20 tpd sludge to lead smelter. One operator per shift.	pH 10				Sludge dewatered to 50% supernatant; sludge pond then freeze-thaw air dried. Pond has sand bottom with drain pipes.		6,500-13,000 m^3/d	C$9 Million (1981)	C$600,000/Yr. (1981)	11 tpd	
Noranda Mines Ltd.	Waste-Amulet Restored Copper-Zinc Mine and Mill	Quebec	Sulfide Mill Tailings and Surface Drainage Mine Drainage	HDS lime precipitation, Lamella thickeners, 242 acre feet storage, 3.3 acre polishing 3.3 acre polishing pond. Lime slurry 1/3 HP Lightnin and Eductor 0 gpm 0 30% lime slurry, two 15,000 lp tanks for 20 minutes residence including recycle 23 minutes without recycle. Primary neutralization 400 scfm at 15 psi (10.66 scfm/tpm). Mixer Polymer Liquid Metronic Pump Model D73, static mixer and 300' hose for acing. Special Noranda design. Clarification: 0.2-0.5 lpm/ft^2 20' x 20'Φ thickener with Axel Johnson LCS-T3200-55 Lamella Plate Pack Rake Mechanism to bring sludge to a central discharge point for recycling. Sludge-slurry premix tank 15 min. residence. Installed a sludge storage tank. Solid state Logic Controller as designed by Rotter Sensor, GECO Division.	10.0	pH 2.3-4.7 Fe 400-1000 Cu 5-15 Cd 0.05-0.2 Zn 40-95 Mn 5.12 Pb LT 0.05 Ni 0.06 Acidity mg/l $CaCO_3$ 890 SO_4 3000-5000 S/S 5-50 Polishing Pond Discharge: pH 9.53 Acidity 0 Conductivity 1500 Cu LT 0.2 Zn 0.02 Cd LT 0.005 Mn LT 0.02 Fe 0.30 SO_4 9.30 Pb LT 0.05 Ni LT 0.05	0.00 1.40 LT 0.03 LT 0.00 0.20 LT 0.02 LT 0.05 LT 0.05 0.00 1020 Low	45-50%	Slit centrifugal pump, or direct dreamed sludge 6000 l/m, two 3" x 3" Berthingson rubber lined slurry pumps selected for slurry recycle and sludge waste pumps. Heavy duty AC motor and a single controller. Gallagher sump pump backup. Magnetic flowmeter Taylor mag-pack to monitor recycle flow rate. Sludge is dewatered in a pumice pond with sand bed and drain pipes. Freeze thaw and in winter.	1984	Design: 660 lpm 9320 m^3/d Actual: 900 lpm Steady Flow	C$1,600,000	Lime: $231,000 Polymer: 12,000 Manganese: 15,000 Electrical: 32,000 $330,000	Est. 23 lbs/1000 gal. Est. 1,600 t/a Bulk Lime @ C$140.10/t 3.3 Kg/m^3	Guidelines pH 5.5-9.5 Fe 3 Cu 0.15 Cd 0.05 Zn 0.5 S/S 25
Co-Pb-Zn Mine @ 2750 stpd Cu, Pb, Zn, Ag Sulfide Ore	Mine-Mill	Ontario	Tailings Dam Decant Solution	1) Lime Addition and Aeration 2) Sludge Recycle 3) Two Agitation Tanks 4) Flocculation 5) Pilot-scale Lamella Thickener 6) Sludge Storage Tank 7) Use Liquid Flocculant Dosed by Noranda System	9.5	Summer / Winter / Summer / Border pH 7.1 6.0 9.3 10.0 °C 16.5 10. Cu 0.01 0.04 0.01 0.01 0.06 Pb 0.00 0.02 Zn 3.14 5.07 0.1-0.3 0.00 Fe 0.00 4.79 0.66 0.16 S_2O_3 tr 43.1 tr S/S 1.0 25.0 1.0 7.0 Spring runoff pH drops to 3.0		Unknown	Sludge added to zinc concentrate thickener shipped to smelter contains 15-20% Zn June 1981 sludge density 9.5%. July 1981 sludge density 21.5%	1981	4000 m^3/d capacity operated at 1270 m^3/d 450 lpm 2610 m^3/d		Use 1 ppm Percol 155 flocculant 1983 per 1,000 Gal. Lime 50.048 Floc 00.107 Power 00.054 Labor 00.300 01.93 lpd per m^3 Lime US$0.15 Floc US$0.02 Power US$0.12 Labor US$0.05 US$0.34/m^3 5 ppm Percol	10.5 lbs/1000 lpd 4.07 lb/m^3	pH 5.5-9.5 Fe 3.00 Zn 0.50 Cu 0.15 Cd 0.05 pH 0.30
Noranda Mines Ltd.	Lac Minerals Callan	Quebec	Acid Mine Water	1) HDS-Up to 50% Recycle 2) Two Reactor Tanks and Sludge Recycle Lime Mix Tank 3) Flash Mixer (Dry Flocculant) 4) Thickener - Two Lamella Plate Packs 5) Automatic Sludge Discharge to Sludge Basin 6) Polishing Pond for Effluent, then Discharge to Kinogevis River 7) 65' Wide x 100' Long x 25' High Building Plus Garage 8) 50' High Butter Bolt x Tank, Lime Storage with Vibrating Screw Feeder and Bin Activator	9.5	pH 3.50 Fe 866 Zn 530 Cu 0.26 Cd Pb	6.5-9.0 0.750 0.45 0.020 0.071 0.160									

ENVIRONMENTAL CONTROL

Mine and tailings effluent treatment at the Kimberley, B.C. operations of Cominco Ltd.

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ABSTRACT

Complex facilities which provide for the collection, management and treatment of effluents emanating from the Sullivan mine and concentrator tailings were made operational in October 1979. Key features of the system are the use of upgraded tailings ponds for the storage of up to 800 million litres of metals-contaminated effluents, a treatment plant employing lime in a high-density sludge process and a sludge-impoundment facility designed for maximum long-term environmental safety. The completed works are capable of satisfying a difficult range of operating requirements imposed by highly variable weather conditions, drainage flows and soluble metals loadings. Final capital expenditures for the project approached $10 million and annual operating costs are about $0.8 million.

This paper discusses the Kimberley effluents treatment project and the major considerations in its development. The treatment process, major plant equipment and initial operating experience are also described.

Introduction

Cominco Ltd. has worked the Sullivan orebody at Kimberley, B.C. since 1909 and has operated a concentrator some 5 km distant from the mine since 1923. Over the last 70 years, in excess of 120 million tonnes of ore have been mined, and production continues at an average rate of 6,500 tonnes per day. It is a well-known fact that the contribution of this operation to Canada's mining industry and, in particular, Cominco's development has been significant. However, this success has not been without some undesirable side effects.

Unfortunately, the Sullivan is one of only a few major Western Canadian orebodies which may be classed as "acidic" in nature. That is, the primary economic minerals, galena and marmatite, are enclosed in a siliceous host rock with abundant pyrrhotite, but with little or no accompanying alkaline gangue minerals such as calcite and dolomite. The unavoidable consequence of mining such an ore is that contact with air and water generates an acid mine drainage containing various soluble metals orginally present as minerals.

This problem also arises in the concentrator's tailings ponds, which, in the case of the Sullivan, are two separate impoundments of different materials. The 1,100 tonnes/day of "iron" tailings are primarily pyrrhotite which is surplus to the requirements of a separate operation that produces sulphuric acid as an intermediate to phosphate fertilizers. Inert gangue minerals with only a minor sulphide content are the main constituents of the 1,200 tonnes/day of siliceous tailings. Corresponding to the relative proportion of sulphides in the solids, the decant from the iron tailings is substantially more contaminated than that from the siliceous pond.

Until 1979, both the mine and tailings effluents eventually reported to the St. Mary River, south of Kimberley, without treatment. A noteworthy feature of these effluents, however, is that the principal contaminant is soluble iron with smaller proportions of the more toxic heavy metals, such as lead and zinc. Biological monitoring in the river downstream from the effluents' points of entry has continued to show an abundance of aquatic life forms, and the concentrations of heavy metals have been far below acutely toxic values even without treatment. The impact most evident has been discoloration of stream beds by iron staining.

Cominco was originally issued an effluent discharge permit in 1967 under terms of the B.C. Pollution Control Act, which was promulgated in the same year. A subsequent amendment required the company to undertake treatment of the mine and concentrator effluents to specified values by the end of 1977. Studies were started in 1974 with the intent of meeting this objective, but it was not achieved due to a number of delays, some of which were beyond Cominco's control. An application to extend the compliance date to December 31, 1979 was eventually successful and the facilities constructed to satisfy permit requirements were officially commissioned on October 19, 1979.

Mine and Concentrator Effluents

As is common in most mining operations, the Sullivan mine drainage is a combination of surface water that has infiltrated

W.J. Kuit

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Keywords: Environmental control, Effluent treatment, Tailings, Cominco Ltd., Water treatment plants, Lime, Flocculents, Clarifiers, Impoundment.

through the fractured orebody and that pumped in for drilling. The drainage leaves the mine through the 3900 level portal, and about 70% of the total flow is intercepted and discharged by gravity. Water penetrating the lower levels is collected in sumps and pumped a total lift of 480 m to the 3900-level ditch. The cyclic nature of the lower-level drainage pumping normally causes substantial instantaneous variation in the mine discharge rate. Retention in the mine's natural hydraulic system is such that the full impact of high surface infiltration rates requires at least one week to be reflected in drainage volumes. The average annual discharge rate is about 3,000 L/min. in a rage of 1,200-10,000 L/min. Typical soluble metals concentrations and other properties of the mine drainage are given in Table 1.

Periods of high flow and high metals concentrations often are simultaneous, such as in the spring freshet due to a "flushing" of sulphate salts accumulated in rock fractures. Virtually all of the dominant parameter, soluble Fe, is present in the ferrous (Fe^{++}) oxidation state.

Prior to this project, the drainage was acutely visible to the community of Kimberley, as it directly discharged to Mark Creek, which flows through the town before entering the St. Mary River. Because both the city and Cominco draw water from an upstream location on the creek, the mine drainage has been a substantial proportion of the total flow during dry periods.

TABLE 1. Mine drainage properties

Parameter	Range
Fe, mg/L	200 - 1,000
Zn, mg/L	30 - 200
Mn, mg/L	20 - 75
Al, mg/L	35 - 150
Pb, mg/L	2 - 5
Suspended Solids, mg/L	200 - 900
pH	2.8 - 4.0
Temperature, °C	8 - 12

TABLE 2. Iron tailings decant properties

Parameter	Range
Fe, mg/L	300 - 2,500
Zn, mg/L	10 - 50
Mn, mg/L	5 - 30
Pb, mg/L	2 - 8
Suspended Solids, mg/L	25 - 100
pH	3 - 4.5
Temperature, °C	0 - 15

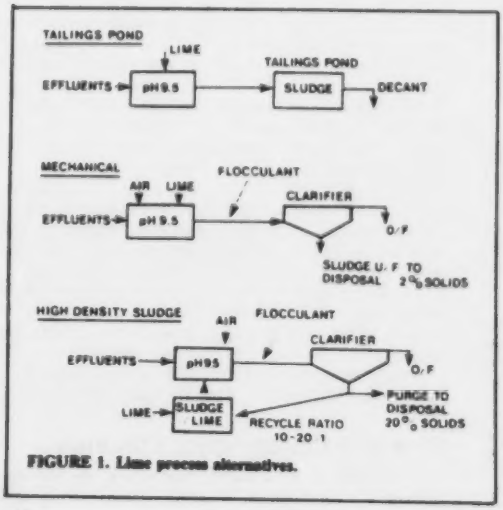

FIGURE 1. Lime process alternatives.

The impact of precipitation and run-off is even more severe on the decant volumes from the concentrator's iron and siliceous tailings ponds, which cover areas of 240 and 112 hectares (590 and 280 acres) respectively. Rapid snow melt during warm spring days and heavy rains cause extremely high rates of water influx that can change, virtually on an hourly basis. Dyke protection has, until the present, dictated that the decant pool sizes be minimized and, consequently, little or no attenuation of these flows was possible.

The quality of the effluents from these two sources is quite different. Because the siliceous tailings are largely inert gangue minerals, decant from this pond usually contains only minor contamination, but soluble Mn and Fe concentrations can reach 15 mg/L and 75 mg/L, respectively, on rare occasions. As a rule, the pH is near 7.0 and most bio-assays fail to demonstrate acute toxicity. Instantaneous maximum decant flows can approach 23,000 L/min., but the annual average is about 4,000 L/min.

Decant from the iron tailings is, as would be expected, significantly more contaminated, because the 240 hectares surface area of essentially pyrrhotite is for the most part exposed to the atmosphere. Oxidation generates the same soluble metals as are present in the mine drainage, but in different proportions, and Fe is even more dominant, as Table 2 indicates.

An important feature (with respect to treatment) corresponding with the mine drainage is that all of the Fe is present in the ferrous (Fe^{++}) form. Peak instantaneous flows of 55,000 L/min. have been recorded, but 6,000 L/min. is a typical annual average.

Both tailings decants have been transported by 0.64-m (24-in.) clay-tile piping to adjacent Parshall flumes south of the ponds. There combined, the flows formed James Creek, which discharged into the St. Mary River.

Effluents Treatment Alternatives

Studies originally commenced in 1974 were primarily directed toward developing the most viable process option for the treatment of mine drainage alone, because this was, at the time, considered to be the most urgent effluent problem. This was soon followed in 1975 by a change in scope to incorporate tailings effluent treatment, and several engineering studies ensued. The complexity of the project increased substantially as it became evident that options were available in the following key areas:

(1) treatment process;
(2) location of treatment facilities; and
(3) plant flow design—single or split stream.

Treatment Process

Preliminary investigations were conducted at Cominco's Technical Research Centre on a variety of treatment methods, but it became clear that viability could only be achieved using lime as a neutralizing reagent and metal precipitant. The relevant chemistry has been well documented and a review here is not required, but the practical process options merit discussion.

The first scheme, outlined in Figure 1, essentially involves the addition of lime to the contaminated effluents and mixture with a concentrator's tailings discharge. Sludge solids clarification and storage is then an integral part of tailings impoundment. Very low in cost and applied successfully at other operations, such as Heath Steele Mines[1], it was evaluated as being technically unsuitable for use at Kimberley.

The direct "mechanical" process requires an independent plant incorporating a major vessel for lime reaction and aeration (to oxidize Fe^{++} to the more stable Fe^{+++} state), followed by a clarifier or settling pond. Although widely used and highly efficient with respect to achieving good final effluent

quality, the process can suffer from a difficult-to-manage sludge handling problem due to low solids densities. This factor can be particularly severe where high soluble metals concentrations are involved. One mine drainage treatment operation has been documented in which the volume of sludge generated was up to 80% of the effluent volume treated[2].

The high-density sludge (HDS) version of the basic lime process offers the attractive potential for minimizing waste sludge volumes and was intensively researched for application at Kimberley. Originally discussed by Kostenbader and Haines[3], the HDS process recycles a substantial proportion of clarifier underflow (U/F) sludge, which is blended with lime slurry required for neutralization prior to the main reaction vessel. This pre-mix is a key function in achieving an inherent modification of sludge solids from a fluffy slime to an almost particulate texture. Incentive for the process is illustrated by Table 3, which correlates the daily volume of sludge to be handled by a facility operating at various U/F consistencies. Calculated values are from a Kimberley case of treatment at 18,000 L/min. and 1 g/L sludge solids production. The impact of this data plant operation and sludge disposal requirements is readily evident.

TABLE 3. Sludge volume - solids content relationship

U/F Solids, Weight %	U/F Volume, L/Day
2	1,310,000
5	505,000
10	245,000
20	119,000
30	75,000

HDS process superiority was confirmed in extensive continuous-flow "mini-plant" studies with a small unit operating at up to 1 L/min. Both the B.C. Pollution Control Branch permit requires and the Federal Guidelines for the mining industry could be satisfied on the full range of Kimberley effluents. Furthermore, the excellent sludge properties arising from recycle were accompanied by near complete control of gypsum scaling as an additional benefit of higher solids loading.

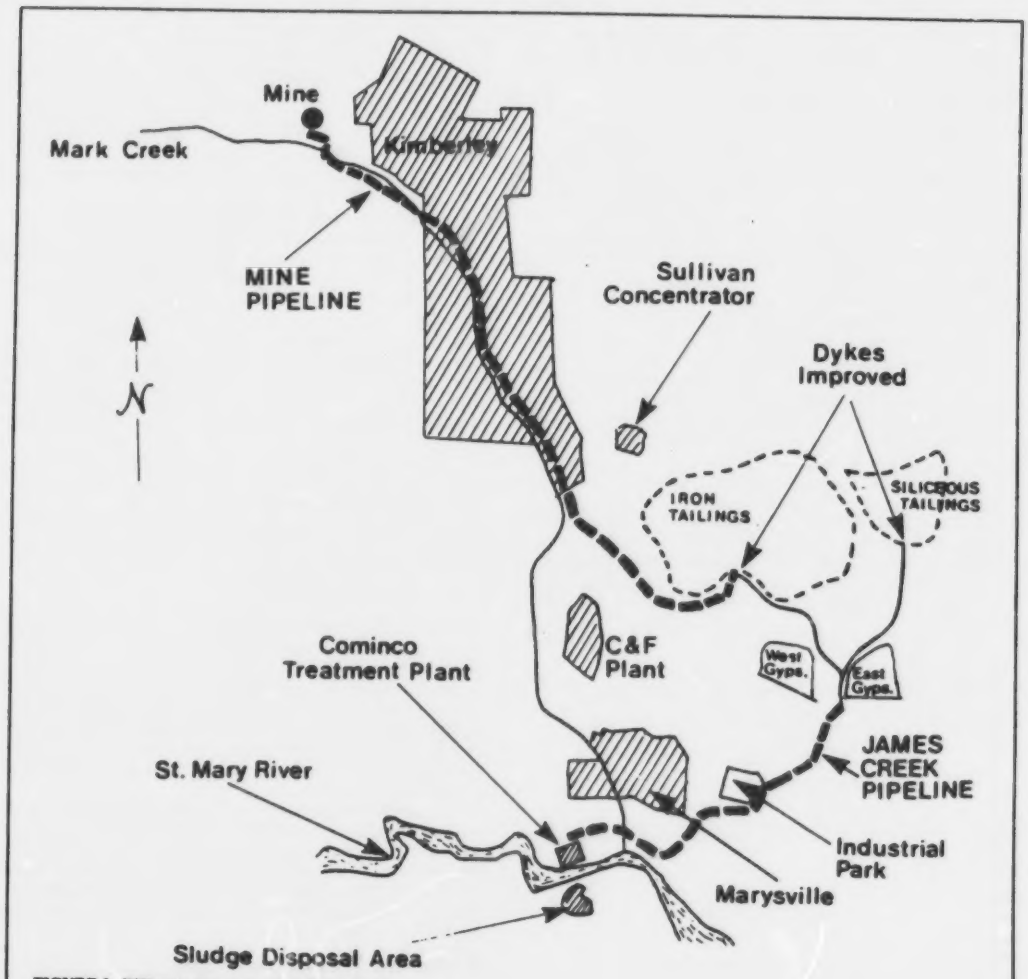

FIGURE 2. Effluents management and treatment.

Treatment Plant Locations

The process studies clearly defined lime-HDS as the treatment system of choice, but plant location was a question to be resolved. Included as important criteria influencing site selection were a recognition of the needs for safe sludge impoundment and sufficient system flexibility to handle long-term treatment requirements.

Separate plants to treat mine and tailings effluents were evaluated in engineering studies, which firmly concluded that such a strategy would not be viable. Costs were extremely high and serious technical differencies became apparent, particularly with respect to the mine plant. Another proposal consisted of a single facility to handle all effluents located near the tailings ponds with direct piping of the mine drainage to the plant. However, sludge impoundment in either of the tailings ponds was not practicable and ground conditions in the vicinity were found to be unfavourable for the construction of a separate diked storage area.

Soon thereafter, locating the plant immediately adjacent to the St. Mary River, about 8 km south of the mine and 3 km southwest of the tailings ponds, became a viable option. A substantial area of land across the river was found to be suitable for long-term sludge storage requirements. Separate piping of the mine and tailings effluents to the river location was a feature of this proposal.

Flow Design Concept

The river location study was completed through to the engineering feasibility level on the basis of a "twin-gut" treatment plant. That is, the retention requirements of key components such as reaction vessels and clarifier were split between duplicated systems to ensure maximum facility reliability. Without the capacity to store exceptionally large volumes of contaminated effluents ahead of the plant, this design concept would at least provide a "compromise level" of treatment in the event of mechanical breakdowns. The design treatment capacity of the plant was 18,000 L/min. (14,000 L/min. annual average rate), which could be forced to 27,000 L/min. with some sacrifice in effluent quality.

However, the problem of dealing with rates above 27,000 L/min. during the spring freshet remained, and the operation was to be scheduled on the basis of the following order of treatment priorities: mine drainage > iron tailings decant > siliceous tailings decant. Substantial volumes of untreated effluent would have been discharged annually, and the need for correcting this deficiency and simplifying the plant operation was recognized. Therefore, Dames and Moore was retained to study the feasibility of actually using the tailings ponds to store effluents and regulate their discharge. This investigation, which proved the concept to be technically sound and viable, permitted the plant design to be reduced to a "single-gut" system with improved costs and superior reliability.

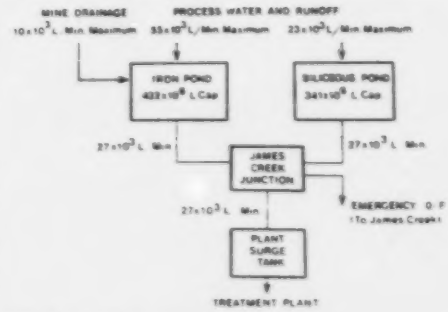

FIGURE 3. Drainage water flow management.

Subsequently, the project was mobilized starting in January 1978, and construction was largely completed by the late summer of 1979. Important locations in the Kimberley system are illustrated in Figure 2, and features within the major scope areas will now be described.

Effluent Collection and Management

Mine Drainage

The collection system at the mine provides for the pick-up of the major effluent (3900 level drainage), mine dry septic tank overflow and miscellaneous waste dump drainages. Prior to being piped to the "iron pond", the flow is passed through a "grit chamber" which consists of parallel rectangular settling tanks for the capture of heavy solids which might otherwise settle and accumulate in the line at low flow rates. The pipeline is constructed of 0.36-m (14-in.) diameter polyethylene and extends for 6,900 m to the iron pond, with Air-Vac and blinded drain valves built in at strategic locations. Its design capacity is 11,500 L/min. under gravitational head alone. The line is fitted for "pig" injection and recovery, a procedure which is routinely implemented with a radio tracer-equipped Polypig.

Effluents Management

Creation of a water management capability in the tailings ponds has required a major dyke upgrading program. The lifts placed have been designed for the safe retention of about 2 m of additional hydraulic load. Compacted siliceous tailings were used for construction, with volumes of 124,000 m^3 and 36,000 m^3 being placed on the existing iron and siliceous dyke structures, respectively.

The objectives of the pond storage system are illustrated in Figure 3 (maximum instantaneous pond influx rate are indicated to emphasize the importance of flow management). About 800 x 10^6L capacity has been provided for the control of peak freshet volumes. It is expected that during spring, the treatment plant will operate at a 27,000 L/min. rate for periods of time which are essentially controlled by weather conditions. Effluents storage will permit plant shutdowns for maintenance and some degree of "blend-optimization" of the different strength decants. Additional benefits are the levelling of strength fluctuations and improved suspended solids control.

The effluents management phase of the project was not fully complete until the late spring of 1980, when remote control valve assemblies in the decant structures were made operational. These allow full flow control from the treatment plant and prevent fluctuations that would otherwise be caused by relatively small head changes.

Treatment Plant Feed

The two pond effluents are directed through the existing decant lines and flow measuring flumes which are recorded in the plant. They are then combined in a junction box which is designed to allow dumping of the less contaminated siliceous decant in emergency situations. The James Creek pipeline varies from 0.46 m (18 in.) to 0.56 m (22 in.) over a total length of 3,600 m. It is designed for a maximum flow of 34,000 L/min. and is fitted with protective devices similar to those on the mine drainage line.

The combined effluents flow discharges to a 900,000-L-capacity surge tank constructed of acid-resistant concrete at the plant site which is operated by level control instrumentation. Storage of the effluent volume contained in the James Creek line will be possible in the event of a forced plant shutdown, or this vessel can be bypassed with the flow going directly to the plant.

Effluents Treatment Plant

Design is based on achieving optimum performance at a normal maximum of 18,000 L/min., but operation at a forced rate

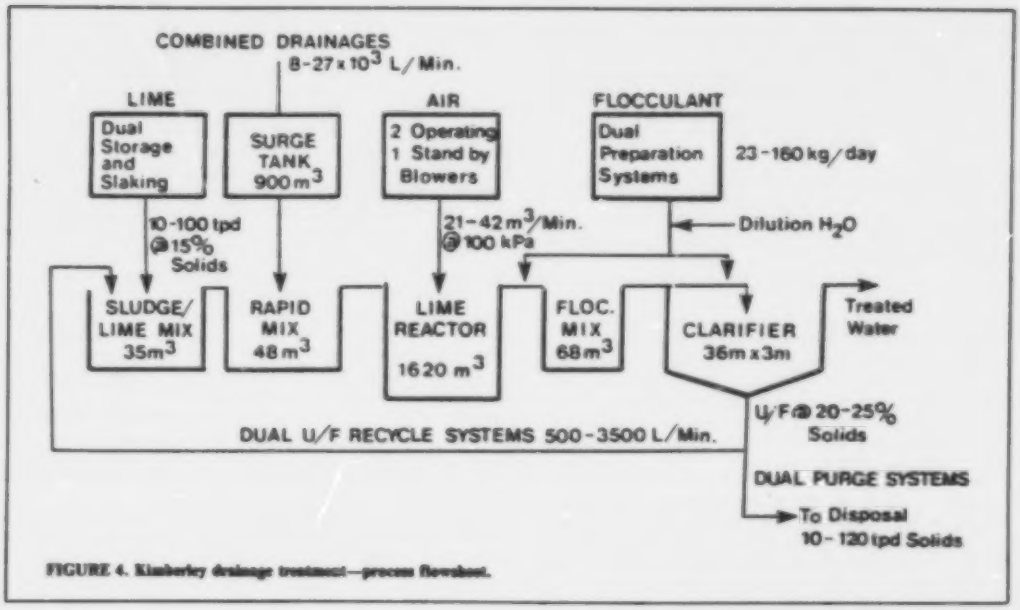

FIGURE 4. Kimberley drainage treatment—process flowsheet.

of 27,000 L/min. during the spring can be managed. The key reagent supply systems (lime, air, flocculant) are sized on the basis of forecast peak demand, but shortened retention times may cause some deterioration in final effluent quality. Process design was based on extensive mini-plant testing conducted previously at Cominco's Technical Research Centre in Trail, B.C. All possible operating parameters, including effluent temperatures as low as 0°C, were simulated in the small-scale unit, which obviated the need for pilot-plant confirmation.

Plant Process

The process flowsheet and ranges of major parameters associated with the operation are illustrated in Figure 4. Important features of the system will now be reviewed.

Lime slurry and recycled clarifer U/F sludge are blended in the sludge/lime mix tank at the head of the process. This step is of vital importance with respect to maintaining satisfactory sludge properties. The sludge/lime mixture discharges to the rapid mix tank, which achieves a partial neutralization of the contaminated effluent entering the plant. Smooth final pH control at the optimum value of 9.5 in the subsequent large reaction tank depends on feed-back regulation of the lime slurry based on the pH in the vessel.

The principal treatment tank, the lime reactor, provides a retention time of about 50 min. at the maximum combined flow of raw effluent and sludge recycle. Near complete precipitation of metals as hydroxides occurs directly at this stage according to:

$$(Zn^{++}, Pb^{++}, Mn^{++})\,MSO_4 + Ca(OH)_2 \xrightarrow{H_2O} M(OH)_2 + CaSO_4 2H_2O \quad (1)$$

$$(Al^{+++}, Fe^{+++})\,M_2(SO_4)_3 + 3Ca(OH)_2 \xrightarrow{H_2O} 2M(OH)_3 + 3CaSO_4 2H_2O \quad (2)$$

However, optimum process chemistry and physical performance require complete oxidation of ferrous hydroxide to the more stable ferric hydroxide as indicated by:

$$Fe(OH)_2 + \tfrac{1}{4} O_2 \rightarrow Fe(OH)_3 \quad (3)$$

Virtually all of the plant feed soluble iron is in the Fe^{++} form, and oxidation by aeration under high shear agitation provides the following:

Optimum Chemistry—Co-precipitation and absorption phenomena associated with $Fe(OH)_3$ formation result in lower soluble heavy metals concentrations than those derived from hydroxides alone.

Clarifier Performance—"Oxidized iron" solids exhibit superior settling properties and form a sludge that is much less viscous than the non-oxidized solids.

Sludge Stability—Incomplete Fe^{++} oxidation during treatment can result in chemical instability of impounded sludge and re-dissolution of heavy metals.

With the chemical reactions completed, the discharge from the lime reactor is treated with dilute flocculant solution prior to entering the gently agitated floc mix tank. This vessel was incorporated into the process to ensure good floc formation prior to clarification.

The clarifier O/F discharge to the river is monitored for flow rate, turbidity and pH, with daily composite samples taken for metals analyses. Thickened U/F sludge of about 20-30% solids content (250-350 g/L) is then either recycled or purged to the impoundment area. The recycle rates are so controlled that 10-20 Kg of solids are returned to the head of the process for every Kg precipitated from the plant feed. Therefore, 90-95% of the solids loading in the system is recycled material.

The frequency and duration of sludge purging is determined by the rate of production. Under peak metals loading to the plant, the frequency can be once every day for a maximum of 6 hours of pumping. A total solids inventory of about 200 tonnes is probably the operating maximum that can be ac-

TABLE 4. Typical operating parameters

lime (CaO) consumption:	20 tonnes/day
flocculant consumption:	(3 mg/L) 80 Kg/day)
sludge solids production:	26 tonnes/day
sludge volume production:	(250 g/L) 104,000 L/day)
recycle rate:	(15/1) 1,100 L/min.
sludge purge frequency:	once (150 tonnes) every 6 days

cumulated without having a detrimental impact on the plant (i.e. clarity, clarifier mechanism torque).

Operating parameters will vary greatly, but typical conditions can be illustrated from the plant treating 14,000 L/min. containing, as the major soluble metal, 400 mg/L Fe.

Plant Equipment

The general arrangement of the main plant components is illustrated in Figure 5. A fundamental design criterion of the facility was that it eventually should function with a minimum of attention, including periods when an operator would not be present. Therefore, manual labour requirements in the plant are minimal, with key systems being duplicated and interlocked.

Lime System—Twin 140-tonne silos equipped with bin activators provide pulverized quicklime storage. Screw feeders of 15 cm (6 in.) diameter supply BIF slakers, which are each rated at 3,200 Kg/hr. lime, producing a slurry of about 15% consistency. This is stored in an agitated tank below floor level which has 1.5 hour storage capacity at the peak lime demand of about 100 tonnes/day. Interlocked 15-hp Morris vertical pumps, rated at 900 L/min. each, supply the pressure-controlled lime feed loop.

Flocculant System—The two interlocked flocculant solution preparation and feeding packages are automated and utilize the BIF Polypac systems. These disperse dry flocculant particles by the drum-wetting principle to ensure solution preparation with minimal "fish-eye" formation. The feed hoppers of each unit are occasionally charged by a Vac-U-Max loading system from ground-level storage. Metering pumps feed solution at 5 g/L concentration, and this is reduced to 0.25 g/L with fresh water in a Kenics static mixer before application.

Air Supply—Three 75-hp Gardner-Denver "cyclo-blowers" are installed below the elevated rapid mix tank to supply air for iron oxidation in the lime reactor. Each has a capacity of about 21 m³ (750 cf)/min. at 100 KPa (15 psi). Normal plant operation will utilize only one blower, with two being on line during peak requirements. The third is intended as a stand-by unit during this period.

Process Tanks—The main process flow through the plant (sludge/lime mix to clarifier) is by insulated launders which are designed for 34,000 L/min.

Sludge/Lime Mix	: Mild steel construction, 3.6 m dia. by 3.9 m, 10-hp Denver, spindle bearing agitator.
Rapid Mix	: Stainless construction, 4.2 m dia. by 3.9 m, 15-hp Denver, spindle bearing agitator.
Lime Reactor	: Concrete construction, 15.2 m dia. by 9.7 m, 150-hp Lightnin, reducer drive, 48 rpm. Flat-blade disk turbine impellor, 2.1 m dia. (crown plate distributor below turbine.)
Flocculant Mix	: Concrete construction, 4.8 m dia. by 4.2 m, 3-hp Denver, reducer agitator.

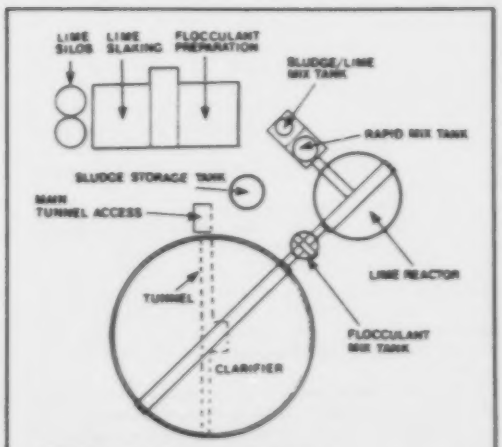

FIGURE 5. Treatment plant arrangement.

Clarifier—The vessel is concrete and measures 36 m dia. by 3 m. Peripheral O/F is provided by submerged ports, with a weir controlling the level, and the vessel is designed to operate with an ice cover. The mechanism is an Envirotech-Eimco type B heavy-duty unit operating at .08 rpm. One 5-hp drive is installed, which gives a torque rating of 240,000 Nm (175,000 ft lb), but this can be doubled by the installation of a second drive. The rake blades are attached to the arms by 0.7-m "thixo-posts", a design that facilitates raking of the viscous sludge. An automatic rake lifting and lowering system is another feature of the mechanism.

Clarifier U/F Handling—Two independent pumping systems are located in a service tunnel beneath the clarifier.

Sludge recycle is by two Canadian Allis Chalmers SRL pumps driven by interlocked 25-hp Asea D.C. variable-speed motors. The capacity of each is 3,800 L/min. under an 18-m head. Separate 20-cm (8-in.) lines feed a nuclear densitometer-equipped Parshall flume, which discharges directly to the sludge/lime mix tank. The recycle system is also designed to fill and pump from the 6-m-dia. by 6-m emergency sludge storage tank shown in Figure 5. This feature will only be used in the event of a plant shutdown which requires the clarifier to be emptied. A stock of dense sludge is a process necessity to ensure that equilibrium operating performance prevails immediately after the plant is re-started.

Sludge purging to storage about 700 m from the plant is done with parallel 60-hp Morris SRL pumps capable of pumping 4,000 L/min. of the thixotropic material. Additional lime, equivalent to approximately 4% of the sludge solids, is added to the sludge during discharge. The two 15-cm (6-in.) diameter, insulated steel lines have four primary discharge locations in the impoundment area and are graded to drain back to the plant. Clarifier O/F is used to flush the lines following each purge.

Sludge Impoundment

The sludge impoundment facility in current use will provide a minimum of 5 years storage capacity based on an average volume accumulation of 55,000 m³/year. Only modest dyke construction, requiring 19,000 m³ of local borrow material, was necessary to provide this Stage I storage capacity. Further development of the site can provide sludge impoundment for in the order of 90 years of plant operation if required. A practical utilization method for this material is obviously desirable, and this search will continue.

It must be emphasized that the impoundment technique is not one of slurry ponding. There is no decant from the stored sludge, as the underlying ground is a mixture of sand and cobble which provides good drainage characteristics without solids escape. Studies have demonstrated that the rapid drainage of water originally present in the sludge or from subsequent precipitation is essential to the development of properties that will ensure long-term environmental safety.

The desired changes which occur in sludge discharged to the impoundment area are illustrated in Figure 6. Initially, the material naturally de-waters to about 50% solids, with the drainage reporting to the water table and eventually the St. Mary River. The quality of the drainage water is the same as that which the plant directly discharges to the river, and this is being monitored by sampling from wells installed at strategic locations. During the winter, freezing of the sludge is a limiting factor, but this effect results in enhanced drainage characteristics following spring thaw. Summer drying removes additional moisture, causing shrinkage which allows the ingress of air. This initiates the function of the extra lime intentionally added before discharge from the plant. Atmospheric

carbon dioxide (CO_2) reacts with the lime, forming a calcium carbonate ($CaCO_3$) matrix in the relatively porous solids, thus providing a measure of physical stability and assisting the permanent fixation of heavy metals. Table 5 illustrates a typical chemical analysis of the sludge, showing the significant metals present.

The discharge points in the impoundment area are cycled to give deposited sludge the maximum exposure time possible before being covered by fresh material. Lengthy cycle times are augmented by the plant's capacity to store sludge solids with only intermittent purging. Leach tests on sludge which has undergone this impoundment cycle have yielded virtually no dissolution of heavy metals under the range of natural conditions prevalent in the area.

Operating Experience

As the facilities have been operational for only about one year, a full assessment of long-term performance cannot be made at this time. At least several years will be required to confirm water management and treatment plant capabilities under the complete range of operating demands.

Mine drainage piping to the iron tailings pond was operational in April 1979, and this system has performed satisfactorily, achieving an immediate improvement in the quality of Mark Creek water which has drawn favourable community reaction.

Plant Operation

The initial operating trials commenced in early September and the plant was officially commissioned on October 19, 1979. An operator and a helper initially manned the plant on each shift, seven days per week, but the complement is now one man per shift and further reductions are planned.

The time requirement for bringing the HDS treatment process to an operating equilibrium was not experienced in the Kimberley plant start-up due to a rather unusual method of preparation. This involved obtaining about 110 tonnes of sludge containing 40% solids from The Bunker Hill Co., Kellogg, Idaho, which operates a similar treatment process[9]. "Seeding" the system using this material proved to be highly effective, as the fresh sludge produced was immediately about 20% solids and high consistencies were readily maintained. The plant initially operated for a period of two weeks at an average feed rate of 10,000 L/min., producing 11 tpd solids, before any sludge was purged to storage.

The over-all operating performance of the facility has been highly satisfactory and the break-in problems normally prevalent in a new plant have been minimal. Key mechanical systems, such as those supplying reagents, and the process control instrumentation have generally operated very well. From the outset, there were no process or mechanical difficulties that prevented the plant from being fully operational. Scheduled shutdowns have been necessary for several minor modifications, but effluents were stored in the ponds during these periods.

Some difficulty was initially experienced with the lime reactor agitator in that the power draw was unacceptably high with only one blower running. Two blowers (42 m^3/min. air) had to be run continuously to ensure sustained operation of the agitator, but this was corrected by reducing the impeller diameter from 2.13 m (84 in.) to 2.06 m (81 in.). Another minor deficiency soon apparent was an inadequate degree of fluid motion in the sludge/lime mix tank caused by the thixotropic properties of the recycled sludge. Air injection to augment the agitator was necessary, but merely removing the tank baffles and increasing the agitator speed corrected the problem.

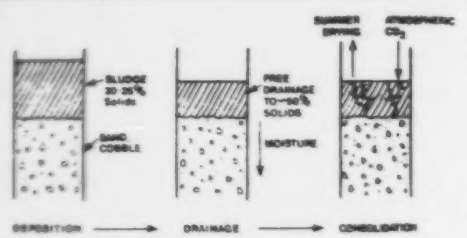

FIGURE 6. Changes in impoundment sludge.

TABLE 5. Metals content of sludge

Metal	Weight %
Fe	19.5
Ca	9.5
Mg	6.0
Si	3.1
Zn	2.1
Al	1.8
Mn	1.2
Pb	0.3

Development work on the flocculant application system was effective in resolving a slight deficiency with respect to clarity of the plant discharge that developed folowing start-up. Operation with clarifier O/F suspended solids concentrations of about 25 mg/L was found to be "aesthetically" unsatisfactory, even though it was within the permit requirements. The use of one of several efficient anionic flocculants in a split application method (Fig. 4) now produces suspended solids values of consistently less than 15 mg/L, with the desired visual impact.

Treatment Performance

Results from the first few months of operation have generally been gratifying. The treatment rate has thus far varied from 7,000 to 27,000 L/min., with the feed consisting of both tailings pond decants in a range of proportions. This variation has resulted in diverse feed strengths which are illustrated by the major soluble metal, Fe, being in the range of 30-500 mg/L.

The quality of the treated effluent discharged to the St. Mary River has normally been superior to that yielded by the lab-scale mini-plant studies. It is also remarkable that metals analyses of the final effluent have been very consistent and essentially independent of the loading to the plant. Performance, to this point, has been well within the standards set

TABLE 6. Plant treatment performance

Parameter, Total Values	Plant Feed	Federal Guidelines	Plant Effluent (mg/l)
Fe mg/L	250	—	<1.0
Zn mg/L	22	0.5	<0.2
Pb mg/L	5	0.2	<0.1
Cu mg/L	0.15	0.3	<.05
As mg/L	.02	0.5	<.01
Suspended Solids mg/L	75	25	<15
pH	4.5	min. 6.0	9.5

down by both Environment Canada and the B.C. Pollution Control Board. To illustrate this with an example that is meaningful to the industry across Canada, Table 6 compares the typical metals concentrations present in the plant feed and effluent with the monthly average objective values in the Federal Guidelines.

With respect to the plant's other product, impounded sludge, substantial time will naturally be required to prove long-term environmental acceptability. However, initial observations indicate that the desired drainage and consolidation are occurring satisfactorily and there is confidence that expectations will be met.

Conclusion

The completion of this project is the culmination of extensive efforts over several years by various groups within Cominco Ltd. and a capital expenditure of nearly 10 million dollars. Adding to this commitment, of course, is the anticipated annual operating cost of the facility, which will be in the order of 0.8 million dollars. It can be appreciated that these cost burdens are a particularly harsh reality when there is no opportunity for monetary return. Moreover, the operation of the treatment plant will have to be maintained long after the closure of the mine and concentrator at Kimberley, beause the oxidation and leaching of residual sulphides will continue.

However, the facilities were constructed with the objective of providing a comprehensive solution to a difficult effluents management and treatment problem, with emphasis on the criteria of reliability and process effluent quality. Value can only be derived, therefore, from the degree to which results fulfill planning. Although the operating record of the Kimberley system is only brief to this time, performance is confirming the project to be a substantial contribution to the improvement of environmental quality.

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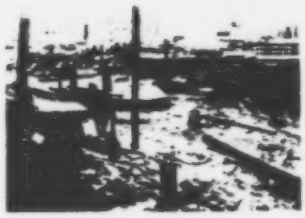
1982 ENVIRONMENTAL ENGINEERING DESIGN AWARD

Cominco Ltd is the winner of the second Environmental Engineering Design Award of the Association of Professional Engineers of BC. Cominco's Effluent Treatment Plant at the Trail Metallurgical Operation was judged the best design for 1982 and their submission is published here in full.

The Award was presented by APEBC President Ken Williams PEng to authors Roger Watson PEng and John Turnbull PEng at the West Kootenay Branch Meeting in Castlegar on March 24, 1983.

Seven other submissions were received from coal mines, pulp mills, engineering consultants, municipalities and government departments. Extracts from these submissions were prepared by Kelly Kline PEng of the Environment Committee and, with the authors' permission, are published in this issue.

1982 Environmental Engineering Design Award Winner



Cominco Ltd's Effluent Treatment Plant at its Trail, BC, Metallurgical Operation

R H Watson PEng, Manager
J D Turnbull PEng, Assistant Manager
Trail Modernization Project

INTRODUCTION. Cominco Ltd's huge metallurgical complex is located in Trail, British Columbia, a city with a population of 10,000 located in the Columbia River Valley in the West Kootenays, 18 km north of the Canada-US border. The lead-zinc production complex is the largest in the world with an annual capacity of over 400,000 tonnes combined lead and zinc. As a consequence of this installation, 30 tonnes of silver and over 325,000 tonnes of chemicals and fertilizers are produced annually. Gold, cadmium, bismuth, antimony, arsenic, and indium are also recovered as by-products.

John D Turnbull PEng, Assistant Manager, Roger H Watson PEng, Manager, Trail Modernization (centre), receive the APEBC 1982 Environmental Engineering Award from Ken Williams PEng

Trail Operations' Effluent Treatment Plant is part of the modernization and expansion program announced by Cominco in 1977. To the end of December 1982, Cominco has expended about $335-million. It is expected that the modernization program will cost in excess of $700 million when completed and that the internal and external aspects of environmental control will amount to approximately $200-million.

From its earliest days, Cominco has demonstrated a responsible corporate attitude towards the environment and has made concerted efforts to minimize the impact of its metallurgical operations on the environment. Its efforts with respect to environmental control date back to 1927 when it undertook steps to control sulphur dioxide and heavy metal particulate emissions from its smelting operation with the installation of a chamber plant to produce sulphuric acid from zinc roaster gas.

Cominco's efforts, which anticipated environmental legislation by several decades, have paid handsome environmental dividends over the years. The Columbia River at Trail has continued to be a favourite among local sportsmen whose fishing activities range from shoreline angling to trolling from boats. Fish caught above and below the Trail plants are of excellent quality and comply with Canadian and foreign standards for food as shown by studies carried out between June 1977 and October 1981. Studies concerning blood-lead levels, lung function and

general health of local residents have shown that Trail is a good place in which to live and bring up children.

NEW WASTE MANAGEMENT BRANCH REGULATIONS

Notwithstanding the fact that Columbia River water downstream from the Trail plants was well within drinking water standards for metal content, it was anticipated that new, discharge-related Waste Management Branch regulations would ultimately necessitate an effluent treatment plant. Consequently, Cominco Engineering prepared a feasibility proposal which outlined the process and plant design, project schedule and capital cost. Funds for the project were appropriated and the project team was mobilized in October, 1978.

On November 29, 1978, Cominco Ltd was issued Pollution Control Permit No PE-2753. The permit requires that the contaminant loadings in effluents discharged into the Columbia River from Trail metallurgical operations be reduced to meet specific maximum levels of contamination by January 1, 1983. The effluent treatment plant was to operate in conjunction with various metallurgical process improvements and other environmental projects to achieve the stringent quality objectives specified in this permit.

PROCESS TECHNOLOGY

The Trail Operations Effluent Treatment Plant uses the high density sludge (HDS) version of the basic lime precipitation process which was researched intensively by Cominco Ltd. Cominco's first application of this process was the $10 million Effluent Treatment Plant at its Kimberley Operations, officially opened in October 1979.

The HDS process recycles a substantial proportion of the clarifier underflow sludge. This material is blended with the lime slurry necessary for neutralization prior to mixing in the main reaction vessels. The pre-mix is an important feature of the process that modifies the physical characteristics of the sludge solids from a fluffy slime to an almost particulate texture.

In the course of pilot plant testing of Trail Operations effluent, Cominco Technical Research personnel simulated various upset conditions in order to be able to design a plant that would handle the combination of varying flow rates and effluent characteristics from various sewer systems of the complex metallurgical operation.

$9-MILLION TREATMENT PLANT

The $9-million Effluent Treatment Plant for Cominco's Trail lead-zinc operation is one of several environmental projects that ultimately will allow Cominco to meet the new Provincial environmental standards.

Because the plant is located next to a residential area, it was built with aesthetic considerations in mind. Extensie landscaping and an attractive exterior were features of the design.

The plant has a treatment capacity of 4500 litres of effluent process water per minute, but because of the incorporation of a large holding tank for incoming feed, the plant can handle emergency surges of up to 9000 litres per minute. Flows from various sewer systems from 20 separate areas at the Trail metallurgical complex are treated in the plant.

The collection system connecting the various industrial sewers to the treatment plant involved the construction of an underground gravity flow piping system. Thirteen effluent streams from the zinc operations are collected and drained to the treatment plant. The major flow from the zinc plants, roaster off-gas cooling water, is stripped to

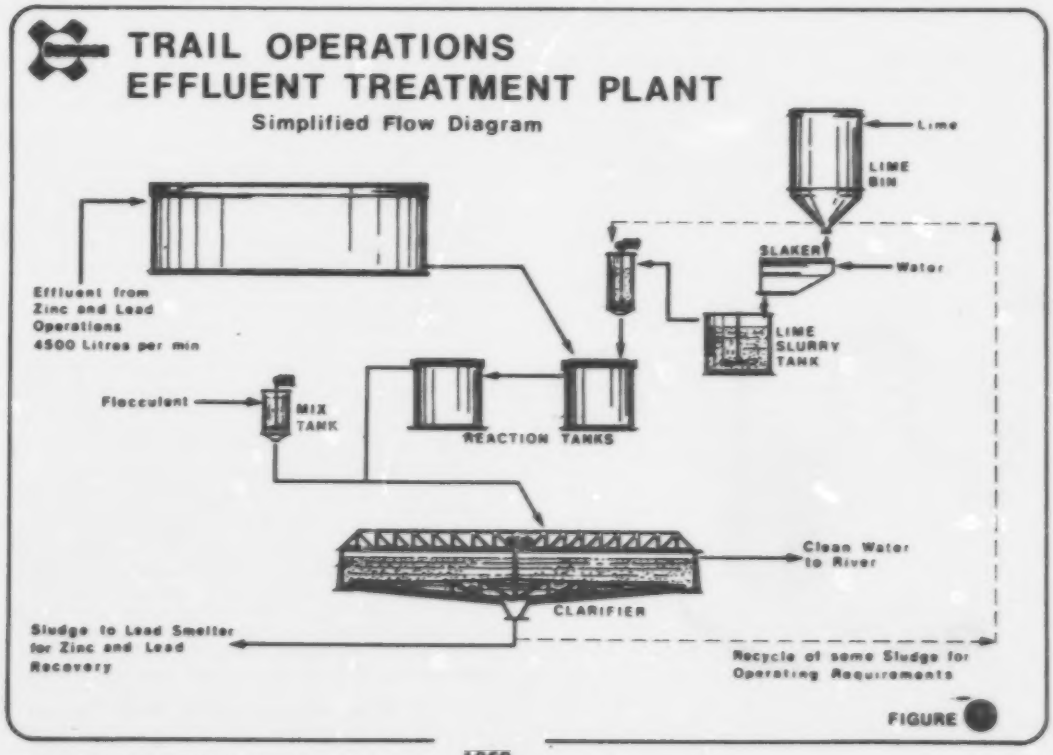


FIGURE 1

SO_2 prior to being sent to the treatment plant, thereby minimizing sludge production. Effluent streams from the lead smelter are first collected in a thickener where they are neutralized to pH 6.5. Thickener overflow is then pumped to the plant for treatment.

Effluent streams from the lead smelter and zinc operations are received in a 23-metre diameter mild steel storage tank lined with neoprene rubber for corrosion resistance. The tank is aerated to keep the solids in suspension. Tank exhaust air is water scrubbed and the scrubber effluent water is sent to the reaction tank for neutralization. The storage tank provides a 13-hour surge capacity for blending of the varied feed streams, dilution of acid spills and allows for short-term plant maintenance shutdowns.

From the storage tank, a controlled flow of the combined effluent is pumped to the first of two 106,000-litre fibreglass reinforced plastic (FRP) reaction tanks in series, for neutralization with lime to pH 10. Both reaction tanks are baffled and agitated to ensure proper mixing.

Pulverized quicklime is received pneumatically in a 150-tonne bin from a bulk delivery truck. The bin is provided with a vibrating bin discharger bottom that ensures a continuous flow of material and prevents bridging and rat-holing in the bin. Air is exhausted via a pulse jet bag filter mounted on top of the silo.

A variable speed screw feeder meters the quicklime into a paste-type lime slaker where it is hydrated. The lime slaker is essentially a mild-steel conveyor trough in which lime and water are mixed with rotating paddles. Hydrated lime is stored as a 10% lime slurry in a 106,000-litre FRP tank. The tank has four internal baffles and is agitated to maintain a homogeneous mixture. Quicklime is drawn off the tank by centrifugal pumps and pumped to a 4000-litre capacity opened top FRP tank where it is pre-mixed with recycled clarifier underflow sludge.

The combined slurry overflows the premix tank and is mixed with the effluent in the reaction vessels where neutralization and precipitation is accomplished. The pH in the reaction tanks controls the lime slurry flow rate to the premix tank.

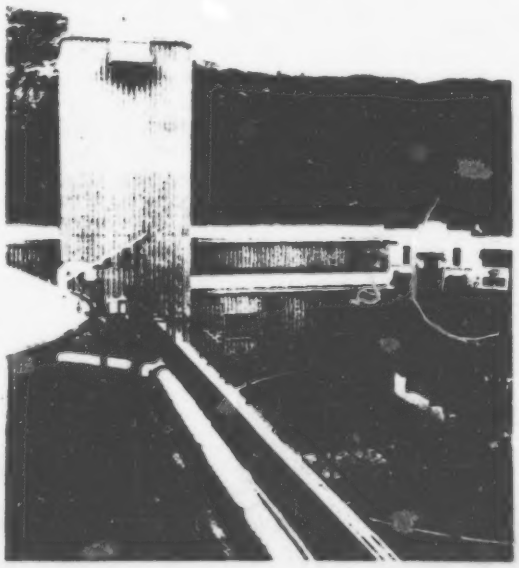
Neutralized effluent slurry from the reaction tanks is mixed with a flocculant in a 3500-litre mix tank which overflows to a clarifier for liquid-solid separation. The flocculant, an organic polymer, is added to improve the settling characteristics of the fine precipitate. This promotes rapid settling of the sludge particles in the clarifier producing a clear effluent overflow for discharge to the Columbia River. This overflow is continuously monitored for turbidity and pH.

The clarifier is a 25-metre diameter by 3-metre deep concrete tank with a slow moving rake mechanism that draws the settled solids to the bottom center cone while allowing incoming solids to settle undisturbed. Settled sludge is removed from the clarifier at about 25% solids. A major portion of this sludge is recycled and mixed with the lime slurry used for neutralization. The balance is pumped intermittently, depending on the sludge production rate, to the Lead Sinter Plant. In the Sinter Plant, the sludge is combined with a reclaimed lead slurry stream, dewatered on a drum filter and mixed with zinc leaching plant residue slurry for treatment and recovery of the metal values. The filtrate joins other Sinter Plant effluent streams for return to the Effluent Treatment Plant.

A simplified flow diagram of the plant is shown in Figure 1.

Interior of the main process building of the Effluent Treatment Plant showing the bottom of the lime bin and the lime slaker (beside the operator).

Detail of Cominco's Effluent Treatment Plant at its Trail Operations. At the left is the surge tank, in the background is the main process building and to the right the clarifier.



PLANT PERFORMANCE

Plant commissioning proceeded in an orderly manner with no major problems and the plant was started on June 8, 1981. The startup went smoothly and the maximum design rate was achieved after only three days of operation. Design limits on the discharge turbidity and pH were met from the very first day.

Since startup, the new plant has performed as expected.

Recovery of zinc, lead and cadmium from the processed streams has been good:

	% Recovered
Zinc	98.9
Lead	99.5
Cadmium	97.5
Suspended Solids	92.9

The Effluent Treatment Plant has contributed to an overall reduction in heavy metals in the effluent leaving the Trail plants. Columbia River water quality data are shown in Table I.

Operating costs have averaged $50,000 per month with lime cost contributing 40% of the total. The metals recovered in the plant, after subsequent reprocessing costs and other associated savings, serve to offset the operating costs to a large extent. Typical of most environmental control projects, there is no return on the capital invested.

An unexpected benefit of the treatment plant is that it has acted as a "policeman" to the metallurgical operation. Any short term process upsets that previously resulted in unrecognized discharges to the river are now readily detected, their origin traced and corrective action taken. During such upsets, the Effluent Treatment Plant, with its conservative design and surge capacity, acts as an effective buffer to prevent the discharge of metallic effluents to the Columbia Rover.

ENGINEERING AND CONSTRUCTION

The Effluent Treatment Plant was designed to meet the strict requirements of the BC Ministry of the Environment. The process and design specifications which served as the basis for detailed design (see Table II) were established by Cominco Technical Research and the Trail Modernization Group. Because of the environmental focus of the plant, extreme attention was paid to minimizing periods of plant downtime. As a consequence of this philosophy, features such as 100% surge capacity, double piping in certain areas, and installed standby pumps were included in the design criteria.

Project management, project services, overall design responsibility and construction were provided by Cominco Engineering. Hatch Associates Ltd of Toronto were responsible for the detailed design work while process technical services were provided by Cominco Technical Research.

The technology, design, construction and operating expertise developed as a result of this project is now being made available to third parties through Cominco Engineering Services Ltd (CESL), a wholly-owned subsidiary of Cominco Ltd.

ACKNOWLEDGEMENTS. Successful implementation of a project of this nature required the broad spectrum of technology, know-how and experience of a large number of professional engineers, technicians, technologists and specialists from within the Cominco organization. Particular acknowledgement is accorded the following key members of the project team:
P Huszti, Operations Representative
W J Kuit, Assistant Manager, Environmental Control
A R Babcock, Research Chemist
D A Burnett PEng, Project Superintendent
H M Ichiyen PEng (Ontario), Design Superintendent (Hatch Associates Ltd.)
D K MacDonald PEng (Alberta), Construction Superintendent

Table I. Typical Columbia River water analysis above (Stoney Creek) and below (Waneta) Trail discharges for 1982

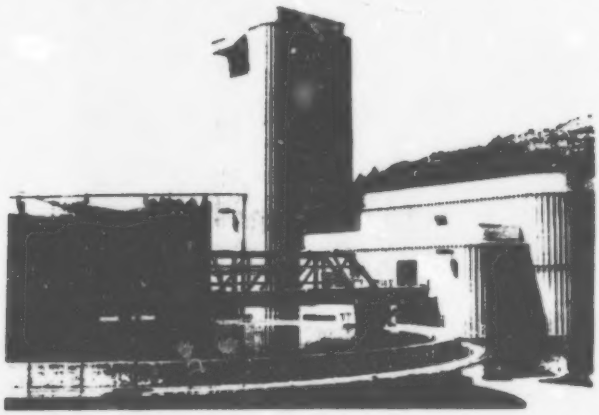
	Stoney Creek	Waneta	Drinking water standard
pH	7.6	7.5	6.5-8.3
Conductivity	153.0	153.0	
Turbidity	2.0	2.0	
	mg/l	mg/l	mg/l
Hardness	67.0	68.0	<180.0
Sulphate	7.9	11.0	<500.0
Fluoride	0.09	0.14	<1.0
PO_4, total	0.03	0.09	<0.2
Mercury, total	<0.00005	0.00005	<0.001
Iron, dissolved	0.04	0.04	<0.3
Lead, dissolved	0.02	0.02	<0.05
Zinc, dissolved	0.02	0.03	<5.0
Copper, dissolved	<0.005	<0.005	<1.0
Arsenic, dissolved	<0.005	<0.005	<0.05
Cadmium, dissolved	<0.005	0.005	<0.01

Average flow = 2,380 m/sec

Table II. Effluent Treatment Plant Data

- Capital cost: $9.0-million
- Completion: June, 1981
- Effluents treated: Contaminated streams from 20 areas in Lead and Zinc Operations
- Effluent collection capacity: 4500 LPM normal; 9000 LPM surge capacity
- Surge tank: 23 metre diameter; 3.6-million litres capacity
- Lime silo: 150 tonnes quicklime
- Lime slaking capacity: 1.8 tonnes per hour
- Process
  - Feed: 4500 LPM normal; 6000 LPM maximum
  - Reactors: two in series, 20 minutes retention time each
  - Lime neutralizes acid and precipitates metal present (usage 11 tpd).
  - Flocculant: use 6 kg/d; added to assist solids settling in clarifier
- Clarifier: 25 metre diameter; 1.7-million litres capacity
- Products: clean water to river; 20 tonnes of sludge per day to Lead Smelter
- Labour: 1 operator per shift
- Operating cost: $50,000 per month

The Effluent Treatment Plant at Cominco's Trail Operations. At the left is the surge tank, to its right the main process building with a tower housing the lime bin and in the foreground the clarifier from which the overflow reports to the Columbia River and the underflow back to the metallurgical plants for the recovery of metal values.



Lime in gold and uranium mining

How ERPM uses lime to solve unique underground water problem

The demand for lime in the South African gold and uranium industry is soaring as mines expand and new uses are found. This article — the first of two discussing the usage of lime in mining — describes how lime is used in a unique, high density sludge process at ERPM gold mine in a plant now regarded as highly successful and the biggest of its kind in the world.

LIME IN THE FORM of calcium oxide, slaked to calcium hydroxide, as well as agricultural lime is used extensively in the South African gold and uranium mining industry. Lime is used in the manufacture of calcium cyanide and is added to the gold bearing pulp to protect the cyanide from decomposing. It also plays an important part in settling pulp. The excess barren sulphuric acid solutions generated in the uranium extraction plants, as well as the acidic uranium residues, are neutralised with hydrated lime before being disposed of.

Iron pyrite (FeS_2) is present in gold bearing ore (conglomerate), oxidising to iron compounds which contaminate underground water. This water always requires liming, oxidation and settling before being disposed of. If the conventional neutralisation method is applied a voluminous sludge is formed, rendering disposal thereof almost impossible. The High Density Sludge (H.D.S.) process has been applied with success by Rand Mines' technical advisers to E.R.P.M. Sludges containing up to 70 g suspended solids per 100 ml suspension have been produced.

INTRODUCTION: About 34 per cent (565 000 t/a) of the total lime production in South Africa is used in the mining industry, the majority of this for the production of gold and uranium.

The South African gold bearing ores always contain iron pyrite which, on exposure, oxidises to sulphuric acid and iron sulphate, giving rise to relatively large volumes of contaminated underground water. This water must receive some kind of lime treatment before being pumped to surface. Neutralisation is necessary to prevent excessive corrosion of equipment and also to meet certain legal requirements prior to disposal. This application forms the major part of the total lime consumption in the above-mentioned industry.

The author, Dr C.M. van Staden, Pr Eng, DSc, F.S.A.I.M.M., is a consulting metallurgist at Rand Mines Limited. The articles are based on a paper he presented to the 4th International Lime Congress (Technical) held in Hershey, Pennsylvania, United States.

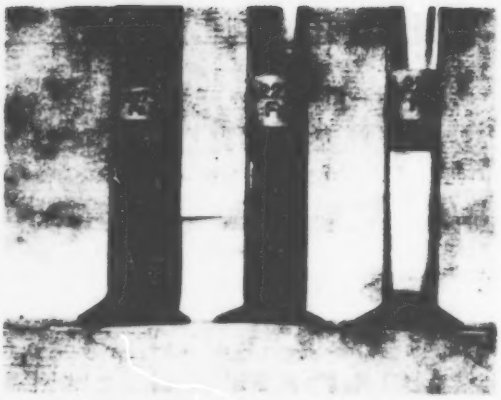
Pollution prevention

When the conventional method is used to neutralise underground waters with lime, voluminous sludges, which are difficult to dispose of, are obtained. A solution to the problem as encountered at the East Rand Proprietary Mines Limited (E.R.P.M.) (one of the Rand Mines Group of Mines), is described here.

In terms of the Atmospheric Pollution Prevention Act[1] it is necessary to suppress the dust caused by wind erosion from the mine's residue disposal dams. Various methods to achieve this have been tested by the Research Laboratories of the Chamber of Mines (C.O.M.), and it has been found that planting of vegetation on these dams is the most practical and suitable method. The surfaces of these dams are usually acidic due to the oxidation of pyrite contained in the deposited residue; agricultural lime and hydrated lime are used to treat the surfaces prior to and after the establishment of vegetation.

NEUTRALISATION OF UNDERGROUND WATER: Gold in South Africa is found in the conglomerate ore which was formed about 2,5 x 10^9 years ago and which consists mainly of weathered rock and quartzite pebbles. The gold content of this ore averages 9 g/t[2] with a pyrite content of between one and three per cent expressed as sulphur. Pyrite exposed underground by the mining operations is bacteriologically oxidised to yield sulphuric acid and

Sludge at ERPM after lime treatment ready for use in neutralisation of underground water.



At left, underground water with lime and no aeration; the iron is in the ferrous state. Centre, underground water with lime and aeration; the lime is in the ferric state. Right, underground water treated with the high density sludge process. All these samples are shown after 24 hours of settling. Note the same Fe content but the different sludge volumes.

water soluble iron salts. A simplified version of the oxidation process is as follows:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$

The result is fairly acidic underground water, pH 3,0, with an iron content as high as 1 500 mg/l.

To enable mining to be carried out this water must be pumped out of the mines. It is necessary to raise the pH of the water to about 5,0 to 5,5[3] (which is the critical corrosion pH for mild steel under these conditions) and thereby to protect the pumps and pipe columns underground.

The conventional lime neutralisation process is shown diagramatically in figure 1. Underground water is neutralised with milk of lime in an agitated tank. Aeration is necessary if the underground water contains ferrous iron, which must be converted to the ferric state for precipitation. The treated water flows to a settler where the ferric hydroxide is settled. The clear overflow (pH 7,5) is utilised in the reduction plant or disposed of in a public stream. The sludge is mixed with reduction plant residue and disposed of on a residue dam.

The establishment of the High Density Sludge (H.D.S.) Process at E.R.P.M.: At E.R.P.M., one of the gold mines in the Rand Mines Group, a unique problem regarding underground water pumping and treatment developed following the closure of neighbouring mines. Pumping started at the South West Vertical (S.W.V.) shaft of this mine in March 1967 at 49 level, 2 030 m below surface, and continued until February 1975. The volume of water pumped and treated was about 6 800 m³ per day. The conventional method of lime neutralisation was used (see Fig. 1.) and clarifier underflow containing about 4 g/l of suspended solids was obtained.

Before February 1975 mining operations and underground water pumping were curtailed or stopped by a number of mines in the area which was about 40 km from East to West and 10 km North to South of E.R.P.M. This had a very important effect on the underground water situation at E.R.P.M., which was still in operation and also the deepest mine in the area. It was therefore obvious that E.R.P.M. had to plan for the pumping of the additional underground water.

For economic and practical reasons it was decided to stop pumping from 49 level (which was a two stage pumping operation), plug the flow at this level by casting concrete plugs with a total overall length of 13,7 m in the drive (and other drives where necessary) and allow the water to rise behind the impervious wall to 24 level, 1 050 m below surface, from where the future pumping would be done in a single stage operation. The pumping arrangement at this level is described in detail by Tyser.[4]

Planning and Investigation

During the planning and investigation stages it was decided that provision should be made to treat an average flow of 45 454 m³/day of underground water.

Design of the surface treatment plant was based on this figure. It was also decided to partially neutralise the water underground with lime to protect the pumping equipment and pipes and for practical reasons it was decided that no settling would be done underground.

The only underground water available for experimental purposes was that from 49 level before the

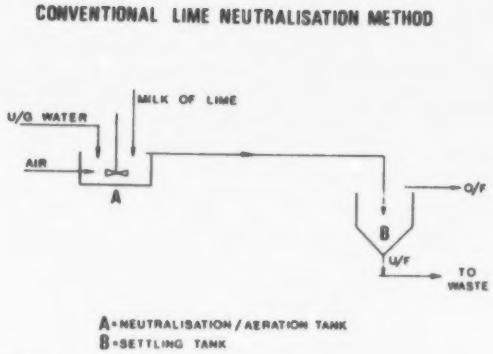


Figure 1

plug was cast. It was hoped that the quality of the water would not deteriorate but rather improve during the time it took to reach 24 level. This was later found to be the case.

At the time of the test the water of 49 level had the following composition:-

pH	→ 3,2
Total dissolved solids	10 000 mg/l
Fe^{2+}	1 400 mg/l
Fe^{3+}	100 mg/l
* Precipitatable solids	5 500 mg/l

Problems encountered: The first question which had to be answered was what quantity of lime would be required, with aeration to oxidise the iron, to raise the pH of the water to 7,5.

*This represents the amount of solids in suspension after neutralisation to pH 7,5 with milk of lime and aeration to oxidise the ferrous iron completely.

Evaluation of H.D.S. process

This was determined from a graph (Fig. 2) of pH vs. amount of lime added to a litre of raw, aerated, 49 level plug water. Using this graph it can be shown that 89 t of lime, containing 90 per cent available CaO, will be required by 45 545 m^3 of underground water per day. It was found later that this figure agrees fairly well with the actual requirement.

The analysis of the 49 plug water indicated that 5 500 mg/l of precipitatable solids, which is equivalent to 250 t, had to be disposed of per day.

If the conventional process of lime treatment had been used a sludge containing a maximum of 4 g suspended solids per 100 ml suspension would have been obtained, equivalent to a sludge volume of 6 250 m^3/day. The only practical method of disposal would be to mix the sludge with gold plant residue and pump the mixture to the residue disposal dams, the sludge replacing make-up re-pulping water. The maximum volume the Reduction Plant could dispose of in this way was only 2 727 m^3/day.

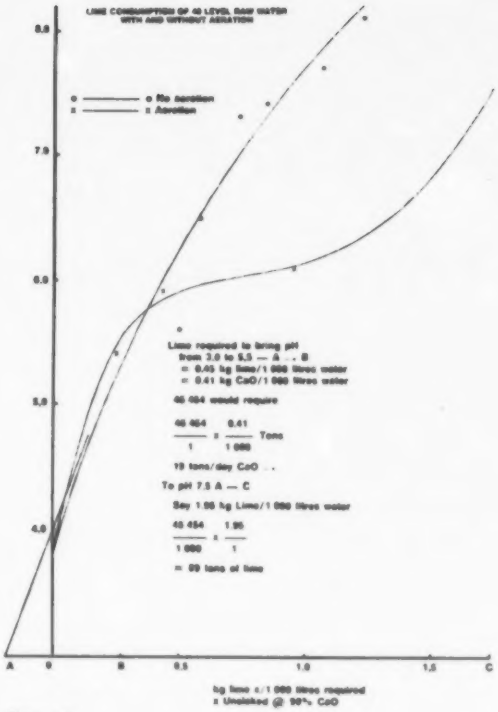


Figure 2

The mine was thus faced with a serious problem, and as the inflowing water behind the plug was rising at a rate of about 0,8 m/day, a solution to the problem was urgently required.

Evaluation of the H.D.S. Process: Various methods to treat the water were considered and it was finally decided to evaluate the H.D.S.[5, 6] process developed by Bethlehem Steel, Pa., in detail. Rand Mines, entered into an agreement with that company to evaluate their process and, if suitable, to use it.

A schematic flow diagram of the H.D.S. process is shown in figure 3.

Three plants at Bethlehem Steel

The important feature are:

☐ That milk of lime must be mixed with the sludge, and this sludge-lime mixture used to neutralise the underground water on surface. If this is not done, the required sludge density is not obtained.

☐ That return sludge rate is such that 25 parts or more of solids are returned for every one part of solids that will be precipitated from the incoming underground water.

At the time of the investigation three H.D.S. plants

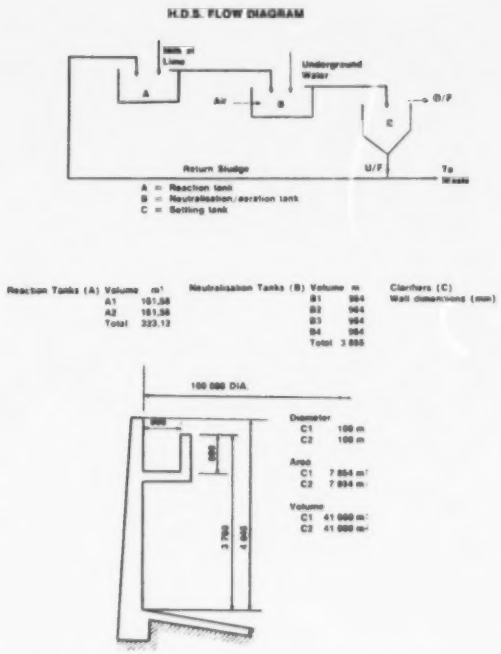


Figure 3

belonging to Bethlehem Steel were visited. Their capacities were as follows:

Plant No.	Volume Average	m³/day Maximum	Total Fe mg/l
1.	5 500	5 500	100
2.	24 500	24 500	250
3.	20 000	40 000	
	50 000	70 000	
E.R.P.M.	45 454	90 000	1 500

The plant required at E.R.P.M., judged by existing world standards, had to be relatively large.

What was not known was the amenability of the E.R.P.M. underground water to this treatment process, particularly in the light of the pre-neutralisation step underground.

The following tests with 49 level plug water were therefore conducted at E.R.P.M.:

1. Batch tests trying to simulate a continuous process.
2. Laboratory scale continuous pilot plant runs, feeding underground water at the rate of 125 ml per minute.
3. The conventional water treatment plant at the S.W.V. shaft was converted to the H.D.S. process for the evaluation of the process on a larger scale.

In all three cases positive results were obtained and sludges containing 25 g suspended solids per 100 ml were produced. On the basis of these results, and on basic information provided by Bethlehem Steel, it was decided to use the H.D.S. process and the E.R.P.M. plant was designed.

Description of the E.R.P.M. H.D.S. Plant:

Underground: Four stainless steel pipes feed the water from the plug to a common mixing chamber, where lime slurry is added under gravity from surface to achieve the pre-neutralisation. Very little iron precipitation takes place at this stage. Four pumps are fed from the mixing chamber and the water is pumped via two 356 mm diameter mild steel columns to surface. Each pump, driven by a 4 000 kW motor has a pumping capacity of about 17 000 m³ per day against a head of 1 050 m. In each case two pumps serve one column to surface.

Performance of the H.D.S. plant

On surface (Ref. Fig 3 and 4): Two mixing tanks (A) and four aeration tanks (B) were designed to treat a total flow of 90 000 m³/day. Therefore a 100 per cent stand-by capacity was installed.

The two clarifiers (C) were designed on the basis of sludge settling curves.

The plant dimensions and capacities are given in figure 4.

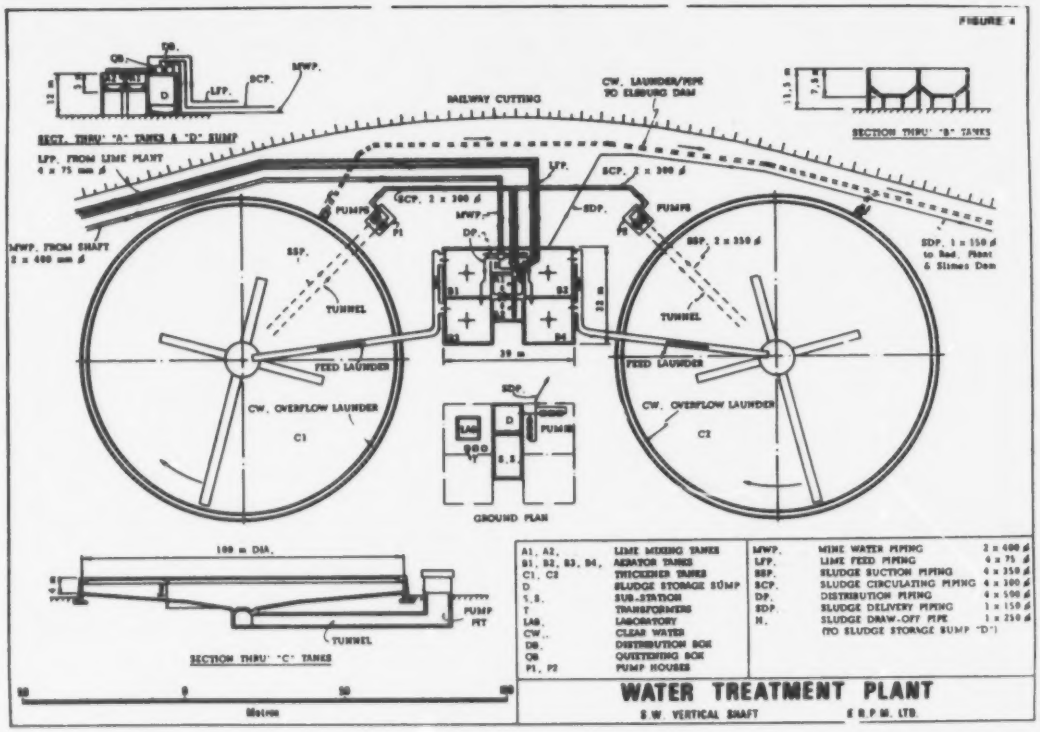
Considerable process flexibility exists between the mixing tanks and aeration/neutralisation tanks.

Lime Plant: Ground unslaked lime (−2 mm) is supplied by The Northern Lime Co Ltd from its plant at Lime Acres in the Cape Province. The lime arrives at the shaft in special rail tankers, and is pneumatically off-loaded into seven storage and one feed silo. Each silo has a capacity of 200 t.

The lime is slaked in two Omega slakers operating in parallel, to give a milk of lime with a relative density of about 1,05, which is equivalent to a concentration of about 5 g CaO per 100 g suspension. The milk of lime is passed through a settler to eliminate coarse particles which may be carried over from the slakers and which would damage the multi-stage pumps underground. The settler of an old water treatment plant, which is about 50 m from the lime plant, was used for this purpose.

A flow diagram is shown in figure 5. The settler overflow only is piped underground for pre-neutralisation. The lime settler underflow is pumped to the H.D.S. plant. About 10 per cent of the total lime consumption for this process is used for pre-neutralisation underground, the remainder being consumed in the H.D.S. plant.

Performance of the H.D.S. Plant: Pumping at 24



level started during October 1976. The average volume of water pumped and treated per day is about 34 000 m³ (See Fig 6).

The water level behind the plug is monitored by recording the water pressure (Fig. 6) and the pumping rate is varied accordingly. The lime consumption is about 40 t/day for two pumps.

The analyses of underground water and the clarifier overflow are as follows:

ANALYSIS OF WATER

	Directly from the plug at 24 level	O/F of Clarifiers
pH	3,6	7,3
Fe^{2+}	650	Nil
Fe^{3+}	30	Nil
T.D.S.	7 500	5 600
Ppt.S	1 650	15 (ss)

T.D.S. = Total dissolved solids
Ppt.S = Precipitatable solids
SS. = Suspended solids
All figures in mg/l except pH.

There has been an appreciable improvement in the quality of the water obtained at 24 level compared with the water of 49 level which was used originally for experimental purposes.

The clarifier overflow is discharged, under permit from the Government Department of Water Affairs, to the nearest public stream. According to legal requirements the pH of the overflow water must be kept between pH 5,5 and pH 9,5 and the suspended solids level to less than 25 mg/l. Thus far these requirements have been met with ease. Also, the clarifier overflow has not contained soluble iron. Unfortunately there is no simple solution to the fairly high dissolved solids content of the water.

Sludge densities as high as 50 g per 100 ml are readily obtained.

The total capital costs of erection of the plant are as follows:

On surface	R3,2 x 10^6
Underground	R1,9 x 10^6
Plug 49	R0.5 x 10^6
	R5,6 x 10^6

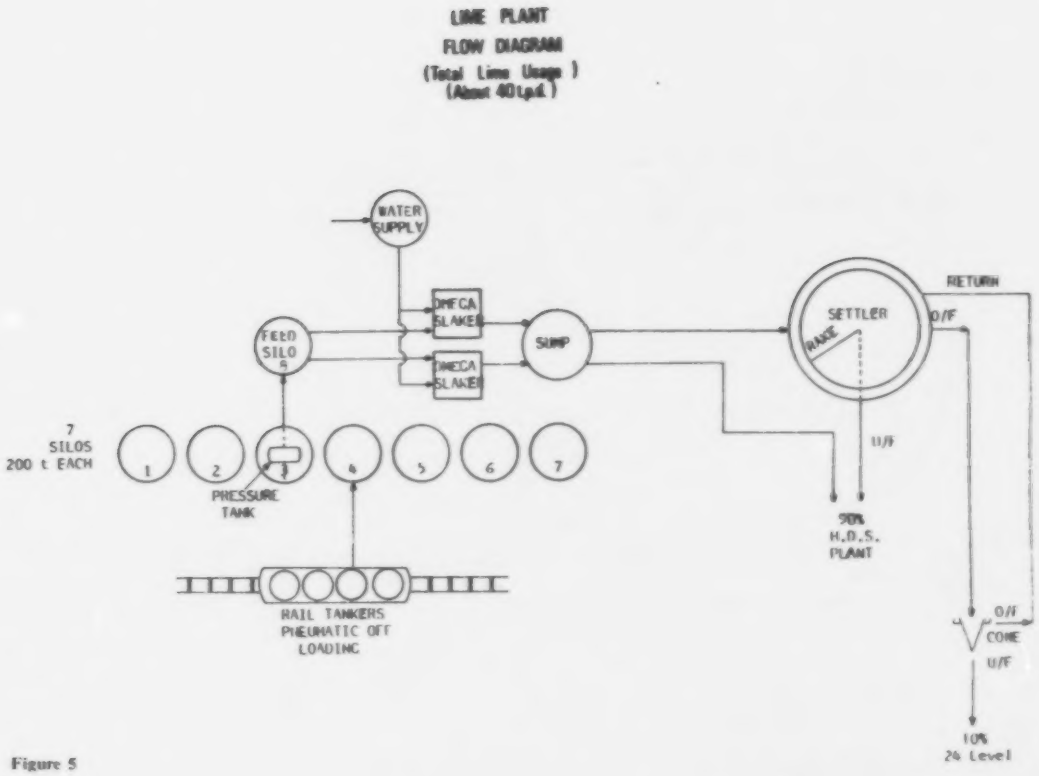


Figure 5

The direct treatment cost of the underground water is about 14 c/m³.

No process, chemical or chemical engineering problems have been encountered at the plant, even during the commissioning period. Rand Mines regard this plant and process as one of the major developments in the mining industry over the past 25 years.[7]

A civil engineering problem was encountered with Clarifier No. 1 where the seals between the floor panels leaked due to bad bonding, but this problem was rectified within a few months.

FUTURE WORK:

☐ One of the investigations which may be carried out in future is the feasibility of mechanically separating the iron hydroxide from the calcium sulphate in the sludge.

☐ One method of H.D.S. sludge disposal, used in Pennsylvania is to deposit the sludge in worked-out underground areas. However, before this can be done it has to be established whether the precipitated iron hydroxide re-dissolves in acidic underground water.

☐ What has also to be determined is where the economic break-even-point between the conventional method and the H.D.S. process lies, taking into account the hydraulic flow of the system and the total underflow tonnage which has to be disposed of.

THE HIGH DENSITY SLUDGE PROCESS
AN IMPROVED TECHNOLOGY FOR HYDROXIDE PRECIPITATION OF HEAVY METALS

by: S. T. Herman
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Bethlehem, Pennsylvania 18016

ABSTRACT

The High-Density Sludge (HDS) process is an improved cold-lime neutralization technique developed by Bethlehem Steel Corporation and originally applied to produce dense sludges in acidic iron-bearing wastewaters such as coal-mine drainage and pickling rinsewaters from steel plant operations. The results of recent laboratory studies are presented that demonstrate the ability of the HDS process to precipitate efficiently, other heavy metals. In laboratory tests with dilute solutions containing copper, cadmium, nickel, lead, and zinc the HDS process was able to reduce all of the soluble metal concentrations to less than 0.1 ppm at a single pH level. This has not been possible with conventional neutralization. Settled sludge concentrations were greater than 20% solids as compared with a normal 1% solids achieved by conventional neutralization techniques.

INTRODUCTION

In the late 1960's Bethlehem Steel's Research Department developed the High-Density Sludge (HDS) process to treat iron-bearing acid mine drainage (AMD) from its bituminous coal mining operations. The process is shown schematically in Figure 1. The main advantage of the HDS process over conventional cold-lime neutralization of AMD is that it can produce a sludge containing up to 50% solids by weight. By comparison, the conventional process generally produces sludges containing 1 to 2% solids by weight. Thus, there is a very substantial reduction in the volume of sludge generated. The HDS process produces a dense sludge by mixing a controlled amount of previously precipitated solids with the an alkaline agent in a separate reactor and using this mixture to neutralize the acidity and precipitate the soluble metals in the wastewater.

In 1979 and 1980 Bethlehem evaluated the potential for using the HDS process to remove both iron and manganese from an AMD discharge at its anthracite mining operations near Tamaqua, Pennsylvania. The bituminous AMD's which Bethlehem had successfully treated with the HDS process contained high ratios of iron to manganese concentrations, e.g., 150 ppm to 200 ppm of iron and 2 to 3 ppm of manganese. The manganese removal was thus enhanced by co-precipitation of relatively large amounts of iron. The anthracite AMD, however, contained only 30 ppm of iron and 13 ppm of manganese. Thus, the beneficial effects of co-precipitation of iron on manganese removal would be much smaller. As part of this program, a small-scale HDS plant was operated on-site for several months. The results of those on-site tests showed that the HDS process reduced the soluble manganese concentrations to levels much lower than expected. A pH of approximately 9 in the HDS process produced manganese removals equivalent to conventional neutralization at a pH of about 10. The HDS process also produced sludge containing up to 50% solids while conventional neutralization sludge contained about 2-3% solids.

In order to study these observations further, additional laboratory studies were carried out with synthetic solutions containing varying amounts of manganese and iron. The results of those studies, shown in Figure 2, demonstrated that: (1) The HDS process precipitated manganese at a lower solution pH than conventional neutralization; (2) the benefits of the co-precipitation of iron on manganese removal in conventional neutralization were carried through and enhanced by the HDS process; and (3) the HDS process produced dense sludges from all of the solutions tested, including one which contained 50 ppm of manganese but no iron. Because of the success seen in these manganese precipitation studies, the test program was expanded to compare the conventional neutralization process and the HDS

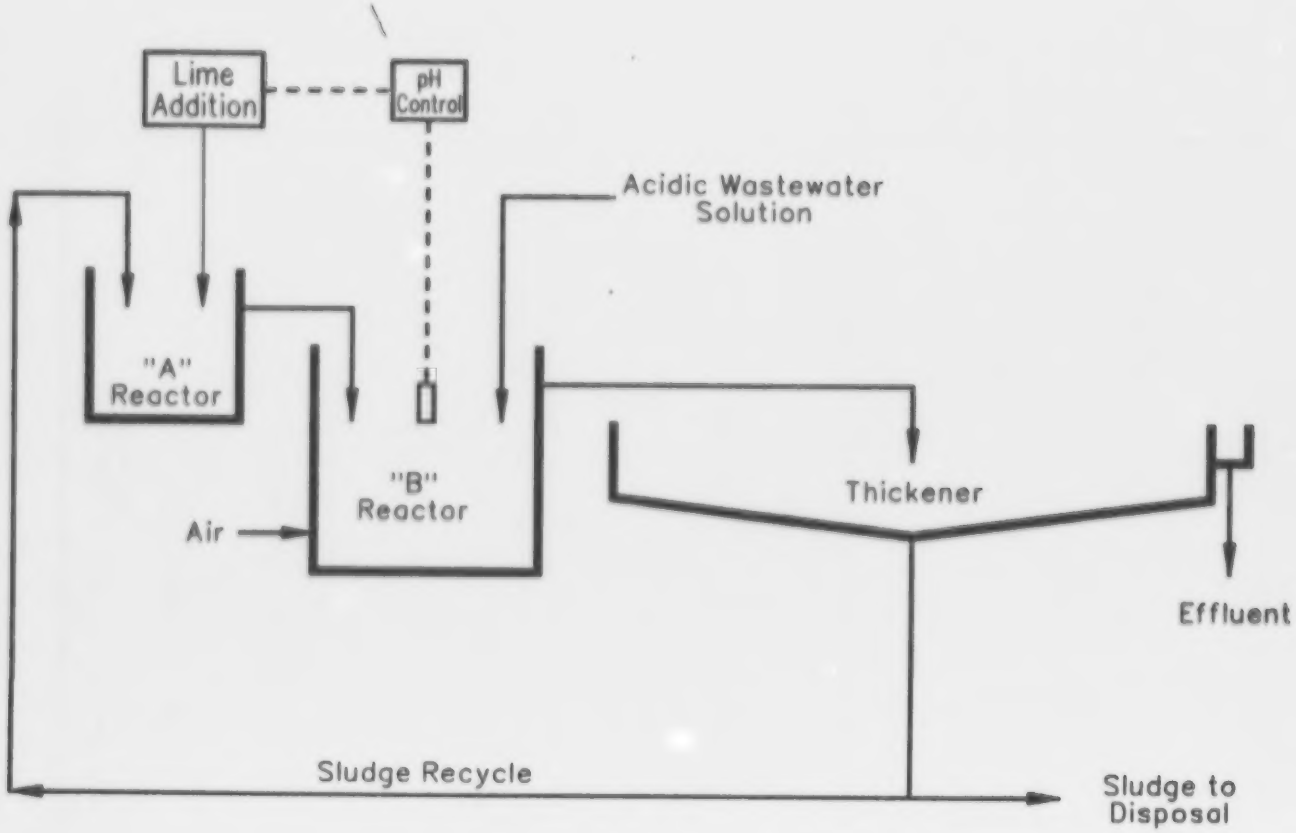
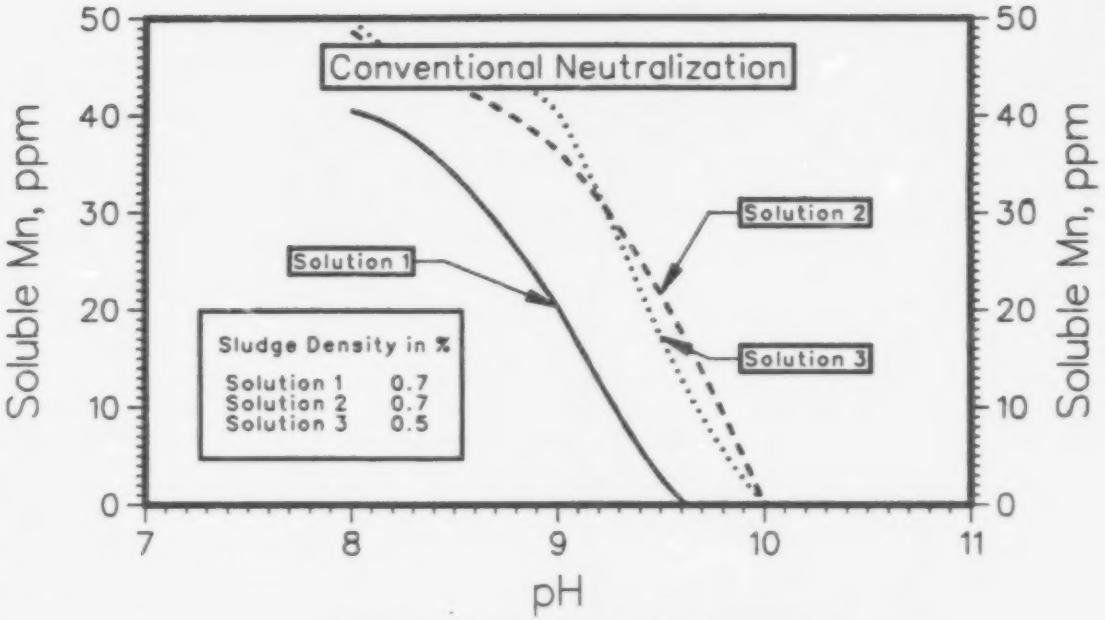


Figure 1. Schematic Diagram of the High Density Sludge Process



SOLUTION CHEMISTRY

Soln #	Fe, ppm	Mn, ppm
1	200	50
2	20	50
3	0	50

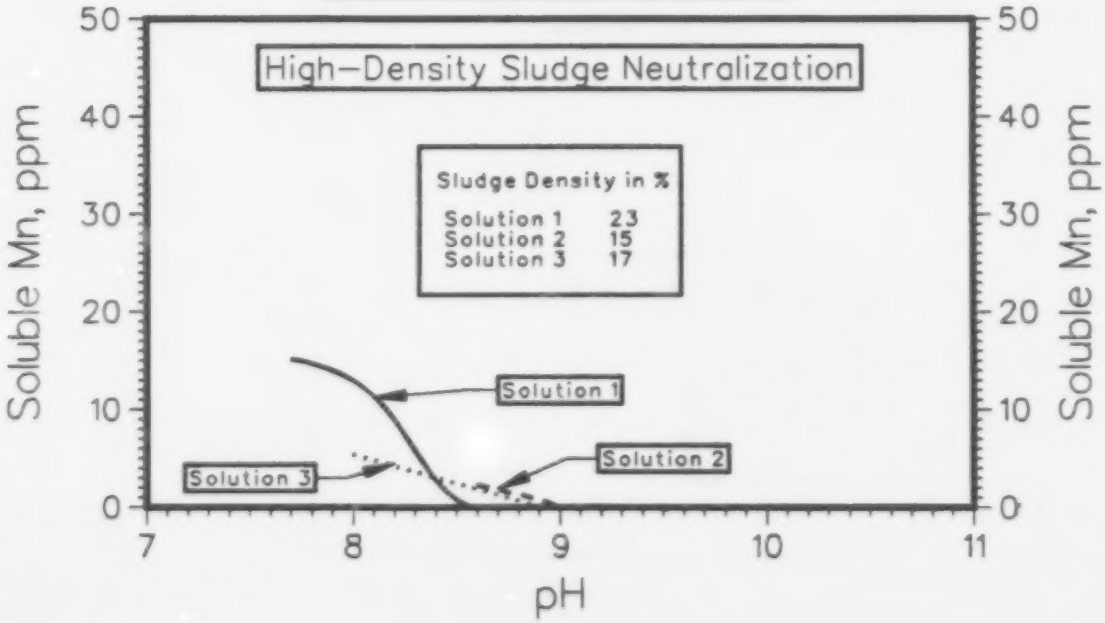


Figure 2. Comparison of Conventional Neutralization and the High–Density Sludge Process for the Precipitation of Manganese

process for the precipitation of other heavy metals, including the effects of co-precipitation of iron on both processes.

TEST PROGRAM

Sets of soluble, heavy metal concentrations versus pH were generated for both conventional and HDS neutralization of synthetic solutions containing cadmium, nickel, zinc, copper, and lead. The initial metal concentrations of the seven solutions tested are given in Table 1. The free acidity of all solutions was maintained at 245 ppm, which was sufficient to assure complete solubilization of the metal chloride salts. The effects of co-precipitation of iron were determined by varying the amount of soluble iron in the synthetic wastewaters. All metal analyses were performed by flame and carbon furnace atomic absorption spectrophotometry. It must be emphasized that this study deals only with soluble metal concentrations, not total metal concentrations upon which effluent discharge limitations are based.

CONVENTIONAL NEUTRALIZATION

Test Procedure

The variables in the experiments were the iron to total non-ferrous heavy metal ratio, the concentration of non-ferrous heavy metals, and the pH of the neutralized solution. Conventional neutralization tests were conducted by neutralizing a 25 or 35-liter sample of the synthetic solution with lime slurry. All solutions were aerated during neutralization, and samples were taken at pH 8.0, 8.5, and then every 0.25 pH unit until pH 11.25. After standing for about three hours, the neutralized samples were filtered and the filtrates analyzed for heavy metals. The lime demand and the solids formed upon neutralization were also determined at each pH level. The percent solids at final dilution (concentration of solids after the slurry had settled for 24 hours) were determined at pH 10 for all solutions. Three replicate neutralizations were run for each of the solutions. Figures 3 and 4 and the top plots in Figures 5 through 9 present the results of the conventional neutralization tests. The concentration of soluble iron in the neutralized samples never exceeded the minimum detectable limit of 0.01 ppm and thus is not shown in any of the plots.

TABLE 1. SOLUTION CHEMISTRIES TESTED AND SLUDGE SOLIDS CONCENTRATIONS PRODUCED BY CONVENTIONAL AND HIGH DENSITY SLUDGE NEUTRALIZATION

Solution #	Metals Concentrations, ppm						Percent Solids in the Sludge			
							Conventional Neutralization		HDS Neutralization	
	Fe	Cd	Ni	Zn	Cu	Pb	% Solids	pH	% solids	pH
1	250	50	50	50	50	50	0.8	10.0	30	9.5
2	25	50	50	50	50	50	0.8	10.0	23	9.5
3	250	5	5	5	5	5	0.6	10.0	20	8.5
4	25	5	5	5	5	5	0.6	10.0	Not Tested	
5	138	28	28	28	28	28	1.0	10.0	Not Tested	
6	0	50	50	50	50	50	0.9	10.0	25	10.2
7	0	5	5	5	5	5	1.0	10.0	28*	9.0

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* Iron sludge generated separately was used as the recycle slurry.

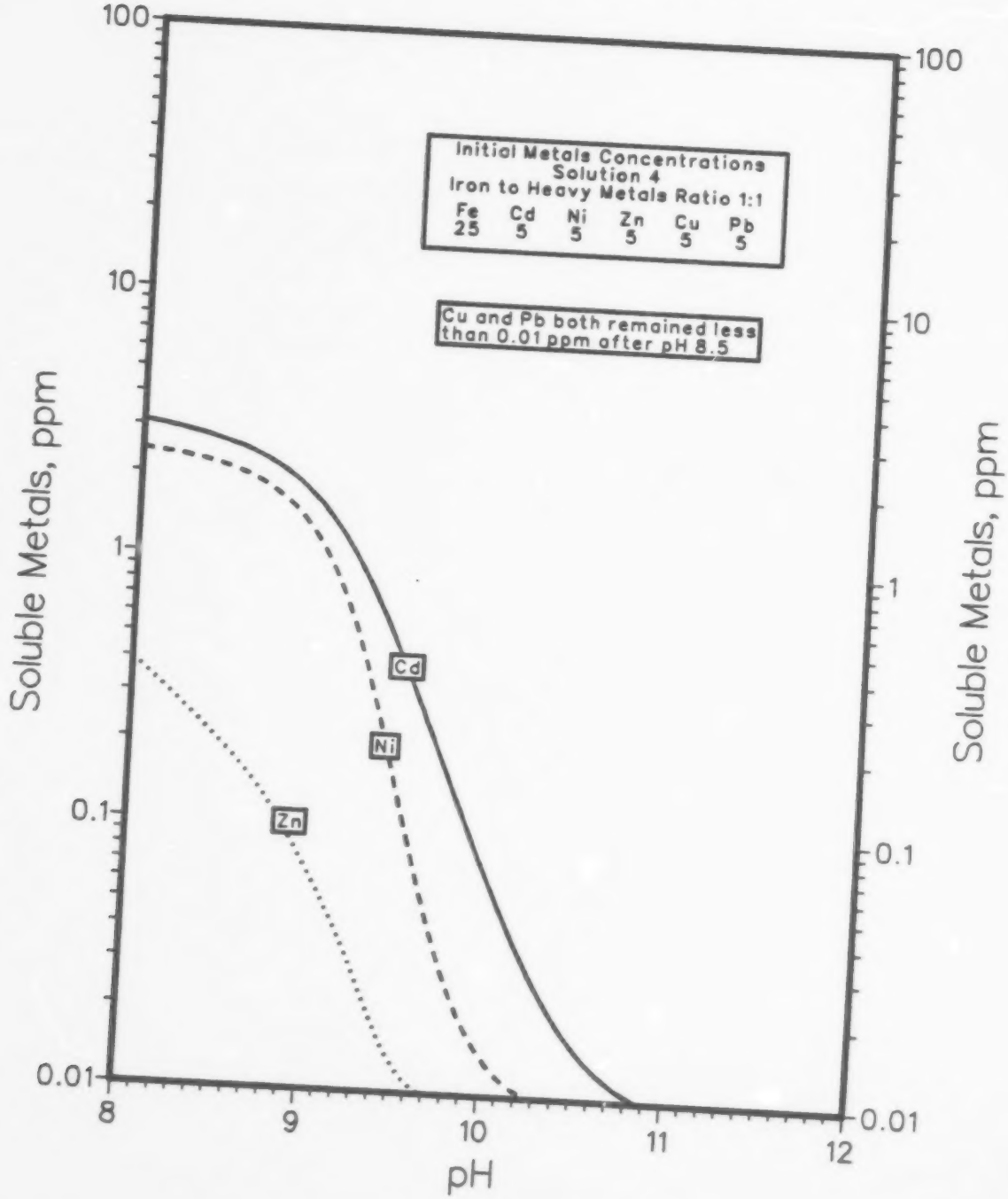

Figure 3. Conventional Neutralization of Solution 4

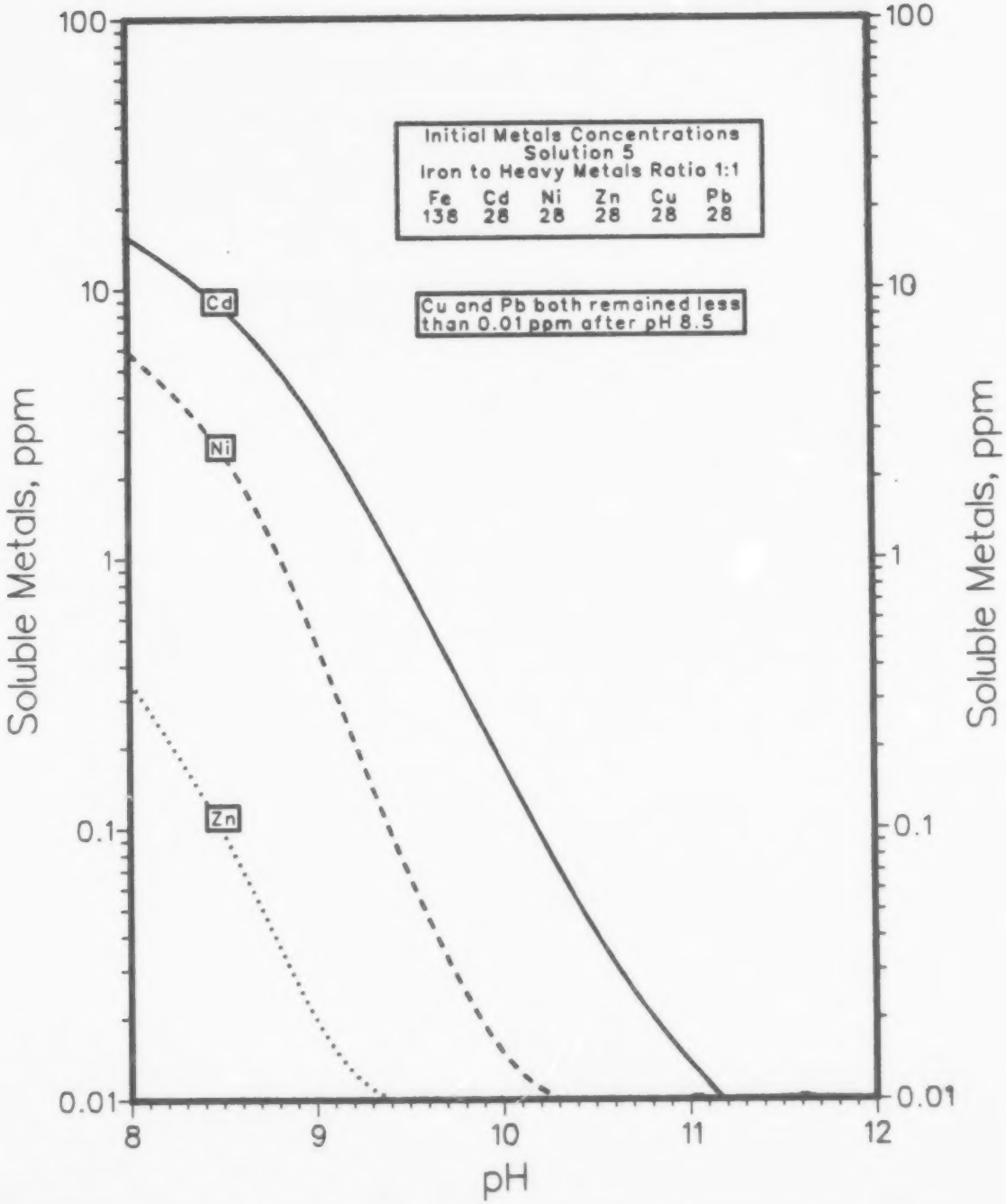

Figure 4. Conventional Neutralization of Solution 5

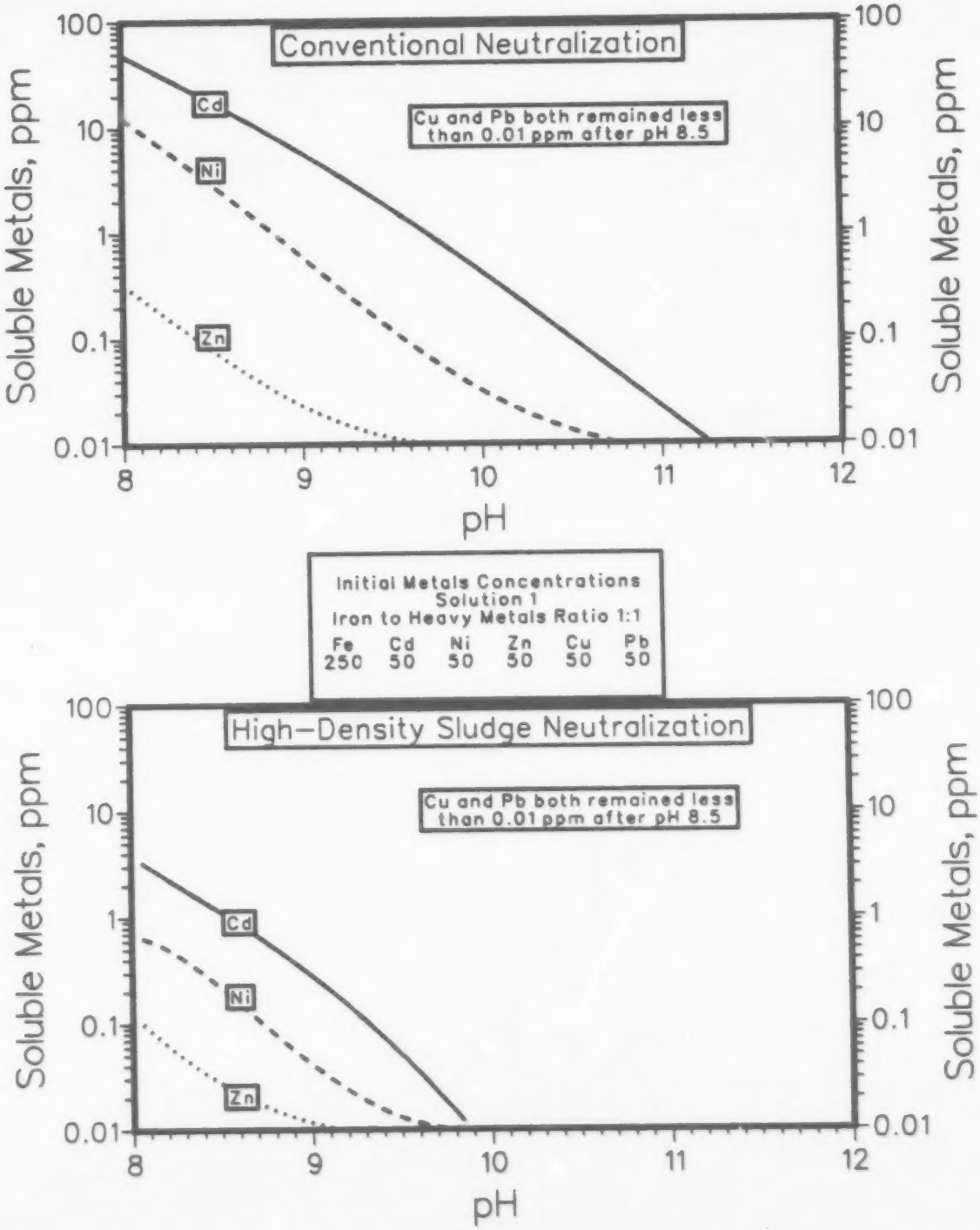

Figure 5. Comparison of Conventional and High-Density Sludge Neutralization of Solution 1

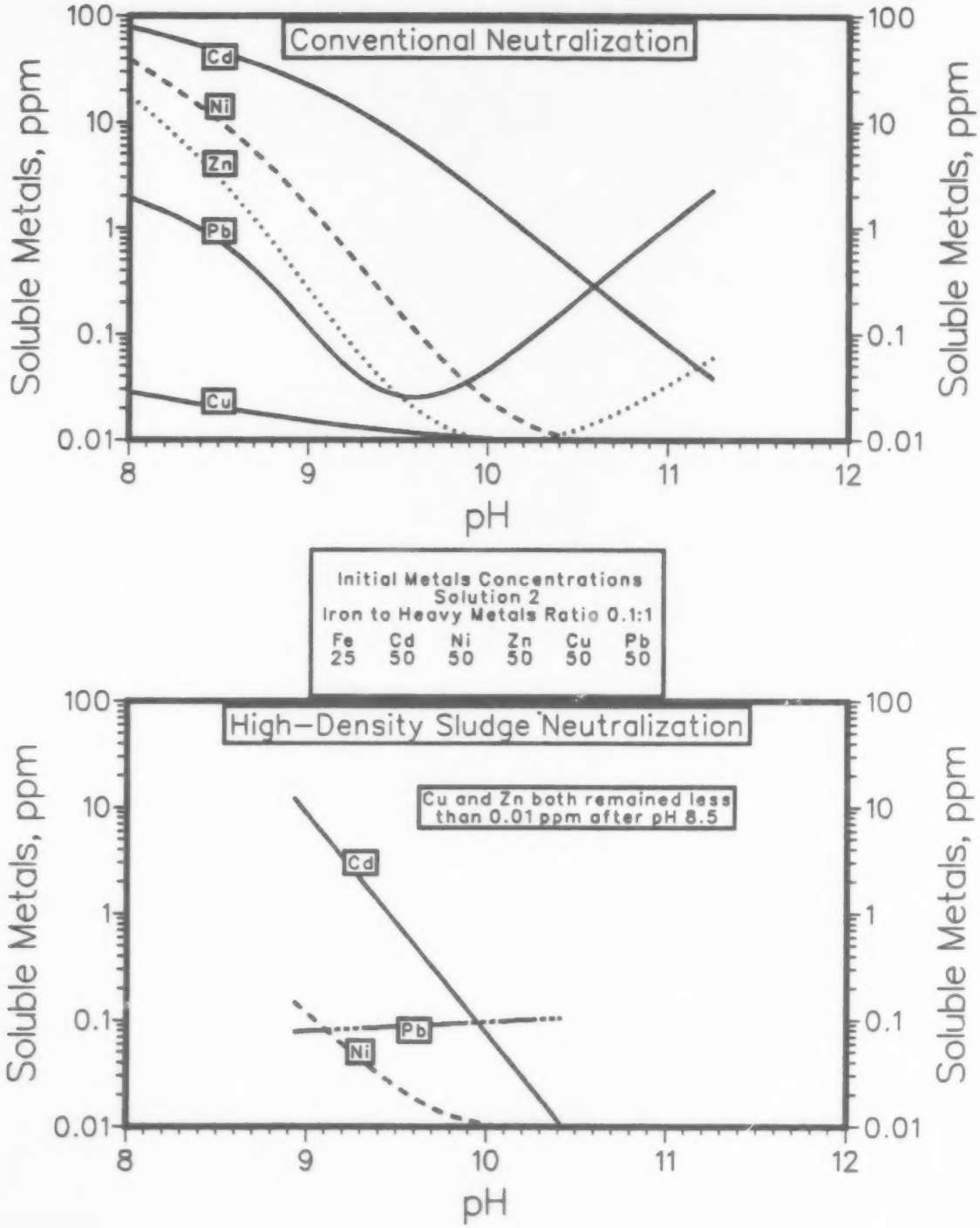

Figure 6. Comparison of Conventional and High–Density Sludge Neutralization of Solution 2

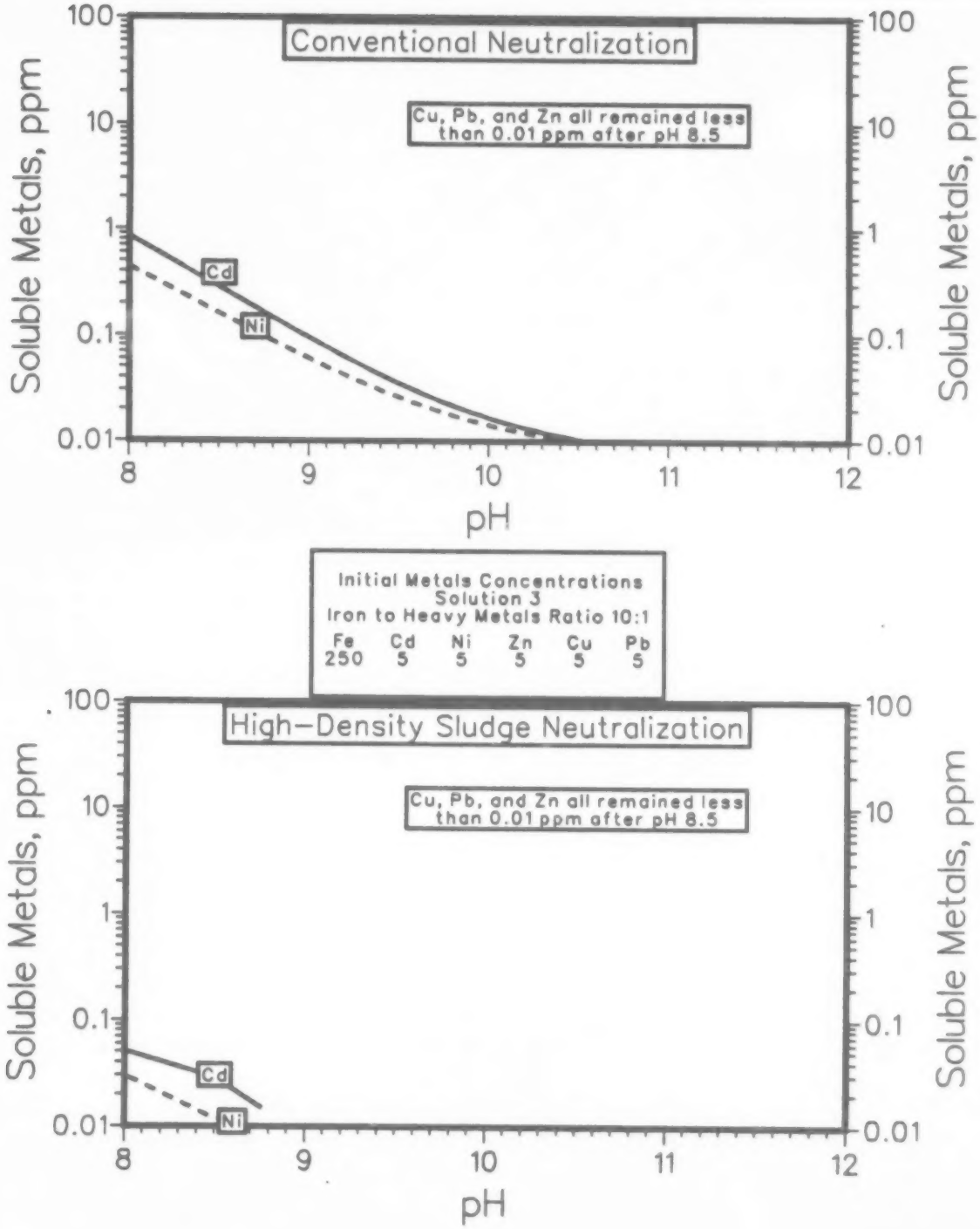

Figure 7. Comparison of Conventional and High-Density Sludge Neutralization of Solution 3

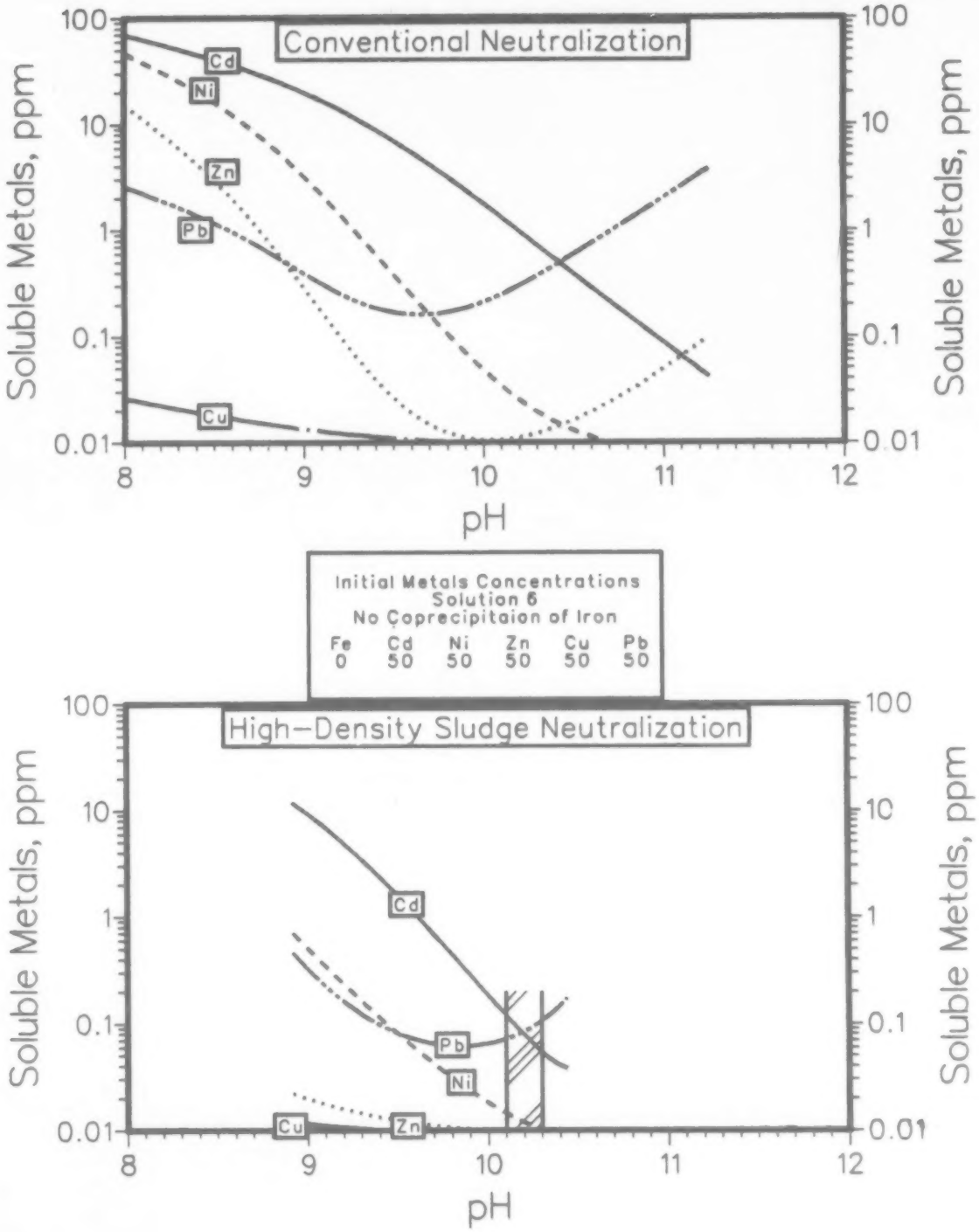

Figure 8. Comparison of Conventional and High-Density Sludge Neutralization of Solution 6

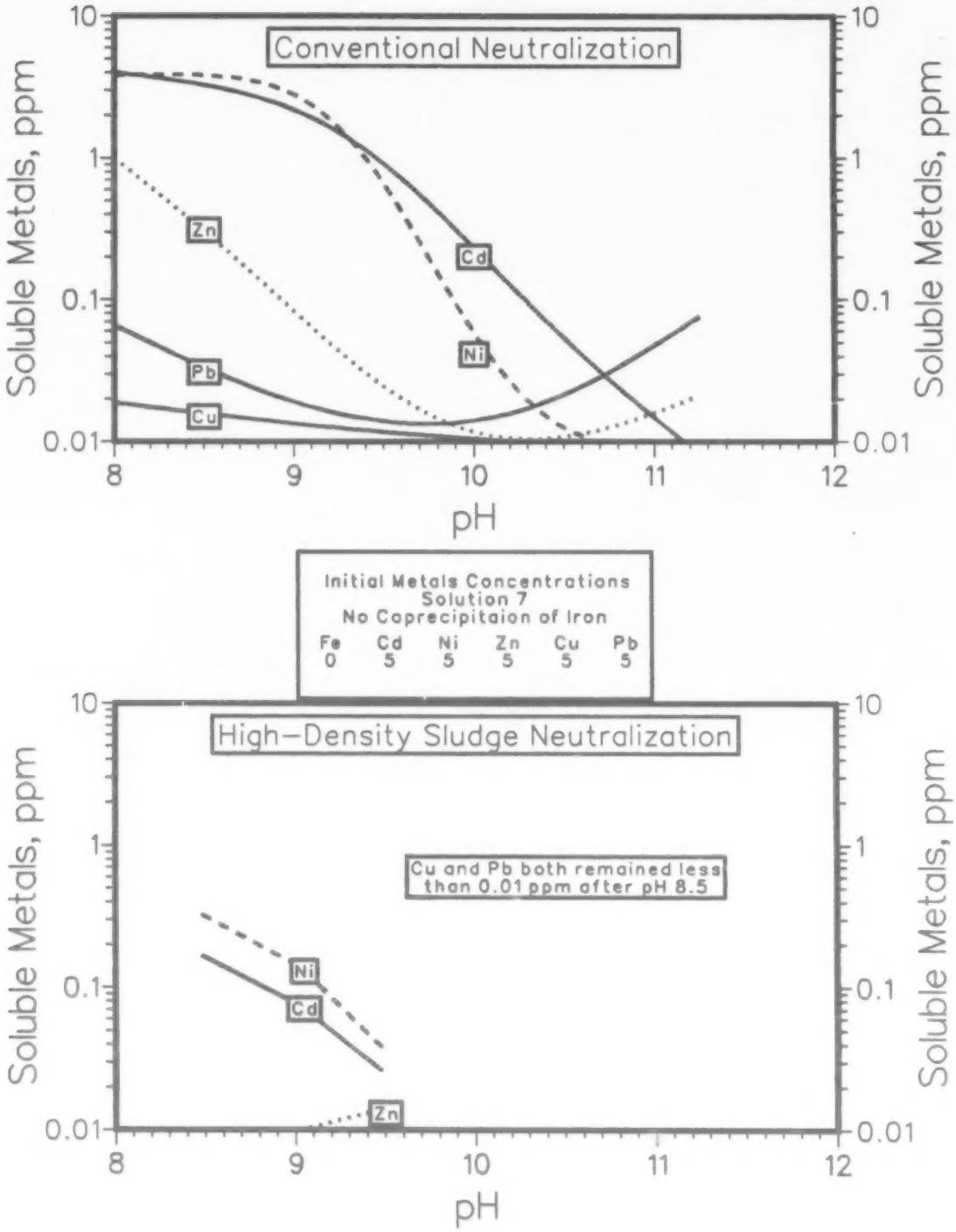

Figure 9. Comparison of Conventional and High–Density Sludge Neutralization of Solution 7

Tests with No Iron in Solution

The top plots in Figures 8 and 9 represent the results of neutralizations of solutions containing 50 ppm each and 5 ppm each of the non-ferrous heavy metals but no iron. In all cases the metal concentrations in these two figures are lower than those predicted from solubility data. This is probably due to co-precipitation effects of one metal on another, e.g., the precipitation of copper affects the precipitation of nickel and so on. For the purposes of this test program, the data in the top plots in Figures 8 and 9 were considered the base cases for determining the effects of co-precipitation of iron, and also the effects of the HDS process, on the solubilities of the non-ferrous heavy metals.

Effects of Iron on Metals Precipitation

As expected, the data show that the co-precipitation of iron both reduces the pH necessary to precipitate the non-ferrous heavy metals and reduces the minimum solubilities attainable by hydroxide precipitation. At the higher iron concentrations tested, the amphoteric properties of lead and zinc were eliminated, i.e., the metal hydroxides did not resolubilize as the pH was increased. The data further show that the effects of co-precipitation are more pronounced as the ratio of iron to non-ferrous heavy metals is increased. For example, comparison of the top plots in Figures 5 and 6 show the results of conventional neutralization of two solutions which both contained 50 ppm each of cadmium, nickel, zinc, copper, and lead. The solution in Figure 5 also contained 250 ppm of ferrous iron (iron to total non-ferrous metals ratio of 1:1) while the solution in Figure 6 contained only 25 ppm of ferrous iron (iron to total non-ferrous metals ratio of 0.1:1). Comparison of these plots shows that the higher iron to non-ferrous heavy metals ratio reduced the pH necessary to precipitate the non-ferrous metals and also eliminated the amphoteric properties of the zinc and lead. Similar results can be seen when comparing Figure 3 (iron to total non-ferrous heavy metals ratio of 1:1) with the top portion of Figure 7 (iron to total non-ferrous heavy metals ratio of 10:1). The data also show that, for a given iron to total non-ferrous heavy metals ratio, the beneficial effects of co-precipitation, especially for cadmium and nickel, are more pronounced for lower initial non-ferrous heavy metals concentrations. This can be seen by comparing Figures 3, 4, and the top plot in Figure 5. All of these solutions have an iron to total non-ferrous heavy metal ratio of 1:1. However, as the initial cadmium and nickel concentrations increase, the pH required for their precipitation increases.

Sludge Density

One of the major drawbacks to the use of conventional lime neutralization is the generation of a difficult-to-dewater sludge which contains very low solids concentrations. Table 1 lists the final dilution solids concentrations obtained in the conventional neutralization tests. Although the addition of ferrous iron aided in the removal of the non-ferrous heavy metals, it also greatly increased the volume of sludge generated. For example, the addition of 250 ppm of iron to a solution containing 50 ppm each of cadmium, nickel, zinc, copper, and lead doubled the solids formed upon neutralization.

HIGH-DENSITY SLUDGE NEUTRALIZATION

Test Procedure

All HDS tests were performed in a laboratory-scale unit which was operated 24 hours per day, five days per week at an acid flow rate of approximately 145 ml/min. The process was considered to be in equilibrium when the solids concentration of the recycled sludge reached 10%. Each pH test point in the HDS program was maintained for a minimum of one week. Daily samples of the raw acid solution and thickener effluent were taken for soluble heavy metals analysis. The solids concentration in the thickener underflow and the lime demand were also determined daily. Due to time constraints, only five of the synthetic solutions tested in the conventional neutralization study were tested in the HDS system.

Test Results

The results of the HDS neutralization studies are presented in the bottom plots in Figures 5 through 9. The concentration of soluble iron in the thickener effluent never exceeded the minimum detectable limit of 0.01 ppm and thus is not shown in any of the plots. Several conclusions can be drawn by comparing the HDS neutralization curves with those for conventional neutralization of the same solutions.

- At any given pH, the HDS process produced lower soluble cadmium and nickel concentrations than conventional neutralization.
- For the amphoteric metal hydroxides (zinc and lead), the HDS process produced minimum solubilities at approximately the same pH level as conventional neutralization. However, even without the benefit of the co-precipitation

of iron, the HDS process reduced the amount of lead and zinc which resolubilized when pH levels were increased above the minimum solubility point.

- There was only one case, lead in solution 2 (Figure 6), in which the HDS process failed to produce minimum soluble metal concentrations as low or lower than those achieved by conventional neutralization.

- For those solutions which contained no iron, the HDS process was able to reduce all the soluble heavy metal concentrations to less than 0.1 ppm in the pH range 10.1 to 10.3. Conventional neutralization techniques were unable to reduce the soluble metal concentrations of all of the metals to less than 0.1 ppm.

HDS Treatment With Separately Generated Iron Sludge

The HDS testing of solution 7, which contained 5 ppm of each of the non-ferrous heavy metals but no iron, was conducted in a different manner from the other HDS tests. Since solution 7 generated very few solids upon neutralization, it would have taken an extremely long time to generate enough sludge to recycle. A dense sludge was generated by using the HDS process to neutralize a solution containing 500 ppm of ferrous iron. This sludge was then used as the recycle slurry to test the removal of non-ferrous heavy metals from solution 2. The results of this test are shown in the bottom plot of Figure 9. This was the only test in which cadmium was removed at a lower pH than nickel. Also, while the average metal concentrations were reduced to low levels at relatively low pH values, the individual daily analytical results were the most widely scattered of all the tests. Although time constraints did not permit additional experimentation, this variation of the HDS process could be very useful for treating solutions containing low initial concentrations of soluble heavy metals.

Sludge Density

The HDS process produced dense sludges for all five solutions tested. Table 1 lists the sludge densities produced from each solution by conventional and HDS neutralization. It is obvious that the HDS process greatly reduces sludge disposal problems, especially if co-precipitation of iron is utilized to obtain minimum heavy metal concentrations. For example, conventional neutralization of 500 gpm of solution 1 would produce about 55 gallons per minute of sludge containing 0.8 % solids. The HDS process would produce 1.2 gpm of sludge containing 30 % solids by weight.

Lime Requirements

Although the HDS process removes metals at a lower pH value than conventional neutralization, the lime demands for both processes are the same for identical metals removal efficiencies.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

BETHLEHEM INTERNATIONAL ENGINEERING CORPORATION
A SUBSIDIARY OF BETHLEHEM STEEL CORPORATION

BIEC TECHNOLOG
ISSUE 4 • JULY 1982

High-density sludge process—an improved technology for treating acidic metal-bearing wastewaters

Many wastewaters from steel plant and mining operations have traditionally been difficult to treat effectively prior to approved discharge into public waters. The reason: conventional neutralization processes that treat acidic metal-bearing wastewaters produce very dilute sludges and are not efficient in precipitating mixtures of dissolved heavy metals. Bethlehem International Engineering Corporation is authorized to license a high-density sludge process that does this job better and more economically than conventional processes.

Also applicable to the treatment of acid mine drainage, the process may reduce costs to build and operate a treatment facility. This economy results from: (1) a substantially higher-density sludge, (2) improved slurry filterability; (3) improved reduction of metal concentrations, and (4), in some cases, the smaller size of the clarifier/thickener required.

The process is in operation at three Bethlehem Steel Corporation plants, five Bethlehem Mines Corporation bituminous coal mines, and a South African gold mine. A new facility for a Bethlehem Mines Corporation anthracite coal mine is under construction. (See Table, Figure 3, on reverse side of this sheet.)

This technology is now available for licensing from Bethlehem International Engineering Corporation.

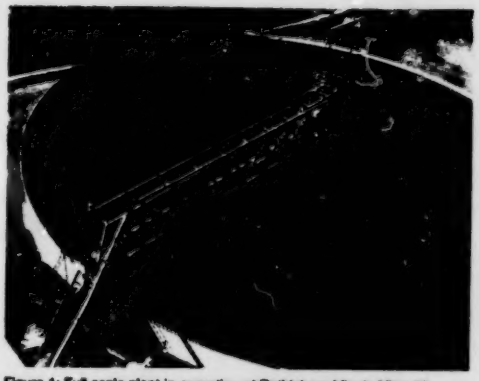

Figure 1: Full-scale plant in operation at Bethlehem Mine's Mine 38, Cambria, Pa.

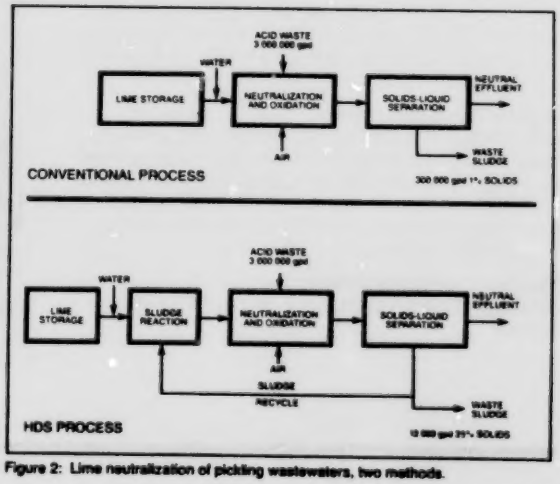

Figure 2: Lime neutralization of pickling wastewaters, two methods.

Technical description of High-Density Sludge Process
This is a neutralization technique which, unlike conventional processes, produces a dense sludge while improving the efficiency of precipitating heavy metals from solution.

Applications:
Federal, state, and local environmental control regulations require removal of most heavy metals from wastewater prior to discharge to public waters. The process is used to precipitate heavy metals from wastewaters while producing a dense sludge which is more easily disposed of than that produced by conventional neutralization processes. The process is applicable to most acidic wastewaters containing soluble heavy metals. For example:

- ☐ Acid mine drainage
- ☐ Steel plant pickling rinse waters
- ☐ Blowdown streams from steel plant recirculating water systems.

Advantages to users:
Compared with conventional neutralization techniques, the high-density sludge process:

1. Reduces the sludge volume by a factor of 10-50
2. Improves the slurry filterability
3. Reduces metal concentrations to levels below the published theoretical solubilities at a given pH
4. In some cases, reduces size of clarifier/thickener

Due to the above advantages, the process reduces the capital and operating cost for facilities to handle, store, and dispose of the sludge generated. For some solutions, the reduced pH at which the metals are precipitated can eliminate the need for a final pH adjustment of the clarified wastewater.

Installation requirements:
Construction of a high-density sludge facility usually requires less real estate and major capital equipment for sludge disposal when compared with conventional neutralization techniques. A second, small reactor tank plus slurry recycle pumps are also required for the high-density sludge process.

Maintenance requirements:
Similar to those for a conventional neutralization system.

Figure 3: **EXISTING FACILITIES**

Installation	Flow Rate m^3/day	(M gal/day)
Acid Mine Drainage, Bituminous Mine 77, Cambria Division, Bethlehem Mines Corporation	2,195	(0.58)
Acid Mine Drainage, Bituminous Mine 31, Cambria Division, Bethlehem Mines Corporation	18,550	(4.90)
Acid Mine Drainage, Bituminous Mines 32-33, Cambria Division, Bethlehem Mines Corporation	39,255	(10.37)
Acid Mine Drainage, Bituminous Mine 78, Cambria Division, Bethlehem Mines Corporation	2,725	(0.72)
Acid Mine Drainage, Bituminous Mine 38, Cambria Division, Bethlehem Mines Corporation	1,630	(0.43)
Wire Mill and Pickling Rinse Waters, Johnstown Plant, Bethlehem Steel Corporation	4,355	(1.15)
Galvanizing and Pickling Rinse Waters, Lackawanna Plant, Bethlehem Steel Corporation	13,625	(3.60)
Pickle Liquor and Pickling Rinse Waters, Lebanon Plant, Bethlehem Steel Corporation	1,100	(0.29)
Acid Mine Drainage, Gold Mine Rand Mines, Limited, Johannesburg, South Africa, (Bethlehem Steel Corporation acted as consultants for Rand under a licensing agreement)	46,335	(12.24)
Acid Mine Drainage, Anthracite Panther Valley Division, Bethlehem Mines Corporation (Plant is under construction).	65,410	(17.28)

Additional information: If you wish to discuss the high-density sludge process in more detail, please write: Marketing Division, Bethlehem International Engineering Corporation, General Sales Office, Bethlehem, PA 18016 U.S.A. Or:

- ☐ **Telephone:** (215) 694-7597
- ☐ **Telex:** 847417 MESBETH
- ☐ **Cable:** MESBETH

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A SUBSIDIARY OF BETHLEHEM STEEL CORPORATION

TREATMENT OF ACID AND METAL-BEARING WASTEWATERS BY THE HIGH-DENSITY SLUDGE PROCESS

By F. M. TEMMEL

Manager, Metallurgical and Chemical Process Research
Homer Research Laboratories
Bethlehem Steel Corporation

ABSTRACT

BETHLEHEM STEEL HAS for many years studied neutralization methods for the treatment of acid wastewaters from mining and steel processing operations. This research has resulted in the development of a high-density sludge (HDS) process to treat acidic, metal-bearing wastewaters. The sludge generated during treatment amounts to as little as 1/50th of the volume produced by conventional neutralization.

The significant operating parameters which affect sludge density and plant design in this new treatment method are:

- Ferrous to ferric iron ratio
- Ratio of solids recirculated to solids precipitated
- Point of alkalinity addition
- Neutralization pH
- Detention time in reaction tanks

Prepared for presentation at San Francisco Regional Technical Meeting of American Iron and Steel Institute, November 18, 1971.
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To date Bethlehem Steel has in operation three HDS plants designed to treat 11,000,000 gallons a day of acidic iron-bearing wastewaters, two treating acid mine water and one treating steel plant acid rinsewaters. One additional plant for 4.0 million gallons a day of acid mine water is in the construction stage and another for 2.0 million gal/day of acid rinsewater is in the design stage.

INTRODUCTION

Many technical articles have been written about conventional lime neutralization processes for the treatment of acid wastewaters from mining and steel processing operations. These conventional processes produce voluminous, gelatinous sludges that contain only 1 to 2 per cent solids and are not economically amenable to further dewatering by filtration or centrifugation. This limitation has been and still is the dilemna of conventional neutralization. Sufficient land areas in most cases are not available for the large volumes of sludge produced by conventional neutralization. Today there are about 200 treatment plants in Pennsylvania alone using one form or another of conventional neutralization for treating acid mine waters, and the resultant sludge handling and accumulation problems are staggering. It is in this problem area that Bethlehem Steel developed a treatment method which generates a sludge amounting to as little as 1/50th of the volume produced by conventional neutralization. This improved neutralization method is called the High-Density Sludge (HDS) Process.

In Pennsylvania it has been estimated that approximately 2 billion gal/day of acid mine waters from coal mines are being discharged to clean streams, i.e., 200 million gal/day (834,000 tons/day) from active mines and 1.8 billion gal/day (7,500,000 tons/day) from inactive and abandoned mines. The sulfuric acid and iron contents of waters from the active mines are estimated to be 460 and 180 tons/day, respectively. If we assume that all of Pennsylvania's acid mine water were neutralized by conventional lime treatment, about 100 million gal/day of sludge would be generated. In contrast, if this same volume of acid mine waters were treated via Bethlehem's High-Density Sludge Process, only 4 million gal/day of sludge would be produced. This hypothetical illustration clearly indicates

the need for a neutralization process which would produce a smaller quantity of sludge for disposal.

The acid mine water discharges from Bethlehem's Cambria Division alone total approximately 11 million gal/day. The treatment of these waters by conventional neutralization would produce about 500,000 gal/day of sludge, whereas treatment with the High-Density Sludge process produces only about 20,000 gal/day of sludge. For this reason Bethlehem is installing facilities for treating these waters by the High-Density Sludge process.

PROCESS DESCRIPTION

The primary differences between the High-Density Sludge process and conventional neutralization can be seen in Fig. 1. Conventional lime neutralization consists of:

- Mixing high-calcium or dolomitic lime with water to produce a lime slurry
- Neutralizing the acid wastewater with the lime slurry at

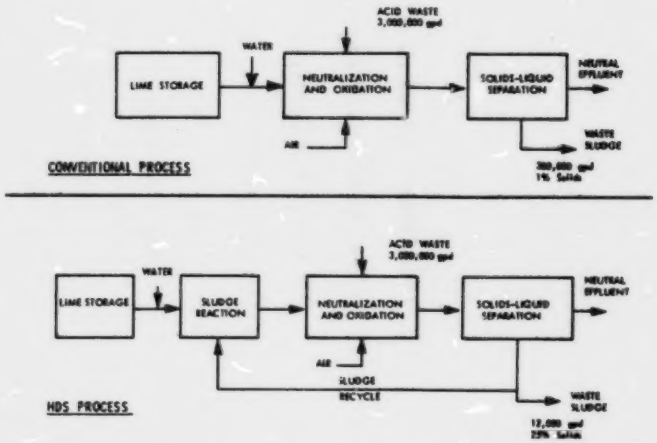


Fig. 1—Lime Neutralization of pickling wastewaters.

ambient temperature in a stirred reaction tank, either with or without aeration

- Settling the solids precipitated from the acid wastewater in a clarifier, thickener, or settling pond
- Discharging the neutral, clarified overflow and disposing of the voluminous, gelatinous sludge *somewhere!*

As shown in the lower half of Fig. 1, neutralization by the HDS process differs from conventional neutralization in that provisions are made for:

- Recycling a controlled volume of the settled sludge
- Mixing the recycled sludge with lime slurry in a reaction tank prior to the neutralization and separation steps.

As shown, the volume of sludge generated using this process is only about 1/25th that which would be generated using conventional neutralization. Actually, sludge volumes from the HDS process vary from 1/15th to 1/50th, depending on actual controlled process conditions.

Operating Parameters

The significant operating parameters which affect sludge density and plant design are:

- Ferrous to ferric iron ratio of acid wastewater
- Ratio of solids recirculated to solids precipitated
- Point of alkalinity addition
- Neutralization pH
- Detention time in reaction tanks "A" and "B"

Ferrous to Ferric Iron Ratio. All test work showed that the ratio of ferrous to ferric iron in the acid wastewater to be treated had a direct effect on the maximum concentration of settled solids that could be produced by this process.

The effect of ferrous iron content on settled sludge density is shown in Fig. 2. Little effect on sludge density was found when the ferrous content of the total iron was less than about 70 per cent; however, at ferrous iron percentages of greater than 70 per cent a very significant increase in sludge density was noted—up to about 50 per cent solids for 100 per cent ferrous iron.

Ratio of Solids Recirculated to Solids Precipitated. The ratio of solids recirculated within the system to the solids precipi-

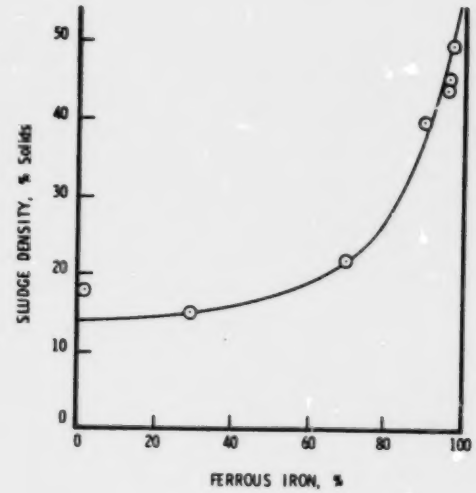


Fig. 2—Effect of ferrous iron concentration on sludge density.

tated from the acid mine water by the neutralization reaction was found to be of primary importance in controlling sludge density. The effect of this ratio on sludge density for the ferric acid mine water from Mine 31 and the ferrous acid mine water from Mine 32 is shown in Fig. 3. The two curves show that the solids concentration increased rapidly as the recirculation ratio was increased to 20:1, the rate of increase in concentration decreased in the ratio range of about 20:1 to 30:1, and the percentage increase in concentration was relatively small in the ratio range of 30:1 to 80:1. The optimum range was 25:1 to 30:1, which is consistent with good process control, the production of near-maximum sludge densities, and minimum area requirements for sludge settling and thickening. It

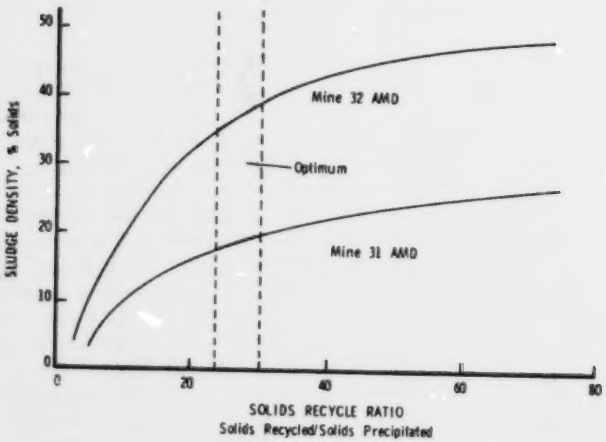


Fig. 3—Effect of solids recycle ratio on sludge density.

is of interest to note that this optimum solids recirculation ratio range was the same for both ferrous and ferric waters.

Point of Alkalinity Addition. The HDS process gains its ability to produce maximum-density sludges from the practice of mixing lime slurry with recycle slurry before reacting the high pH mixture with acid mine water. This is of primary importance. In a short-term test it was shown that mixing lime slurry, recycle slurry, and acid mine water in a single reaction tank resulted in process failure. Similarly poor results were obtained when the acid mine water and recycle slurry were mixed in the neutralization reactor.

Neutralization pH. The neutralization pH was found to have a significant effect on the physical characteristics of the neutralized slurry and on the thickener area required for sludge settling.

- The optimum pH range from overall process considerations was 7.2-7.7. Within this range, the oxidation rate of the ferrous iron was satisfactory, sludges of maximum density were produced, and thickener area requirements were at a minimum.

- A neutralization pH range of 6.0-6.5 reduced the alkalinity requirements, but the oxidation and precipitation rates of the iron were too slow for practical consideration in sizing the neutralization reactor.
- A neutralization pH range of 8.2-8.7 reduced the turbidity of the clarified effluent but decreased the settled solids concentration from 35 per cent to 20 per cent and increased the settling area requirements by a factor of 1.6.
- A pH range of 9.0-9.5 resulted in the production of a rubbery sludge that could only be pumped with difficulty and increased the torque on the thickener rakes to the extent that the rakes became inoperative.

Detention Time in the Reaction Tanks. The results of laboratory tests on the effect of detention time on the overall process showed that a detention time of one minute in the sludge reaction tank was sufficient to produce and maintain sludges of maximum density, and that a detention time of ten minutes in the neutralization-oxidation tank ensured oxidation and precipitation of the ferrous iron from the acid mine drainage at any pH value above 7.2. A maximum detention time of one minute in the sludge reaction tank is considered to be a good design number for an HDS system, but detention time in the neutralization tank is a function of both the initial ferrous iron concentration and the neutralization pH.

DEMONSTRATION PLANT

A flow diagram of the 1 million gal/day HDS Demonstration Plant at Mine 32 near Ebensburg, PA is shown in Fig. 4. This plant was designed from data obtained from laboratory and pilot-plant studies. The HDS plants studied in the laboratory and pilot plant are shown in Figs. 5 and 6, respectively. The basic equipment in this treatment system consists of a lime storage bin, lime slaker, sludge reactor, neutralization reactor and thickener. Fig. 7 shows the Demonstration Plant with its lime storage bin, sludge reactor, neutralization reactor, and a 60-ft thickener. The plant operation, shown in Fig. 4, is as follows:

- The acid mine water is pumped from the mine to the neutralization reactor (Reactor "B").

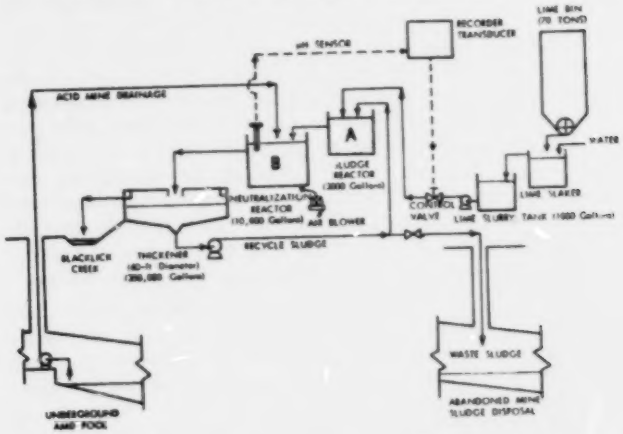


Fig. 4—Flow diagram: HDS demonstration plant at Coal Mine 32.

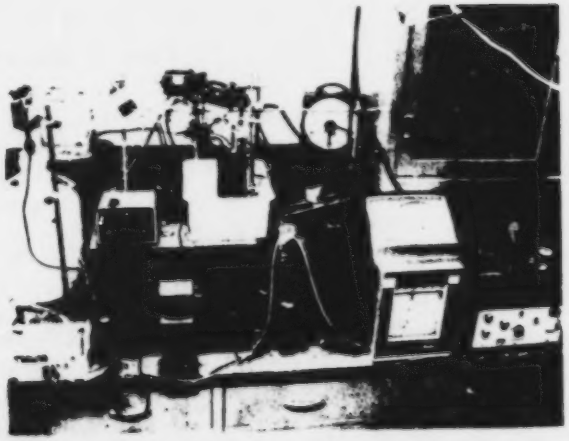


Fig. 5—Laboratory high density sludge plant.

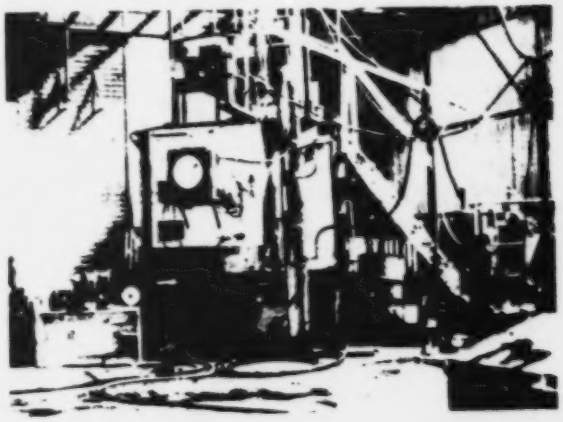


Fig. 6—High density sludge pilot plant.

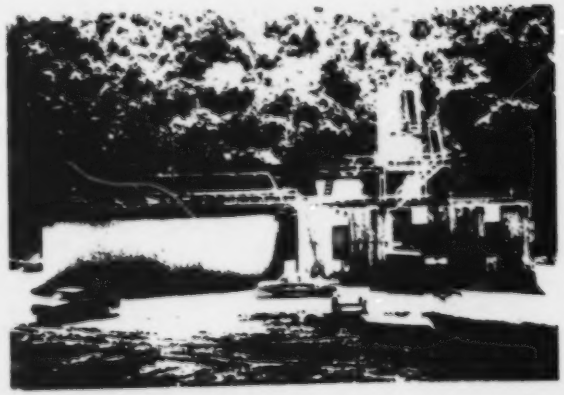


Fig. 7—High density sludge demonstration plant.

- The lime slurry is pumped to the sludge reactor (Reactor "A"), where it is mixed with sludge recycled from the thickener underflow.
- This sludge mixture flows by gravity from reactor "A" to reactor "B", where it is mixed with the acid mine water and aerated. Here the pH is controlled at about 7.5, the ferrous iron is oxidized to the ferric form, and the iron is precipitated as ferric hydroxide.
- The neutralized slurry then flows by gravity from reactor "B" to a thickener, where it settles to about 35 per cent solids.
- The thickener overflow is discharged to public waters, and the sludge produced is discharged once a day through a borehole to an abandoned section of the mine.

FULL-SCALE PLANTS

The demonstration plant at Mine 32 was redesigned and enlarged to treat 6.2 million gal/day. This plant was put into operation in February 1971. Fig. 8 shows the full-scale HDS plant at Bethlehem's Mine 77 after startup in November 1969. This plant was designed to treat an estimated 1.8 million gal/day based on a planned expansion of Mine 77; at present it treats 0.8 million gal/day of acid mine water. In addition to these two operating plants, a third plant capable of treating 4.0 million gal/day of acid mine water is being constructed now with startup scheduled for October 1971.

Having successfully demonstrated the feasibility of the HDS process for treating acid mine waters we decided to study the applicability of this new method to treating acid rinsewaters from steelmaking operations. The transition was not obvious since the makeup of the two waters is somewhat different. Whereas iron and sulfuric acid are the major components in acid mine water, the acidic rinsewaters produced in our operating steel plants contain other metals and/or mineral acidity which also require treatment. For example, acidic rinsewaters from continuous galvanizing operations contain zinc and sulfuric acid; rinsewaters from continuous picklers contain iron and hydrochloric acid and rinsewaters from a typical wire mill

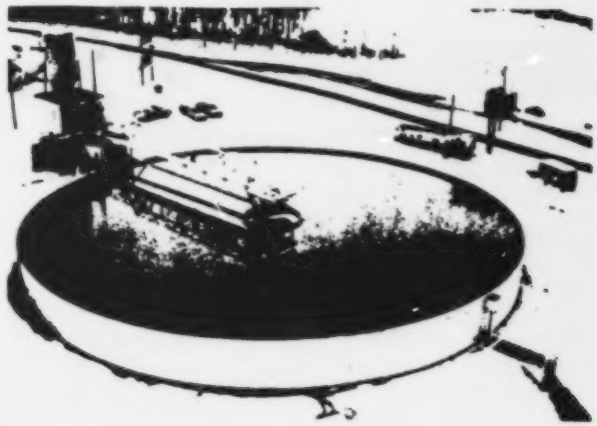


Fig. 8—Full-scale high density sludge plant treating acid mine water.

operation contain iron and zinc as well as dilute sulfuric and hydrochloric acid.

Our first effort to extend the HDS process capability was based on laboratory tests using feed with the composition of rinsewater from a typical hydrochloric acid pickling operation. After successfully demonstrating the process at this level, a pilot program was conducted at our Lackawanna plant to get design data for a full-scale plant to treat acidic rinsewaters from the continuous picklers and galvanizers. Upon completion of the test, a 3 million gal/day HDS plant was designed and built to treat these acidic rinse waters. The full-scale facility was started up at Bethlehem's Lackawanna Plant in December 1970. The flow diagram, Fig. 9, for this system is similar to the flow diagram for the Demonstration Plant at Mine 32 shown in Fig. 4, except that the excess sludge from this system is disposed of by trucking to a dump. The HDS plant at Lackawanna was designed for treating acid wastewater containing 440 ppm Fe, 40 ppm Zn, 600 ppm Cl, 1370 ppm SO_4, and 2280 ppm total acidity as $CaCO_3$, and producing an effluent that will meet the New York State water quality criteria. These criteria are pH 6.5 to 8.5, less than 15 ppm Fe, and less than

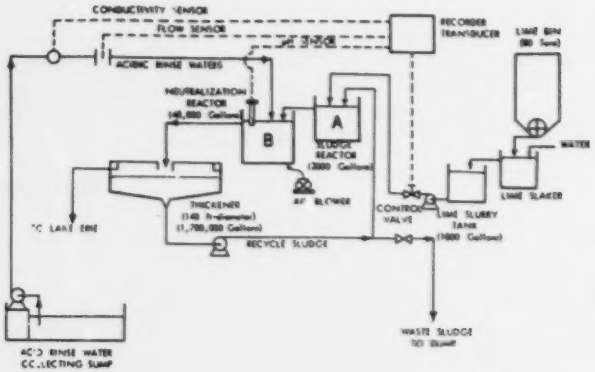


Fig. 9—Flow diagram: HDS plant at Lackawanna Steel Plant.

40 ppm suspended solids. Because the acid wastewater flow and composition vary drastically in the Lackawanna HDS plant, more sophisticated controls are required for maintaining the pH in reactor "B" than the controls in HDS plants for treating acid mine waters. The control system installed consists of measuring conductivity and flow of the acid wastewater in a feed-forward circuit and a pH feedback circuit. Since January 1971 the Lackawanna HDS plant has been satisfactorily treating 800 to 1900 gpm of acidic wastewater. During the month of June 1971, the most recent month for which operating data are available, the continuous picklers operated 151 turns and the galvanizing mill ran 55 turns. The average wastewater volume treated was 1700 gpm; the wastewater contained from 150 to 695 ppm Fe and from 340 to 2330 ppm total acidity as $CaCO_3$. Treated effluent averaged 13 ppm Fe, 27 ppm total suspended solids, and pH of 8.2. By using the HDS principle, the volume of sludge to be disposed of was only about 10,000 gpd with a 30 per cent solids concentration instead of the 300,000 gpd of sludge that would have been produced from a conventional neutralization plant. The estimated cost to treat 1,000 gallons of acid rinse waters is 20 cents; of this amount, 10 cents is for labor and supervision and five cents is for

chemical lime. Fig. 10 shows the outside of the No. 7 Water Treatment Station at Lackawanna, which consists of the HDS plant and an ultrahigh-rate filtration plant for treating oily wastewaters from the cold reduction mills. The thickener in

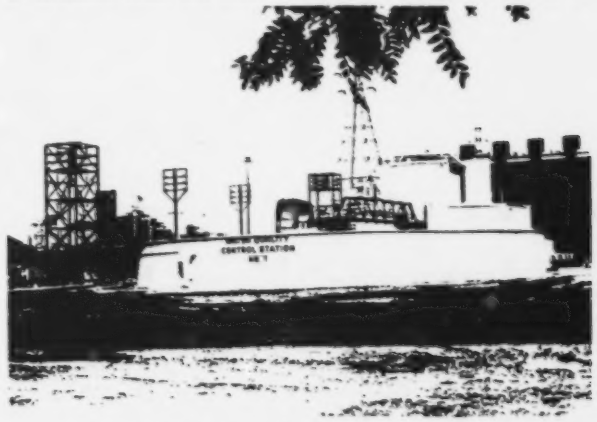


Fig. 10—Full-scale high density sludge plant treating steel plant acid rinse waters.

Fig. 11—Laboratory facilities at Water Treatment Station No. 7.

the foreground is part of the HDS system. Laboratory facilities at this location are shown in Fig. 11.

A 2-million gal/day HDS plant is presently being engineered to treat acid wastewaters from the Wire Mill at our Johnstown Plant. As shown in Fig. 12 the system is similar to the one at Lackawanna, except that the flow is split and sent to two parallel treatment facilities after exiting from reactor "A". The parallel network was selected primarily because of space limitations; however, it offers the added advantage of at least a 50 per cent operation in the event of equipment failure.

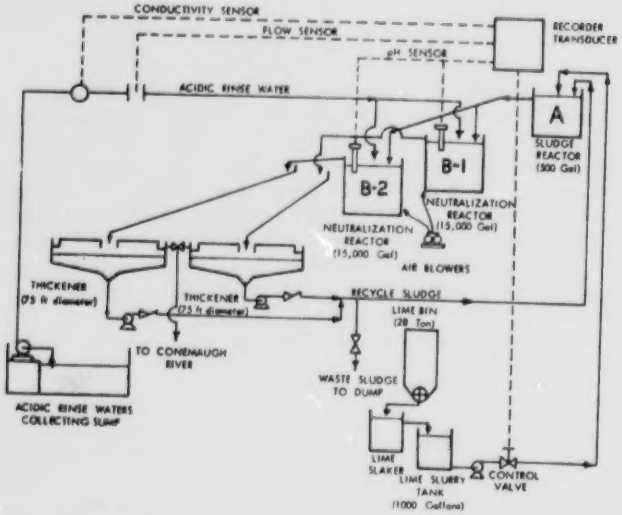


Fig. 12—Flow diagram: HDS plant at Johnstown steel plant.

SUMMARY

In summary, the high-density sludge process proved its effectiveness in comparison to alternate methods of treatment and has been applied full-scale not only to all of our acid mine water discharges at the Cambria Division of Bethlehem Mines but also to the 3 million gal/day acid rinsewaters from

our continuous descaling lines at our Lackawanna Plant. Finally, we are in the detailed engineering stage of an HDS plant for handling the 2 million gal/day acid wastewaters from our wire mill descaling operations at Johnstown.

To date, Bethlehem has spent approximately $4,000,000 in HDS plants. As shown below, the plants have the capacity to treat 17,000,000 gal/day of acidic, iron-bearing wastewaters.

BETHLEHEM STEEL CORPORATION HDS PLANTS

Location	*Design Capacity*	*Startup Date*
Johnstown	2,000,000 gpd	At Engineering Stage
Lackawanna	3,000,000	December, 1970
Cambria Division Mines		
Mine 31	4,000,000	October, 1971
Mine 32	6,200,000	February, 1971
Mine 77	1,800,000	November, 1969
Total	17,000,000 gpd	

The total sludge volume that will be produced by treating 17,000,000 gal/day wastewaters will be 43,000 gal/day instead of the 990,000 gal/day if conventional neutralization were used.

Having identified several HDS plant installations and provided a description of their operation, performance, and cost, it remains to summarize some of the operating and design parameters to identify several innovations. Some of the problems are also described, as well as measures used, to overcome them in operating plants.

1. Bethlehem Mines Corp, Panther Valley Division

This large HDS plant is designed to treat 12,000 gpm or 65,000 m^3/d minewater pumped from a deep open pit anthracite coal mine. The interesting aspect is that pH is 6.8, but the minewater contains a ferrous iron level of 30 ppm and 13 ppm Mn, which is a low Fe^{2+} to Mn ratio for HDS. HERMAN and KORB (?), in describing the pilot testwork, found that:

- Aeration of AMD prior to neutralization reduces lime demand by abut 40%. This requires one 50HP Fuller Corp. wisp blower to reduce the CO_2 level in this water by aeration at 600 scfm, discharging below two 25HP turbine mixers in the aerator reactor.

$$H_2CO_3 = HCO_3^- + H^+$$
$$H_2CO_3 = H_2O + CO_2$$

  By a vigorous aeration, the CO_2 is blown off, thereby reducing bicarbonate levels according to the above equations.

  Aeration can increase the pH of the feed from 6.3 to 7.2-7.3.

  The way to test whether pre-aeration will reduce lime consumption is to measure the pH during aeration in the laboratory. If the pH rises, this indicates that there will be a saving. Also, the amount of lime required to achieve a given pH with and without aeration can be measured in the laboratory.

- Aeration prior to lime addition reduces the solids precipitated at pH 10 by 35%.

- After aeration, the water is agitated in B reactor by 300 cfm air introduced under two 25HP turbine mixers to oxidize ferrous to ferric iron. The lime slurry with thickener underflow sludge are mixed in A reactor using a 7.5 HP agitator and pumped to B reactor to be mixed with the aerated minewater.

- Neutralized AMD is pumped to a 250 foot (76m) diameter thickener which was constructed by modifying an existing 200 foot Ø thickener to save cost. A 9 foot side water depth was maintained. The steel walled thickener has a concrete floor.

BETHLEHEM MINES CORPORATION
No.10 SHAFT
PANTHER VALLEY DIVISION
PHASE 2
HIGH DENSITY SLUDGE ACID MINE DRAINAGE TREATMENT PROCESS

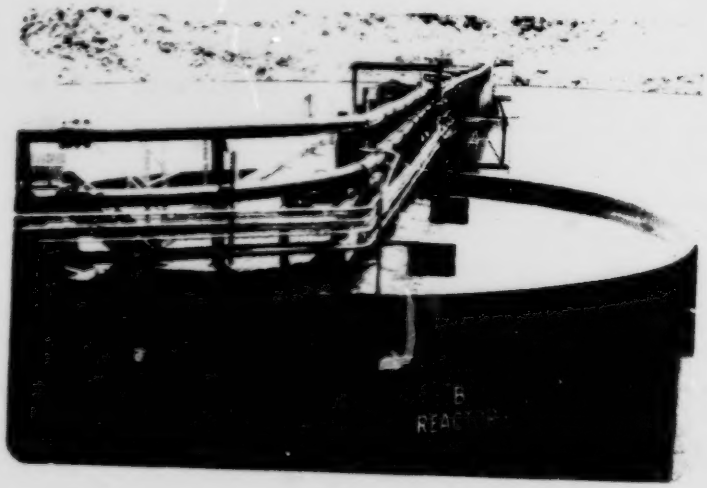
ANTHRACITE PIT SHOWING MINEWATER WHICH REQUIRES TREATMENT

HDS SLUDGE IS DISCHARGED BACK TO THE PIT

BETHLEHEM MINES CORPORATION

AERATION REDUCES CO_2 LEVEL IN WATER

HDS CLARIFIER



B REACTOR - NOTE BAFFLES

- Submersible centrifugal pumps are utilized to recycle sludge from the thickener to a reactor. Thickener effluent is used to slake the high-calcium pebble lime.

- No polymer use is required.

- Even at the approximate ratio of Fe^{2+}:Mn of about 2.5:1, the HDS process reduces the volume of sludge to only 10% of that from conventional precipitation.

  The Panther Valley plant was operated to yield a 34% solids density sludge. The sludge is pumped to the pit at SG 1.15-1.25 through a 5500' pipeline of 6" Ø. It would be possible to achieve densities up to 50% solids at which it is like a paste and impractical to pump.

  Using conventional neutralization, about 20 m^3 of sludge would be generated for each 1000 m^3 treated or about 1300 m^3/d at the design capacity. This would fill a pond 100m x 100m x 3m deep every month, and the sludge would not be amenable to further dewatering.

- Using conventional precipitation if there is not excess iron to coprecipitate manganese, the latter readily goes back into solution if the pH is dropped below pH 9.

- Lime demand to reduce Mn concentration to less than 1 ppm was the same by HDS and conventional precipitation. However, HDS was able to reduce Mn to less than 1 ppm at pH 9 as opposed to pH 10 by conventional neutralization.

- pH control is smoother using HDS.

- Calcium carbonate scale formation occurred in the conventional neutralization process but not in the HDS test as $CaCO_3$ is forced to precipitate in B reactor sludges.

- The minewater temperature remains at 54°F yearround, so there is no temperature effect on the process.

- The Panther Valley lime addition is controlled by a Leeds & Northrop pH meter in reactor B that controls the lime slaker flowrate to maintain pH 8.9 in Reactor B. Ultrasonic cleaners for the pH probe were not successful at this plant.

- All lime slurry addition is by gravity flow.

- The lime slaker was supplied by:

BIF CORP.
Unit of General Signal Corp.

- Polyethylene piping used for water and sludge disposal is found to be very resistent to scale and corrosion as there is no easy surface for scale forming bacteria to attach themselves to.

- The HDS plant now operates without the addition of flocculant, said to be a characteristic of this process when operated properly.

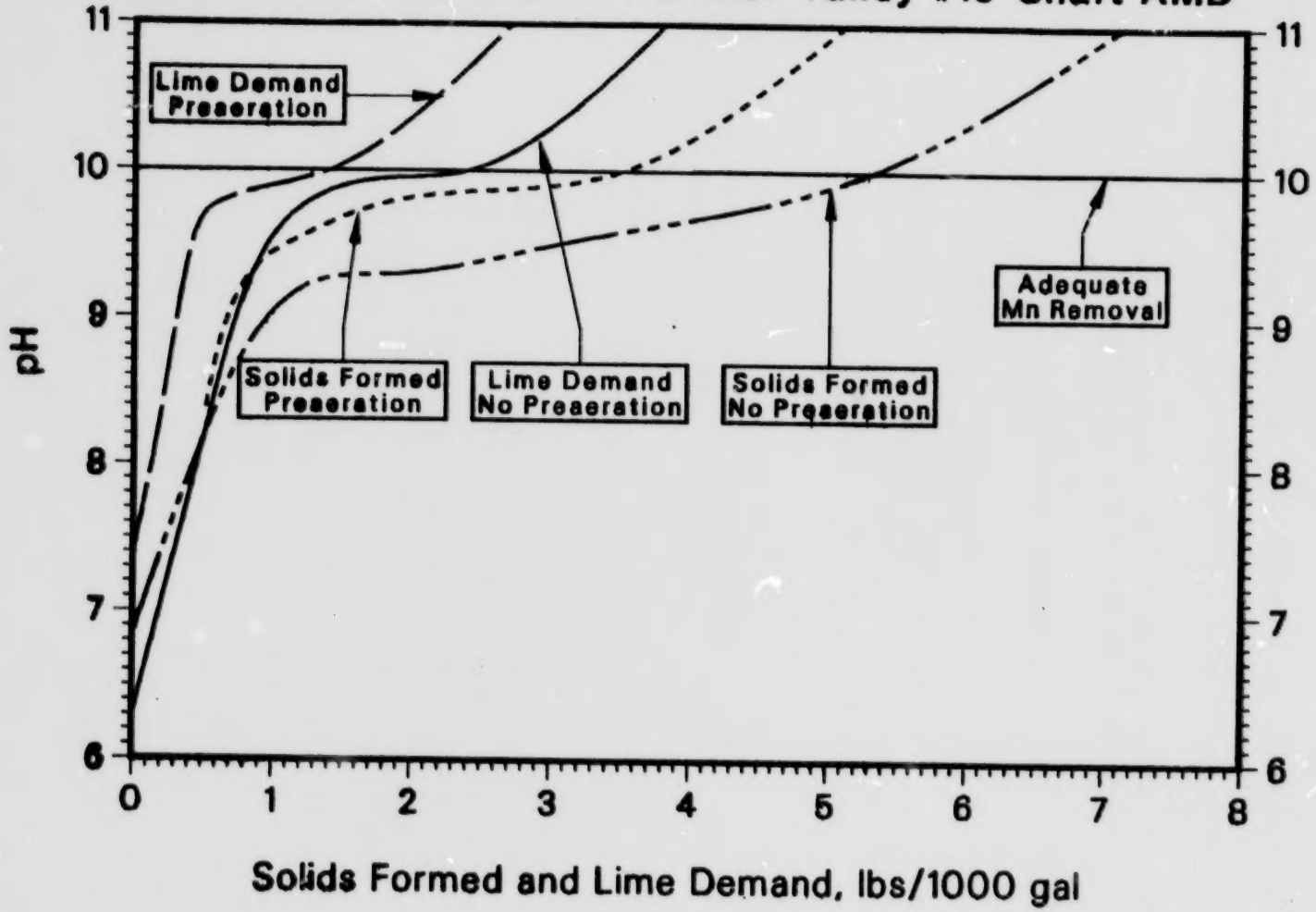
More information on this operation and requests to visit it can be directed to:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18016
(215) 694 2424
Telex: 847417 MESBETH
Mr. Jim Forand
Mr. Stewart T. Herman

ANALYSES OF FULL-SCALE THICKENER EFFLUENT AND UNDERFLOW
PANTHER VALLEY #10-SHAFT HDS PLANT

pH	TSS ppm	Total Fe ppm	Total Mn ppm	Underflow Solids Concentration Percent
9.06	15.2	1.4	<1.0	15
8.70	22.4	1.9	1.5	22
8.90	15.6	1.4	1.3	16
8.90	14.8	1.5	1.3	15
8.72	13.6	1.0	1.0	14
8.69	18.4	1.4	1.6	18
8.66	16.0	1.6	<1.0	16
8.63	24.4	1.8	<1.0	24
8.62	18.8	1.4	1.0	19
8.94	21.6	1.4	<1.0	22
9.10	16.0	1.4	<1.0	16
8.80	18.8	1.4	1.4	19

Figure 4 - pH Versus Solids Formed and Lime Demand With and Without Aeration Prior to Neutralization Conventional Neutralization - Panther Valley #10-Shaft AMD



ANALYSES (1) OF BENCH-SCALE HDS THICKENER EFFLUENT
PANTHER VALLEY #10-SHAFT AMD

pH	TSS (2)	Fe		Mn	
		Total (2)	Soluble	Total (2)	Soluble
8.35	43	6.3	N.D.	4.0	2.7
8.70	34	5.0	N.D.	1.9	1.0
8.75	35	4.9	N.D.	1.8	1.1
8.65	29	4.3	N.D.	2.0	1.1
8.75	47	6.7	N.D.	2.2	0.9
8.75	39	6.3	N.D.	2.0	0.8
8.65	37	6.2	(3)	2.5	1.2
8.75	39	6.8		2.3	1.5
8.80	39	6.5		2.2	1.2
8.65	41	7.2		2.6	1.4
8.65	43	7.2		2.5	1.4
8.60	32	6.4		2.2	1.4
8.70	34	6.2		2.3	1.2
8.70	39	7.1		2.1	1.1
8.75	36	6.8		2.2	1.2
8.80	30	6.2		1.7	1.2
8.75	36	6.5		1.4	0.6
8.75	33	6.0		1.7	0.7

1 - All results except pH are in parts per million.
2 - The total suspended solids and total metals analyses cannot be used as a direct scale-up factor due to unavoidable short circuiting in the small thickener.
3 - Analyses discontinued due to the low results consistently obtained.

Source: HERMAN & KORB (1984)

2. Kromdraai Coal Mine HDS

An HDS plant was installed in the early 1970's at the restored Coronation Colliery site at Kromdraai, near Witbank, Transvaal to treat 14,000 m^3/d acid mine water pumped from underground.

Conventional lime neutralization and clarification yielded the following results in tests described by BOSMAN (1974).

	Influent	Effluent
pH	2.7	7.5
Acidity $CaCO_3$:	1000	
Conductivity/m	18.0×10^6	
TDS mg/l	1750	1800
Fe^{2+} mg/l	0-140	1
Fe^{3+} mg/l	30-200	30
Fe_T mg/l	175	

	Influent	Effluent
Al mg/l	90	1
Ca mg/l	30	450
Mg mg/l	10	20
Na mg/l	5	
K mg/l	3	
$SO_4^=$ mg/l	1150	
Cl^- mg/l	5	
Suspended Solids		60

The Kromdraai HDS plant was visited in December, 1983, and several observations were made:

- Product water after HDS neutralization is now used at 93AD army headquarters nearby for lavatories and showers. An initial attempt to use the water as a potable source had the army "on the trot," due to its high $SO_4^=$ content.

- Lime consumption to neutralize 14,000 m^3/d AMD at pH 2.2-2.4 amounted to 750 tpm, i.e., 2.5 Kg lime per m^3 (2.5g $Ca(OH)_2$/l).

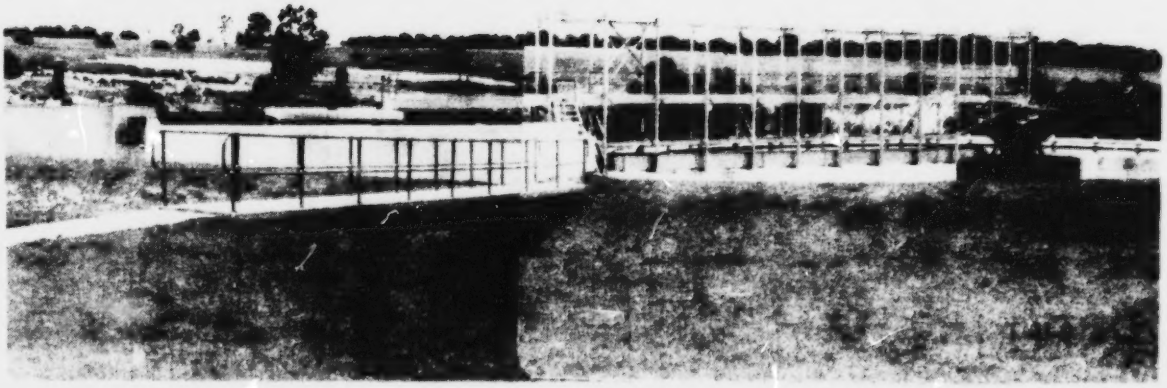
- The HDS operation has been run at between 15% and 25% solids in the sludge and occasionally up to 34% solids. This is possibly because of the low ferrous to ferric ratio which is an important parameter for sludge density although, since there is more than ample sludge storage capacity at the site, there has been no need to optimize the process. A higher sludge density would only serve to increase pumping problems. The sludge disposal ponds are located 5500 feet from the plantsite.

The equipment installed at the plant is as follows:

Lime Silo	1.5 HP Vibrator Feeder
Lime Slaker	
Air Compressor	Godfrey
Compressor Cooling System	60HP
Premix Tank	
Reactor-Aerator	60HP Moyno Pump
Thickener-Clarifier	Est. 150'Ø

Valves and piping are shown on the attached sketch.

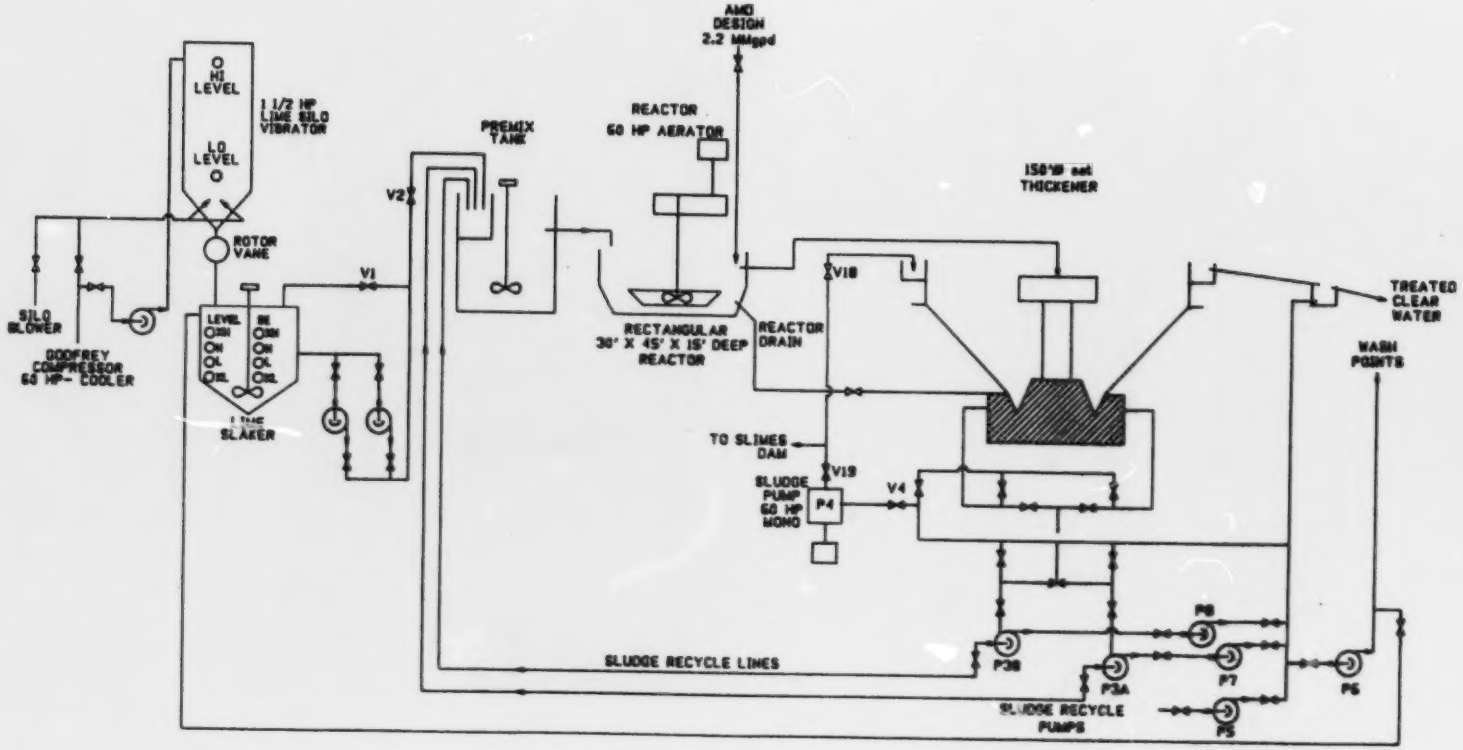
- Suspended solids in the thickener overflow from the full scale plant is much lower than the 60 ppm s/s in the pilot plant.



:AAI COAL MINE HDS PLANT

HIGH DENSITY SLUDGE IS STABLE

HDS PLANT
OLD CORONATION MINE, KROMDRAAI



- The plant is operated and maintained by one operator and two unskilled assistants.

- The original plant was installed with an underground 3"Ø line to feed slaked lime slurry from the lime slaker tank to the sludge premix tank. The line diameter proved too large resulting in inadequate flow velocity and the settling out of solids resulting in the line clogging. The problem was solved by installing a 1½"Ø flexible plastic line above ground level to transfer lime slurry to the premix tank.

- Although designed for automatic control, it has proven more practical to operate the plant manually.

- Sludge settles and dries to a very stable material. It is very low density but stable enough to easily support a man's weight and is suitable for permanent restoration of the ponds upon completion.

- According to BOSMAN (1974), the thickener is designed for a rising velocity of 0.4 m/h compared with 0.57 m/h in the pilot plant which yielded 60 mg suspended solids/l. This compares with Bethlehem Steel Corp. effluents with less than 7 or 8 ppm iron at a rising velocity of 0.7 m/h.

- The operator recommends that flanged sludge recycle lines be installed in any new plant to facilitate unclogging as needed.

- No scale problems are experienced, probably because of the low $CaSO_4$ concentration in the water, and low carbonates.

3. Noranda Mines Ltd., Waite-Amulet, Quebec

This operation is designed to treat 4320 m^3/d (660 lgpm) acid mine drainage from 8,000,000 tons sulfide tailings in a 100 acre pile and mine drainage from a restored zinc mining site near Noranda Quebec. This plant was designed and constructed after examining all the HDS plants then operating in Canada. It therefore represents the best of Canadian experience.

- Plant Startup: 1983.

- Water Treatment (Average for 1984):

	Influent	Treated	Polished and Treated
pH	2.8	9.7	9.3
Fe	246	2.2	0.5

	Effluent	Treated	Polished and Treated
Mn	5.3	2.2	0.05
Cu	3.1	LT 0.02	LT 0.02
Cd	0.004	LT 0.005	LT 0.00[illegible]
Zn	19.2	0.02	0.02
Pb	0.05	LT 0.05	LT 0.05
Ni	0.06	LT 0.05	LT 0.05
Acidity mg/l $CaCO_3$	922	0	0
SO_4	1,940	1050	1,100
S/S	5-50	--	--
Conductivity m Mhos/cm	2588	1331	1584

- Capital Cost: Estimated C$1.7 million (1983).

- Operating Cost (1983 Projection):

Lime	C$231,000	C$0.10/m³
Polymer	C$ 12,000	C$0.005/m³
Labor	C$ 55,000	C$0.023/m³
Power	C$ 32,000	C$0.0135/m³
Total	C$330,000	C$0.142/m³

- Water treatment costs were significantly reduced by reducing the watershed that drains into the affected area from 1000 acres to 313 acres through various diversion projects. Through successful revegetation of the sulfide rich dumps, an attempt has been made to reduce the rate of acid and dissolved metal generation.

- Being located in a cold climate, the Waite-Amulet treatment plant, including thickeners, is installed indoors in a building measuring 42' wide x 65' long x 34', i.e., 2730 ft².

- To accomplish the compact plant, a lamella platepack thickener is used inside a small indoor indoor clarifier tank.

- The Waite-Amulet system includes:

  - Acidic water retention pond--adequate for one in 25 year rainfall containment; 252 acre-feet.

- Water treatment plant for 660 Igpm allowing 20% margin over the required one in ten year maximum inflow to be treated.

- Polishing pond for treated effluent.

- Three division sludge storage and dewatering ponds with porous sand floors.

- Provision to add lime at the decant point to any excess effluent over and above the capacity of the treatment plant that might have to be released in an emergency to Lake Default.

° The HDS plant consists of the following:

- Lime storage; 60 ton skirt supported lime silo outdoors.

- Lime slurry preparation system 1/3 HP Lightin mixer, 3-4 minute retention, deep vortex mixing, Schutte and Koerting water jet eductor, lime slurry pump.

- Lime-recycle sludge mixing tank; Prochem 10HP mixer.

- Two neutralization reactors, each 15,200 I gallons mixed by Prochem agitators with baffles and air lances at 7 psi.

- One 26'Ø x 20', 60,000 I gal. thickener fitted with an Axel Johnson LGS-T3200-55 Lamella Plate Pack. The thickener has a rake mechanism to bring sludge to a central discharge point.

- 12'Ø x 15'6" h. sludge storage tank, 10,400 I gal.

- 400 cfm blower system 15 psi.

° The HDS plant at Waite-Amulet was required to reduce the volume of precipitate sludges generated by treating the AMD. A 3.3 active acre lagoon would have been adequate storage for 3-6 months sludge generated by conventional neutralization.

° The HDS plant was designed by Noranda in conjunction with P. W. Shipley of P. W. Shipley Associates.

° Cost of lime at the Noranda, Quebec site is $144/st in bulk. Lime demand in 1984 was 12 lbs. per 1,000 I gallon or 1.2 Kg lime/m^3.

- The Waite-Amulet HDS plant is designed to be completely automatic. Controls and sensors place the plant on hold when there is a shutdown and indicate a problem at at the Horne Division Control Room.

- The plant is operated at a steady flow of 800 lgpm provided by a pump at the pond. To achieve a trouble free operation the plant is operated at a steady flow. When there is inadequate water in the pond to achieve this flowrate, the plant shuts itself off.

- Flowrate is measured using an ultrasonic device on a Parshall flume, which measures flow and solids density of the underflow, made by:

  MARIG, INC.
  #230, 3300 Boulevard Cavendish
  Montreal, Quebec H4B 2M8
  (514) 487-1024
  Telex: 055-66305

- For the automated plant, hydrated lime was selected over quicklime to avoid the need for a slaker or storage reservoir and to minimize operator and maintenance requirements. At the time of the visit, NORANDA had not yet reached a final conclusion about quicklime vs. hydrated lime relative merits.

- Lime discharge from the feeder is connected to a totally enclosed polyethylene mixing tank. Makeup water is piped through the lid of the tank at a constant flow rate to produce 30% slurry at maximum lime demand of 20 lbs/minute. The water nozzle is positioned to induce a deep vortex in conjunction with a 1/3 Greey-Lightnin mixer. Lime flowing into the vortex is carried to the downdraft impeller where it mixes instantaneously to produce a lime slurry. The mixing tank has a 3-4 minute retention time to give a fast response to the control loop.

- A submerged overflow from the lime mixing tank flows into an enclosed funnel which discharges to the suction port of a "Schutte and Koerting" type 264 carbon steel water jet eductor. Even though a 1 1/2" water jet eductor can handle 5/16" particles, the submerged overflow at the mixing tank prevents any non-dissolved lime from reporting to the eductor. The system delivers 8 gpm of 30% lime slurry against 15 psi back pressure. The system has proven itself to be simple and reliable to convey a lime slurry for short distances and with small lifts. This system elevates the slurry 22 feet to the delivery point.

By enclosing the rotary feeder discharge, the lime mixing tank, and the eductor funnel, a slight negative pressure is created in the lime system and the escape of lime dust is minimal. This system is installed at both Geco Division and Waite-Amulet with successful results.

- Sludge-Lime Mixing

  Sludge is recycled to the lime-slurry mixer fitted with a Prochem 10 HP Type 640 ft. 10 agitator at 44.6 RPM. The baffled sludge recycle tank measures 12'Ø x 6' high with 3200 Igal. (14.5m^3) storage capacity, designed for 15 minutes retention. This modifies the sludge solids from a fluffy slime to an almost particulate texture.

- Neutralization Reactor Tanks

  Two reactors, each 15,200 I gallons (69 m^3 each), are sized for 23 minutes residence time not counting sludge recycle and 20 minutes including sludge recyle, which indicates 27 m^3/h sludge recycled.

  The tanks are of mild steel with mixing and discharge baffles and a cone bottom discharge. All wetted parts are coal-tar-epoxy coated. Agitation uses Prochem agitators, one in each tank, and 7 psi aeration.

- Air was to be injected in the primary neutralization reactor at 15 psi and 400 scfm (0.6 scfm/Igpm) to convert ferrous to ferric. The idea was to minimize gypsum scaling by keeping an accelerated motion of the particles while they formed.

  During the visit, however, air was injected at 7 psi via four removable air lines per tank inserted below the Prochem mixers.

  To prevent spillage, and to contain any foam that might occur, the tanks have a 2.5' freeboard.

Polymer System

Liquid polymer is used which is much simpler to use than a dry polymer makeup system. Liquid polymer systems are currently in use at two INCO plants and at NORANDA MINES LTD., Geco Division.

Alchem HC35 flocculant was in use at the time of the visit, although Alchem 8C26, 8C35 and 87079 had been tested.

Liquid polymer was to be introduced via a variable speed "Liquid Metronic" model D73 pump. However, during the visit to the actual plant, a Stanco Polyblend Bradley Illinois polymer pump was in use. This pump was reputedly invented at NORANDA's Geco Division. The flocculant is mixed into thickener of water bleedstream via a T static mixer and then passes through a 300' clear plasic 1"Ø pipe acting as an aging coil before being injected into a 5gpm stream for a second dilution which carries it to the delivery point which is achieved by inserting the end of the diluted flocculant solution into the overflow

upcomer at the discharge of the second neutralizing tank allowing flocculant to disperse in the water as it cascades down the trough leading to the clarifier.

The use of flash mixers for flocculant mixing was dispensed with after NORANDA staff visited several installations using the static mixers or propeller mixers were found to have been removed.

Solid/Liquid Separation

NORANDA tests indicated a clarifier rate at 0.2-0.5 lgpm/ft^2 (0.54-1.36 m/h). To enable the clarifier to operate indoors a lamella clarifier was selected. Conventional thickeners operated in Canada alsoexperience interference due to surface currents on the sludge blanket. A circular thickener 26 ft Ø x 20 is installed and fitted with an Axel-Johnson LGS-T3200-55 Lamella plate pack and a rake mechanism to bring sludge to the central discharge point.

Sludge level is detected using a Sensall device supplied by:

NATIONAL SONICS DIVISION
Sensall Control
Xertex Corporation
Hauppauge, NY 11787

The Lamella plate packs are made by:

AXEL-JOHNSON LTD.
Montreal

Sludge Handling

Based on experience at NORANDA, Mattabi Division, where the original Moyno pump was replaced by an SRL type centrifugal pump, the latter was installed at Waite-Amulet. Positive displacement pumps normally prefered for this type of job require so much maintenance that the benefits do not offset the greater reliability of SRL centrifugal pumps. floc breakage can be overcome by a little extra flocculant dosage.

At COMINCO's Kimberly, B.C., plant two SRL Allis Chalmers pumps are installed, each capable of recycling 850 lgpm sludge. At Kimberly the pumps are fitted with DC variable speed motors, and one pump operates at a time. Cominco reportedly initially experienced problems with constantly changing polymer dosage requirements created by the solid mass flow not being uniform. The RPM of the motor is now controlled to draw a constant amperage. In this way a change in sludge viscosity or density caused by a sudden slide of material to the thickener discharge cone is taken care of by a change in pump rpm.

To achieve 25-30% sludge density, 95-98% of the sludge must be recycled. At Waite-Amulet, two Worthington 3" x 3" horizontal rubber-lined slurry pumps were installed as slurry recycle and sludge waste pumps. One heavy duty AC motor and a single controller were selected for the variable speed sludge recycle pump.

The sludge recycle pump and sludge waste pump are located in a pit under the thickener which minimized the length of the suction line to the pumps. One Galligher sump pump acts as a backup for either the recycle or waste sludge pump. The sump is designed to discharge its overflow to the clear water overflow ditch.

Recycle flow monitoring is by a Taylor mag-pipe flowmeter installed on the sludge recycle line. The purpose of the sludge flow measurement is to be able to optimise the flocculant/recycle ratios and to shut the plant down automatically if the recycle sludge volume drops below a preset limit.

Sludge Disposal

Once sludge density has been reached, the sludge waste pump is activated for a timed period by an ultrasonic sludge level detector supplied by:

NATIONAL SONICS DIVISION
Sensall Control
Xertex Corporation
Hauppauge, NY 11787

To minimize the amount of spare parts, this pump is identical to the recycle pump but with a standard AC motor which is feasible because the sludge pond is only 300-400 feet from the treatment plant and at the same elevation.

The sludge disposal line is insulated and has a 1½% slope back to the treatment plant. After every sludge purge the line will be flushed. The waste pump header is connected to the upper part of the clarifier and, by means of automated knife valves, some of the clear water will be used for the flushing of the line by the waste pump. After the flushing sequence has been completed an automated knife dump valve will be activated to drain the line.

Sludge production is estimated at 2.6 acre-ft/year, and a 10 acre-ft sludge disposal pond has been constructed adjacent to the plant.

The sludge impoundment system is fitted with a porous base of sand and pebble size slag drains to drain the sludge to 50% solids. The impoundment is divided into three sections which are cycled to provide maximum drying before being covered with fresh material.

During winter, dewatering is limited but as the spring thaw arrives, the drainage characteristics of the once frozen material is greatly enhanced. In summer, drying will remove additional moisture causing shrinking and cracking which allows air to come into contact with the sludge. There will be some conversion from ferric hydroxide to the carbonate as well. This results in a very stable dry sludge.

Leach tests of a similar sludge by COMINCO at Kimberly, B.C., are said to have resulted in virtually no dissolution of heavy metals but more information on this could be requested from:

MR. WALTER KUIT
Cominco Ltd.
200 Granville Street
Vancouver, B.C.
V6C-2R2
(604) 682-0611

At Waite-Amulet, the storage ponds are about 300 feet x 500 feet long divided into three sections with clay dikes and a usable storage height of 5 feet.

Dry sludge production rate is estimated at 4,000 tpa or 2.6 acre-ft/year. A truck hauling program will be instituted when needed to move dry sludge to one of the tailings sites for final deposition.

The drainage pipes from the sludge depositions exit to a drain for gravity flow to the acid feed water reservoir. In the future, this water could be diverted to the clear overflow ditch once its good quality has been confirmed.

Control System

A very innovative automatic control system has been installed at the Waite-Amulet water treatment plant. The heart of the system is a programable Texas Instruments micro-processor which is equipped to handle on/off analogue input/output as well as timing, counting and arithmetic functions. The input/output configurations are simple and easily traceable in the event of malfunction or logic error.

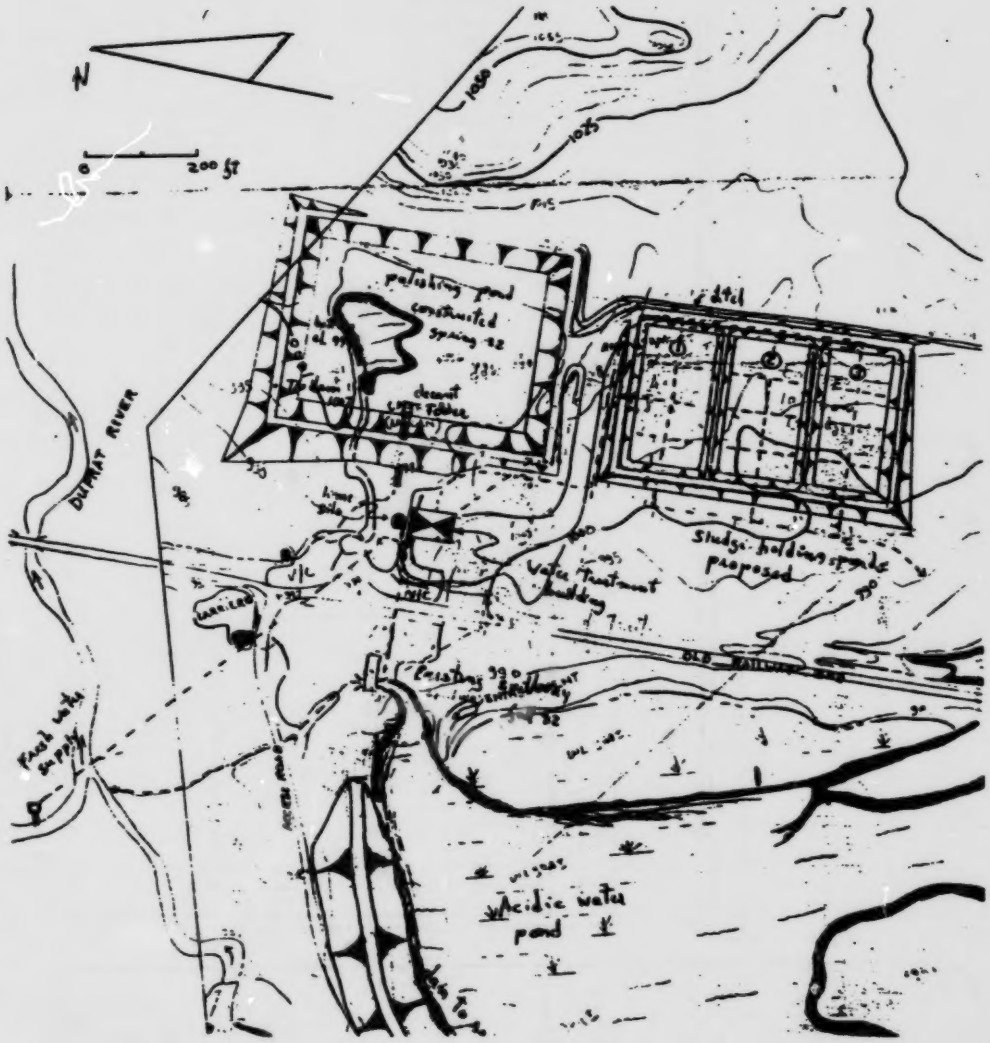
The micro-processor has three prime functions:

1. Generating temporary shutdown on critical alarm.
2. Monitoring and recording of plant operation.
3. Restarting the plant after power failure.

The plant is also equipped for manual operation by manual on-off switches on the central control panel although it is intended to operate the plant as a remote, unmanned automatic unit.

Proposed Water Treatment Plant at Waite Amulet

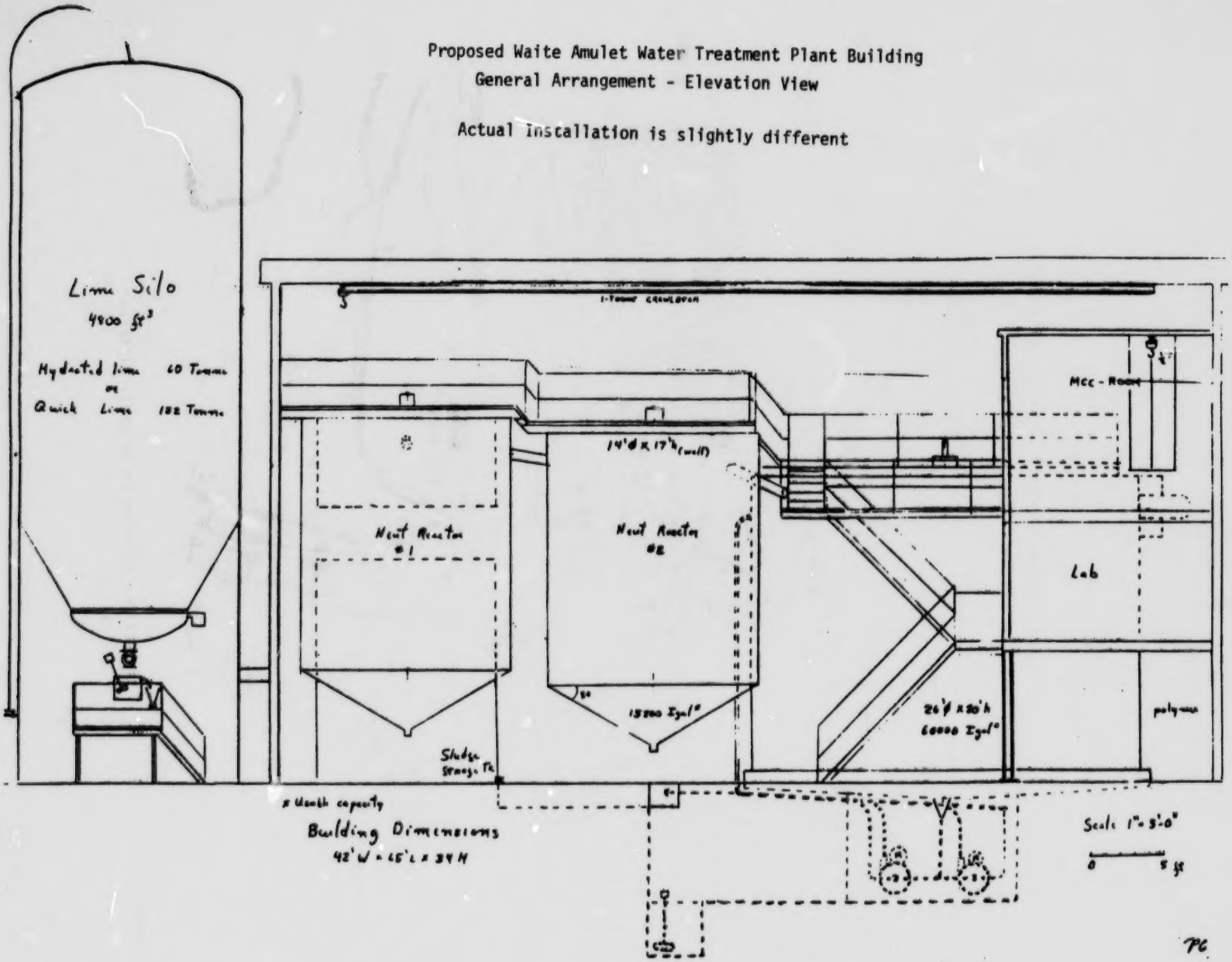
Site Arrangement



Actual Installation is slightly different

Proposed Waite Amulet Water Treatment Plant Building
General Arrangement - Elevation View

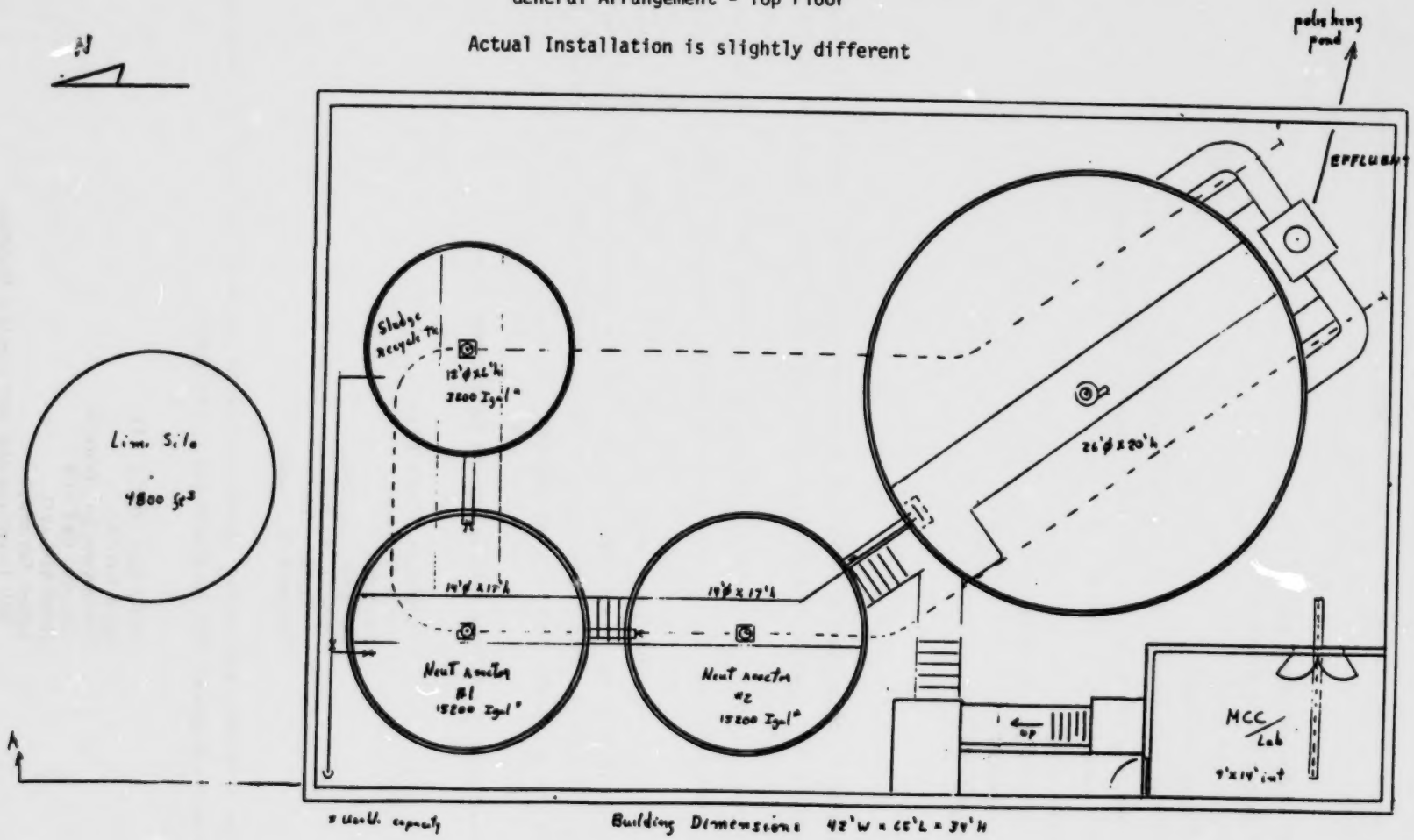
Actual Installation is slightly different



Proposed Water Treatment Plant at Waite Amulet

General Arrangement - Top Floor

Actual Installation is slightly different



The microprocessor is programmed to handle a variety of contact switches associated with field instruments:

- High pH at neutralization tank #1.
- Polymer delivery line pressure.
- High sludge bed level.
- High efficient turbidity.
- High clarifier rake torque 70% of maximum rated torque.
- Medium high clarifier rake torque at 40% of maximum rated torque.
- Low pH in neutralization tank #1.
- Low water supply pressure.
- Low compressed air pressure.
- Low raw water pond level.
- Low sludge recycle flow.

Services

The water treatment plant facility totals 150 HP installed power and 75 KW for heating during the coldest days. Cost of installing the 25KV line for the installation was $55,000.

The microprocessor is connected by telephone line to the Horne Division to continuously transmit plant operating status and for communications with the plant operator.

The plant also needs 60 igpm fresh water to operate. This is supplied by installation of one two-stage Flygt pump in a heated well alongside the Duprat River about 1500 feet from the plant to provide fresh water for polymer preparation, lime slurry preparation and transport, pump glands, and for floor washing.

More information on this excellent installation can be obtained from:

NORANDA MINES LTD.
Horne Division
BP 4000
Noranda, Quebec
Canada J9X 5B6
(819) 762-7764
Bernard W. Brooks

Details on the excellent programable control system for an automated plant can also be requested from the engineer that developed the system first.

NORANDA MINES LTD.
Geco Division
Manitouwadge, Ontario
Canada P0T 2C0
(807) 826-3211
Walter Sencza,
Mill Environmental and Control Engineer

Acid mine water treatment at Les Mines Gallen, Noranda Mines Limited

N. LECUYER
Chief Engineer, Chadbourne Division
Noranda Mines Limited
Noranda, Quebec

ABSTRACT

During early 1980, pre-production work commenced at the "Les Mines Gallen" project, north of Noranda, Québec. As a result of the acid mine water associated with this property, a major pre-production phase included the installation of a water treatment plant to render the water environmentally suitable.

This paper emphasizes the planning, installation and operational factors of the treatment plant necessary to the success of the mining operations and the maintaining of a clean environment.

Introduction

The Gallen Project is a zinc, gold and silver open-pit mining operation approximately 10 kilometres north of Noranda, Québec. This property has a long history, with initial diamond drilling done in the early 1930s and underground mining taking place between 1953 and 1962. This property was reactivated in 1980, with production scheduled at a rate of 45,000 tons per month.

Included in the reactivation plans for the property was the installation of a water treatment plant to treat the acidic mine water.

Plant Design

The requirements for the Gallen water treatment plant were two-fold. Firstly, it was necessary to neutralize the acid water and secondly to produce a sludge containing metal hydroxides and sulphates which would be stable when stored, and a clarified overflow meeting governmental regulations to be discharged to the environment.

The flow sheet (Fig. 1) will explain the process in treatment of the acid water.

Acid mine drainage is treated with lime to increase the pH to 9.50. Metals in solution are precipitated as metal hydroxides and the SO_4 as calcium sulphate. The precipitate slurry is then aerated to convert ferrous iron to ferric iron, which is more stable for storage and disposal.

The precipitate is next flocculated with a polymer flocculant and settled in the thickener to produce a sulphate/hydroxide sludge and a final effluent discharged to the environment.

The initial plant design was based on a flow rate of 400 l.g.p.m. From this, the plant specifics, such as reactor capacities, flow rates, thickener capacity, etc., were designed. The consultant for the design stage was P. Shibley and Associates, with Mining Corporation of Canada responsible for all engineering drawings, including all fabrication and erection details.

Construction on the plant building was started in August 1980, with plant start-up initiated in early April 1981.

Norman Lecuyer

Norman Lecuyer is a native of Noranda, Québec. He is a graduate of the Northern College, Haileybury School of Mines, and a graduate of Queen's University in mining engineering. His work experience includes various positions with Pamour Porcupine Mines Ltd. and Mining Corporation of Canada Limited. He is currently chief engineer with Noranda Mines Ltd., Chadbourne Division.

Keywords: Underground mining, Les Mines Gallen, Water treatment, Noranda Mines, Environmental control, Acid mine water.

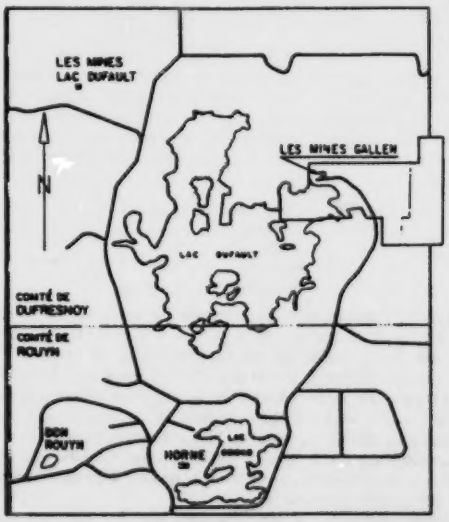


FIGURE 1. Location of Les Mines Gallen.

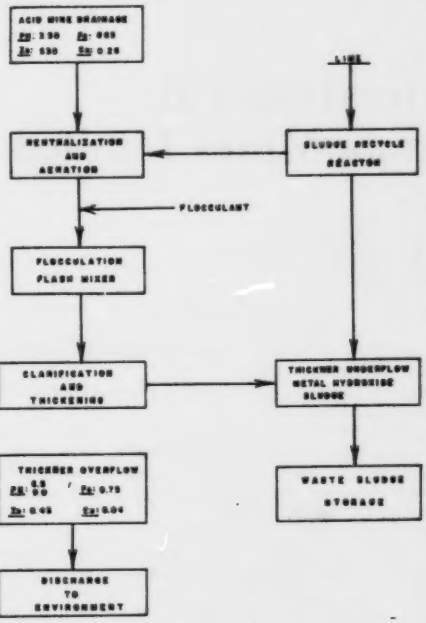


FIGURE 2. Block diagram of the Mines Gallen flow sheet.

Theory of Operation

The plant operation can best be explained by the use of a schematic flow sheet (Fig. 2).

Prior to plant start-up, it is necessary to perform bench tests to determine neutralization and flocculation requirements in order to start nearest to the optimum lime and flocculant flow rates.

The acid mine water flows into neutralization reactor 1 from the mine, where lime is added on initial start-up. Once all tanks are filled, the lime is introduced to the sludge recycle tank. Neutralization takes place in the two reactors, the second of which is utilized to provide for retention time for the reactions to complete. These reactions may be summarized as follows:

$$Ca(OH)_2 + \text{Metals} - \begin{array}{ll} CaSo_4 \text{ ppt (insoluble)} & \\ Cu(OH)_2 \quad \text{ppt} & \\ Zn(OH)_2 \quad \text{ppt} & \\ Fe(OH)_2 \quad \text{ppt} & \\ Mn(OH)_2 \quad \text{ppt} & \end{array} \left.\right\} \text{insoluble ppt}$$

The hydrated lime slurry increases the pH from an average of 3.50 to 9.5. Achieving a pH of 9.5 is very important, because this provides for the best formation of sludge in the thickener. The lime is stored in a 100-ton lime bin and fed via a vibrating screw feeder into a cone where water is added to produce a slurry, which is then pumped to the recycle tank.

The lime flow is automatic. The pH meter, located in neutralization reactor 2, feeds a signal through an interface controller which increases or decreases the lime feed rate depending on the pH in the tank.

From reactor 2, the overflow goes into the thickener via a flash mixer, where the flocculant is added to promote flocculation and rapid settling of the sludge. The flocculant is prepared in the B.I.F. (basic inflow) system and pumped to the flash mixer. To date, the flocculant used is the dry polymer, Percol 156. The flocculant is prepared as a 0.1% solution or as required, depending on the flow rate of the incoming water.

The sludge precipitates in the thickener to approximately 35 per cent of the original inflow, but will be of a very low density. To provide for a high-density sludge, the High-Density Sludge System was incorporated whereby recycled sludge from the thickener underflow is premixed with lime for neutralization before adding it to the incoming mine water. This provides a change in the physical chemistry of the sludge which promotes the growth of larger and consequently faster-settling high-density sludge. Sludge densities of over 20 per cent have been obtained to date.

The thickener is equipped with two Lamella plate packs which provide high surface area for clarification. The thickener underflow is split between the sludge discharge and sludge recycle. The sludge recycle volume can be up to 50% of the mine water flow.

The sludge discharge is automatic. A sludge level control system is utilized, which consists of an ultrasonic sensor which activates the sludge discharge pump when the sludge attains the desired level in the thickener. This sludge is discharged to the sludge basin for storage and will eventually be covered and revegetated.

The thickener overflow or effluent is discharged to a polishing pond, from where it discharges into the Kinojevis river system.

Plant and Associated Construction

Construction for the treatment plant consisted of the plant itself as well as the sludge basin (necessary for storage of the sludge), polishing pond, diversion ditch and a fresh-water line from Lake Dufault.

The sludge basin area selected was an area where a natural depression existed that would facilitate construction. The sludge basin and polishing pond area required some 90,000 cubic yards of excavation. The overflow of the polishing pond goes into the diversion ditch, a ditch 1,500 feet long to drain the water into the Kinojevis river system.

The process water line from Lake Dufault is a 3-inch-diameter line, approximately 2,500 feet long, which supplies the plant process water for the polymer mix system and the lime feed system.

The plant is housed in a 45-foot-wide, 100-foot-long, 35-foot-high building. The building also houses the two-bay garage, and both plant and garage can be serviced by a 3-ton overhead crane.

Lime storage is provided for by a 56-foot-high by 15-foot-diameter Butler bolt-a-tank, which is equipped with a vibrating screw feeder and bin activator.

The thickener tank is a 26-foot-diameter by 20-foot-high tank constructed of quarter-inch steel and having a working capacity of approximately 63,000 Imperial gallons. The reactor tanks are 12-foot-diameter by 16-foot-high tanks having a working capacity of approximately 9,000 gallons each.

Flocculant preparation is done using the B.I.F. (basic inflow) system. Dry polymer is fed automatically into a mixer, mixed with water and flows into the mixing tank (200 gallon cap.). After mixing, the solution is transferred to the holding tank (400 I. gallon cap.), from where the solution flow to the thickener is effected by a metering pump set to deliver the required concentration of flocculant solution.

The nerve centre of the plant is the control room. The control room houses the motor control centre, control console and the instrumentation panel. The operators control console permits the operator to see at a glance that all plant systems are functioning. The instrumentation panel continuously records the mine water inflow, the pH in reactor two and the effluent discharge and the turbidity of the discharge. The instrumentation also provides for automatic plant shutdown. A plant shutdown is effected when a critical point in the system fails. These critical points include:

(1) drainage inflow variation below set-point;
(2) significant fluctuation of the pH;
(3) turbidity of effluent above the set limit;

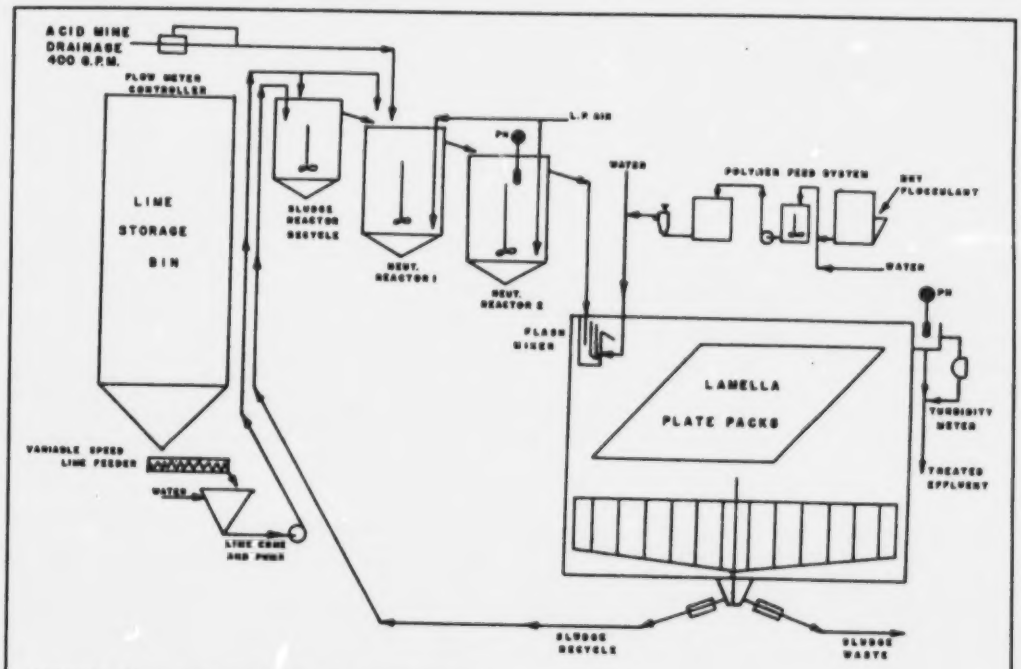


FIGURE 3. Schematic diagram of the Mines Gallen flow sheet.

(4) fresh water supply failure to flocculant or lime system;
(5) air supply for aeration failure below set limit;
(6) high sump level; and
(7) high level on effluent discharge.

Capital costs for the plant are approximately one million dollars, which includes the building, foundation, plant electrics, tanks, pipelines, plant equipment, engineering, etc.

Plant Operation

The Gallen treatment plant started operations on the 4th of April, 1981.

Initially, the drainage inflow was limited to approximately 25 per cent of plant capacity due to an undersized pump. Initial problems included discoloration or suspension of the precipitate in the thickener tanks as a result of ineffective flocculation. The problem was resolved by adjustment of two items. Firstly, it was apparent that initial flocculant preparation or mixing was not sufficient, whereby the polymer was coagulating due to insufficient mixing. Secondly, the point of injection of the flocculant was moved 5 to 6 feet upstream of the flash mixer to provide more contact time with the precipitate. It was also found that the flash mixer tended to break up the effect of the flocculant and this was removed from the system. With the above-mentioned adjustments, the flocculation and settling took place rapidly, with a clearing up of the thickener solution and excellent effluent quality.

Combined with the above, it was necessary to balance the flocculant dosage, which required a period of time, with the present consumption at 6 p.p.m.

Adjustments and changes to the lime system were also required. The initial 1-inch lime slurry line proved to be undersized, and installation of a 2-inch line to reduce losses eliminated plugging. Problems were also experienced with the screw feeder, which tended to plug on occasion due to its intermittent operation, based on lime demand from the pH loop in reactor two. This was solved by assuring that the screw feeder rotates at a slow speed when lime demand is low rather than stopping completely. Lime consumption to date is averaging 18.5 pounds per 1000 gallons.

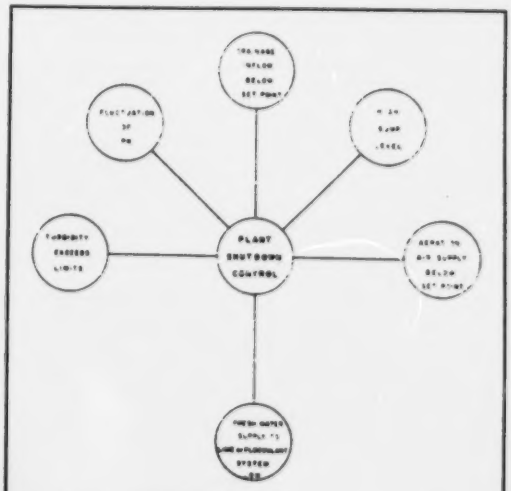


FIGURE 4. Plant shutdown control.

The sludge recycle rate is now 145 I.g.p.m., or about 50 per cent of the drainage inflow to the plant. At this rate, the flocculation and settling rates are very good. The per cent solids on the sludge discharge and recycle has built up to a point where the averages for the months of June and July 1981 were 9.5% and 23.53% respectively.

Although there were some problems with effluent quality during the first month or so because of balancing of the plant, the effluent quality is now within the governmental regulations, as indicated by the following comparison:

Gov. Requirements (p.p.m.)		Plant Effluent (p.p.m.)
Cd	0.05	0.021
Cu	0.15	0.039
Fe	3.00	0.750
Pb	0.20	0.160
Zn	0.50	0.45
pH	5.5 to 9.5	6.5 to 9.0

It is apparent that the plant is doing its job. There is also room for improvement here on the optimum flow rates, concentrations and recycle rates. This of course, comes with operating experience and requires some time.

An estimate of plant operating costs is as follows. It must be pointed out that this is based on the first four months of operation, during which time flow rates were not at maximum and balancing of the plant was required.

Item	Cost/1000 I. Gallons
Hydrated Lime	.848
Flocculant (Percol 156)	.107
Power	.658
Labour	.300
TOTAL	$1.913

The above figures are those for a single operator. Eventually, it is planned to operate the plant without a full-time operator, whereby plant tests for sludge quality, etc., can be performed on a routine basis which should require only several hours per week. Thus, costs at that time would be in the order of .1 to .2¢ per Imperial gallon treated.

Conclusions

Although it required some time to balance the treatment plant at Gallen, present results are very good. Most problems have been mechanical ones to date—pumps, motors, electrical defects, etc.

Most important is the fact that the sludge densities sought have been obtained with an effluent discharge that meets governmental requirements. Work is also continuing to optimize and reduce costs where possible.

Our main object is to carry out the mining operations at Gallen while maintaining or improving the environmental conditions, which in this day and age have become a prerequisite for the mining industry.

5. Cu-Pb-Zn Mine-Mill M, Ontario

Note: This data has not been verified and may be unreliable.

This early HDS water treatment plant is of particular interest here because acid mine drainage, consisting mainly of tailings reclaim water is high in zinc relative to iron. In other words, this HDS plant removes a sludge with a high zinc/iron ratio which is atypical of the other plants discussed to date.

HERMAN (1983) showed that zinc can be effectively removed in an HDS operation even in the absence of iron.

Composition of tailings pond decant solution, i.e., feed to the treatment plant, varies in summer and winter as follows.

	Winter		Summer		
	Treatment Plant		Treatment Plant		Retention
	Influent	Effluent	Influent	Effluent	Pond Effluent
pH	10.0	10.2	7.0	10.5	9.3
Fe	0.10	0.48	0.88	0.04	0.88
pB			LT 0.06	LT 0.02	0.02
Zn	0.80	0.76	3.14	0.20	0.1-0.3
Cu			LT 0.01	LT 0.01	LT 0.01
S_2O_3			Tr	4.1	Tr
S/S	7.0	Tr	1.0	Tr	1.0
Temp.			16.5°C	17°C	14°C

LT = Less Than

The HDS water treatment plant treats 600 Igpm (3900 m^3/d). It is noted that the quality of the reclaim tailings pond water varies from summer to winter. In summer dissolved Zn levels increase to over 3 ppm, and the pH of the tailings return water is lowered.

Recycle sludge from the Lamella thickeners is mixed with lime in a ratio 90:10 using air to mix the sludge. The process is operated at pH 9.5 and also uses Lamella thickeners. However, this time Pilkenrood Lamella plate thickeners were used.

Following two stages of neutralization, flocculant is added in two points into a long series of S-bends carrying the solutions ahead of the Lamella thickener.

Percol 155 flocculant is added at a dose of around 1 ppm.

The sludge from the thickener-clarifier runs 15-20% Zn, and operators say that sludge density must be kept up in order to keep the clarifier working correctly. The precipitation process, being mainly zinc-oriented, is operated at pH 9.5. It is found that if the pH gets above 10, then the flocs are light and tend to get lost in the clarifier overflow.

In this case, the precipitated sludge at 15-20% zinc represents an economic value, and the sludge has at times been disposed of by adding it to the zinc concentrate for shipment to a refinery.

CONVENTIONAL NEUTRALIZATION

Conventional neutralization of AMD can be achieved by reaction with several reagents including lime, limestone, sodium hydroxide, soda ash, and ammonia. Ammonia may be the most effective and least costly in several locations, but it is unsuitable for AMD treatment for dischargeable effluents because of the undesirable environmental effects on fish to which ammonia at high pH is toxic down to 10 ppb. One of the main disadvantages of lime precipitation is the voluminous sludge that requires very large impoundments and which takes many, many years to stabilize for site reclamation.

Unstable Voluminous Sludge from Conventional Lime Precipitate of AMD

An example of the different results that can be achieved when using some of the various neutralizing reagents to treat AMD from a South African coal mine is illustrated in the following graph from BOSMAN (1974):

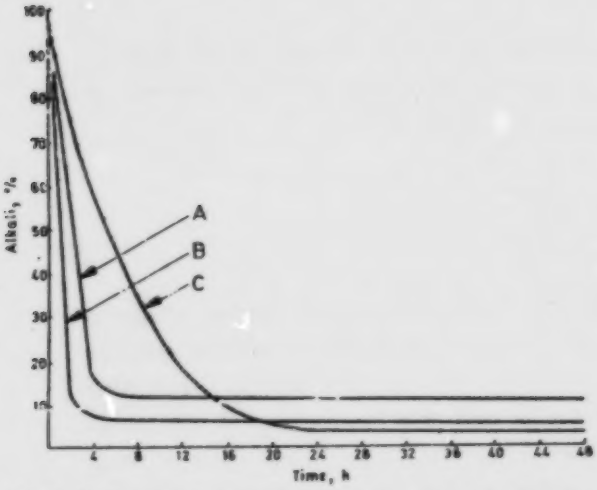
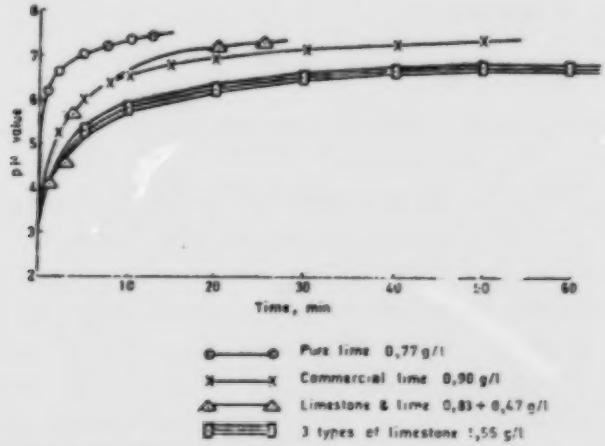


Fig. 1—Settling rate of precipitate from Kromdraai neutralized water
A—Lime 0,875 g/l Solids in sludge 0,8%
B—Limestone 0,83 g/l + lime 0,47 g/l Solids in sludge 1,7%
C—Limestone 1,10 g/l Solids in sludge 2,7%



—Neutralization of Kromdraai acid drainage with different types of lime and limestone

A comparison of various treatment processes including the cost of various neutralizing agents was published by HOLM & SIMPSON (1981) for a Colorado mountain location and reported as follows:

Estimated Range of Costs for Treatment

Method	Estimated Cost Range, dollars/1000 gal.
Lime neutralization	0.20 to 1.30
Limestone neutralization	0.15 to 1.00
Soda ash neutralization	0.40 to 3.00
Sodium hydroxide neutralization	0.50 to 3.50
Reverse osmosis treatment	1.00 to 5.00
Ion exchange treatment	1.00 to 7.00

Although probably not based on a rigorous engineering study, the ranges of costs in the above table do illustrate the relative costs quite well. Additional discussion of the relative merits and performance to be expected by lime and limestone precipitation is included in the following excerpt from a 1975 review on the subject prepared by Environment Canada. One item in particular that was found to be interesting was the fact that even ferric hydroxide forms higher oxide complexes, and that ferric hydroxide is also amphoteric, as well as zinc, copper, and aluminum.

OXIDATION OF FERROUS TO FERRIC IRON

BOSMAN pointed out the wellknown fact that if conventional air agitation is used, then the rate of ferrous to ferric oxidation is highly pH dependent, being much higher at pH 8 and 9 or above than in the acid pH range.

Also, if iron can be converted into the ferric state, it can be removed from solution by precipitation as ferric hydroxide at relatively low pH values, thereby requiring less lime or NaOH addition.

MIHOK (1969) reported the interesting phenomenon that ferrous iron can be efficiently oxidized to ferric iron even at low pH values around pH 2.5 using a short contact time with activated carbon and air.

Ferrous iron content of an acid minewater flowing through an aspirated activated carbon column was reduced from about 700 ppm to about 10 ppm in less than a minute.

MIHOK (1969) reported that activated carbon was used repeatedly with little loss in efficiency, no discoloration, and no solids deposition. In the batch tests, about a third of the iron was adsorbed by the carbon but with continuous flow, little iron adsorption was expected.

Excerpt from: MINE AND MILL WASTEWATER TREATMENT

By

Environment Canada WPCD Staff
Report EPS 3-WP-75-5 Dec. 1975

4. WASTEWATER TREATMENT PROCESSES

The specific wastewater problems and treatment requirements of a particular mine are subject to the influence of local circumstances. These include the mineralogy of the ore body and surrounding area, climate and topography. However, the overall problem faced will be composed of an aggregate of discrete units determined by the contaminating factors described in Section 3.

In this section, descriptions are provided of the basic wastewater treatment processes. Emphasis is placed on demonstrated, practicable solutions applicable to Canada.

4.1 Acid Neutralization and Heavy Metal Removal

Acid is generated through the oxidation of iron sulphide minerals. This acid is then available for leaching metals from the minerals.

The characteristics of a range of typical acid waters is given in Table 2. In their untreated form, these wastes are extremely toxic to fish and other forms of aquatic life and do not comply with many basic requirements for potable water. Any process used to neutralize acids will also remove dissolved heavy metals through the formation of insoluble metal hydroxides. The conditions necessary for hydroxide formation are considered below.

4.1.1 Hydroxide formation

Heavy metal precipitation occurs as a result of the reaction $M^{++} + 2OH^- \rightarrow M(OH)_2$, where M is the metal cation. Many metal hydroxides are in fact precipitated as the hydrated metal complex $M(OH)_2 \cdot nH_2O$, even from simple solutions of the metal.

The precipitation of heavy metal hydroxides can be predicted by using standard solubility relationships where the solubility product, Ksp, for the above general reaction is given by:

$$KsP = (M^{++})\ (OH^-)^2$$

Since the OH^- ion concentration is a function of hydrogen ion concentration, the degree of precipitation of a given metal hydroxide is directly related to pH:

$$(OH^-) = 10^{(pH-14)}$$

TABLE 2. TYPICAL ASSAYS OF ACID WATERS IN CANADA

(All Concentrations are mg/l except pH)

Type of Operation	Cu - Pb - Zn (Mine & Surface Drainage)	Cu- Pb -Zn (Mine Water)	Uranium (Seepage)	Cu - Zn (Active Mine)	Base Metal (Abandoned)	Uranium (Abandoned Mine)
pH	4.0	2.0	2.0	3.0	2.6	2.0 - 2.8
Suspended Solids	8.8	690	Nil	-	-	25
Total less solids	79	24,000	-	-	9,200	13,440
Hardness	293	2,960	-	-	1,390	
Ca	-	-	416	-	454	-
Mg	-	-	106	-	178	-
Cu	17	11	3.6	0.0	2.5	2.2
Zn	118	1,090	11.4	0.4	34	9.4
Pb	0.4	58	0.7	0.11	0.5	-
Fe (total)	79	1,830	3,200	11.7	1,300	300
Mn	21	0	5.6	0.4	8.2	3.6
SO_4	36	16,560	7,440	885	4,050	6,900
COD	-	245	270	-	110	-

Thus, for simple precipitation, if the solubility product constant is known, a plot of metal ion concentration against pH can be drawn from which the optimum level of precipitation and corresponding pH can be determined.

The calculations are more complex if the precipitated compound is amphoteric or if the composition of the waste is such that several compounds precipitate simultaneously.

Amphoteric precipitates, such as many heavy metal hydroxides, exhibit minimum solubility at a distinct pH level and an increase in solubility as pH is shifted in either direction. The pH level of minimum solubility can be evaluated from solubility product and chemical equilibrium relationships of the appropriate ampholytes. Such an exercise has been attempted for copper, zinc, lead and iron and the resulting plots are presented in Figures 1 to 4.

Several factors preclude the possibility of theoretically deriving absolute values for best residual levels of metal ions. Not the least of these is the extremely broad range of solubility products for most of the metallic salts in question.

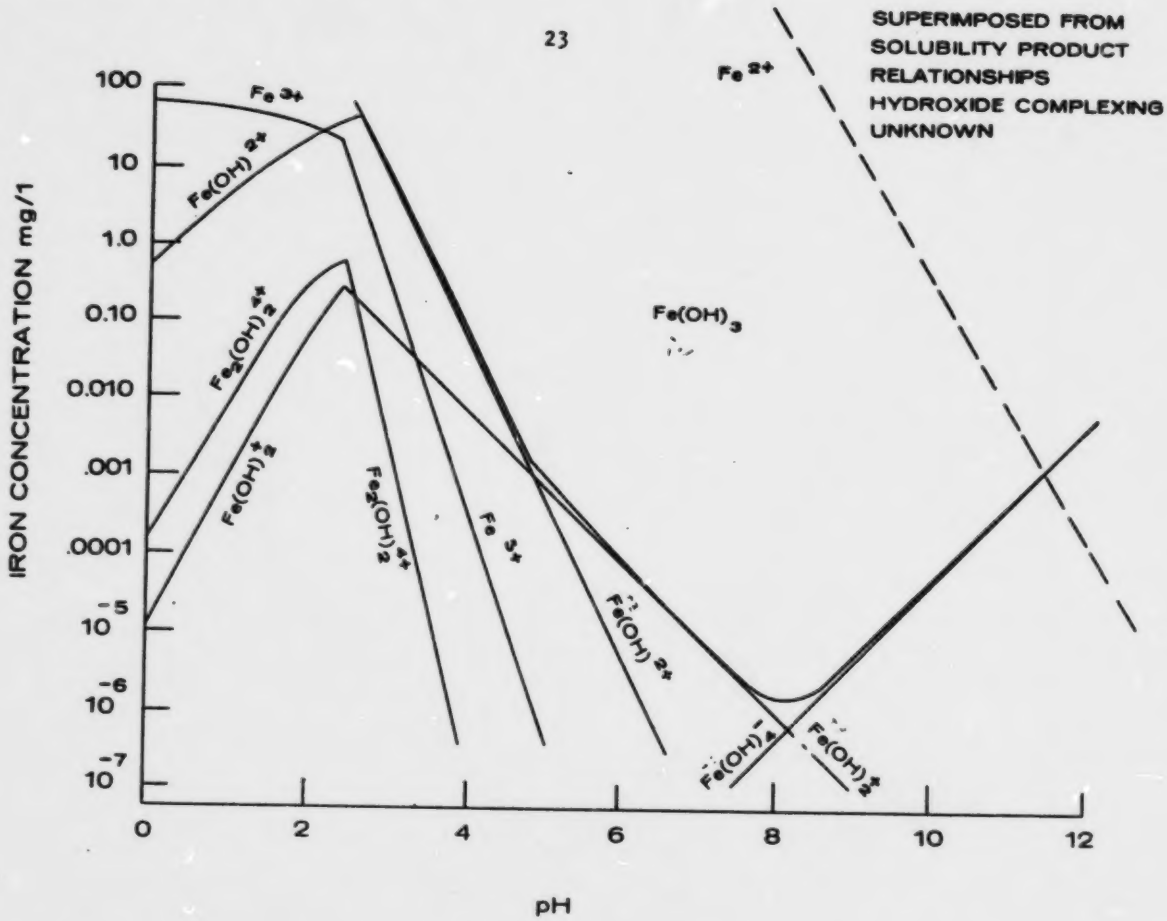
Bearing in mind the above-mentioned limitations, the following ranges of residual metal concentrations and optimum pH values appear to be theoretically feasible if total precipitate removal from the decant can be achieved.

Cu	1 - 8 µg/l	pH 9.5
Zn	10 - 60 µg/l	pH 10
Pb	< 1 µg/l	pH 8
Fe (total	< 1 µg/l	pH 8 (if totally oxidized to ferric)

It is evident that, at best, theoretical solubility product relationships can give only a broad indication of the metal concentrations attainable by treatment methods using precipitation.

Figures 1 to 4 indicate that the following pH sequence should theoretically result in an optimum removal of metals from solution:

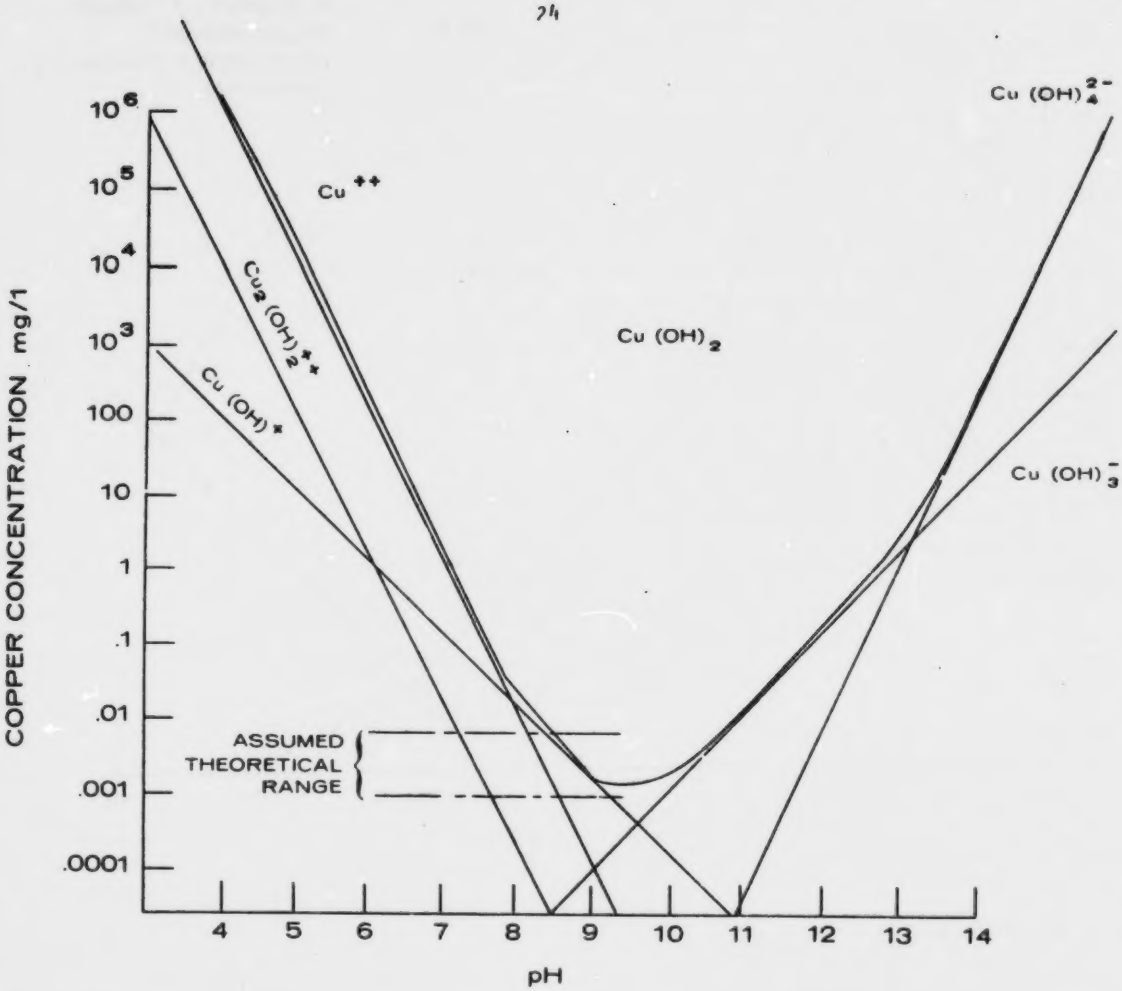
pH 8 - maximum removal of iron as $Fe(OH)_3$ and lead as $Pb(OH)_2$



REACTIONS:

$Fe(OH)^{+2} = Fe^{+3} + OH^-$	$K = 1.5 \times 10^{-12}$
$Fe(OH)_2^+ = Fe^{+3} + 2\ OH^-$	$K = 5.6 \times 10^{-22}$
$Fe(OH)_3\downarrow = Fe^{+3} + 3\ OH^-$	$Ksp = 10^{-38}$
$Fe(OH)_4^- = Fe^{+3} + 4\ OH^-$	$K = 10^{-33}$
$Fe(OH)_2^{4+} = 2\ Fe^{+3} + 2\ OH^-$	$K = 7 \times 10^{-26}$
$Fe(OH)_2\downarrow = Fe^{+2} + 2\ OH^-$	$Ksp = 3.2 \times 10^{-14}$

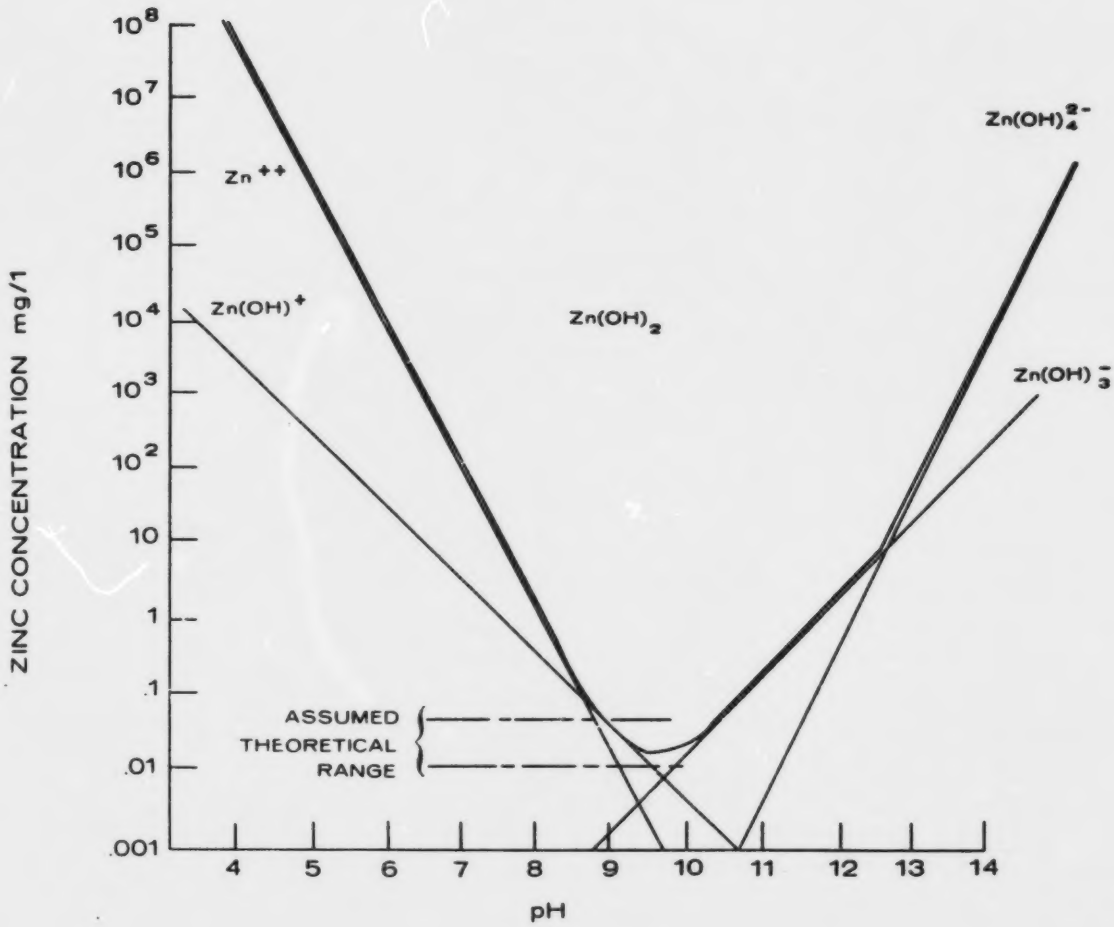
Figure 1. Iron Solubility (3)



REACTIONS:

$Cu(OH)^{+} = Cu^{++} + OH^{-}$	$K = 10^{-6}$
$Cu(OH)_2 = Cu^{++} + 2\ OH^{-}$	$Ksp = 2 \times 10^{-19}$
$Cu(OH)_3^{-} = Cu^{++} + 3\ OH^{-}$	$K = 6.2 \times 10^{-16}$
$Cu(OH)_2^{-} = Cu^{++} + 4\ OH^{-}$	$K = 7.7 \times 10^{-17}$
$Cu(OH)_2^{++} = 2\ Cu^{++} + 2\ OH^{-}$	$K = 10^{-17}$

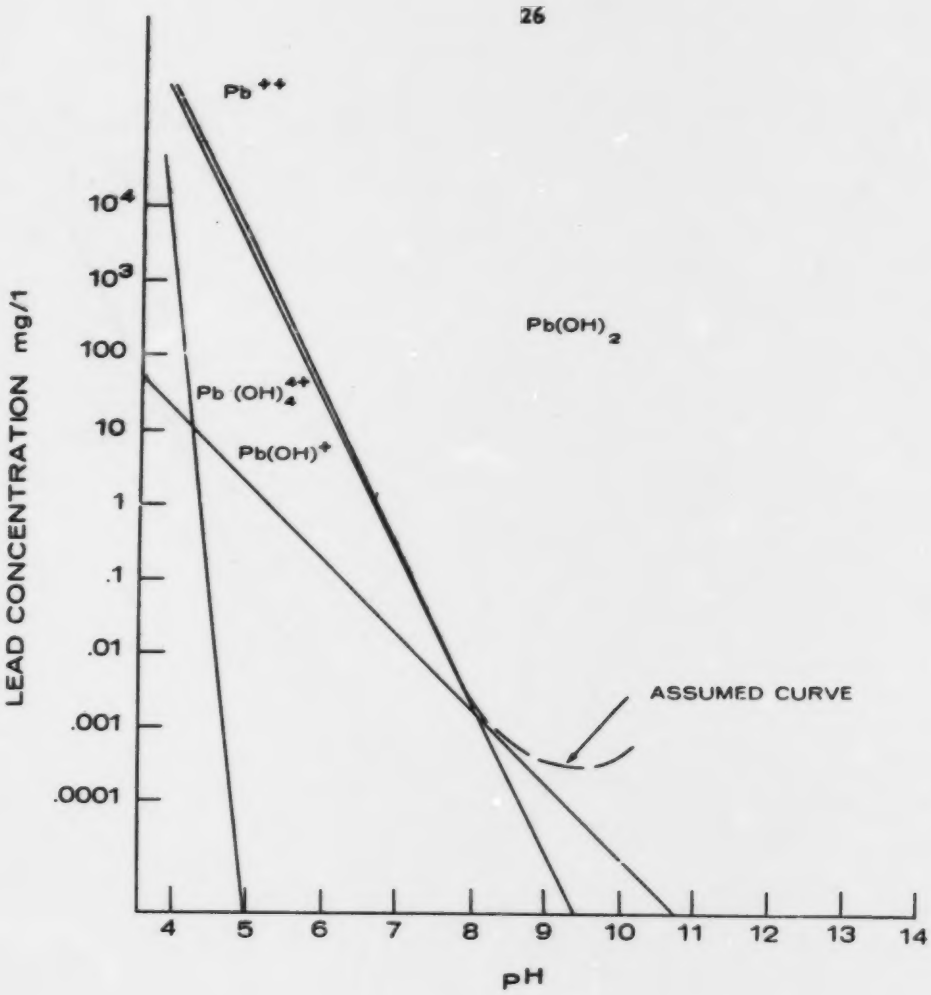
Figure 2. Copper Solubility(3)



REACTIONS:

$Zn(OH)^+ = Zn^{++} + OH^-$	$K = 9.1 \times 10^{-6}$
$Zn(OH)_2\downarrow = Zn^{++} + 2\ OH^-$	$Ksp = 4.5 \times 10^{-17}$
$Zn(OH)_3^- = Zn^{++} + 3\ OH^-$	$K = 1.75 \times 10^{-14}$
$Zn(OH)_2^- = Zn^{++} + 4\ OH^-$	$K = 8 \times 10^{-16}$

Figure 3. Zinc Solubility (3)



REACTIONS:

$Pb(OH)^{+} = Pb^{++} + OH^{-}$ $\quad K = 1 \times 10^{-6}$

$Pb(OH)_2 \downarrow = Pb^{++} + 2\ OH^{-}$ $\quad Ksp = 1.1 \times 10^{-20}$

$Pb_4(OH)_4^{4+} = 4\ Pb^{++} + 4\ OH^{-}$ $\quad K = 1.8 \times 10^{-37}$

Figure 4. Lead Solubility (3)

pH 9 - 9.5 - maximum removal of copper as $Cu(OH)_2$

pH 10 - maximum removal of zinc as $Zn(OH)_2$

In practice, it is unlikely that such a sequence would be either feasible or worthwhile. In cases where the theoretical relationships apply, it is probable that better overall results and reliability would be achieved by closely controlling the pH at 9.5 to 10. In this way good copper and zinc precipitation should be achieved with only slightly less efficient removals of iron and lead.

Ferric iron precipitation commences at pH 3 and is complete by about pH 8. Harrison (4) reports that total ferrous removal is achieved at pH 9.5 but other sources (3) suggest that higher pH values may be required as indicated by the superimposed Fe^{++} solubility line on Figure 1.

Other factors precluding the derivation of absolute values include:

- The effect of mixed metal hydroxide complexes of the general form $(M_1)_a(M_2)_b(OH)_c \cdot nH_2O$ is difficult to predict. Solubility product calculations can be applied accurately only if the ratio of concentrations of the precipitating substances is stable. This is unlikely in most practical applications.
- Data on ampholytes are limited but, where available, such data have been used in the derivation of Figures 1 to 4. The assumption that all indicated ampholytic species of a metal will exist in a solution is conservative. For example, in the case of copper it has been assumed that $Cu(OH)_2$ precipitates, and $Cu(OH)^+$, $Cu(OH)_3^-$, and $Cu(OH)_4^=$ remain in solution.
- Chelation of metal ions by organic compounds in the tailings pond can further influence actual ion concentrations.

4.1.2 Neutralizing reagents

Reagents which have been used for neutralization of acid mine water include:

- limestone,
- lime,
- sodium carbonate, and
- sodium hydroxide.

In the iron ore industry, where flotation is practiced, the circuit is quite often run at a pH of 9 - 11.5. For effective flocculation of slimes in tailings the pH should be neutral. The neutralizing agent most commonly used is sulphuric acid.

The relative costs and advantages of these reagents are summarized in Table 3. This information was developed on materials costs and supplies at a particular location in New Brunswick. Transportation costs, reagent purity, and the availability of materials may provide a different cost analysis in other parts of the country. It is evident that on a cost basis alone, limestone and lime are the most attractive, with limestone being the cheaper when compared in terms of relative basicities. The effect of dolomite content has not been considered but can be a major factor. Several serious disadvantages are associated with the use of limestone, particularly its inability to produce pH's higher than about 7 and its tendency to produce a surficial layer of gypsum ($CaSO_4$) and gelatinous metal hydroxides, which reduces its reactivity unless mechanically removed by sparging or tumbling. Lime is, therefore, the most common reagent used for pH adjustment in base metal mine effluent treatment and results in the metal being precipitated as the hydroxide.

In certain instances it is advantageous to consider the use of mixtures of limestone and lime. In such cases limestone is applied initially with final pH adjustment made with lime. The factors which have to be assessed include:

(i) unit reagent costs and daily tonnage requirements;
(ii) availability of supply;
(iii) reaction period necessary for neutralization (limestone can require up to 48 hours contact before the reaction is complete);
(iv) capital and operating costs of dual materials handling system;
(v) sludge handling and stability;
(vi) process control; and,
(vii) freight costs for reagents.

TABLE 3. ALKALI CHARACTERISTICS

Reagent	Formula	Basicity Factor*	Approximate Cost (¢/lb)	Relative Cost/ Unit Basicity (cents)	Relative Advantages and Disadvantages
Limestone	$CaCO_3$	1	0.4	0.4	Suitable for pH < 7 only. Lower reactivity than lime. Potential surface coating problems with gypsum. Handling costs may be relatively high - crushing, high bulk storage, etc. High CO_2 production.
Lime	$Ca(OH)_2$	1.75	1.25	0.71	High reactivity - relatively easy bulk handling, high pH attainable.
Ammonium Hydroxide	NH_4OH	2.85	8	2.80	Nitrogen nutrient enrichment has eutrophication implications in some regions. NH_3 toxic to fish at high pH and low DO.
Sodium Carbonate	Na_2CO_3	0.91	3	3.30	Less basic yet more expensive than limestone or lime. High CO_2 production.
Sodium Hydroxide	NaOH	1.25	5	4.0	Cost prohibitive - very fast reacting, complete pH range effectiveness.

* $CaCO_3$ = 1 (100% utilization of available alkalinity assumed)

Finally, it must be emphasized that the reactivity and thus the cost/effectiveness of different sources of lime and limestone vary tremendously. Generally, dolomitic limestone and high magnesium lime are less reactive than low magnesium sources.

Reactivity should generally be assessed on the basis of available CaO or $CaCO_3$. It is recommended that each application be individually assessed.

It should be noted that metals precipitated by both limestone and sodium carbonate may be in the form of basic metal carbonates; these may be less soluble than the equivalent hydroxides. Sodium carbonate also has the advantage of dispersing slimes that might otherwise float on the surface of the tailings pond and be discharged with the overflow.

The use of ammonia for neutralization is not recommended. Ammonia is an acutely toxic substance even at low concentrations and it is the recommendation of this working group that the use of ammonia for neutralizing acid wastewater be prohibited.

4.1.3 Point of addition

Some basic observations may be made with respect to the point and manner of addition of the neutralizing reagents. Both lime and limestone require a finite reaction time before the neutralizing capacity is fully realized. The required reaction time is very much larger in the case of limestone. This must be taken into account in the original process design, which must establish conditions of intimate contact between the reacting species for as long as is necessary. Clearly this is not achieved if the neutralizing agent is allowed to settle out in a tailings pond or lagoon before it has reacted with the bulk water phase. It may be necessary to provide vessels or use a slurry pipeline or launder as reaction chambers.

4.2 Ferrous/Ferric Oxidation

In order to precipitate ferrous hydroxide a solution pH of 9.5 is required. On the other hand, ferric iron precipitates sufficiently by pH 4.5, although the minimum level as previously indicated is reached at a pH of 8. Thus, there are substantial potential advantages in being

able to oxidize ferrous iron to the ferric form and complete the precipitation at lower pH values. Both chemical and biological oxidation processes have been evaluated. The general equation:

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (18)$$

describes the reaction.

4.2.1 Chemical oxidation

Ferrous iron may be oxidized by atmospheric oxygen. The reaction is strongly pH dependent and occurs almost instantaneously (less than 1 minute) at pH values greater than 7.2. At a pH of 6.5 the reaction takes in excess of 1000 minutes. See Table 4.

The importance of the pH has a major cost impact on two interrelated factors: the size of the oxidation reactors; and, the neutralizing agent used for pH adjustment. If the cheaper limestone is used, then a substantial equilibration period is required to approach, if practical, pH values in excess of 7. Thus, large reaction chambers would be required for both neutralization and oxidation. Alternatively, lime could be used to provide rapid neutralization to a pH level sufficient for almost instanteous oxidation. The attendant implications with respect to sludge production and handling are discussed in Section 4.5.

In the majority of installations treating solely iron bearing acid waters lime or limestone/lime combinations are employed. Different cost evaluations must be applied to waters containing dissolved zinc, nickel, etc. In these cases pH values in excess of 9 will be required to precipitate the metal hydroxides. Consequently, lime handling facilities will be required independent of what material is used to facilitate the iron oxidation process.

4.2.2 Biological oxidation

Biological oxidation of ferrous iron can be effected by the acidophilic bacterium *Thiobacillus ferrooxidans*. The process consists of controlled bacterial oxidation in a balanced nutrient medium. The process is conducted under acid conditions in the range of pH 1 to 4. The potential advantage of this process is that ferrous iron oxidation is carried out under acid conditions, and thus the converted ferric iron

TABLE 4. DETENTION TIMES (MINUTES) REQUIRED TO OXIDIZE FERROUS IRON (Temperature 10°C)

pH	100 mg Fe/l	500 mg Fe/l	2500 mg Fe/l
5.0	7.8×10^5	1.1×10^6	1.4×10^6
6.0	7.8×10^3	1.1×10^4	1.4×10^4
7.0	7.8×10^1	1.1×10^2	1.4×10^3
8.0	7.8×10^1	1.1×10^0	1.4×10^0

TABLE 5. FERROUS IRON OXIDATION RATES AT VARIED INITIAL Fe^{++} CONCENTRATIONS AND TEMPERATURES

Initial Fe^{++} Conc. mg Fe/l	Temperature °C		
	10	20	35
10	0.001*	0.003	0.003
100	0.009	0.013	0.018
500	0.011	0.035	0.053
1000	0.017	0.040	0.080

* oxidation rate g Fe/l/hr

may be precipitated at pH values readily attainable through limestone neutralization. Completely stirred tank reactors (CSTR) can meet process requirements. However, the bacteria do not possess satisfactory auto or induced flocculation characteristics. This means that clarification and sludge recirculation cannot be practiced, with the result that bacterial populations are limited by those generated in a single pass oxidation process. If bacterial populations could be increased then the kinetics of the process would improve proportionately. This has been achieved through the use of fixed film reactors. In this approach, bacteria are developed on inert surfaces and exposed to the liquid. As the population increases, so does the number of bacteria exposed to a unit volume of iron bearing wastewater. Both packed column and biodisc treatment processes function in this way, with the biodisc exhibiting a higher efficiency than the packed column.

The process is first order dependent on the ferrous iron concentration and oxygen pressure, and directly proportional to the second power of the hydroxide ion concentration.

Oxidation rates are also strongly temperature dependent at any given pH. See Table 5. This results in residual ferrous iron concentrations that are too high and thus still require pH elevation to 9.5 for complete removal. This is especially the case at low temperatures, i.e. less than 5°C. Further process development is underway.

4.3 Co-precipitation and Adsorption

Co-precipitation is a phenomenon associated with the precipitation of one component from a multi-component system. Component 'A' may be converted to an insoluble form and in so doing may remove a fraction of component 'B' from solution. Under equilibrium conditions component 'B' should have remained in solution.

This phenomenon may be employed advantageously in the precipitation of metal hydroxides. Rapid pH adjustment, resulting in maximum instantaneous hydroxide formation, should result in increased co-precipitation effects, i.e. removal of dissolved materials. This would be in comparison with gradual addition of neutralizing agents and sequential equilibration. The precipitate of calcium sulphate from saturated solutions may also be effective in this regard.

The co-precipitation of radium with barium sulphate is considered in Section 4.8.

Chemical and physical adsorption processes can also be used to advantage in heavy metal removal. Both siliceous and calcareous materials in tailings exhibit affinities for dissolved heavy metal ions. Silica has a zero point of charge in the range of 3 to 4 pH units. At higher pH values it is negatively charged and will adsorb heavy metal ions through electrostatic adsorption. This would also apply to oppositely charged particulates, such as hydroxide particles. This property may be exploited by bringing siliceous gangue into contact with acid waters prior to neutralization. There would probably be a supplementary benefit through improved hydroxide settlement characteristics and sludge consolidation.

Calcareous gangue would act in a manner similar to siliceous materials. It would also effect pH neutralization and hydroxide precipitation. With both classes of materials there would be a finite adsorption capacity which, in practical terms, could not be regenerated. The long term stability of the absorbed contaminants must also be considered. The data available at this time are limited but since the processes are based on ion exchanges it is reasonable to suppose that the absorption is reversible under certain conditions. If large volumes of material are likely to be used in this manner, then stability tests should be run under a variety of field conditions. It should also be recognized that some ions are more easily adsorbed than others. Figure 5 lists data for adsorption on clay of small amounts of metal ions in the presence of large amounts of calcium and sulphate.

4.4 Flocculation/Clarification

In the heavy metals removal process, precipitated hydroxides must be separated efficiently. Gravity sedimentation is universally employed, generally in stilling basins provided by tailings impoundments or lagoons and more rarely in mechanical clarifiers/thickeners. The design and operation of these units is considered in Section 5.

In the majority of cases the hydroxide precipitates are highly flocculated, possess excellent settling characteristics and provide low residual particulates in the supernatant under quiescent conditions.

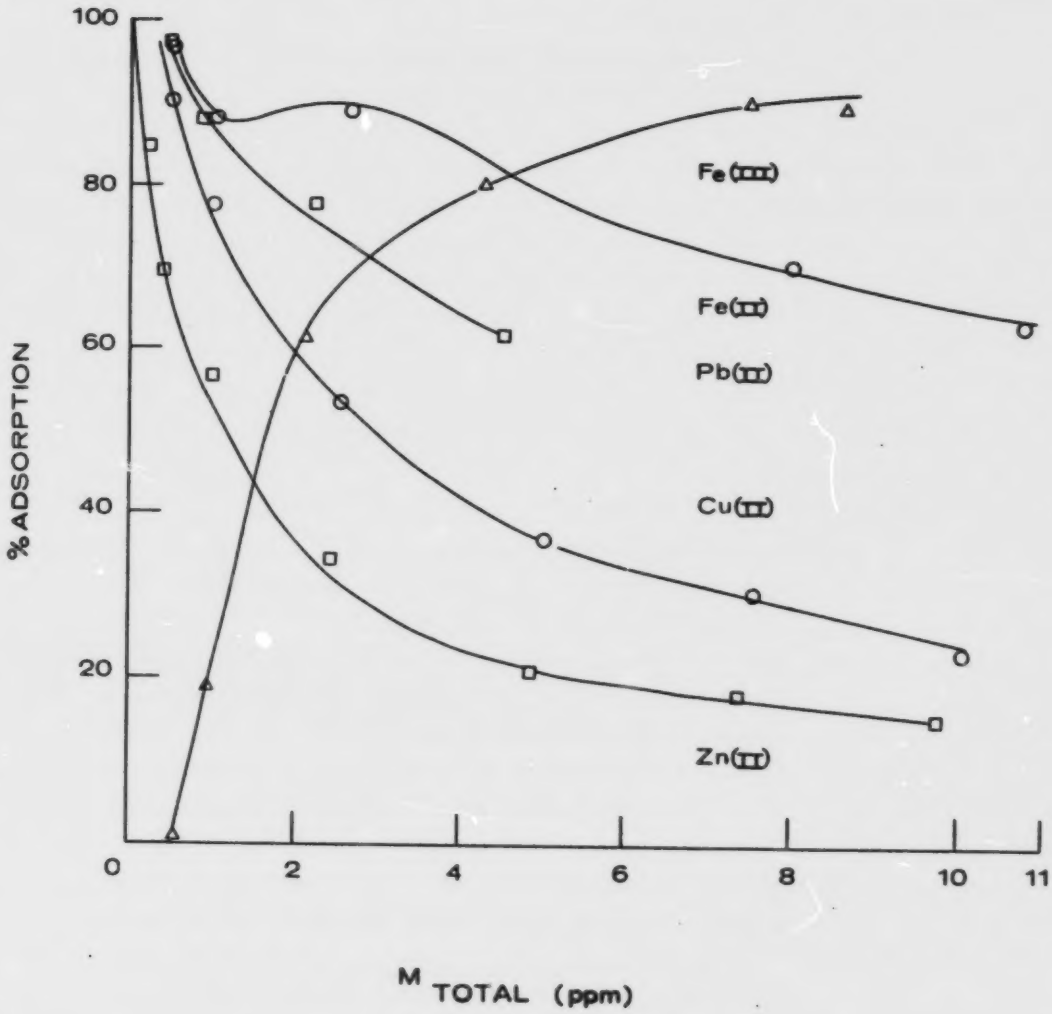


Figure 5. Metal Ion Adsorption on Clay(5)

The basic factors affecting the settling characteristics are the density of the particulates and the occupied volume. A high proportion of sludge will result in a rapid transfer from free settling to hindered settling, or even zone compaction.

Although by far the great majority of the metals settle rapidly in the flocculated mass, improvements in supernatant quality have been recorded for settling periods of up to three days in the laboratory. This has been attributed to initial supersaturation and gradual equilibration of the hydroxides, with consequent precipitation and sedimentation.

In certain instances the occurrence of pin point, near colloidal flocs with poor settling and supernatant characteristics has been reported. This is especially predominant when low total metal concentrations, in the order of 25 mg/l, are precipitated. Also, exposing well flocculated materials to high shear rates e.g. centrifugal pumps, can result in floc degradation with similar results on settling and supernatant clarity.

When these conditions exist, the flocculant characteristics of the precipitates can be improved through the following:

(i) Recirculation of the settled solids will increase interparticle collision frequencies and thus increase the rate and extent of flocculation.

(ii) Collision frequencies may be increased by gentle mixing; conventional design considerations used in potable water treatment would be applicable.

(iii) Organic flocculants would be effective in improving the efficiency of adhesion of interparticle collisions. It is hypothesized that cationic substituted derivatives of polyacrylamide would be most efficient, although polyethyleneimine could possess the additional advantage of scavenging trace metals from solution through chelation. Moderately hydrolysed charboxy' substituted polyactylamides would be applicable if sludge conditioning was the dominant concern.

4.5 Sludge Characteristics

The metal hydroxide sludges produced in a wastewater treatment process represent a highly concentrated stream of contaminated material.

It is imperative that they be efficiently separated from the purified water and disposed of in such a fashion that they will never re-enter the environment. As the majority of mining operations providing treatment to acid waters use the tailings impoundment as a settlement zone and sludge collection device, this is not recognized as a major problem by the industry. However, the problem can assume striking proportions to those employing separate lagoons for treatment. Also, the advent of mechanical equipment treatment systems will further accentuate the problem. To set the problem in focus, the waste sludge flow from a system treating a concentrated acid water may constitute up to 30% by volume of the raw feed water. At one mine this is equivalent to 9 cu ft of sludge per ton of mill capacity or 50% of the tailings volume.

4.5.1 Basic properties

The basic characteristic of metal hydroxide sludges is their loose fluffy appearance. On standing they consolidate into a gelatinous thixotropic mass that rarely exceeds 2 to 3% solids by weight. The very low density is caused by chemically bound water which resists conventional physical means of dewatering. It is suggested that the water is attached mainly through hydrogen bonding. If the solids concentration of the waste sludge could be increased, then the physical problems of sludge handling and storage would be reduced. Only a freeze/thaw technique appears to hold potential for the dewatering of the low density sludges. In the freezing step the bound water is "stripped" from the hydroxide to form ice crystals. When thawed the water melts and does not rehydrate the precipitates. The resultant sludge consists of comparatively coarse particulates which settle readily to 30% by weight solids. Such a process would be most applicable in those areas that could rely on natural freezing. It is noted, however, that in one location, faced with the disposal of aluminum hydroxide sludges with similar characteristics, a mechanical freezing plant was justified for full scale application.

A different approach is employed in the "high density sludge" process developed by the Bethlehem Steel Corporation. In this method , sludge is returned from a final clarifier and blended with lime before being processed through a chemical ferrous oxidation reactor with the

raw acid water. The waste sludge may be thickened to up to 50% solids by weight. The densification process is dependent on Fe^{++}/Fe^{+++} ratios and its effectiveness in the presence of other heavy metals has not been established. Although the densification process has been attributed to an ion exchange mechanism, this is in dispute.

Certain extremely acid waters have been reported with sulphate concentrations in the order of 20,000 mg/l. In the presence of calcium ions, introduced through lime or limestone, massive calcium sulphate precipitation will occur. This will dramatically improve the sludge concentration. Sludge densities in excess of 35% solids by weight have been achieved.

Similar benefits are reported when a limestone produced sludge is compared with a straight lime sludge. The combined influence of compaction through unreacted limestone particulates, adsorption on the surface of these particles and the probable formation of dense basic carbonates assist in producing a more consolidated sludge. Heat treatment of precipitated ferrous hydroxide to 80°C has the effect of converting it to the dense magnetite form. This process has not been conducted on a demonstration scale.

4.5.2 Sludge stability

The stability of the sludge with respect to the release of metals is generally indicated by the solubility relationships presented in Figures 1 to 4.

If sludge is stored in surface lagoons it will come into contact with precipitation. Rainwater consists of a weak solution of carbonic acid with typical pH values ranging from 5 to 6 units. In industrialized areas pH values as low as 3.2 to 3.5 have been measured in rainwater and snow and are attributed to the presence of sulphur dioxide. Under equilibrium conditions rainwater will redissolve many heavy metal hydroxide sludges, especially zinc, nickel, ferrous and, to a lesser extent, copper hydroxides. Only ferric iron precipitates may generally be considered to be stable when exposed to the atmosphere. The rate of equilibration is slow and may mask the immediate impact of the process under practical conditions. Nonetheless the data indicate that either (a) the sludge must be converted into a completely stable form; or, (b) affected precipitation must be collected and treated; or, (c) sludge must be disposed of so that

it does not come into contact with atmospheric precipitation; or, (d) the metals contained in the sludges must be recovered.

Table 6 lists data illustrating the problem. A sludge was formed using lime neutralization of water from a Cu-Pb-Zn operation. The treated water was of high quality. The sludge formed was then leached for several days at the pH values shown. Even at pH 5 significant amounts of Cu and Zn are leached.

TABLE 6. DISSOLUTION OF Cu-Pb-Zn SLUDGE (14)
(mg/l)

pH of Leach Solution	4.0	5.0	7.0
Cu	1520	47	0.3
Zn	2330	570	5.3
Fe	4.7	0.2	0.5
Wt. Loss (%)	4.0	1.6	1.2

Various sludge conversions to stable forms have been proposed. They include the formation of stable carbonates and silicates, as well as the use of organic gels. The feasibility of applying these techniques to sludges containing zinc, nickel etc. has not been demonstrated. The treatment of contaminated sludge runoff implies a never ending treatment process. Underground disposal of sludge has not been demonstrated in Canada, although the disposal of ferruginous sludges in abandoned mines has been employed in the United States. Zinc and iron have been recovered from sludges at one location in Germany but no applications are reported in Canada.

4.6 Effluent Stability

The stability of effluents from mining operations should be such that no adverse chemical or biological conversion of the compounds contained in the effluents will occur in the receiving environment. The two basic sources of effluent instability are thiosalts and milling reagents.

4.6.1 Thiosalts

The origin of thiosalts in mining effluents is described in Section 3. The impact of these materials on ambient water quality can be pronounced. Biochemical oxidation of thiosalts with various species of *Thiooxidans* bacteria in the receiving stream results in the formation of sulphuric acid and consequent pH depression. Although the manifestations of this phenomenon have been recognized for a long time, the cause has been established only during the last few years. Recent evaluations indicate that the problem is much more widespread than hitherto suspected. Three basic approaches have been advocated.

(a) Biochemical Oxidation

Bacterial action by a group of autotrophic aerobic bacteria can convert sulphur and its reduced compounds to sulphate. Table 7 indicates several species and their characteristics. Although some recent development work has been undertaken with the bacterium *Thiobacillus thioparus*, most data are available for *Thiobacillus thiooxidans*. The properties of the latter species are considered further.

The optimum conditions for bacterial oxidation are a pH of 3.5 and a temperature of 35°C, in the presence of adequate nutrient supply, oxygen etc. Both completely stirred tank and fixed film reactors are capable of providing the necessary process conditions as described in Section 4.2.2.

A CSTR design has been proposed by Schmidt (7) which incorporates a residence period of six days and is capable of completely oxidizing 1000 mg/l of thiosalts. This would utilize oxygen transfer rates of 5,700 lb/thousand gallons*. If such a process design were to be applied to Canadian mining conditions it would necessitate an outside lagoon or aeration basin which would operate at temperatures of near 0°C in the winter months. The reaction rate of the bacterial oxidation process tends to zero under these conditions and thus would be incapable of providing effluent stabilization in a practicable manner. Field data have confirmed this.

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* Unless otherwise noted, gallons referred to in this report are imperial gallons.

TABLE 7. CHARACTERISTICS OF THE *THIOBACILLI* (7)

Name	Substrates Utilized Other than Thiosulphate	pH Characteristic	Remarks
T. thiooxidans	Sulphur Tetrathionate	Optimum pH 2.0 to 3.0 Range 1.0 to 6.0	Acidophilic; oxidizes thiosulphate rapidly to sulphate.
T. ferrooxidans	Ferrous iron Sulphur Trithionate Tetrathionate	Optimum pH near 3.5 Range 2 to 6	Acidophilic; unable to use sulphur rapidly. Optimum pH for oxidation of sulphur compounds is apparently pH 4 to 5.
T. concretivorus	Similar to *T. Thiooxidans* but differs principally in that it can use both ammonia and nitrate.		
T. thioparus	Sulphur Trithionate Tetrathionate Dithionate	Optimum pH near neutrality	Oxidation of substrate causes the medium to become acid.
T. denitrificans	Sulphur	Optimum pH near neutrality	Under anaerobic conditions uses nitrate as a terminal respiratory electron acceptor.
	Cultivated aerobically this bacterium is indistinguishable from *T. thioparus*.		
T. thiocyanoxidans	Thiocyanate Sulphur Sulphide	Optimum pH near neutrality (pH 6.8 to 7.6	Produces acid, oxidizes thiosulphate rapidly.
T. novellus	Various organics	Optimum pH near neutrality	Grows slowly, produces acid. Of all the above *thiobacilli* this is not an obligate autotroph but a facultative autotroph.

Note: All the *thiobacilli* oxidize thiosulphate to sulphate although the precise pathways have not yet been agreed upon.

Fixed film reactors show the same trends in oxidation kinetics but, due to their higher microbial population, exhibit faster and more complete reaction per unit reactor volume. These reactors are at the developmental stage and possess a high potential for in-plant treatment of warm streams containing high concentrations of thiosalts. Recent data have indicated that the oxidation reaction is now always carried through to the sulphate, and that intermediate oxidation products of the polythionate class may be present in significant quantities in process effluents. The causes and significance of this have not been established.

It must be emphasized that, while thiosalts may be found in many mining wastes in sulphidic areas, the concentrations may not be sufficiently high to warrant the installation of specific treatment operations to stabilize them. In many cases, the oxidation provided by normal retention times in a tailings pond may be sufficient without seriously lowering the pH in the system due to thiosalt oxidation. While such removal rates may be reduced during the winter months, it must also be borne in mind that the rate of biological oxidation of the residuals in the receiving streams will also be at a low level and the impact of small thiosalt residuals in such cases may not be significant.

(b) Chemical Oxidation

The chemical oxidation of thiosalts may be achieved through the use of chlorine, ozone, sodium chlorate, sodium hypochlorite and hydrogen peroxide. A cost analysis (see Section 5.4.6) indicates that oxidation using chlorine and ozone is most feasible although more expensive than bacterial means. It is worthwhile noting that the oxidation of thiosulphate by atmospheric oxidation is theoretically possible. Some evidence suggests that the catalytic influence of cobalt, nickel salts etc. may be dominant. Unfortunately, this process has not yet been successfully demonstrated.

The following equations have been proposed to describe the oxidation of thiosalts by chlorine and ozone.

Chlorine:

$$S_2O_3^{=} + 4Cl_2 + 5H_2O \rightarrow 2SO_4^{=} + 10H^+ + 8Cl^- \qquad (19)$$

Ozone:

either $2S_2O_3^{=} + 5O_3 + 2H_2O \rightarrow 4SO_4^{=} + 7/2O_2 + 4H^+$ (20)

or $5S_2O_3^{=} + 2O_3 + 7O_2 + 5H_2O \rightarrow 10SO_4^{=} + 10H^+$ (21)

All chemical and biological oxidation processes for thiosalts will result in acid formation and reductions in the pH of the process liquor. This may be of advantage through the precipitation of elemental sulphur.

$S_2O_3^{=} \rightarrow SO_3^{=} + S$ (slow) (22)

$SO_3^{=} + \frac{1}{2}O_2 \rightarrow SO_4^{=}$ (fast) (23)

$6H^+ + 5S_2O_3^{=} \rightarrow 2S_5O_6^{=} + 3H_2O$ (24)

Equations (22) and (23) indicate that substantial effluent stabilization may be expected through sulphur precipitation under acid conditions. At pH 3 up to 80% yield as elemental sulphur has been reported. Equation (24) indicates that higher thionates, probably in the form of polythionates and sulphurous acid, are formed. Thus, after complete precipitation of sulphur, residual concentrations of polythionates will exist which may require stabilization.

It may be concluded that both chemical and biological oxidation processes will be influenced by the dissociation of thiosalts under acid conditions.

(c) Addition of Buffer Solutions

The addition of sodium bicarbonate, soda ash, lime or other chemical buffers to the effluent stream provides a possible means of counteracting acid generation by thiosalt oxidation in the receiving stream. Costs, which are summarized in Section 4.1.2, are relatively high and the concept of applying chemical treatment in the receiving stream is not encouraged.

4.7 Process Reagent Stabilization

Although oxidizable organic process reagents are frequently inherently toxic materials (see Section 3.2.1) water quality problems are rarely attributed to this source. The majority of these reagents are subject to biological and/or chemical degradation under the conditions which exist in the tailings impoundment. A 30 day theoretical hydraulic

retention period is generally provided in the pool section of the tailings impoundment and it is inferred that this is sufficient for degradation to occur. In the event that a nondegradable toxic reagent is encountered, the use of a degradable alternative should be encouraged.

In certain instances, the hydrophic characteristics of many reagents may result in the formation of a monomolecular layer on the surface of the tailings pond. This may skim rapidly over the surface and report in the overflow. The provision of baffles and the use of submerged decant weirs can counteract this problem.

It should be noted that the breakdown products of nitrogen and phosphorus containing reagents may enrich the receiving stream and result in symptoms of eutrophication. Phosphates may be precipitated by the use of lime or limestone under alkaline conditions and, where acid conditions are being counteracted by these materials, no additional treatment is generally necessary.

4.8 Radium Removal

Uranium is extracted by leaching processes of two types. Acid leaching is used in the Elliot Lake District, while carbonate leaching is employed at Eldorado because of the high natural carbonate level in the gangue. In most operatins the mine water is directed to the mill for removal of dissolved uranium and is subsequently discharged as part of the ion exchange barren solution.

The liquid barren is recombined with the washed filter cake and discharged as mill tailings. Carbonate leach mills require no additional pH adjustment since the net discharge is at pH 8-9. The acid leach tailings are neutralized with lime or a limestone-lime combination and discharged at a pH of 8-10. Since the solid tailings may generate acid, it is desirable to have excess limestone available as a buffering agent. Effluents at pH 8-10 contain very little heavy metals (after sedimentation of hydroxides) and also contain reduced levels of Ra 226 after neutralization, typically from 400-800 pCi/l. The Ra 226 in the barren solution ranges from 3000-4000 pCi/l.

Radium is removed by co-precipitation with $BaSO_4$ by adding $BaCl_2$ to the effluent in the presence of excess sulphate (typically 0.01

to 0.1 lb/ton wastewater).

$$BaCl_2 + Ra^{++} + 2SO_4^{=} \rightarrow 2Cl^- + BaSO_4 \cdot RaSO_4 \qquad (25)$$

The treatment does not remove Ra effectively if the initial suspended solids are high since barium displaces radium from the solids. The co-precipitate settles slowly and adequate lagoons are needed to reach acceptable levels in the final effluent. The sludge formed may also be unstable if the sulphate level decreases to the point where $BaSO_4$ redissolves. A low input level of Ra 226 to the $BaCl_2$ system appears to be beneficial but this result has not been specifically confirmed.

The level of Ra 226 achieved in the final effluents from the various uranium mines varies somewhat because of minor differences in treatment practice and, in particular, because of variations in the sizes of the settling lagoons used. It is difficult, however, to identify specific cause and effect relationships between the effluent levels and the various treatment parameters since there are only three case studies available in Canada at this time (23).

A detailed study and review of the data available was conducted by the Radioactivity Expert Group as a subgroup of the Mining Regulations Task Force (23). This study showed that, using data for filtered samples (3 μ filter), a monthly average level of 10 pCi/l Ra 226 could be achieved using best practicable technology.

4.9 Suspended Solids

The most obvious environmental concern of a mining operation is to eliminate the discharge of tailings into the environment. This can be achieved through the use of an appropriately designed and operated tailings impoundment area. Canadian practice in this regard is considered in Section 5.3.

Although settling rates for the tailings may be measured and used as a process design consideration, this is generally not the controlling factor dictating tailings pond design. Other considerations, such as reagent stabilization requirements, decant design, topography, etc., are usually limiting factors. This results in substantial safety margins for the settling requirements. In those instances where solids carry-over is observed, physical modifications to the side to eliminate

possible short circuiting effects, and to alter the manner of tailings deposition and the depth of the stilling basin at the decant structure, are often able to rectify the situation. If necessary, this may be augmented by improving the settling characteristics through pH adjustment or the addition of flocculating agents.

4.10 Untreated Contaminants Present in Mining Effluents

As we increase our appreciation of the conditions necessary to sustain or improve our environment, we develop a progressively more conservative approach to the allowable discharge of contaminants. In the past, crude observations of parameters such as fish mortality guided the setting of pollution control requirements. The increased awareness of sublethal effects and synergism alert one to the harmful effects of substances that were previously considered completely harmless or were not even known to be present in the effluents from mining operations. Between the identification of a problem and the development of a solution there is always a delay. When the problem is in the field of water pollution abatement from an industrial source, the onus is upon the industry to develop practicable solutions for application to that particular sector or specific location.

The materials listed below are found in mining effluents. They do not occur universally and even when they do occur it is not suggested that they automatically constitute a problem.

The one common characteristic that they possess is that there is no generally accepted means of providing treatment for them as they appear in mining effluents. The alternative approach to that of developing treatment processes is to make in-plant or process modifications to eliminate the contaminant at source.

Typical contaminants are:

(a) sulphates
(b) ammonia
(c) nitrate
(d) hardness
(e) chlorides

LIME/LIMESTONE AMD NEUTRALIZATION PLANTS

Examples of operations visited or reviewed by Randol International Ltd. during this investigation where limestone or lime were used to treat acid mine drainage were:

Lime

1) Falconbridge Sudbury Operations, Falconbridge, Ontario
2) INCO Sudbury Operations, Ontario
3) St. Joe Minerals, Balmat Operations, New York State
4) Falconbridge Onaping Operations, Strathcona Mill, Ontario
5) Kidd Creek Mines Ltd., Kidd Creek Mine, Ontario
6) Kidd Creek Mines Ltd. Timmins Mill Tailings Decant

Limestone

1) Falconbridge Onaping Operations, Moose Lake, pH adjustment.
2) Rössing Uranium Ltd.,passive neutralization of seepage.
3) Schullsburg Mine, passive neutralization by dolomitic limestone with disastrous results.
4) Gold Field of South Africa Ltd., Greenside Colliery, South Africa (abandoned due to lack of success).
5) Limestone column tests by Noranda Mines Ltd. at Heathe Steel Mine, New Brunswick.
6) U.S. Bureau of Mines, limestone neutralization process tests 1967-68 and process demo, 1982.
7) Pennsylvania Bureau of Abandoned Mines, reclamation test.

Interesting variations on the theme of lime neutralization, precipitation, and solid/liquid separation include the use of dissolved air flotation for flotation and also the Dravo Lectroclear flotation system. The latter is installed at an expensive but efficient AMD treatment plant at AMAX Molybdenum Division's Mount Emmons operations at Crested Butte, Colorado, which is described in detail in a trip report included in Appendix I.

Falconbridge Sudbury Operations

The Falconbridge integrated mine, mill, smelter, and refinery complex at Falconbridge, Ontario, has achieved remarkable improvement in effluent and environmental quality. Much of the improvement can be attributed to a change in some of the pyrometallurgical processes and also to the systems approach adopted in managing and treating water in a macro recycling system.

It would not be proper to refer to the lime neutralization plant at Falconbridge without referring to this exceptional example of what can be achieved by applying a systems approach. The Falconbridge operations at Falconbridge, Ontario, and at Onaping, Ontario, are included as trip reports in Appendix I. In addition, excellent accounts of the wastewater treatment system at Falconbridge, Ontario, are provided by MICHELUTTI (1981) and NORMAN and MICHELUTTI (?).

Here, only some details germaine to lime neutralization are summarized to illustrate an example where conventional lime neutralization works particularly well.

A new tailings area and wastewater treatment system was put into operation at the end of 1978 at a cost of around C$3 million. After the first two years of operation, the following results had been achieved.

1. Integrated air pollution control measures at the smelter complex reduced fallout contribution to metal levels in Falconbridge effluents.

2. The tailings and the polishing ponds required 13 weeks to fill their operating levels for a total of 368×10^6 Imperial gallons (1.75 million m^3).

3. The settling pond downstream of the neutralization plant has a retention time of approximately 15 days at 2,900 Igpm <u>inflow</u> (19,000 m^3/d) with a volume of 63×10^6 Imperial gallons (286,373 m^3). The settling pond, which formerly was barren wasteland, sprang to life on becoming flooded with shallow alkaline water. The prolific plant life and algae in the pond acts as a high surface area polishing pond to remove whatever metal hydroxide particles do not settle on their own.

   The inflow is made up of 1566 Igpm: (10,000 m^3/d) tailings and process water; 500 Igpm (3,300 m^3/d) groundwater; 742 Igpm (5,000 m^3/d) precipitation.

4. The average flow leaving the treatment plant during 1979-80 was 2,511 Igpm (16,000 m^3/d). The total flow discharged as a final effluent to Coniston Creek was 5,480 Igpm (36,000 m^3/d) during the same period.

5. Sulfate concentrations decrease with distance from the source.

6. pH values are 3.5 during the summer and 6.5 during the winter in the tailings ponds. This is due to the varying oxidation rates of sulfo-salts by chemical and/or bacterial action.

7. Nickel concentration in the wastewater inflow dropped considerably from 1979 to 1980 (0.7 ppm to 0.1 ppm).

8. Dissolved nickel concentrations increase downstream from the inflow as well as downstream from the treatment plant. A possible explanation was solution pickup of nickel from the bog area, the area having formerly been exposed to airborne fallout from the smelter-roaster. Nickel in the bog is not perfectly "fixed" at the operating pH.

9. The suspended solids two-year average leaving the settling pond was 5.8 ppm indicating that a clarifier is not warranted. It was estimated that it would require 65 years to accumulate 1" of sludge in the settling pond at the 1981 rate of deposition.

10. pH depression caused by organic acids in the bog area downsteam of the treatment plant was corrected by discharging excess lime.

11. The treatment plant treated 3.6×10^6 lgpd (16,400 m^3/d) at a cost of 4.6 cents per 1000 gallons \$0.01/m^3 during 1980. On average, 0.84 tons hydrated lime/d were consumed in 1980.

12. Treated alkaline wastewater has resulted in a rapid colonization of the denuded bog by aquatic plants and wildlife. As a result, the area is now a designated "Conservation Area."

13. It is concluded that conventional lime neutralization followed by polishing in a large shallow settling pond filled with aquatic plants with a very high surface area can represent an extremely economical way to adjust the pH of AMD and remove dissolved metals. There remain some questions as to nickel removal at the operating pH.

Additional information is available in the excellent papers on the subject referred to above, the trip report included in Appendix I or from:

FALCONBRIDGE NICKEL MINES LTD.
Falconbridge, Ontario POM 1S0
(705) 693-2761
John K. Weglo, Director,
Environmental Control
R. E. Michelutta, Environmental
Control Engineer

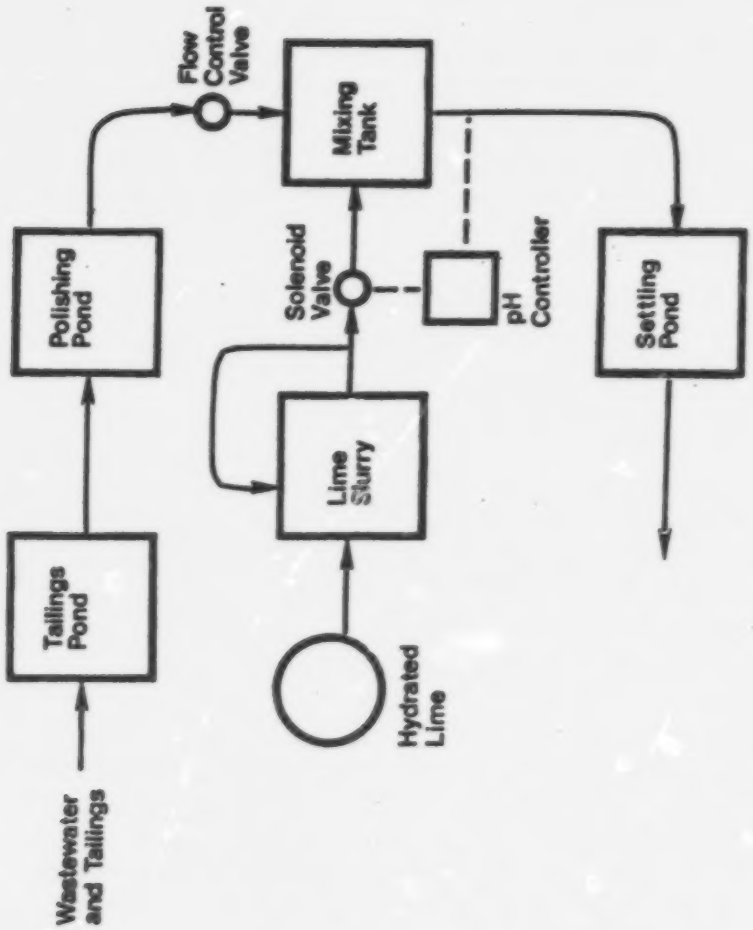

FIGURE 9 - TREATMENT SCHEMATIC

Wastewater Treatment System at
Falconbridge Ontario

East Mine Treatment Plant - Cost Analysis

(to nearest $100.00 Canadian)

	1979	1980
Labour	$ 3,900	$ 200
Supervision	$ 11,700	$ 11,500
Lime	$ 48,100	$ 23,700
Polyelectrolyte	$ 2,200	0
Building Repairs	$ 1,000	$ 800
Equipment Repairs	$ 12,000	$ 6,800
Instrumentation Repairs	$ 23,900	$ 17,100
Supplies	$ 1,800	0
TOTAL	$104,600	$ 60,100

At a flow rate of 3.6 M.G.P.D. the 1980 costs were 4.6¢ per 1,000 gallons treated.

INCO SUDBURY OPERATIONS

INCO LTD. produces 110,000 tpa nickel at Sudbury at their currently reduced capacity. Plant capacity was reduced because of environmental restriction mainly on SO_2 emmissions. INCO LTD. in Ontario operates three lime-settle plants to treat acid water. The one at Copper Cliff is part of a massive integrated water management complex.

Plant Capacity

Plant	Year Erected	Capacity	Capital Cost
Nolen Creek	1975	6.3 mm Igpd 28,600 m^3/d	C$0.69 Million
Copper Cliff	1975	60 mm Igpd 272,000 m^3/d	C$4.1 Million
Port Colbourne	1981	9 mm Igpd 41,000 m^3/d	C$5.1 Million

Plant Throughput

INCO, at the Copper Cliff plant, treats 86,000-160,000 m^3/d water from tailings seepage, decant, and runoff.

Plant Performance

	Raw Feed Water	Effluent After Treatment
pH	4.4	10.2
Cu	0.8 ppm	0.1 ppm
Ni	9.5	0.1
Fe	13.4	0.35
S/S	14.0	2.7

Sludge Properties

The sludge, at around 2% solids of which 3-4% is nickel and 0.2% Cu, is mixed with tailings in a sump pump and discharged back to the huge tailings area.

Treatment Plant Description

Incoming effluent, which includes decant solution from the main active tailings impoundment and runoff, arrives via an open ditch to a raw water well equipped with three submersible pumps, each with a capacity of 15,000 gpm.

Lime is added directly to the ditch about 150-200 feet upstream from the plant, and a considerable amount of precipitation occurs in the ditch. In the wintertime warm sewage is added to the raw water well which tends to reduce frazzle ice.

The water at pH 10 is next pumped to two EIMCO reactor clarifiers. A liquid polymer Aichem 8C26 is added just before the neutralized solution flow reaches the thickeners. The reactor clarifiers have a diameter of 135'Ø with 22' vertical sidewalls and have a capacity of 2.5 mm U.S. gallons, i.e., 9,500 m^3.

Overflow solution from the reactor clarifiers is released to the Copper Cliff stream by gravity flow. Sludge at 2% solids, of which 3-4% is Ni, gets discarded to the tailings area after being blended with the tailings. Each sludge pump can handle 450 gpm (3000 m^3/d).

The INCO water treatment plant uses EIMCO reactor clarifiers operated with a sludge blanket and rakes. To facilitate flow of solution in winter they have been designed with radial launders submerged 3 feet below the surface so that they will operate even when the surface is frozen.

Sludge Stability

The solubility of nickel reaches a minimum of around 0.075 ±0.05 ppm. Raising the pH to 10.5 increases the theoretical solubility of Ni to 0.075 + 0.05 ppm. The sludge is relatively soluble and can redissolve in the tailings dam, however the soluble Ni sludge in the precipitate is low; it is said to be lower than in the tailings themselves.

Cost of Water Treatment

C$0.30/1000g = C$0.07/m^3.

More information on the INCO Copper Cliff water treatment plant can be obtained from:

INCO LTD.
Copper Cliff, Ontario POM 1N0
(705) 682-8342
H. R. Butler, Supervisor
Environmental Control, Ontario Division

Lime Precipitation: Balmat Mine Location

The Balmat Mine location of ST. JOE MINERALS COMPANY in New York State operates an extensive complex of mines and a mill. By rerouting their underground minewater through the Edwards Mill as process water, a significant reduction in suspended solids and dissolved metals was affected as described by REILLY (1979) inserted below. Minewater is already at pH 7-8 due to the carbonate rock types.

Additional inquiries can be addressed to:

ST. JOE RESOURCES COMPANY
Mining Division
Balmat, NY 13609
(315) 287-2500
J. G. (Mike) Reilly,
Administrative Assistant

The following summary should be read in conjunction with the summary on passive AMD polishing at the Balmat Mine location in the next section of this chapter.

MINE WATER TREATMENT SYSTEM AT THE BALMAT MINE LOCATION

J. G. REILLY
ST. JOE ZINC COMPANY
MINING DIVISION
BALMAT, NEW YORK

SUMMARY

A system for reducing the concentration of dissolved metals in mine water effluents was installed and is operating successfully. The basis for this water treatment system is lime/sedimentation, and the design concept was to minimize capital and operating costs by utilizing existing process streams and facilities. This was accomplished by rerouting the waters from the underground mines to the mill for use as process water and by subsequent treatment in the existing tailings lagooning system.

INTRODUCTION

The Mining Division operates mining and milling facilities in St. Lawrence County, New York State. The final product is zinc mineral concentrate and a by-product lead mineral concentrate. The Balmat operations consists principally of #2, #3, and #4 Mines and the #4 Mill. The Mill presently processes Balmat ore as well as ore trucked in from the Edwards Mine and the Hyatt Mine, respectively eleven miles and seven miles in distance from the Balmat operation.

BACKGROUND

The present Balmat Mine water treatment system was developed for the purpose of reducing the dissolved metal content of discharged waters to presently acceptable standards.

In the period following the passage of the Clean Water Act of 1972 the Mining Division began a monitoring program to determine the characteristics of the various discharge waters. In 1974 draft discharge permits and compliance schedules were issued by the EPA. For discharges from mining facilities it was evident that "clean" in appearance would no longer constitute the norm for acceptable discharge quality.

The monitoring program indicated that the effluent from the existing tailings lagooning system was generally satisfactory under the new standards, but that the mine water discharges contained unacceptable concentrations of dissolved metals.

DEVELOPMENT OF THE MINE WATER TREATMENT SYSTEM

Laboratory testing of the discharged waters from the Balmat mines indicated that the lime/sedimentation process, which was specified by the EPA as the Best Practical Technology (BPT), could produce an effluent of acceptable quality to meet the new standards. However, the traditional concept of end-of-pipe treatment system for each mine discharge was economically discouraging when considering the cost elements for multiple installations, buildings and hardware, sludge disposal problems, and daily operating costs (chemicals, labor, maintenance, winter heating, etc.).

As an alternative to the traditional water treatment system, the plan developed and instituted for the Balmat mining complex was oriented toward making the greatest possible use of existing facilities and the minimum increase in additional operating costs.

Basically, the concept of the plan was to gather all of the mine waters together at #4 shaft, to pump to the surface, to re-use the mine water as mill process water which would provide the exposure to high lime concentration (pH 10 to 11) for precipitation of heavy metals during passage through the flotation circuit. The resulting precipitated heavy metals would then follow the path of the tailings slurry for sedimentation in the tailings treatment lagooning system. It was believed that the existing good quality of the discharge effluent from the tailings system would not be adversely affected by the additional heavy metal precipitates.

Simplified flow schematics are shown on Figures 1 and 2 for the original and for the new systems.

INSTALLATION AND OPERATION

Rock excavation began in 1975 for the new pumping station on the 1300 level at #4 Mine shaft. During the next two years the pump station (20,000 cubic feet) and the sump (150,000 cubic feet) were excavated and outfitted. The sump was designed to contain the normal expected inflow of 500 GPM for 14 to 20 hours in the event of power failure. The equipment installed at this underground pump station included three Peerless 12 stage pumps, each at 250 HP and 500 GPM, and the accompanying electrical transformers, distribution and monitoring gear. The installation began partial operation in October, 1977.

For #2 Mine, the mine water (nominally 100 GPM) was re-routed to the new #4 shaft pump station by installing 4400 feet of pipeline in the existing 1300 level drift connecting the #2 and #4 Mines. Two low head pumps were installed at the existing #2 Mine 1300 level pump and connected to the new line. This portion of the system became operational in October, 1977, at which time the existing #2 Mine pumps (to surface discharge) were permanently shut down.

The re-routing of the #3 Mine water (nominally 400 GPM) to the #4 shaft 1300 level pump station was more difficult, because the lowest level at #3 Mine is the 900 level and a new water passage route was required and was established as follows:

A ten foot wide by ten foot high drift was driven for 2000 feet on the 1300 level from the #4 Mine to a location under the #3 Mine 900 level, and several bore holes were then drilled from the #3 Mine 900 level to intersect the new 1300 level drift. Several sources of water intruding into the #3 Mine were found not to be carriers of dissolved metals, and this water was segregated for continued pumping from the #3 Mine 900 level pumps to the surface for direct discharge. A number of problems delayed the #3 Mine portion of the system until start-up in March, 1978.

The surface installations for the mine water treatment system began in the Fall of 1976 by starting the excavation for the three-acre surge pond whose purpose was for receiving the mine water and for mill water supply. This pond, located in a depression adjacent to #4 Mill, was also designed to intercept floor wash from the mill as well as run off from the ore storage area, an improvement which eliminated potentially troublesome discharges to the plant storm sewer system. These surface facilities became operational in October, 1977.

The surface handling of mine water was designed for flexibilities of operation so that mine water pumped could be either stored in the pond or diverted directly (after liming) to the mill tailings system. The system's storage capability also provided the scheduling flexibility so that mine pumping can avoid electric power peaking.

A simplified flow schematic is shown at Figure 2.

OPERATIONAL RESULTS

The following observations are made as a result of the experience to date with the Balmat mine water treatment system:

Based on present standards, acceptable quality discharge effluents can be achieved at this location without the need for traditional end-of-pipe treatment facilities.

Concurrent sedimentation of tailings particles along with the flocs of precipitated heavy metals is believed to exhibit a superior performance to the sedimentation characteristics of the flocs by themselves.

Operating costs have been minimized by making use of the processing streams and the equipment already functioning.

SIMPLIFIED WATER FLOW CHARTS

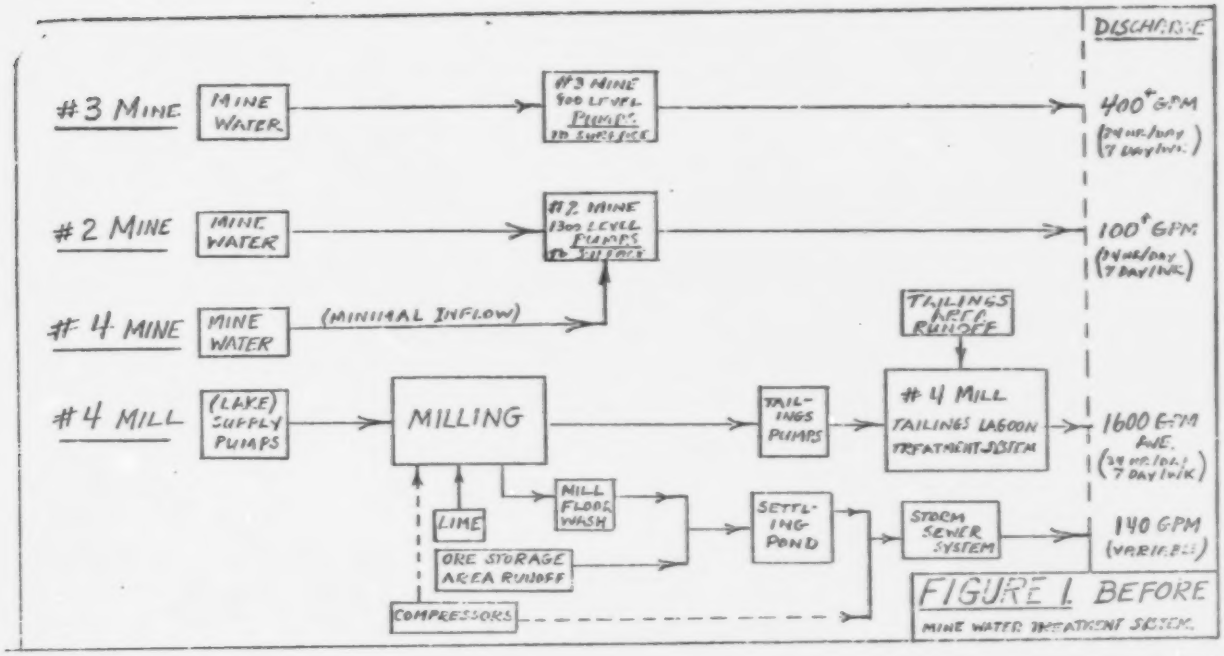

FIGURE 1. BEFORE
MINE WATER TREATMENT SYSTEM.

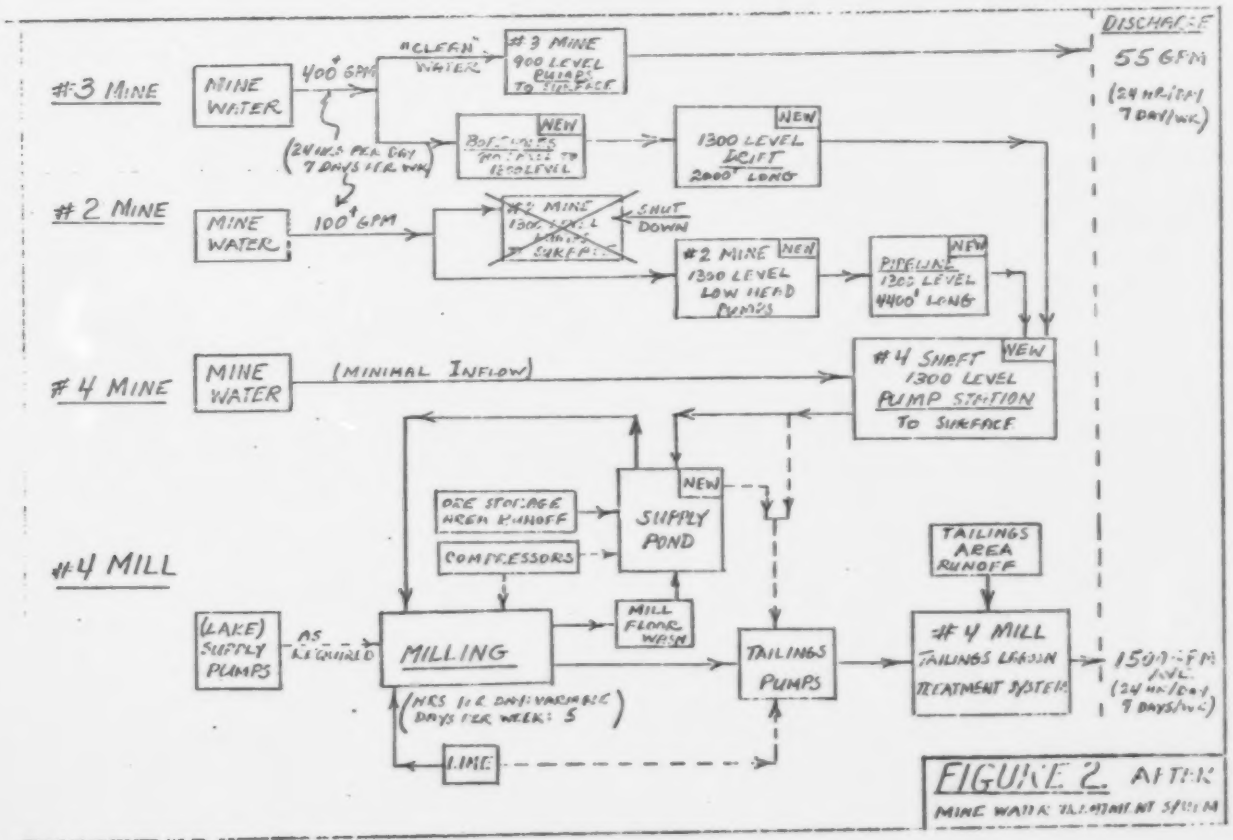

FIGURE 2. AFTER
MINE WATER TREATMENT SYSTEM

JGR 11/6/77

Two former direct discharges to the surface waters have been eliminated completely and another one has been significantly reduced.

A substantial reduction has been made in the quantity of fresh water required for the milling process with no apparent detrimental change in the mill metallurgy.

Table I shows the quality of the discharged water resulting from the completed water treatment system as compared to the former mode of operation.

Table II compares the discharge loading to surface waters for suspended solids and for zinc, indicating reduction of 81% and 92%, respectively, over the former system.

TABLE I

SELECTED DISCHARGE EFFLUENT WATER QUALITY DATA
BEFORE AND AFTER INSTALLATION OF THE MINE WATER TREATMENT SYSTEM
(in mg/l except flow & pH)

	GPM (NOMINAL)	SUSP SOLIDS	pH	Zn	Pb	Cu	Fe	Mn	Cd	REMARKS
#4 TAILINGS EFFLUENT										
Before	1600	6.	7.3	.13	.08	.06	.2	.3	<.01	1976 Ave. Used
After	1500	4.	7.9	.15	.03	.03	.2	.2	<.01	See Note 1.
#2 MINE DISCHARGE										
Before	100+	10.	7.0	11.0	.15	.01	.6	.4	.04	1976 Ave. Used
After	0	(discharge eliminated)								
#3 MINE DISCHARGE										
Before	400	46.	7.5	4.0	.05	.01	1.6	.1	.01	1976 Ave. Used
After	55	<1.	7.8	.34	.01	<.01	.1	<.1	<.01	See Note 2
#4 MILL AREA TO STORM SEWER										
Before	140	20.	7.5	1.4	.05	.06	.5	.1	<.01	1976 & 1977 Used
After	0	(discharge eliminated)								
PERMIT LIMITS										
Average	---	20.	---	.3	.1	---	---	---	---	
Maximum	---	40.	6-9	1.0	.2	.2	2.	1.	.1	

NOTE 1 Averages based on 3 months prior to labor strike and 3 months after.
NOTE 2 Averages based on 6 month period May through October, 1979

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TABLE II

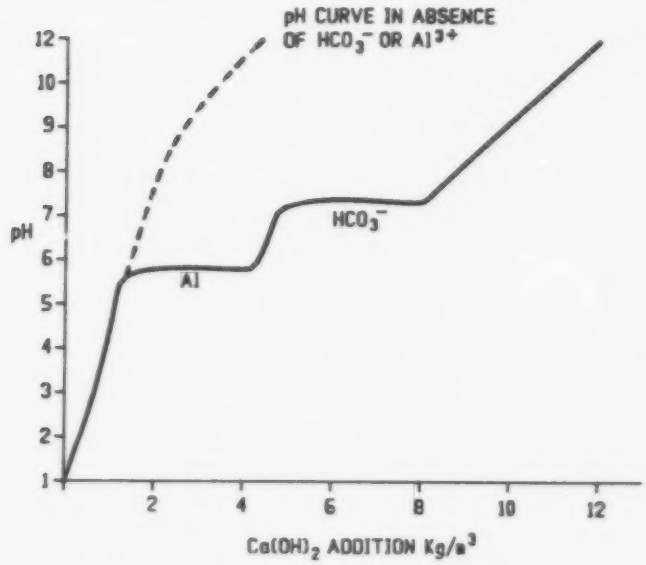
EFFLUENT LOADING TO THE SURFACE WATERS

The values given below are calculated from the data shown at TABLE I and represent the loadings to the surface waters before and after installation of the Mine Water Treatment System.

(IN POUNDS PER DAY)

DISCHARGE LOCATION	SUSPENDED SOLIDS		ZINC	
	Before	After	Before	After
#4 Tails	115	72	2.5	2.7
#2 Mine	12	0	13.2	0
#3 Mine	220	1	19.2	0.2
#4 Mill Area	34	0	2.4	0
TOTAL	381	73	37.3	2.9
Percent reduction	---	81%	----	92%

AFFECT OF CO_2 AND Al^{3+} ON LIME CONSUMPTION



LIMESTONE NEUTRALIZATION: FALCONBRIDGE STRATHCONA MILL

The Falconbridge Strathcona Mill is located at Strathcona, Ontario, a thirty-minute car drive north of Sudbury. A more accurate company-corrected description is included in Appendix I. Through contact with tailings and AMD from the Fecunis Mine and now closed Fecunis Mill, the water in Fecunis Lake in 1984 contains 14 ppm-15 ppm Ni in solution. This water would normally drain into Moose Lake and then to the effluent discharge point for the system.

Moose Lake water was used as process water for the Strathcona Mill. However, since the Moose Lake water is treated with limestone, it contains a high level of dissolved carbonates which consumes flotation reagents.

Rather than the former arrangement of using Moose Lake water in the Strathcona Mill which then is decanted back to Moose Lake after being discharged with Strathcona Mill tailings, and rather than discharging Fecunis Lake water to Moose Lake where it adds significantly to the nickel load, Falconbridge now draws nickel contaminated millwater for the Strathcona Mill from Fecunis Lake. In this way, the nickel in this water is precipitated at pH 10 onto Strathcona Mill tailings which decant to the Moose Lake at less than 1 ppm Ni. Since one of INCO's mines in the area contributes to AMD generation in Fecunis Lake, they contribute a payment to Falconbridge for treating their share of the water.

In the future, the south end wall of Fecunis Lake will be raised by a 5 foot dam causing the lake drainage to flow in reverse toward a new offtake for Strathcona Mill water which will allow water to be taken from the lake immediately adjacent to the mill which will reduce pumping costs significantly.

This is an example of the benefits achievable when a systems approach is employed.

NEUTRALIZATION AND DISSOLVED AIR FLOTATION (DAF)

BOSMAN (1983) pointed out that in some cases, even where HDS can yield a dense sludge, say 39% solids, HDS may still not be the most practical approach. One example of this was AMD from a pyrite mine which, when neutralized, contained only 100-200 mg/l suspended precipitate--a very low solids load. Although HDS achieved good densification, there are perhaps simpler ways to achieve clarification and low sludge volumes.

BOSMAN pointed out that because of the low settling rates of iron hydroxide particles, sometimes less than 1 m/h, solids-liquid separation by means of flotation is a logical alternative for water with such low solids loadings as mentioned above.

BOSMAN considers dissolved air flotation (DAF), electroflotation, and dispersed air flotation to be potential candidates for this job. RAMIREZ and RAMADORAI (1980) showed how molybdenum co-precipitated with ferric or other trivalent ions from AMD could be efficiently removed using DAF. DAF is discussed in greater detail in Chapter 12.

LIMESTONE NEUTRALIZATION

Because of limestone's general local availability and lower cost, there would be a potential economic advantage in using it for neutralization of acidic effluents. If it is not in general use, however. The reasons for this are:

- Limestone is less effective than lime for acid neutralization. Assuming stoichiometric consumption, limestone can only neutralize 57% of the acid that the same weight of lime can neutralize.

- Stoichiometry of limestone neutralization is not as complete as when lime is used. This is because the limestone particles used become coated by a passivating coating of $CaSO_4$ and other precipitates including silica (possibly as calcium silicate).

- Limestone neutralization reactions are not as fast as lime neutralization.

- Limestone addition can raise the pH to no more than 7-8 which is too low to reach the minimum solubility of many base metals which require pH up to 10.

In some parts of the world, limestone is much less expensive than lime. For example, in parts of northern Ontario, limestone may be locally available whereas lime must be trucked or railed several hundred miles.

Considerable development and testwork has been undertaken to find ways to use limestone for AMD treatment. Work in the late 1960's by the U.S. BM is described by MIHOK, et al. (1968), and DEUL and MIHOK (1967) inserted below.

Advantages of limestone, other than cost in certain circumstances, are that it is safer and sightlier to handle and that under certain circumstances it may be particularly appropriate for passive systems, i.e., for treatment of acid mine drainage at worked out mines where economics do not dictate a conventional lime neutralization-oxidation-settle and clarification system such as several of those discussed above. The U.S. Bureau of Mines in particular has been very active in developing experimental and demonstration systems for use at small AMD flow sites, particularly from abandoned coal mining waste dumps and workings where iron is the most common metal contaminant in the AMD effluent. Limestone precipitated sludges often have a higher solids density than lime precipitated

sludges, albeit only around 2-3% solids. The following are accounts of limestone neutralization plants encountered during this investigation.

McDONALD and GRANDT (1981) of the PEABODY COAL COMPANY found that a combination of limestone-lime process has cost advantages with improved effluent quality and sludge settling characteristics. A full-scale neutralization plant was operated to determine the effect of retention times, sludge recirculation flow patterns, and operating pH using limestone and lime separately and in combination. The operation found that the combination of limestone and lime treatment with sludge recirculation in both treatment steps is the most economical. More details can be obtained in EPA-600/7-81-033 (PB81-172645) obtainable from the National Technical Information Service, Springfield, Virginia.

ENOXY COAL, INC., BUCKHANNON, WEST VIRGINIA

In order to inhibit AMD in parts of the West Virginia coal region, several companies, including ENOXY COAL, INC., mix a carbonate waste rock with their coal spoil. High alkalinity carbonate rock effectively prevents the pH from dropping and also removes iron from runoff and seepage water. However, as iron is precipitated, manganese present in the carbonate rock goes into solution and reaches levels of 30-130 ppm which is well over the allowable effluent limits.

Removal of manganese needs a pH over 10, and it is very difficult to remove in the absence of iron. In this case Mn:Fe ratios of 10:1 are typical. A final pH adjustment would then be needed to bring pH down to dischargeable limits 6-9.

ENOXY COAL, INC. has explored several avenues in the search for a practical way to remove manganese:

ENOXY COAL, INC.
Post Office Box 710
Buckhannon, WV 26201
(304) 472-9274
Allan Meek

To date, they had found no practical way for manganese removal. Also, since no environmental reasons have been found for manganese removal, it is possible that the limit on manganese may have been placed there originally because it is a symptom of AMD requiring treatment to remove other metals. Manganese is a problem in potable water because of the black marks it leaves on porcelain, but evidence of environmental damage has yet to be found. A movement is afoot to persuade regulators to change the rules on manganese. (Note: Stewart Herman of BETHLEHEM STEEL indicated at the RANDOL Workshop that the HDS process can be adapted for solutions with low Fe:Mn ratio.)

In the above case, the effective inhibition of AMD by limestone addition to coal spoil, itself resulted in a new effluent problem that is even more difficult to solve, namely soluble manganese.

FALCONBRIDGE LTD., ONAPING, ONTARIO

At Falconbridge's mine-mill complex at Onaping, Ontario, a limestone neutralization plant was installed to treat a flow varying between 30,000 igpm (200,000 m^3/d) during spring runoff and 6000 igpm (40,000 m^3/d) during the driest part of the summer.

Limestone can acheive a pH adjustment approaching pH 7, and the Onaping plant is part of a comprehensive water management and AMD abatement program adopted by Falconbridge and described in Appendix I.

The limestone neutralization plant is described by RIVETT and OKO in the following Deco Trefoil report dated 1972. There has been little change in the plant since then.

The latest annual operating cost figures which are for 1981 are as follows for the limestone neutralization plant.

Labor	$25,500
Fringes	11,000
Supplies	35,000
Electricity	7,500
Maintenance	17,000
	$95,000

1984 operating costs are budgeted at C$108,000 for this plant which works out to C$0.03 per m^3 of water treated (C$0.14 per 1000 I gallons).

BULLETIN NO. G3-B151
Environmental Control
Neutralization of Waste Water

The Moose Lake water system, treatment dam and plants complex. The natural water flow is from bottom to top of photo. At the left is the sluice in the dam where the limestone slurry is added to the lake water. The building on the left center in the foreground is the pump-house, with the water intake point at the shore of the lake. The building on the right in the foreground is the slurry plant housing the DENVER Ball Mill, and also visible are the limestone stockpile, the storage-feed silo, and the slurry pipeline out to the sluice in the dam. In the background at the top right is the Onex Exploration Shaft.

Tailings Disposal, Generation of Acidity from Pyrrhotite and Limestone Neutralization of Waste water at Falconbridge's Onaping Mines

By L. S. RIVETT and U. M. OKO, Falconbridge Nickel Mines Limited

L. S. RIVETT was born in Haileybury, Ontario. He received his engineering degree in chemical engineering at McGill in 1935, and joined Siscoe Gold Mines, northern Quebec. In 1937, he joined Falconbridge Nickel Mines Ltd., where he became mill engineer in charge of experimentation. Between 1940 and 1946, he worked for C-I-I in Hamilton and Copper Cliff, Ontario.

Mr. Rivett rejoined Falconbridge Nickel Mines in 1946 and was steadily promoted to his present position of general superintendent of the Falconbridge Area. He currently lives in Falconbridge, Ontario.

L. S. RIVETT

U. M. OKO

URIEL M. OKO was born in Israel and moved to Canada in 1955. He received his Bachelor of Engineering from McGill in 1961. In 1964, after three years of foundry engineering in Montreal, Quebec and Belleville, Ontario, he returned to McGill for his Master in Mineral Dressing, work which he performed under the direction of Dr. T. Salman in the Metallurgical Engineering Department. In 1969 he received his Ph.D. from the University of Missouri. The research he conducted there involved mine-water pollution abatement.

Dr. Oko joined the Falconbridge organization in 1969, where he is now industrial wastes control engineer in charge of water pollution abatement, Sudbury operations.

FIGURE 1
The Moose Lake System[1]

Introduction

Until recently, the only apparent water pollution problem that required attention in the minerals industry was the separation of the suspended solids from the mine and mill waste effluents. Operators were conditioned to this requirement and generally did an acceptable job.

Over the past few years, however, the situation has altered radically as a result of the considerable increase in our understanding of the effect that various trace elements can have on the ecology of stream systems. Naturally, legislation governing water pollution control has been strengthened to keep pace with the greater knowledge and understanding. In many cases, tailings disposal is now no longer a simple matter of a well-built dam and a clear overflow.

This paper describes special circumstances encountered by Falconbridge Nickel Mines Limited when bringing a large new mine and concentrator (Strathcona) into production.

The water pollution problem associated with the mining and treatment of sulphide ores that has to be resolved is essentially one of acid formation. If this could be eliminated, the problems of dissolved heavy metals and of sulphides would also virtually disappear. However, whenever water comes into contact with the sulphide mineral pyrrhotite that forms some 15 per cent of the Sudbury District ores, in the mining, grinding, flotation or other processing steps, small amounts of sulphur are dissolved to form sulphur compounds that oxidize eventually to sulphuric acid. The rates of dissolution depend on a variety of conditions, but in general the reactions are slow.

The only available water supply for the Strathcona operation was Moose Lake[1], but this was insufficient for the requirement of 3,000 gallons per minute. In addition, the water in this lake had already become acidic (pH 3.7) as a result of an earlier concentrating operation at Fecunis. It was obvious that process water would have to be recirculated.

The solution adopted was to utilize part of the lake as both a reservoir and an ageing or oxidizing basin. A dam and spillway were constructed in order to introduce a continuous stream of finely ground limestone pulp to neutralize the acidity. The limestone neutralization unit was designed to operate continuously and unattended.

This system has operated satisfactorily over the past several years, producing good-quality neutral water at flow rates varying from 6,000 to 30,000 gallons per minute (spring runoff).

Source of Sulphuric Acid in the Lake Water

Falconbridge Nickel Mines Limited started using the Moose Lake watershed for a water supply and for the retention of tailings in 1955, when the Fecunis Lake mill was brought into production. The mill discharged its tailings into a dammed-off marsh which drained into Cranberry Lake (see Figure 1). To prevent suspended solids from reaching Moose Lake, a dam was constructed at the outlet of Cranberry Lake.

During the ten-year period that the Fecunis Lake concentrator had been in operation, up to 1966, the water decanting from its tailings disposal area had resulted in the water of Moose Lake becoming appreciably acid. This is due to the fact that, during grinding and flotation operations in the concentrator, a small amount of sulphur from the mineral pyrrhotite dissolves in the water. The process seems to be independent of water temperature, but is accelerated at an alkaline pH which is normal in the Falconbridge flotation circuits. As a result, the water leaving a typical Falconbridge mill has a chemical oxygen demand (C.O.D.)[2] of approximately 50 parts per million (ppm). This is not a particularly high figure, but the products of oxidation, with the passage of time, generate sulphuric acid, which causes the pH of the water to decrease to levels that are toxic to aquatic life.

The dissolution process of sulphur from pyrrhotite, accelerated in an alkaline environment, is typical of that of other metal sulphides[3],[4]:

$$Fe_7S_8 + 20H^- \rightarrow 7FeS + S^= + H_2O + \tfrac{1}{2}O_2 \quad \ldots\ldots(1)$$

The kinetics of the oxidation of dissolved sulphide to sulphuric acid depend on many factors, such as sunlight, water temperature, pH and the presence of active sulphur-oxidizing bacteria[3],[6]. The intermediate products of oxidation, called polythionates, further oxidize to the ultimate product, sulphuric acid, which results in practically complete elimination of the C.O.D. in the water. Reaction (2) describes the oxidation of the unstable sulphide ion. This accounts for the presence of thiosulphate in the mill effluents.[7]

$$2S^= + 2O_2 + H_2O \rightarrow S_2O_3^= + OH \quad \ldots\ldots(2)$$

Polythionates, identified as $S_3O_6^=$, $S^=O_6$, (n, 4 to 8), are formed as shown below[8].

$$S_2O_3^= + H_2O + 4O \rightarrow 2SO_4^= + 2H^+ \quad \ldots\ldots(3)$$

$$nS_2O_3^= + (n-2)H_2O + 2(5-n)O \rightarrow 2S_nO_6^= + 2(n-2)OH^- \quad (4)$$

Pumphouse, slurry plant, limestone stockpile on banks of Moose Lake. The ½"x¼" limestone chips are wet ground to 90% mesh. The lime slurry is discharged at the rate of 200 g.p.m. over the Moose Lake Narrows Dam to blend with and neutralize the acid water.

and the ultimate oxidation to sulphuric acid is described as follows:

$$S_nO_6^{=} + (n-1)H_2O + (3n-5)O \rightarrow nSO_4^{=} + 2(n-1)H^{+} \quad (5)$$

resulting in the generation of hydrogen ions and a decline in the pH.

Neutralization

There being no known practical economic method of preventing the formation of the polythionates and subsequently sulphuric acid in the ore concentration and tailings disposal system, the only available solution to the problem is to neutralize the acid after it has been found.

In the system under consideration, this meant the neutralization of all the decant solutions from the Fecunis Lake and the Strathcona tailings disposal areas at a location where the sulphur compounds in these solutions had become completely oxidized to sulphuric acid. Of the neutralizing agents available, limestone was the most advantageous with respect to cost and ease of handling. Also, it had the advantage that an excess of limestone could be tolerated without raising the pH of the water above the acceptable limits. Caustic soda or lime would present major control problems and ammonia was unacceptable because of its fertilizing properties. The neutralizing action of limestone is described by equation (6).

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \quad (6)$$

Choice of Tailing Impound for the Strathcona Concentrator

The Strathcona tailings disposal basin had to be large enough to contain an estimated 6,250,000 dry tons of tailings slimes, the quantity that would be produced over the 25-year expected life of the mine, keeping in mind that this disposal area might have to contain several times this amount, as there were distinct possibilities that additional major orebodies would be developed in this general area.

Containing a 25-year output of mine tailings can present a major problem. This was particularly so for Strathcona. The topography of the area is extremely rugged and unsuited for impounding. To further complicate the problem, the area is a checkerboard of mining claims, only part of which belong to Falconbridge. The removal of the sandy portion of the mill tailings for use as fill underground leaves a slime which is useless for dam construction. Thus, material for dam building has to be provided and in this immediate area was limited to small gravel deposits located around the periphery of the lake.

Of the eight areas which appeared worthy of consideration, the northwest arm of Moose Lake, an area of about 2,290,000 sq. ft., seemed to be most favorable. Impounding this area required a short dam, and therefore little gravel, and decant water from this site could be recycled back to the mill as process water, thus alleviating seasonal shortages. The estimated capacity of the impounding area was 139,288,000 cu. ft., adequate for 25 years, if a dam 35 ft. above the original water level were to be constructed at the outlet of the northwest arm.

The choice of this particular tailings disposal area fitted in very well with the over-all water treatment system proposed in that the tailing water effluent from both Fecunis Lake and Strathcona would flow into Moose Lake, which would provide the retention time necessary for the oxidation of the sulphur compounds to sulphuric acid and, by the judicious location of the water treatment facility, would not only insure that treated water would be discharged to the outflowing water course but also that the pumping installation providing water to the two concentrators would also be handling treated water.

Dam for the Strathcona Tailings Pond

The dam was designed to be built from gravel located in a small nearby deposit, using the Ontario Water Resources Commission (O.W.R.C.) specifica-

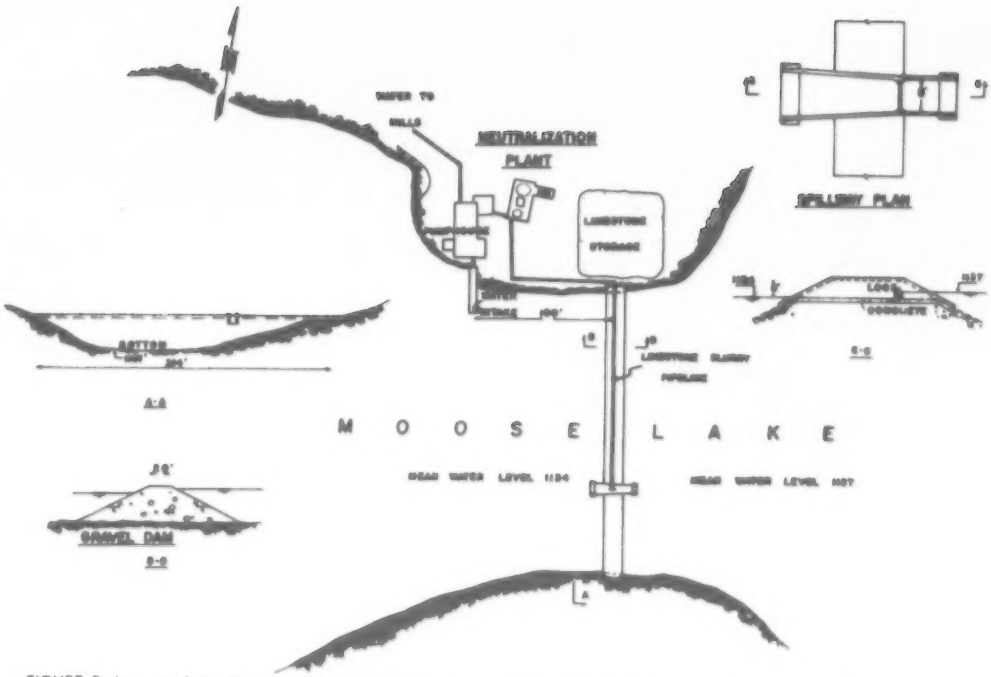


FIGURE 2—Layout of the Moose Lake neutralization plant and the cross sections of the dam across the lake narrows.

tions for slope and width. After approval had been obtained from the O.W.R.C. for the construction of the gravel dam, as much as possible of the sediment and vegetable material on the lake bottom at the narrows was removed with a drag line. For pockets of sediment that could not be reached readily by the drag line, explosive charges were used. A narrow dam was built first across the narrows and then widened to its full width. This sequence of construction is considered to be the best method of displacing any remaining bottom detritus and thus providing for best foundations.

In the initial construction stage, the dam base was built to its full final width and, at the same time, a concrete decant tower was built with provision for later extension as required.

Dam for Moose Lake

To insure that Moose Lake acted as an effective reservoir year 'round, including the relatively dry summer months, O.W.R.C. and the Ontario Department of Lands and Forests approval was obtained to construct a dam across the narrows near the south end of the lake to raise the water in the main body of Moose Lake by about 5 feet. This also permitted the use of a weir in which the limestone slurry could be mixed satisfactorily with the outflow water. A gravel dam was constructed, as shown in Figure 2.

Water at the Moose Lake System

The entire Moose Lake system has a watershed area estimated at 10 square miles and an average annual precipitation of 29.5 inches. The main body of the lake alone has an area of 26,200,000 sq. ft. and is about 50 ft. deep, equivalent to a storage capacity of some 8.1 x 10^{9} Imperial gallons. The annual outflow to the Onaping River amounts to about a third of this storage capacity, which, in other words, means that its retention time is about three years.

Table I summarizes the annual water balance for the lake, including the projected consumption of the Strathcona and Fecunis mills.

The lengthy retention time of the tailings water in Moose Lake allows for complete oxidation of the dissolved Polythionates to sulphuric acid, and the year-'round discharge, despite seasonal fluctuations in temperature and water runoff, has no C.O.D. A comparison between the water quality at the tailings pond outlets during the winter and the Moose Lake system outlet, before and after neutralization, is shown in Table II.

It is evident from Table II that the tailings pond effects essentially complete solid-liquid separation and that the decanted water, with a high C.O.D. is completely oxidized by the time it reaches the Moose Lake outlet. The table also shows that the use of limestone as a neutralizing agent does not greatly increase the dissolved solids content of the water and that the lower reaches of Moose Lake below the neutralization plant provide a settling basin for the precipitate formed by the limestone treatment.

TABLE I—Annual Water Balance for Moose Lake

	Volume in Imp. Gals.
Total Precipitation	4,210,000,000
Mill Effluents	2,290,000,000
Total Inflow	6,500,000,000
Evaporation and Percolation Losses	962,000,000
Total Water to be Neutralized	5,540,000,000
Water for Mills	2,290,000,000
Net Outflow to Onaping River	3,250,000,000

The concentration of polythionates is determined by noting the difference in the sulphate concentration in the water before and after oxidation. The oxidation of polythionates can be performed using conventional analytical procedures.[10],[11]

Moose Lake Neutralization Plant

The factors that were most important in the development of the best over-all plan were: (a) that the quality of water flowing out of the system should be acceptable to the Ontario Water Resources Commission[9]; (b) that the overflow from the Strathcona tailings disposal area should decant into Moose Lake; (c) that a water treatment facility be located so as to be able to treat the decant from both the Fecunis Lake and Strathcona tailings disposal areas; and (d) that the water treatment facility be located upstream from the pumphouse that would deliver the process water to the Fecunis Lake and Strathcona concentrators.

To effect neutralization, it was necessary to contact very large and variable water flows with relatively small amounts of limestone. This could only be achieved by funneling the water through a relatively narrow weir and using the turbulence as a means of mixing finely ground limestone with the water. The water flows varied from a high of 30,000 Imperial gallons per minute during the spring runoff to a low of about 6,000 Imperial gallons per minute during the driest part of the summer. For water with a pH of about 3, this indicated requirements of from 3.5 to about 10 tons of limestone per day.

The scheme finally adopted was to wet-grind limestone chips extremely fine, dilute the wet thick slurry and introduce it at a rate of 200 Imperial gallons per minute into the water overflowing the weir in the Moose Lake Narrows dam. The neutralization plant, shown in Figure 3, consists of a 50-ton limestone bin, a spiral feeder for a 4- by 6-ft. DENVER Ball Mill powered by a 40-hp motor, and a pumping arrangement for the limestone slurry, which is diluted in the wood-stave tank that receives the ball-mill discharge. Table III is a list of the plant equipment and the approximate cost in 1968.

Limestone slurry mixing with Moose Lake water at the Narrows dam to neutralize acid water. The limestone slurry is -325 mesh. Depending on requirements, from 3.5 to 9 tons per day of limestone is consumed.

Operation of Moose Lake Neutralization Plant

Due to the slight excess of limestone normally added and the large volume of the lower reaches of the lake, water discharging into Moose Creek is consistently neutral. This allows for safe and economical m[illegible] control of the neutralization plant. To insure minimum surveillance, it was decided to use limestone that was sufficiently coarse to prevent hangups in the storage bin even when wet, but sufficiently fine to be fed to the system using a conventional screw feeder.

In the neutralization plant, -½ + ¼-inch limestone chips are wet-ground to a fine powder, 90 per cent of which passes a 325-mesh screen, mixed with water and discharged at the rate of 200 gallons per minute over the Moose Lake Narrows dam weir to blend with and neutralize the acid water. The plant was designed and constructed by Falconbridge to operate unattended, with minimum supervision and maintenance.

TABLE II—Effects of Retention Time and Neutralization

Analysis Results ppm	Tailings Water at Tailings Dam	Moose Lake Outlet	
		Before Neutralization	After Neutralization
Dissolved Solids	987.	330.	390.
Suspended Solids	1.5	1.0	1.0
Sulphate Before Oxidation	555.	195.	206.
Sulphate After Oxidation	679.	194.	206.
Total Fe	6.	2.	0.6
Total Ni	0.6	0.3	0.3
Total Cu	0.5	0.1	0.1
pH	6.4	3.5	7.2
C.O.D.	46	less than 1	less than 1

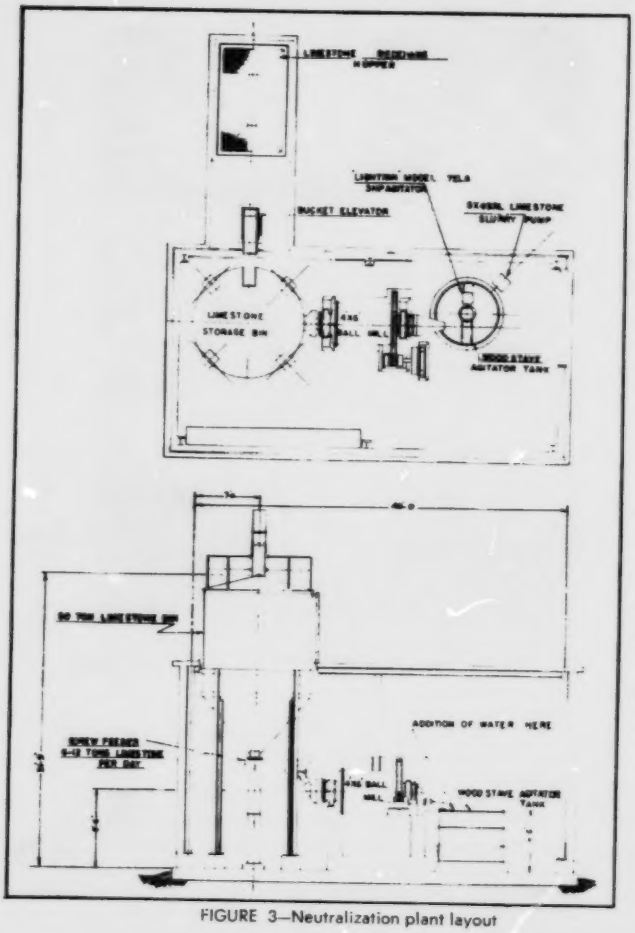


FIGURE 3—Neutralization plant layout

Limestone, stockpiled outside the plant is loaded once weekly, under normal operating conditions, through the bucket elevator into the 50-ton bin. It is fed through the screw feeder at rates varying between 3.5 and 9 tons per day, manually adjusted, depending on the rate of water flow in the weir, directly into the ball mill. Water, added at a rate of 1 gal/min., serves to effect wet grinding at about 60 per cent solids in the mill. The grinding medium consists of 275 lbs. of 2.5-in. diam. and 700 lbs. of 1-in.-diam. steel balls. For the average grinding rate of 5.5 tons per day, about 15 lbs. of steel are consumed.

The annual operating expense of the plant averages $27,000, of which $15,000 is the cost of limestone and $2,000 the cost of power. Equipment repair and maintenance amounted to about $6,000 in 1968, but dropped to about $4,000 in 1969. The ball mill is alarm-coupled to a service station located at the Fecunis mill 1½ miles away to ensure continuous surveillance by maintenance personnel.

TABLE III—Equipment List for Moose Lake Neutralization Plant

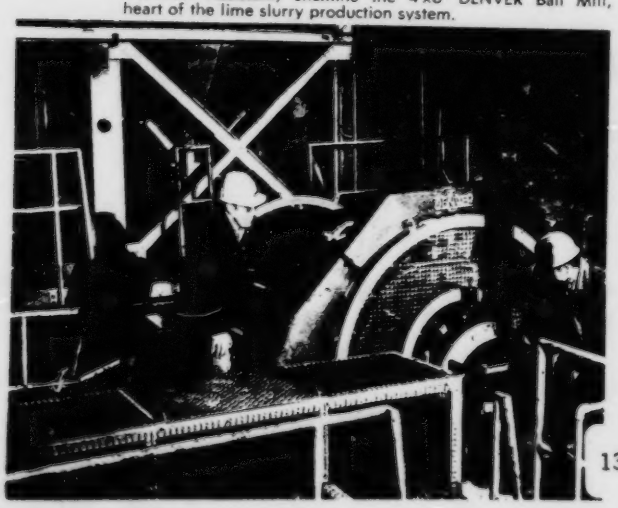
	Cost
Bucket Elevator	$ 3,500
50-ton Limestone Bin	2,500
1/3 Pitch 9-in. 7-ft. long Conveyor Screw Feeder	2,000
Reduction Conveyor	500
Feeder Vibrators	1,400
4- by 6-ft. Ball Mill	16,000
40-hp motor	1,400
3x3 SRL Limestone Slurry Discharge Pump & Motor	1,000
Wood-stave Tank	1,000
Mixing Turbine Agitator and Water Level Controller	2,000
Total Cost of Equipment	$ 31,300
TOTAL COST OF PLANT ERECTED	$100,000

Discussion

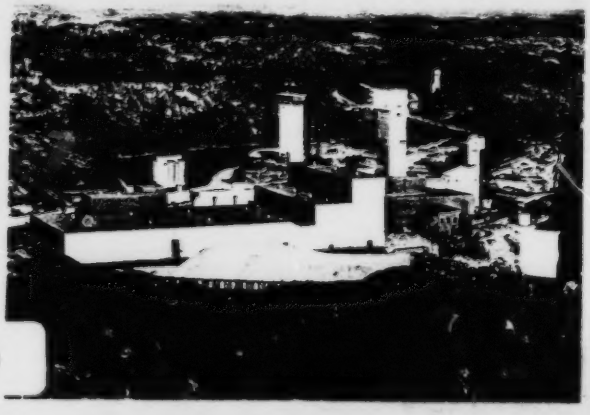
Two unsuccessful approaches to the elimination of acidity in Moose Lake are considered worthy of a brief description.

One initial concept of the problem was that excess alkalinity at the mill may, if sufficiently large, counter the acidity generated in the oxidation reaction. The polythionate-C.O.D. problem was recognized, but its

Onaping's Ron Rhude, pump operator, left, and Brian Potter, Technical Assistant, examine the 4'x6' DENVER Ball Mill, heart of the lime slurry production system.



The Strathcona Mill treating copper-nickel ore in the Onaping, Ontario, area. It is the tailing water from this new plant which is neutralized in the Moose Lake water treatment system



importance was not realized. Thus, a relatively simple solution appeared to be merely to add lime to the tailings disposal lines, utilizing equipment already available in the concentrator. An experiment of this nature was carried out and, although the pH of the decant water from the tailings pond was raised to 9.5, the oxygen demand and the free acid both increased substantially. The reason for this is that the mineral pyrrhotite becomes more reactive in an alkaline solution, resulting in a greater quantity of dissolved sulphur and the subsequent production of greater quantities of acid.

An attempt was also made to develop an intensive biological system that would produce a reduction in the C.O.D. in the same manner that a sewage system operates[12]. The bacteria *thiobacillus thioxidants*, which was identified in the tailings pond, was cultivated in the laboratory and introduced into samples of tailings pond decant solutions. The C.O.D. of these solutions was monitored for a two-month period and, although there was a reduction in the concentration of polythionates, it was insufficient to give any promise of being practically effective.

The water in Cranberry Lake, which receives the effluent from the Fecunis Lake tailings pond, has been monitored for a number of years and the results of 17 consecutive months are shown in Table IV. These results show that the combined chemical and biological processes which result in the oxidation of the polythionates are ineffective in November and December, presumably because of low water temperatures, inoperative under the ice cover from January through April, slow during the first two months of open water in the spring, while the water is warming up, and only truly effective during the months of July through October, during which period all or most of the C.O.D. is removed.

During the months of April, September and October, water samples from Cranberry Lake can indicate unrealistically low sulphate concentrations. These, however, are the months when precipitation in the Sudbury District is highest and the results are a reflection of the dilution which occurs.

TABLE IV—Analysis of Cranberry Lake Discharge Water

Month	Condition	$SO_4^{=}$ Before Oxidation	$SO_4^{=}$ After Oxidation	C.O.D. ppm
May 1969	Open water	441	478	20
June	Open water	703	721	14
July	Open water	760	760	0
Aug.	Open Water	719	719	0
Sept.	Open water	334	342	0
Oct.	Open water	281	289	5
Nov.	Open water	896	1010	40
Dec.	Open water	430	630	70
Jan. 1970	Ice cover	597	692	40
Feb.	Ice cover	694	839	49
Mar.	Ice cover	555	679	49
Apr.	Ice cover	375	437	32
May	Open water	719	832	42
June	Open water	411	491	36
July	Open water	877	880	0
Aug.	Open water	1019	1011	0
Sept.	Open water	996	995	0

200 gallons per minute of limestone slurry are mixed with water in the flume at the Moose Lake Narrows Dam. The System has been effective in raising the pH of water in the Moose Lake outlet from 3.5 before the neutralization to 7.2 after the lime slurry treatment.

The retention period in Cranberry Lake, which receives the water decanting from the Fecunis Lake tailings pond, has been estimated as six weeks. Analysis of water flowing out of this lake during the summer months reveals that complete oxidation of the sulphur compounds has taken place during this retention period. Lacking any other evidence, six weeks is considered to be the ageing time required under optimum conditions to effect complete polythionate oxidation.

There was some concern that the proximity of the discharge from Cranberry Lake to the Moose Lake Treatment System dam might permit unoxidized polythionates to escape during the winter months or early spring if unnatural flow patterns developed in Moose Lake. This has not occurred and, over two winters of operation, no sample taken at the dam has indicated any appreciable C.O.D.

To summarize, it would appear that in order to insure that neutralization will be effective, a retention period of approximately six weeks under open water and an active biological environment must be available

The new nickel-iron refinery of Falconbridge Nickel Mines Limited, at Falconbridge, Ontario. The main mill of Falconbridge Nickel Mines Limited is seen in the background.

Derek Ellot is pictured conducting tests on water sample taken from Moose Lake, to check on water treatment and circulation system. The Space-age instrument in the main analytical laboratories at Falconbridge during this test is an atomic absorption spectrophotometer.

from the time the effluents discharge from the tailings dam to the time the neutralizing limestone is added. In addition, in the spring eight weeks are required from the time the ice has vanished to the time the biological system of the lake becomes sufficiently active to oxidize the polythionates.

The operation of this system has been essentially trouble-free and its effectiveness has been entirely satisfactory. The biological life cycle in the lower part of Moose Lake below the neutralization plant has been restored. In fact, last summer minnows began showing up in the plant's process water system, indicating that the quality of water at the lower reaches of Moose Lake has been restored.

Finally, a few words on the cost of operation of the neutralization plant. The amount of limestone required to neutralize the 18.5-million-gallon average daily outflow from a pH of 3.5 was estimated using equation (6) at 4.5 tons. The cost to date, including the write-off of the plant's equipment, but excluding the cost of the dam, building, etc., is about 0.7 cent per 1,000 gallons of water treated—very reasonable considering that the acceptable cost of treating process water exceeds 10 cents in many parts of North America. Thus, work at Falconbridge has proved that effective acid neutralization for pollution control and improvement of process water quality can be carried out with a modest investment and low operating costs.

Acknowledgments

The writers wish to gratefully acknowledge the encouragement and advice given by W. L. W. Taylor, manager, Technical Services, and the useful criticism offered by J. E. Finlay, assistant general manager, Falconbridge Nickel Mines Limited, Sudbury, Ontario.

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Appreciation

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Application of mineral processing technology to solve certain problems faced by many other industries when treating or disposing of waste water is becoming very important. Thus the timeliness of this report has added significance.

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	Tailings Dam Effluent	Seepage Dam
pH	1.8	6.6
Conductivity Micromhos	20,000	10,000
TDS (ppm)	33,084	13,430
S/S	134	20
Total Hardness (ppm $CaCO_3$)	6521	4729
Calcium Hardness	1685	1436
Magnesium Hardness	4836	3293
Chloride	880	960
Sulfate	20,657	8102
Flouride	98	42
Nitrate	160	72
Iron	1825	0.1
Manganese	1925	1100
Potassium	260	76
Sodium	1075	825
Silica	320	27
As	0.375	0.003
Uranium	17	0.5
Calcium	675	575
Magnesium	1175	800
Aluminum	625	12
Radium 226 (piC/l)	243.4	21.2
Ammonium	401	172

EAGLE-PICHER INDUSTRIES, SHULLSBURG MINE, WISCONSIN

HOFFMAN (1984) described the impact on groundwater quality of the EAGLE-PICHER zinc mines near Shullsburg, Wisconsin, which closed in 1978 and 1979.

The mines were pumped dry during their working life; however, after closure they became flooded, and groundwater was affected to the extent that well water in the area is not suitable for use by humans or for livestock watering.

Closure of underground zinc-lead producing mines appears to have caused degradation of associated ground water resources. Changes in groundwater chemistry implied that acid mine drainage mechanisms were responsible for altering associated private water supplies in the area.

Groundwater quality in the Galena-Plattville dolomite aquifer experienced deterioration due to significant increases in dissolved sulfate (to 3500 mg/l). Other impacts were noted with dissolved iron (to 65 mg/l) and lesser quantities of zinc, lead, and arsenic. Field observations indicated that bacterially accelerated acid oxidation of FeS_2 with precipitation of $Fe(OH)_3$ produced micro-environments that were shielded from neutralization by the surrounding dolomite. Dissolution of relatively soluble iron, calcium, and magnesium sulfates on reflooding were probably responsible for the high values of sulfate. Where acid neutralization occurred, polythionate and thiosulfate salts may have yielded additional sources of sulfate.

The important aspect is that one would have expected dolomitic rock and soils to attenuate the formation of AMD and to avoid excessive levels of sulfate and metals. In this case, due to the high solubility of $MgSO_4$, however, the water quality turned out to be much, much worse than would have been expected at first, and natural attenuation of AMD could not be relied upon.

This is also a practical example of the phenomenon whereby even gypsum precipitation will be inhibited when magnesium is present. In some cases, solutions which, based on their Ca^{2+} and $SO_4^{=}$ levels, should be scaling are not when Mg^{2+} is also in solution.

GREENSIDE COLLIERY, WITBANK, TRANSVAAL

GREENSIDE COLLIERY is part of GOLD FIELDS OF SOUTH AFRICA LTD. and must treat a 220 m^3/h flow of acid mine drainage from the underground mine.

The flow of water into the mine has been reduced as much as possible, but there remains 220 m^3/h to treat. A plant was designed using crushed limestone in an innovative way. A commercial installation was to be installed by mid-1984.

Water was to flow upwards through a multi-compartment, deep trough filled with crushed limestone at minus 19 mm (0.75 inches). It has been found in laboratory tests that pH adjustment would be satisfactory after just six minutes contact time with limestone of this sizing, to comply with South African effluent pH limits of pH 5.5-9.5. Optimum time for

contact between water and the limestone was estimated at ten minutes, and there was not much further increase in the pH from 10-60 minutes contact time. Tests indicated that pH 6.3 could be achieved in 15 minutes and pH 8.5 after prolonged contact.

At regular intervals the activity of the limestone, as it becomes passivated by surface coating of $CaSO_4$, would be restored by vigorous agitation of the limestone in the troughs using an air sparge.

Reaction rate is faster with smaller limestone particles, but there was found to be a minimum practical size for the agitation attrition step without losing the bed.

During the air sparging cycle, the overflow was designed to be temporarily diverted to a lamella clarifier to clarify the neutralized water and settle a sludge.

Limestone could be supplied from a local quarry at a very attractive price compared with lime.

- The sole purpose of this treatment step was to modify pH as metal values meet the discharge limits. Composition of inflow and treated water based on laboratory tests were as follows:

	Untreated	Treated
pH	0.4	6.6
Ca Hardness as $CaCO_3$ ppm	496	553
Mg Hardness as $CaCO_3$ ppm	1340	1527
Total Hardness $CaCO_3$ ppm	1836	2080
Calcium as Ca	198	221
TDS	3500	3700
Suspended Solids	25	27

- In all tests, a fine sludge was formed during the neutralization process. This sludge required flocculation and settling for removal Lamella thickener tests indicated that a 3-4% solids sludge would be achieved which could be dried on "drying beds."

- Unless the process is operated in an upflow mode, the bed was found to "choke" with sludge.

- After treatment in the above way, the water would be suitable for discharge or for recycle to the operation as process water. Greenside Colliery planned to use the water in a coal preparation plant.

- The result of the commercial installation was failure, as indicated by David Blane's letter, due to blinding by ferrous salts.

The limestone neutralization facility was to be installed by:

WATER CARE PTY LTD.
Spartan Centre
Post Office Box 21
19 Newton Street
Isando 1600
(011) 976-2136
Telex: 8-2393
David Blane

More details from the mining company may be available from:

GOLD FIELDS OF SOUTH AFRICA LTD.
Post Office Box 1167
Johannesburg 2000
(011) 639-9111
(011) 672-2459
A. W. Pullen, Group Civil Engineer

U.S. BUREAU OF MINES LIMESTONE NEUTRALIZATION

The U.S. Bureau of Mines at Pittsburgh, Pennsylvania, has developed and demonstrated a system for neutralization of AMD using limestone which is introduced after being grinded very finely in an autogenous mill. A description of this system is included in Bureau of Mines Information Circular No. 8905 by KIM, et al. (1982) inserted below.

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DB/es/85/67

5th February 1985

Randol International Ltd
21578 Mountsfield Drive
Golden
Colorado, 80401
U.S.A.

Attention : Mr. Hans von Michealis

Dear Sir,

RE : LIMESTONE NEUTRALISATION PLANT

Your letter of the 15th October 1984 refers. Firstly my apology for the delay in responding, but we were delayed in the commissioning of the plant, and I wished to give you an accurate assessment of its capabilities.

However I have to report failure. On commissioning we found that the formation of ferrous salts soon coated and then slowly blinded the limestone, rendering the plant ineffective. Our various attempts to overcome this problem have not been successful, and the client is reverting to a lime-slurry neutralisation system.

I was extremely interested to hear of the three plants you have found operating in the USA, and would greatly appreciate any further information you could possible send me, such as location, owners, and any technical details you might have.

Thank you for the interest you have shown in our project.

Yours sincerely,
WATERCARE (S.A.) (PTY) LIMITED

.....

D.G. BLANE
GENERAL MANAGER

2/P.S. .....

report of investigations 7191

BUREAU OF MINES

September 1968

MINE WATER RESEARCH

The Limestone Neutralization Process

by

E. A. Mihok,[1] Maurice Deul,[2] C. E. Chamberlain,[3] and J. G. Selmeczi[4]

ABSTRACT

A pilot plant for treating mine drainage by neutralization with limestone was designed, fabricated, and operated by the Bureau of Mines. The process consists of (1) producing a very fine (minus 400-mesh) limestone slurry, (2) mixing the slurry with the mine water, (3) aerating the resulting mixture to remove carbon dioxide and precipitate iron, and (4) separating the solids from the liquid by sedimentation.

A mine discharge of pH 2.8, containing 1,700 ppm total acidity, 36 ppm ferrous iron, and 360 ppm total iron, was treated at rates from 300 to 400 gpm. The treated water ultimately reached a pH of 7.4 and contained no detectable iron. The resulting sludge compacted to approximately one-third the volume of sludge from mine water neutralized with lime.

The advantages of the limestone process, compared with the conventional lime process are as follows: Widespread distribution and lower cost of run-of-mine, indigenous limestone; simplicity of plant design; reduced hazards and plant operating and maintenance costs accruing from the use of a less reactive chemical agent; higher solids concentration of the precipitated sludge; and no deleterious effect caused by accidental overtreatment.

While total process costs could not be determined, it is conservatively estimated that the cost of treating mine water by the limestone process is one-third to one-half the cost of the lime process, depending on the characteristics of the water to be treated and the availability and quality of limestone used.

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[2]Supervisory geologist, Pittsburgh Mining Research Center, Bureau of Mines, Pittsburgh, Pa.
[3]Chemist, Pittsburgh Mining Research Center, Bureau of Mines, Pittsburgh, Pa.
[4]Development engineer, Research and Development Department, Dravo Corporation, Pittsburgh, Pa.

INTRODUCTION

In 1966, the Bureau of Mines, as a special adjunct to its comprehensive research program on the chemistry of mine water and at the request of a group of coal mine operators, undertook a short-term project to develop an effective treatment process for mine water. The work was primarily concerned with neutralization and iron oxidation, although sludge settling characteristics and dewatering techniques also were studied.

The emphasis on the use of limestone as a neutralizing agent was due mainly to its low cost and easy availability. In 1967, a report was published which showed that coarse limestone was potentially useful for treating mine waters.[5] Additional papers by Mihok and Chamberlain,[6] and by Kim[7] provided information on limestone neutralization and iron oxidation. F. P. Calhoun[8] gave performance and cost data on limestone treatment of a Rochester and Pittsburgh Coal Co. mine effluent.

The original concept in the use of coarse limestone was that the sustained reactivity achieved by vigorous cascading agitation in a rotating vessel (1) provided abrasion to eliminate the coating of limestone particles with precipitated solids, (2) continuously renewed the reactive surface, and (3) removed the CO_2 from solution. A large aeration surface facilitated oxidation of ferrous iron. Adequate treatment for water containing high acidity and moderate amounts of soluble iron was limited to flows of less than 100 gpm. This concept was expanded and improved upon during the pilot plant tests reported here.

ACKNOWLEDGMENTS

The successful prosecution of this research was made possible through the mutual cooperation of the management of the Vesta-Shannopin Division of Jones & Laughlin Steel Corp., who provided unstinting assistance with manpower, material, counsel, and a treatment site where the research could be conducted; and the Research and Development Division of Dravo Corp. which, through a cooperative agreement, provided financial assistance.

---

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We acknowledge with thanks the patience and personal interest of Herbert L. Steinman, chief engineer, Vesta-Shannopin Division, Jones & Laughlin Steel Corp.

MINE WATER TREATED

Preliminary tests conducted with a tube mill reactor were made with synthetic mine water solutions at the Bureau of Mines.[9] To determine the performance of the limestone system with a natural mine water, the tube mill and auxiliary equipment were installed at the Jones & Laughlin Steel Corp. Shannopin No. 1 air shaft borehole treatment site near Bobtown, Greene County, Pa.

An existing 3-million-gallon-capacity holding lagoon was used to level off the variable composition of the water pumped from the mine, and to obtain some reduction in ferrous iron by natural oxidation. This provided a mine water of fairly uniform composition for tests. Typical analyses of the mine water treated are shown in table 1.

TABLE 1. - Analyses of mine water treated

	3-1-68	4-1-68A	4-1-68B	6-14-68
Temperature.....° C..	10	15	15	18
pH.....	2.75	2.9	2.85	2.85
Ferrous iron.....ppm..	140	20	20	24
Total iron.....ppm..	390	355	325	350
Acidity[1].....ppm..	1,730	1,620	1,450	1,690
Sulfate.....ppm..	-	3,996	3,888	-
Calcium.....ppm..	259	244	257	-
Magnesium.....ppm..	130	61	66	-
Aluminum.....ppm..	-	114	113	-

[1]As determined by the hot phenolphthalein method.

TEST PROCEDURE

Limestone Process

The limestone pilot plant consisted of a 3-foot-diameter by 24-foot-long tube mill driven by a 15-horsepower variable-speed motor; a slurry discharge trough and sump; a 60-foot-long, 2-foot-diameter, semicircular mine water feed and mixing trough; and a 60,000-gallon-capacity, earthen, limestone-riprap-lined aeration pond equipped with a surface aerator and air blower sparging system. Later, a 35,000-gallon-capacity sedimentation pond was constructed between the aeration pond and the existing large settling basin. Figure 1 is a flowsheet of the limestone process. The major components of the treatment pilot plant are illustrated in figures 2 through 5.

Mine water from the holding pond was fed by gravity through plastic pipe simultaneously to the tube mill and mine water feed trough. A 1/4-inch screen

[9]Work cited in footnote 6.

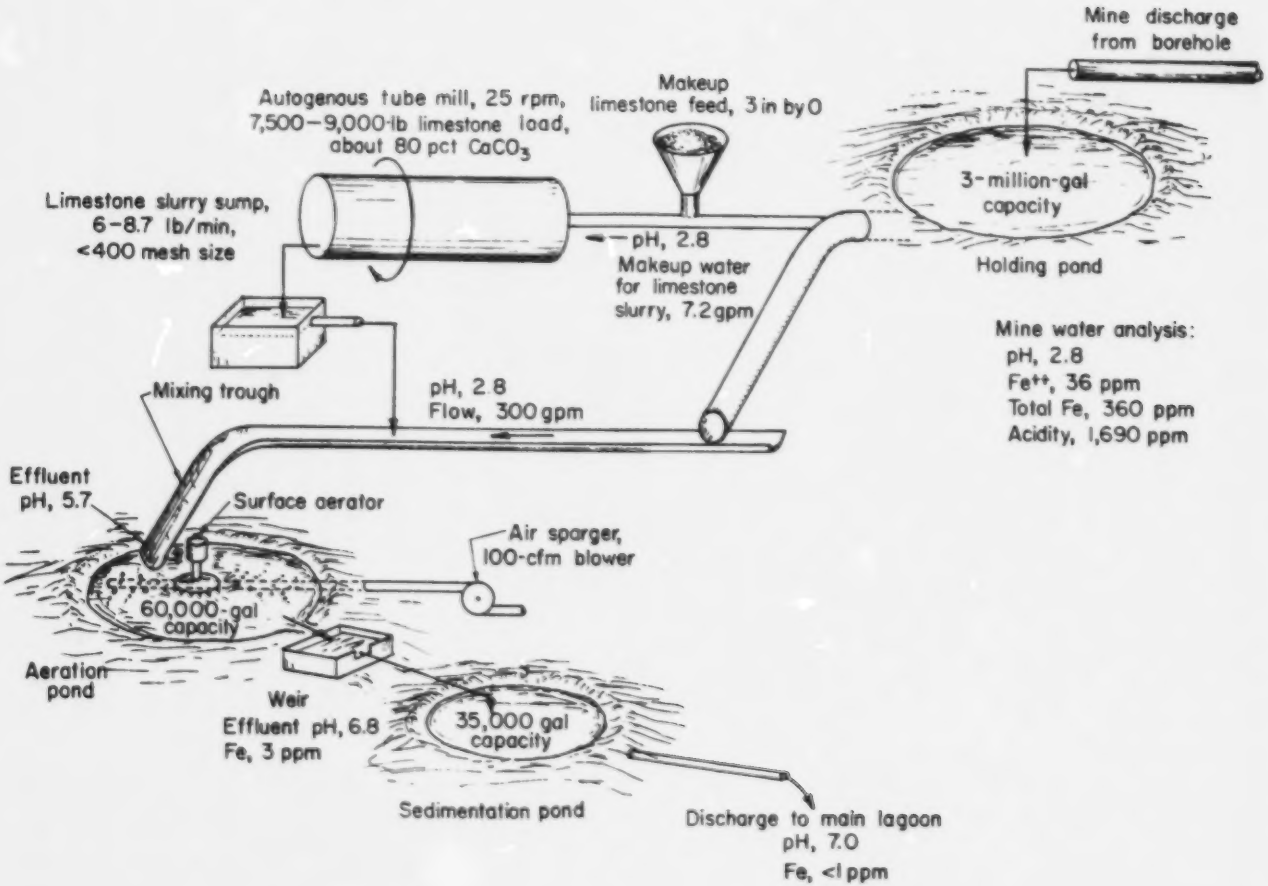

FIGURE 1. - Flowsheet of the Limestone Neutralization Process.

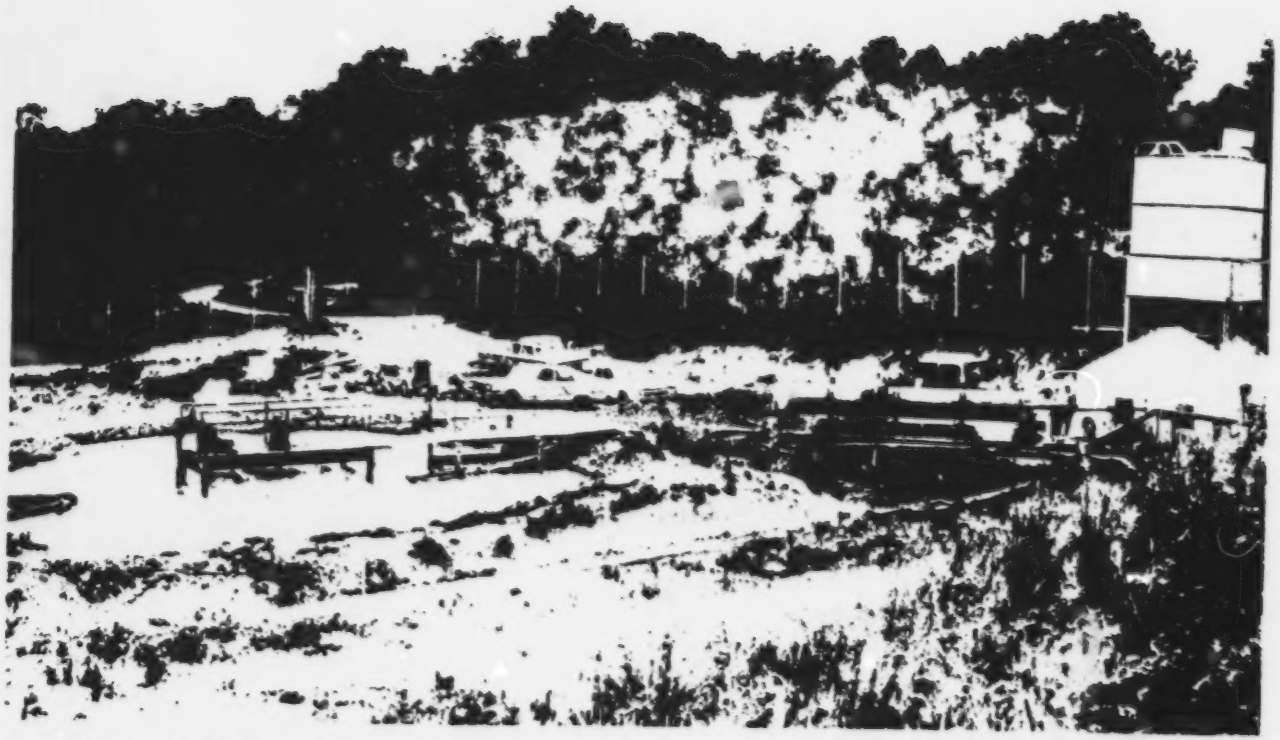

FIGURE 2. - Overall View of Limestone Treatment Plant From Edge of Holding Basin, Showing Tube Mill and Aeration Pond. Building at right is lime neutralization plant not part of this process.

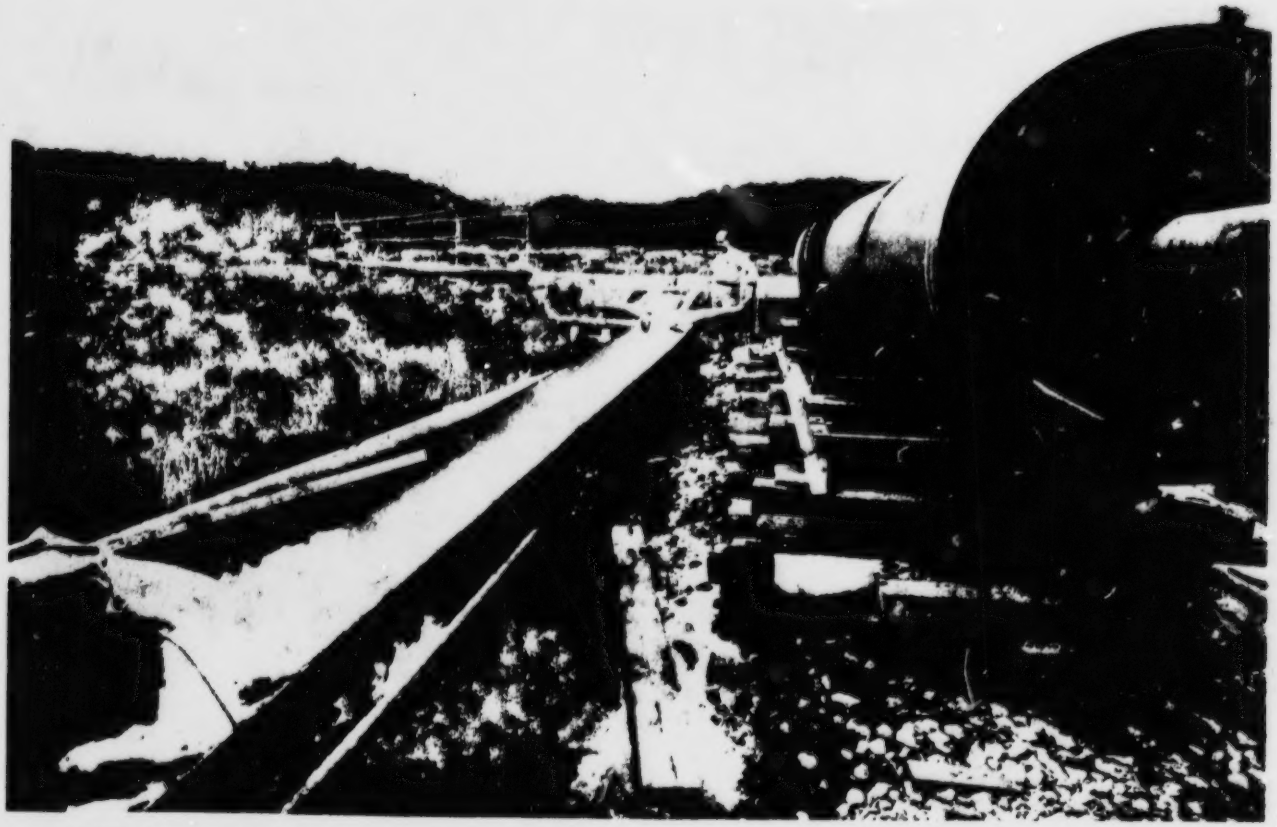

FIGURE 3. - Mine Water Feed and Limestone Slurry Discharge From Tube Mill. Makeup limestone and water for slurry enter through pipe at right.

FIGURE 4. - Limestone Slurry Discharging From Tube Mill to Small Sump and Through Pipe to Mixing Trough.

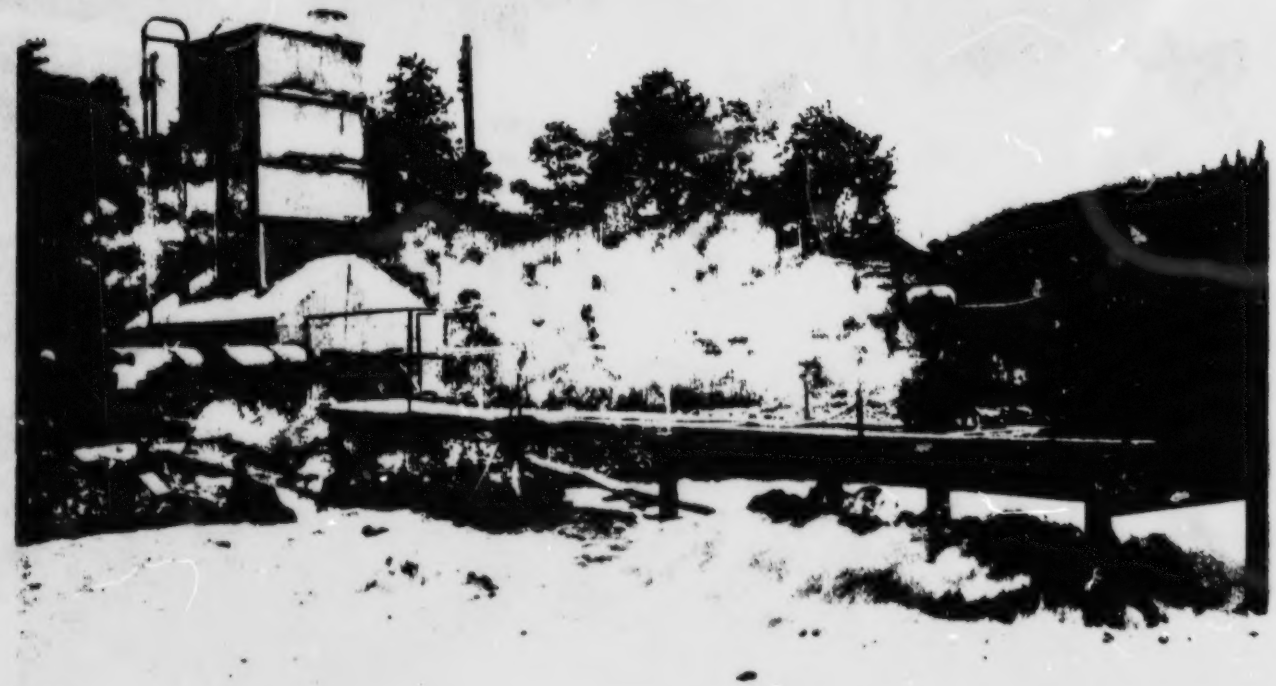

FIGURE 5. - Holding Pond, Upper Right; Tube Mill, Left; Slurry Discharge Pipe to Mixing Trough; and Aeration Pond With Surface Aerator at Right and Localized Air Sparging to Left.

with a 7-inch circular opening was mounted near the feed end of the mill. A similar screen, but without an opening, was located at the discharge end of the mill. A hinged watertight end plate with a 10-inch circular opening, contained the water within the tube mill and provided a hydrostatic head for flow. A 6-inch-diameter plastic pipe carried water into the tube mill, and limestone was added to the mill through an opening in the top of the pipe. Four equally spaced 1/4- by 2-inch angle irons, spirally mounted inside the mill, served as lifters and prevented sliding of the stone. The feed end of the tube mill was raised about 4 inches to permit higher limestone loads.

Limestone Used

The limestones for the tests were obtained locally from quarries at Smithfield, Pa., and Morgantown, W. Va., as standard commercial products. Two low-grade argillaceous limestones, double-screened 3- by 1-inch, and 1-1/2-inch by 0 crusher run sizes, were used. During the testing, a labor strike at one quarry made it necessary to find another source of limestone. The analysis of the limestones is shown in table 2. Both limestones were dark gray and contained undetermined amounts of organic matter; a fetid odor emanated from the tube mill while in operation.

TABLE 2. - Analysis of limestones

	Source of limestone	
	Smithfield, Pa.	Morgantown, W. Va.
Size.....inches..	3 by 1	1-1/2 by 0
Composition, percent:		
$CaCO_3$.....	72.0	82.0
$MgCO_3$.....	5.6	2.4
SiO_2.....	14.6	8.0
Fe_2O_3.....	1.6	1.7
Al_2O_3.....	4.5	1.3

Grinding Tests

The amount of fine limestone generated in the tube mill at 25 rpm was determined in a series of tests with various limestone loads and water throughputs. Results of these tests showed that very fine limestone is generated; over 90 percent passed through 400 mesh. With waterflows of 60 gpm or more through the tube mill containing approximately 7,000 pounds of 1/4- by 3-inch limestone, only 1.6 pounds per minute of fine limestone was produced. With comparable limestone loads at about 10 gpm of water, up to 6 pounds per minute of fine limestone was produced. More than 8 pounds per minute of fine limestone was generated with higher limestone loading (9,000 pounds). Figure 6 shows particle size distributions of the fine limestone produced as determined with a recording microsedimentation balance. A sample of the slurry produced in a 6-hour test contained particles 98.6 percent of which were finer than 400 mesh. The median size of the particles was about 8 microns. A photomicrograph of the limestone slurry (fig. 7) shows a high percentage of

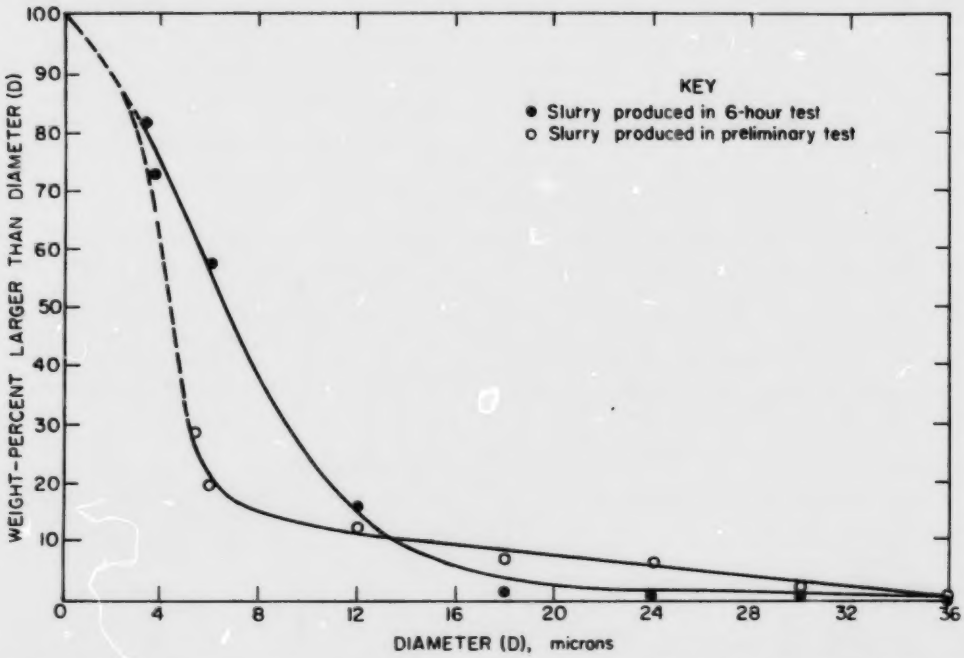

FIGURE 6. - Particle Size Distribution Curves of Limestone Slurry Produced in the Tube Mill.

extremely fine particles in the 1- to 5-micron range. The generation of fine limestone in the tube mill is shown in table 3.

TABLE 3. - Fine limestone generation in tube mill

	Flow through tube mill, gpm			
	11.0	14.6	13.3	7.2
Limestone load.....lb..	5,900	5,900	7,500	9,000
Limestone generated.....lb per min..	4.9	5.1	5.8	8.4
Screen analysis, percent:				
On 30 mesh.....	0.8	5.5	[1]0	[1]0
On 100 mesh.....	0.3	0.2	0.0	0.0
On 400 mesh.....	4.0	1.6	1.0	1.4
Through 400 mesh.....	94.9	92.7	99.0	98.6

[1]Most of the greater than 100 mesh material settled in a small sump located between the tube mill and the mixing trough.

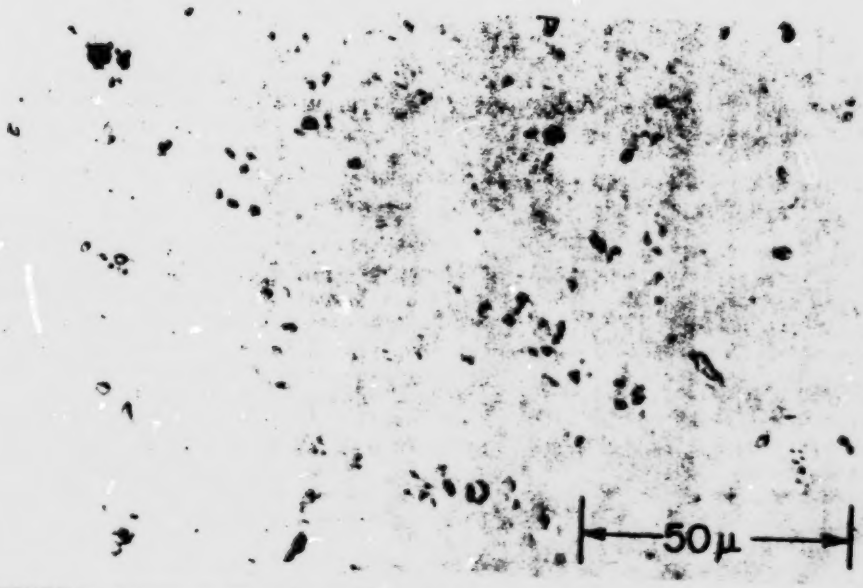

FIGURE 7. - Limestone Particles in Slurry From Tube Mill Produced During 6-Hour Test.

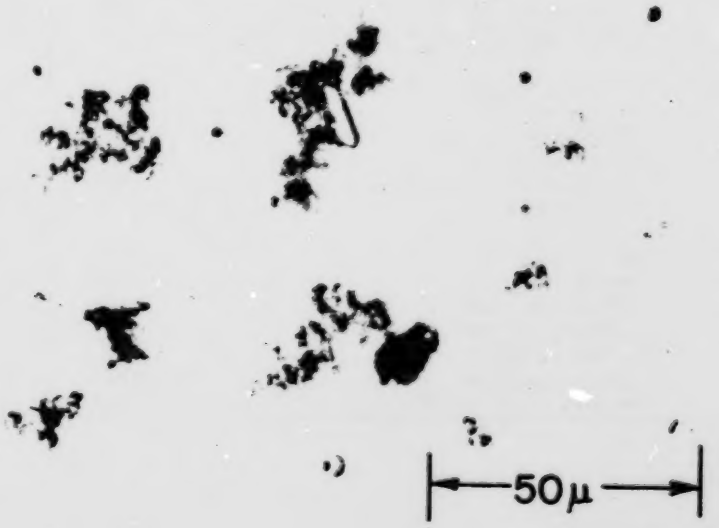

FIGURE 8. - Precipitated Neutralization Products From Mixing Trough. Note small gypsum crystal and floc formation.

TEST RESULTS

If the mine water to be treated must flow through the tube mill, its maximum capacity is about 100 gpm for this particular mine water. By using the tube mill solely as a device to generate a fine limestone slurry, which is subsequently added to the mine water, over 450 gpm could be treated. This rate could not be sustained owing to inadequate power supply. A flow of from 300 to 325 gpm was treated continuously during a 6-hour run.

At the start of the test summarized in tables 4 and 5, the tube mill contained approximately 7,500 pounds of smoothly rounded limestone ranging in size from 1/4 to 3 inches. Three- by 1-inch limestone, assaying 72.0 percent $CaCO_3$ and 5.6 percent $MgCO_3$, was added continuously to the reactor at a rate approximating the consumption rate for the first 2 hours; thereafter, 1-1/2-inch by 0 limestone, assaying 82.0 percent $CaCO_3$ and 2.4 percent $MgCO_3$, was added at a higher feed rate. The mill contained approximately 9,000 pounds of limestone at the end of the test. This resulted in the production of 2.2 pounds per minute more $CaCO_3$ than needed to neutralize the total acidity in the water at the 300- to 325-gpm flow rate. The amount of fine limestone produced was capable of treating up to 480 gpm, which is more than the average discharge from the borehole. If a pure limestone were used, as much as 600 gpm of this water could be treated.

TABLE 4. - Process conditions

Mine water treated:	
Flow rate.....gpm..	300-325
Total volume.....gal..	120,000
Analyses, average:	
pH.....	2.9
Ferrous iron.....ppm..	36
Total iron.....ppm..	360
Total acidity.....ppm..	1,690
Temperature.....° C..	18-19
Tube mill conditions:	
Speed.....rpm..	25
Limestone load, lb:	
Start of test.....	7,500
End of test.....	9,000
Limestone size.....inch..	3 by 0
Slurry flow rate.....gpm..	7.2

TABLE 5. - Process results

Elapsed time, hr	$CaCO_3$, lb per min[1]			Treated effluent		
	Required	Produced[1]	Excess	Before aeration, pH	After aeration pH	After aeration Fe, ppm
0.75	4.6	4.6	0.0	5.15	6.80	-
1.75	4.6	-	-	5.00	6.65	-
3.25	4.7	5.5	.8	5.30	6.80	-
4.25	4.7	6.1	1.4	5.70	6.75	3
5.75	4.7	6.7	2.0	5.70	6.75	-
6.25	4.7	6.9	2.2	5.90	6.80	3

[1]Represents about 80 percent of total solids produced; the other 20 percent is inert material.

Approximately 5 seconds elapses between the time the limestone slurry from the tube mill mixes with the mine water and the time it discharges into the aeration pond (fig. 8). Precipitates are already forming during this brief interval. The pH of samples taken from the end of the mixing trough is greater than 5.0. The suppressed pH is due almost entirely to dissolved carbon dioxide. This phenomenon is discussed more fully later in the report. The surface aeration and limited air sparging applied continuously in the aeration pond was adequate for these tests, but efficient air sparging is essential to achieve the high pH for removal of high concentrations of ferrous iron. Figure 9 shows the dispersed precipitated gypsum and iron hydroxide flocs in the effluent from the aeration pond.

Neutralization Rate

Acid neutralization batch tests in the laboratory, with a fine limestone slurry, indicated that air sparging removes CO_2 from the solution at a significantly higher rate than stirring (fig. 10).

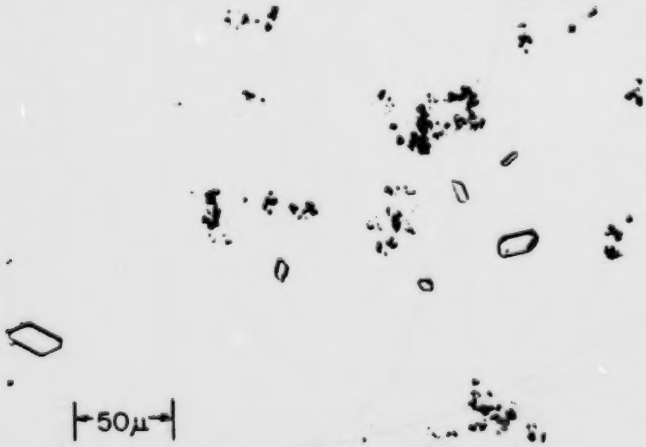

FIGURE 9. - Gypsum Crystals and Precipitated Floc in Effluent From Aeration Pond.

Studies were conducted in the laboratory using mine water with a limestone slurry containing 98 percent minus 400-mesh particles. A 12- and a 60-percent excess of limestone alkalinity were used. Comparable tests with slaked quicklime slurries and mine water were conducted. The limestone- and lime-neutralization rates are shown in figure 11. Air sparging was used during the limestone tests to

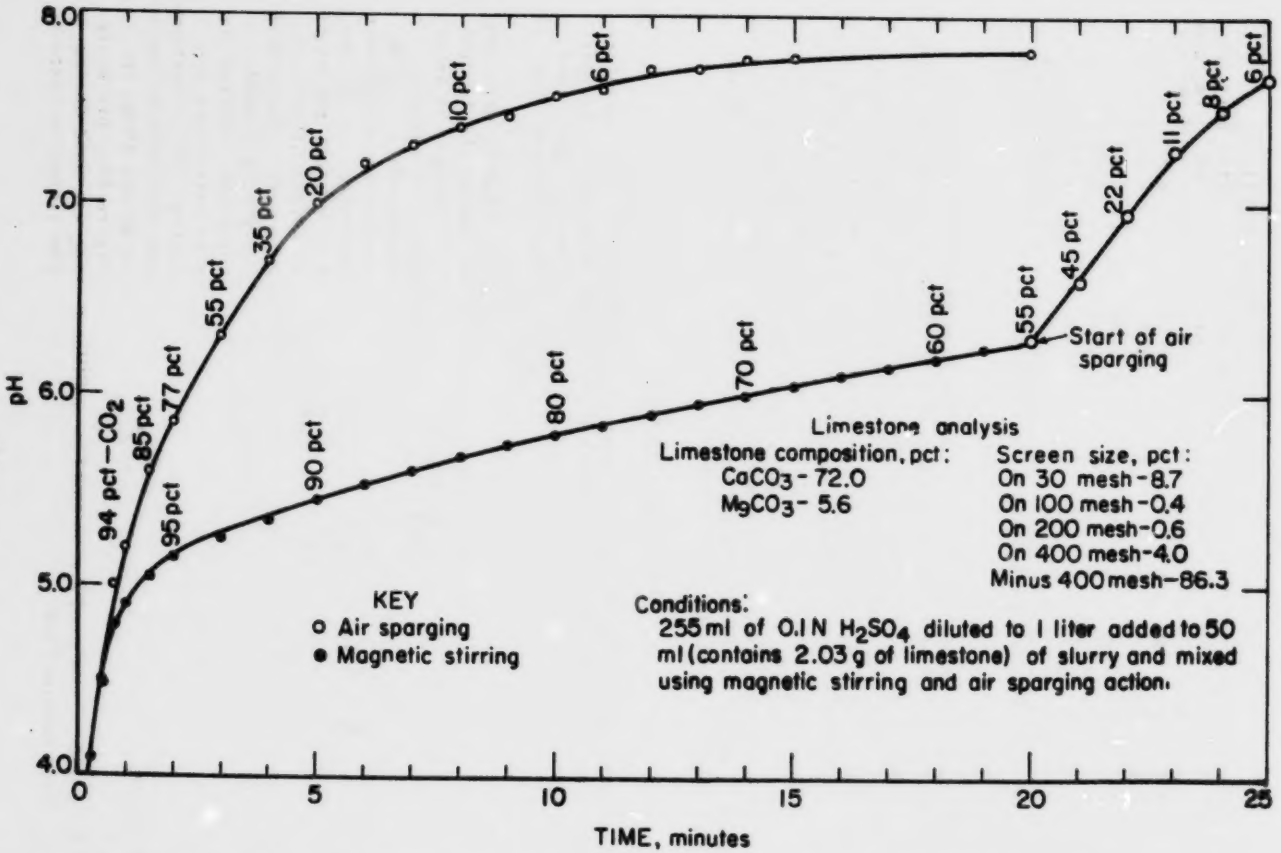

FIGURE 10. - Effect of Carbon Dioxide Removal on pH in Limestone Neutralization of Acid Solutions. CO_2 concentrations based on carbon dioxide-carbonate equilibrium data in aqueous solution (25° C). (Kern, David M. The Hydration of Carbon Dioxide. J. Chem. Ed., v. 37, No. 1, January 1960, p. 17.)

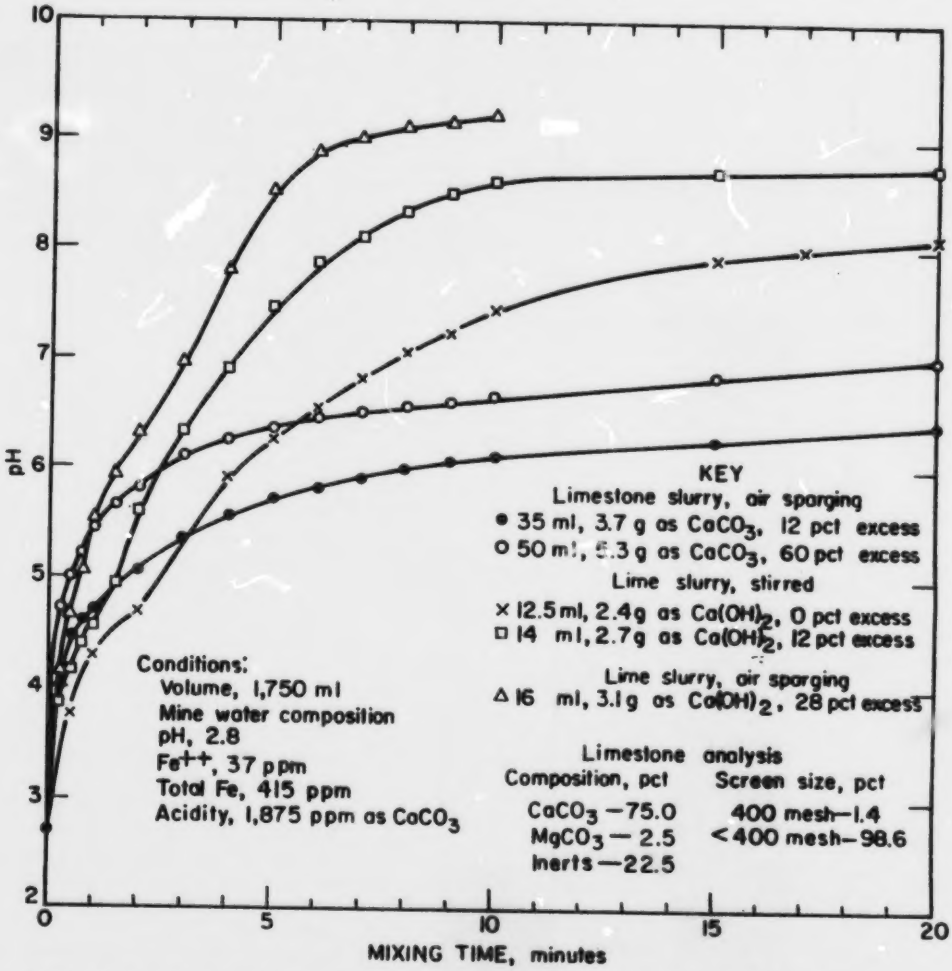

FIGURE 11. - Batch Tests of Neutralization of Acid Mine Water With Lime and Limestone Slurries.

expedite carbon dioxide removal. These tests are not as efficient as pilot tests, in which the more reactive particles are supplied continuously, but they do illustrate the importance of air sparging to remove dissolved carbon dioxide to achieve a high pH rapidly.

Settling and Compaction of Precipitated Solids

Settling and compaction tests were made on lime- and limestone-neutralized mine waters. The water was treated to the same end conditions; that is, to a

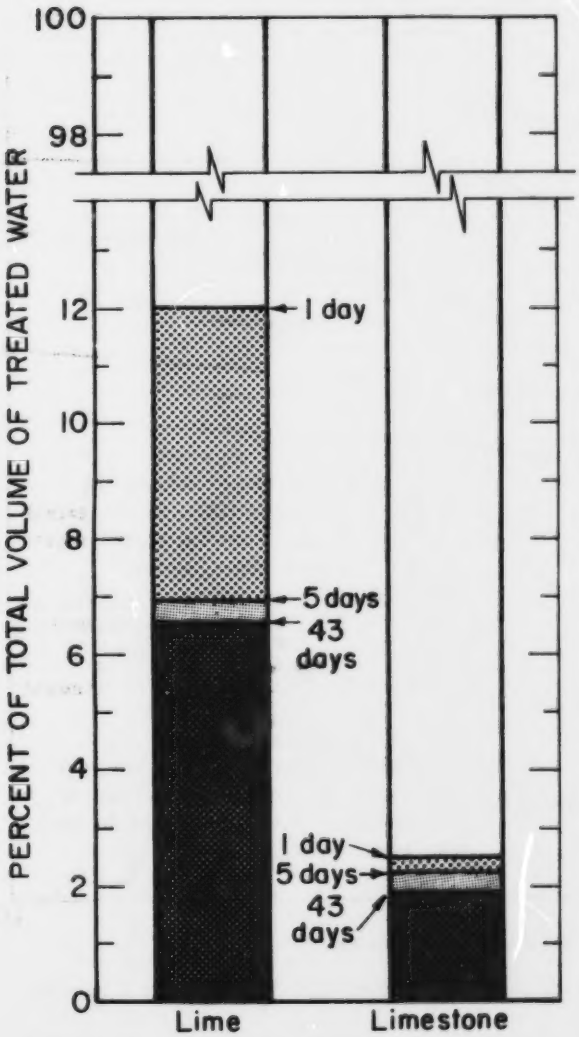

FIGURE 12. - Heights of Precipitated Sludge From Lime- and Limestone-Neutralized Water After Settling for 1, 5, and 43 Days as Percent of Total Volume of Treated Water.

pH of 6.9 and with no detectable iron remaining in solution. Glass cylinders, 2-5/16 inches in inside diameter and 48 inches long, with a capacity of 4.9 liters were used. Lime- and limestone-neutralized waters were put in separate cylinders and allowed to settle. The resulting data are shown in table 6 and illustrated in figure 12. After 1 day, the volume of sludge from limestone neutralization was less than one-fourth the volume produced by lime neutralization. After 43 days, the sludge volume from the limestone process was less than one-third the volume from the lime process. This difference in sludge volumes is significant for treatment plant design and in reducing the volume of sludge to be disposed.

An attempt was made to determine the influence of depth on sludge compaction. equal volumes of sludge were prepared for the test. To produce 4.9 liters of settled sludge after 1 day of settling, 27 liters of lime-neutralized mine water was required compared with 128 liters of limestone-neutralized mine water. The supernate was decanted, and the remaining sludge was allowed to settle in glass cylinders for 42 more days. These data are given in table 7 and illustrated in figure 13 for easy comparison with table 6 and figure 12. This simple scale-up is inadequate to establish absolute sludge compaction properties; however, the data do indicate that there is no compaction for the lime-neutralized sludge and that the limestone-neutralized sludge compacts slightly.

TABLE 6. - Height of settled solids of lime- and limestone-treated waters

Days	Percent of total volume[1]	
	Lime	Limestone
0	100.0	100.0
1	12.0	2.6
5	6.9	2.3
11	6.7	2.1
15	6.7	2.0
20	6.7	2.0
43	6.6	1.9

[1]As percent of total volume (pH = 6.9, no detectable iron).

TABLE 7. - Height of settled solids from 1 day's sludge concentrates produced from lime- and limestone-treated waters

	Percent of total sludge volume[1]	
	Lime	Limestone
Total volume of treated water.....liters..	27	128
Volume of 1 day's sludge.....do....	4.9	4.9
Days:		
0	100.0	100.0
4	50.9	57.6
10	47.3	51.6
14	46.6	50.6
19	46.0	50.6
42	44.7	48.5

[1]As percent of total sludge volume (pH = 6.9, no detectable iron).

The effect of solids concentration on hindered settling in a primary sedimentation pond and the potential for gypsum crystal growth with time are two important factors that could not be studied within the scope of this project.

A high-solids concentration of limestone-neutralized sludge rapidly produces a clear supernate. A low-solids concentration, which permits free settling, requires a longer time for water clarification. This is a well-known phenomenon[10] that should be considered in the design of thickeners, clarifiers, and settling ponds, especially where land area is a prime consideration.

Earlier experiments with limestone neutralization indicated that after agitation, limestone-neutralized solids tended to settle more rapidly as they aged. A possible explanation for this effect is the continual growth of gypsum crystals already present in the sludge. Such growth would affect

[10]Coe, H. S., and G. H. Clevenger. Methods for Determining the Capacities of of Slime Settling Tanks. Trans. AIME, v. 55, 1917, pp. 356-384.

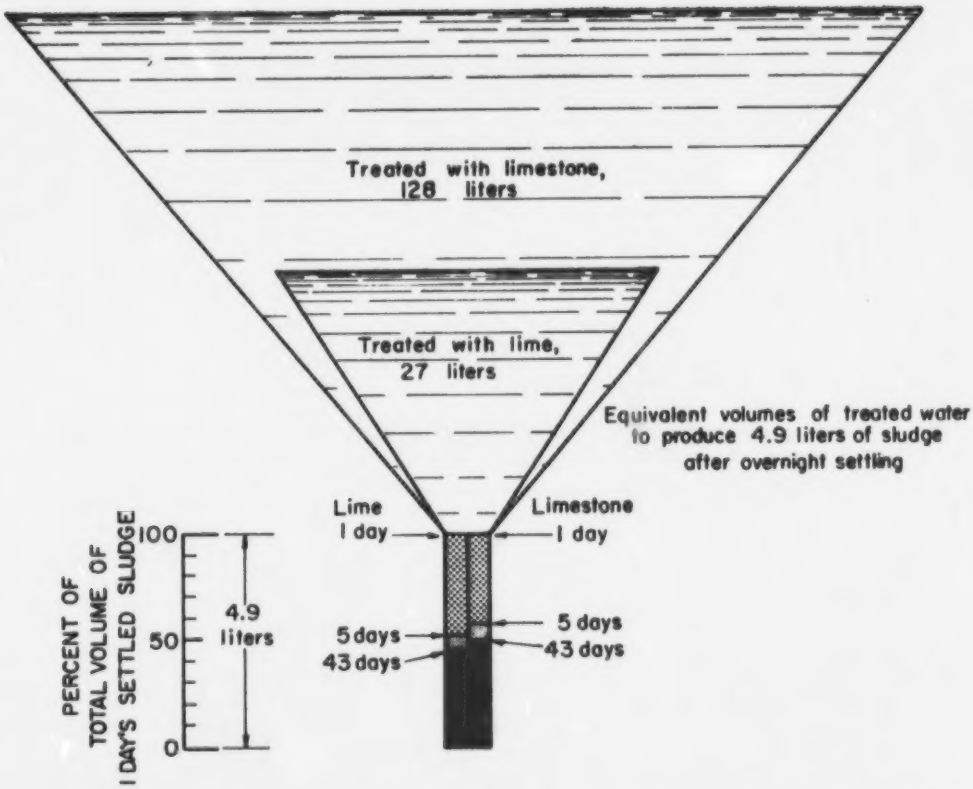

FIGURE 13. - Heights of Sludges Produced From Lime Neutralization of 27 Liters of Acid Mine Water and From Limestone Neutralization of 128 Liters of Acid Mine Water as Percent of Total Volume After 1 Day's Settling.

materially the settling characteristics of the sludge and may be an important factor in liquids-solids separation.

ECONOMICS OF LIMESTONE TREATMENT

The limestone process has inherent advantages over the conventional lime process; namely, lower cost, widely available raw material, simplicity in design and operation, and much smaller volume of precipitated solids. The limestones used in these tests were low grade, argillaceous limestones costing about $3 per ton delivered at the site in small lots. A standard lime product would have cost about $20 per ton.

To treat 1 million gallons per day of mine water, containing 2,000 ppm total acidity as $CaCO_3$, would require 16.6 tons per day of limestone (assuming

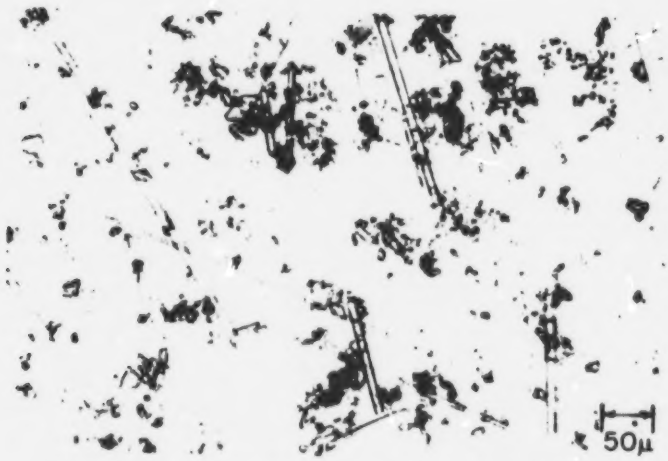

FIGURE 14. - Gypsum Crystals and Precipitated Floc From the Sedimentation Basin.

only 50 percent utilization based on inerts and excess $CaCO_3$) costing $50 per day, compared with 6.2 tons of hydrated lime (assuming 100-percent efficiency) costing about $120 per day. The savings in cost of raw material alone would amount to at least $25,000 per year.

Fine reactive limestone in slurry form can be generated in a simple tube mill and operated with a minimum of maintenance and control. Power requirements for generation of fine limestone in the tube mill are comparable to those of commercial grinding devices. With a power rate of 1.5 cents per kilowatt-hour, the cost of generating 1 ton of fine limestone is approximately 67 cents.[11]

Bulk handling techniques for coarse stone and slurry are available to permit low-cost, efficient operation. Because over-neutralization to a pH greater than 8.4 is impossible, expensive precision controls are not required; standard aeration equipment is adequate.

The rapid settling and higher compaction characteristics of limestone sludges, compared with lime sludges, indicate that settling basin requirements would be reduced considerably. Figure 14 shows the coarse mat of gypsum crystals and flocculated solids from the sedimentation pond. Since solids waste disposal is as much a problem as neutralizing acidity and removing soluble iron, a minimum threefold reduction in sludge volume is a distinct advantage.

CONCLUSIONS AND RECOMMENDATIONS

Limestone neutralization is an effective and low-cost method for treating ferruginous acid waters. This has been demonstrated at a mine discharge site where 300 to 400 gpm of mine water at a pH of 2.8 and containing 36 ppm ferrous iron (Fe^{++}), 360 ppm total iron (Fe), and 1,700 ppm total acidity--determined by the hot phenolphthalein method--was treated to yield a primary effluent containing less than 7 ppm iron, no acidity, and a pH of nearly 7. Overnight settling in a small sedimentation pond produced an alkaline final effluent having a pH of 7.4 containing no detectable iron.

[11] Perry, R. H., C. H. Chilton, and S. D. Kirkpatrick. Chemical Engineers Handbook, 4th ed., McGraw-Hill Book Co., Inc., New York, 1963, sec. 8, p. 47.

The limestone-treatment process, compared with the conventional lime-treatment process, has the following advantages: (1) Widespread distribution and lower cost of run-of-mine, indigenous limestone, (2) simplicity of plant design, (3) reduced hazards and plant operating and maintenance costs accruing from the use of a less reactive chemical agent, (4) higher solids concentration of the precipitated sludge, (5) no deleterious effect caused by accidental overtreatment, and (6) total treatment cost estimated to be one-half to two-thirds lower.

This process has general application for treating mine waters of the wide range of acidity and iron normally encountered, provided enough fine reactive limestone is available in slurry form to neutralize the acidity and sufficient aeration is provided to remove the dissolved carbon dioxide to create the high pH environment required for rapid iron oxidation and precipitation.

Based on the results of these tests it is recommended that, where pollution abatement measures cannot eliminate acid mine drainage, the limestone neutralization process be used to treat the persisting mine water effluent to produce an acceptable discharge. It is further recommended that, to effect maximum economies in treatment costs and in land conservation, consideration be given to use of the limestone neutralization process wherever other treatment processes are now in use or are contemplated. Milling of limestone to micron sizes, techniques of aeration, and sludge handling are aspects of the limestone neutralization process that can be optimized, and it is recommended that engineering studies be conducted in these areas.

INT.-BU.OF MINES,PGH.,PA. 12926

TENNESSEE CLAY DEPOSITS - AMD

Overburden from some ballclay deposits in Tennessee yields acid mine drainage with a pH of around 4, too low to be discharged. The pH is adjusted very simply by allowing the effluent to seep through a pile of limestone. This system works adequately and is completely passive. More information could be requested from:

AMOCO METALS CO.
7000 South Yosemite Street
Englewood, CO 80155
(303) 740-5000
Mark Passarini

ALKALINE MINE DRAINAGE

Occasionally mine drainage may have a high pH and, on standing, an algal bloom develops which increases the pH to 8.5-9.5, which is also too high to discharge. The algae consume CO_2 in the water which results in part of the increase in pH which must be reduced to pH 6-9 for discharge in terms of most NPDES permits. This phenomenon occurs usually in summer, for example in stormwater storage impoundments into which nutrients have been added, e.g., by addition of water reclaimed from secondary sewage treatment or settling ponds used to settle fine coal.

One company brings the pH to within effluent limits by acidifying with CO_2. An alternative way would be to add a small dose of sulfuric acid, but this involves handling, transporting, and storing a hazardous chemical.

report of investigations 6987

BUREAU OF MINES 1967

MINE WATER RESEARCH

Neutralization

by

Maurice Deul[1] and E. A. Mihok[2]

ABSTRACT

A special short-term research project was initiated to develop plant design parameters for treating mine waters to yield an effluent acceptable for discharge into streams and a sludge amenable to effective and economic disposal.

Neutralization was investigated to provide simple and direct treatment of ferruginous acid waters using lime, coarse limestone, and limestone followed by lime. Limestone treatment was accomplished using a small cement mixer as a simple reactor to provide abrasive agitation of limestone and mine water. Results from tests with nine mine waters encompassing a wide range of iron and acid concentrations showed that coarse limestone, one of the cheapest neutralizing agents known, is potentially useful for treating mine water discharges. However, process variables must be defined more completely before the practical applications and limitations of the process can be fully established.

In all the tests a pH of >7.2 was obtained ultimately with limestone. Reaction time to reduce the iron content below 7 ppm in the water was dependent on the original ferrous iron concentration. For waters with high ferrous iron content, treatment with limestone followed by lime rapidly produced an acceptable treated water. Sludges with good settling and handling characteristics resulted when limestone was used for neutralization either alone or with subsequent treatment.

Reaction rates are expressed graphically as pH change and iron depletion curves; characteristic solids settling curves are shown. The temperature dependency of ferrous iron oxidation was verified.

[1]Geologist, Pittsburgh Mining Research Center, Bureau of Mines, Pittsburgh, Pa.

[2]Chemical research engineer, Pittsburgh Mining Research Center, Bureau of Mines, Pittsburgh, Pa.

CONCLUSIONS AND RECOMMENDATIONS

Coarse limestone in a dynamic state with mine water and air has been demonstrated to provide sufficient sustained action to neutralize acid and to remove iron. For mine waters containing low to moderate concentrations of iron, the treated water had a pH of 7 to 8 and an iron concentration of less than 7 ppm; the precipitated solids compacted well. Mine waters high in ferrous iron required long reaction times (>15 min) with coarse limestone, and the treatment had to be supplemented with lime in a second stage to produce acceptable waters in a short reaction time. Nine mine waters of widely ranging acid and iron concentrations were treated by one or more of these methods for comparison with lime neutralization. These exploratory investigations show that coarse limestone, one of the cheapest neutralizing agents known, is potentially useful for treating mine water discharges.

It is recommended that investigations of neutralization processes should continue to (1) study the effect of contributing factors to the overall reaction such as size distribution and composition of limestone, residence time, temperature, degree of agitation and abrasion, and air-liquid-solid interfacial area; (2) design an efficient reactor to treat large volumes; and (3) develop plant design criteria for neutralization of acid mine waters.

INTRODUCTION

The Bureau of Mines, as a special adjunct to its comprehensive research program on the chemistry of mine waters, recently undertook a short-term project to define quickly and clearly the investigative effort that would be required to develop practical plant-design parameters for treating acid mine water. This project was initiated by the Bureau's Director, at the request of a group of coal mine operators, with the long-range goal of yielding an effluent acceptable for discharge into streams and a sludge amenable to effective and economic disposal.

A research program was outlined and implemented, encompassing an extensive field of investigation including neutralization, oxidation, settling characteristics, and sludge dewatering techniques. It was generally agreed that water treatment testing should consist of neutralization with lime, with limestone, and with limestone followed by lime. The emphasis on the use of limestone as a neutralization agent was due mainly to its low cost and easy availability.

ACKNOWLEDGMENTS

The cooperation of many representatives of the coal mining industry is gratefully acknowledged. These included Rochester & Pittsburgh Coal Company; Pittsburgh Coal Company, Division of Consolidation Coal Company; Bethlehem Steel Company; Powell Coal Company; and Jones & Laughlin Steel Corporation. Without their assistance and personal guidance in site selection, their making available temporary field laboratory space, and free access to their records of water analyses, progress of the work would have been much slower. The free exchange of information is exemplified by the disclosure by Rochester &

Pittsburgh Coal Company officials that they had been investigating a promising limestone neutralization process.

We are grateful for their demonstrated concern for maintenance of safe working conditions in crowded and potentially hazardous locations.

We also acknowledge the efforts of C. E. Chamberlain, chemist, and K. D. Curley and Fred Pichi, technicians, for their high efficiency throughout a difficult and arduous field program.

WATERS TESTED

A reconnaissance survey and sampling of mine waters representing a wide range of composition were conducted on sites of the cooperating coal mining companies. Nine mine water discharges were selected. Typical analyses of these waters are presented in table 1.

TABLE 1. - Analysis of mine waters collected during reconnaissance

Mine water	A-1	A-2	B-1	B-2	B-3	C-1	D-1	E-1	E-2
pH	2.80	3.65	2.85	4.20	3.20	3.10	6.70	2.70	6.10
Total acidity[1] ....ppm	1,215	685	775	1,720	1,380	1,050	5	4,530	55
Dissolved solids ....ppm	3,180	([2])	2,520	5,330	3,490	3,310	2,090	([2])	7,680
Total sulfates (as SO_4) ....ppm	2,150	([2])	1,660	3,350	2,180	2,175	1,150	([2])	4,440
Total iron ....ppm	294	168	154	713	406	425	42	1,176	56
Ferrous iron, Fe^{++} ...ppm	98	162	0	699	70	([2])	35	577	42
Calcium, Ca^{++} ....ppm	148	([2])	220	360	188	249	172	([2])	392
Magnesium, Mg^{++} ....ppm	([2])	([2])	83	117	95	109	41	([2])	107
Eh (oxidation potential) ....mv	675	([2])	800	435	600	615	165	([2])	260
Conductivity ....mmho	2,900	([2])	2,430	4,040	2,800	2,811	2,420	([2])	8,300

[1]End point = pH 8.20 at 60° C.
[2]Not determined.

The composition of any mine water discharge is variable and subject to almost daily fluctuation. The waters used in the field tests were taken 1 to 2 months after the reconnaissance sampling. The composition of the mine waters actually tested and the test results are given in the section describing the test results.

TEST PROGRAM

Procedure

The characteristics of mine water change with time; consequently, it was necessary to conduct experimental work at the point of discharge. The field equipment consisted of laboratory analysis facilities and neutralization, settling, and filtration equipment. Samples of mine water were taken from the discharge for analysis and neutralization. The reaction was monitored for pH and for ferrous iron concentrations. In most cases, the initial test was run

beyond the point of complete iron removal to obtain a pH trend in the neutralization process. When that point was determined, additional batches of neutralized water were made to provide sufficient volume for settling and filtration tests. Samples for detailed analysis at the Bureau of Mines laboratories were withdrawn at various stages of treatment. This procedure was substantially the same for all water treated.

Reactor

A modified cement mixer, 1/4-cubic-yard capacity, was used as a reactor (fig. 1). Except for continuous tests, all neutralization tests were conducted on a batch basis, keeping the reactor conditions constant. Rather than design a reactor in the short time allotted this project, it was decided that a cement mixer could impart the necessary interaction between mine water, limestone, and air. The mixer was driven by a gasoline engine at constant speed of 22 rpm. The mixer was held at a set angle of tilt about 20° from the horizontal for all tests to insure containment of the limestone and prevent loss of water by overflow and splashing. The inside surface of the mixer was coated with an inert epoxy resin to prevent contamination of the waters by extraneous iron that might be dissolved by the acid water.

Neutralizing Agents

The neutralizing agents used for the tests were high-calcium, double-screened (1- by 1/2-inch and 1/2- by 1/4-inch) limestones and commercial hydrated lime. The analysis of the reagents is shown in table 2. The limestones were obtained locally from lime and stone companies as standard commercial products.

TABLE 2. - Analysis of neutralizing agents, pct

Composition	Limestone		Composition	Lime
	(1- by 1/2-inch)	(1/2- by 1/4-inch)		
$CaCO_3$	94.27	98.81	CaO	73.17
$MgCo_3$	.21	.58	MgO	1.03
Silica	4.07	([1])	Iron	.22
Iron	.29	.06		

[1]Not determined.

Analytical Methods

Methods of analysis used in the field are as follows:

1. pH. Determined by electrometric measurement by means of the glass electrode.

2. Acidity. Sample was oxidized and boiled to hydrolyze all iron salts and remove CO_2, then titrated with standard sodium hydroxide to an electrometric pH of 8.2 at 60° C.

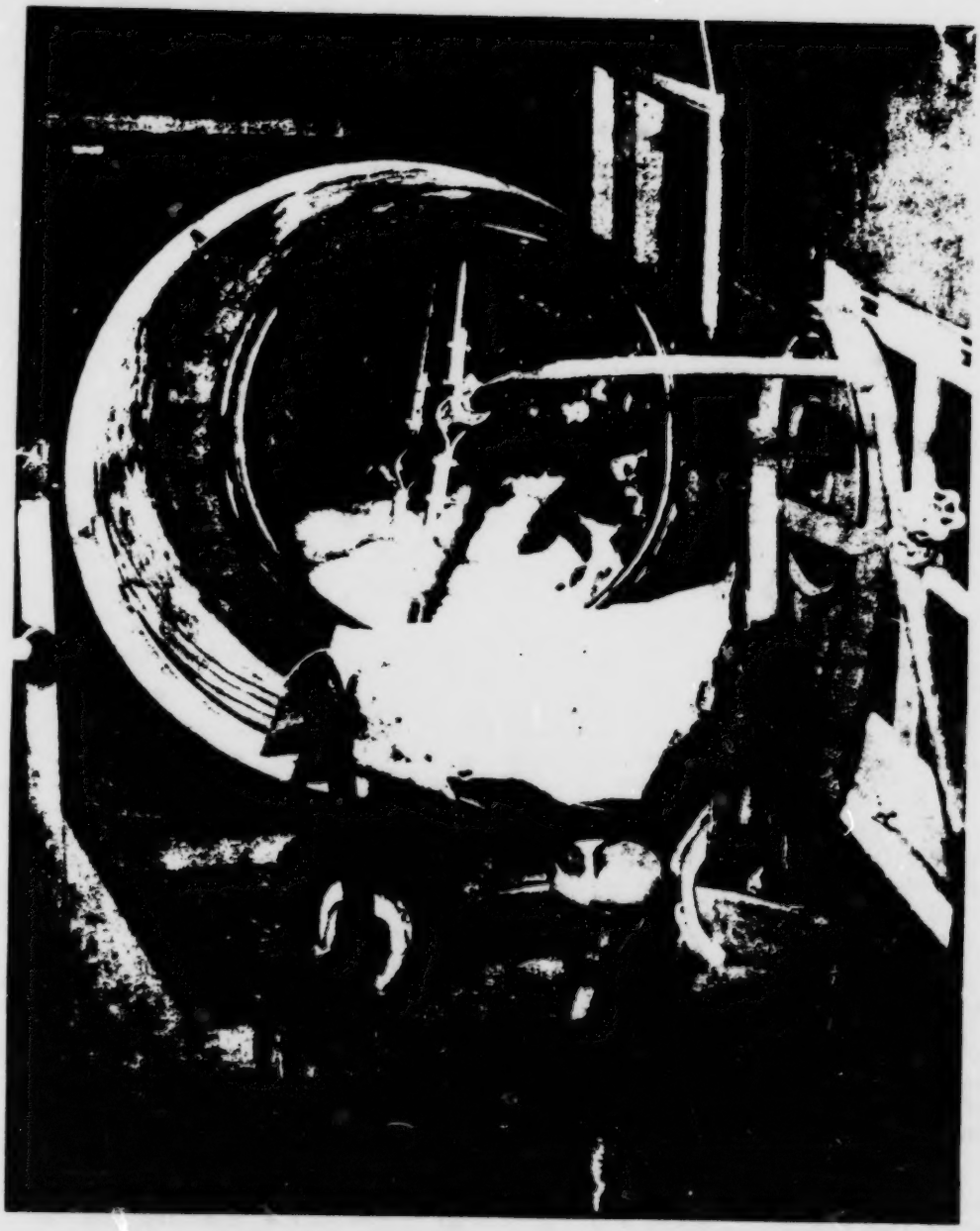

FIGURE 1. - Photograph of Reactor.

3. Iron, ferrous. Sulfuric acid-phosphoric acid mixture and sodium salt of diphenylamine sulfonate indicator were added to the sample and titrated with standard potassium dichromate.

4. Iron, total. Sample was oxidized with bromine water, iron precipitated with ammonium hydroxide, filtered and redissolved with hydrochloric acid, reduced with stannous chloride, and titrated with standard potassium dichromate.

Other determinations were made in the laboratory as follows:

1. Carbon dioxide. Evolved by acid and absorbed in ascarite.

2. Sulfate. Precipitated as barium sulfate and weighed as such.

3. Calcium. Precipitated as calcium oxalate, ignited, and weighed as calcium oxide.

4. Magnesium. Precipitated as magnesium ammonium phosphate, ignited, and weighed as magnesium pyrophosphate.

5. Silica. Hydrochloric acid insoluble material was ignited and weighed; then evaporated with hydrofluoric acid to expel SiO_2. Difference in weight is SiO_2.

6. Water. Sample air dried at 85° F, then dried to constant weight at 105° C.

7. Solids, weight-percent. Net weight of sample obtained by weighing sample plus bottle, and subtracting weight of bottle. Filtered by gravity on weighed filter paper. Paper and contents dried at 105° C to constant weight.

8. Eh (oxidation potential). Electrometric measurement of oxidation potential by means of an electrode pair consisting of an inert (platinum) electrode and a reference (calomel) electrode.

Limestone Neutralization

The literature and laboratory tests on the use of limestone--coarse, powdered, and granular--as an acid neutralizing agent indicate that the terminal pH is usually in the range of 6.0 to 6.5. This pH, however, is not maintained on a continuing basis. The limestone reactivity steadily decreases; this is due in part to the deposition of reaction solids on the surface of limestone particles. Failure to remove carbon dioxide from the solution, resulting in the formation of carbonic acid, also inhibits the neutralizing action.

Exploratory tests in the laboratory using acid mine water with coarse (1- by 1/2-inch) limestone in a small cement mixer, which can be construed to be a tilted revolving chamber with baffles and lifter plates, resulted in a terminal pH above 8. The inordinately high alkalinity obtained gave immediate impetus to reinvestigate this reaction. The present explanation is that this

high pH is achieved by vigorous cascading agitation to provide (1) abrasion to eliminate coating of limestone particles with precipitated solids and continual renewal of reactive surface; (2) large aeration surface for oxidation of ferrous iron; and (3) removal of CO_2 from the solution.

Prior efforts to utilize limestone[3] as an alkaline agent were concerned with stoichiometric proportions or a small excess of limestone. Theoretically, smaller particles should contribute to greater activity. However, this is not the basis to maintain sustained high activity. A great excess of limestone is needed to provide a constantly renewed reactive surface. For most of the batch neutralization tests, the ratio was approximately 1 part water to 2 parts limestone, or 10 gal (83 lb) of water to 150 lb of limestone.

Lime Neutralization

Most industrial acid waste liquors are neutralized with lime. The lime used in the form of a quicklime, or hydrate, usually provides a cheap source of alkalinity. The reactivity of commercial lime is great enough to neutralize economically the acid and precipitate the high iron concentrations normally encountered in industrial waste liquors.[4] Since acid mine drainage, at worst, contains only a fraction of the acid and iron found in industrial acid waste liquors, the use of lime supplies a ready solution. The disadvantages in the use of lime as a treatment of mine waters are (1) the high cost of alkalinity and (2) that the precipitated solids occupy large volumes which must be disposed of with difficulty. The technology of lime treatment of acid wastes is highly advanced so that estimates of treatment costs can be obtained readily.

Limestone-Lime Neutralization

Another method of treating mine waters was investigated using primary treatment with limestone followed by secondary lime treatment. In most cases, the mine water was allowed to mix with the coarse limestone in the reactor for at least 1 min and then the lime was added in small increments until the pH of the solution reached 8 to 9.

Using limestone, long reaction periods were needed to treat mine waters high in ferrous iron. With lime, the same waters were rapidly neutralized, but larger amounts of reagent were required to precipitate all the iron. Therefore, a dual treatment using the two alkaline agents would produce an effect combining the best of both reactions.

---

[3]Boynton, Robert S. Chemistry and Technology of Lime and Limestone. Interscience Publishers, New York, 1966, pp. 370-372.

[4]Hoak, Richard D., Clifford J. Lewis, Charles J. Sindlinger, and Bernice Klein. Lime Treatment of Waste Pickle Liquor. Ind. and Eng. Chem., v. 39, No. 2, 1947, pp. 131-135.

Continuous Limestone Neutralization

The limestone reactor was converted from batch neutralization to continuous operation. A raw water feed line was introduced into the reactor with the discharge outlet submerged in the coarse limestone. A discharge well was provided near the opening of the reactor for insertion of pH electrodes to continuously monitor the treated water discharge. Settling containers also were provided to collect concentrated solids and clarified effluent.

Piping difficulties imposed limitations on the raw feed supply. As a result, a flow rate of only 1 to 1-1/4 gpm was obtained. The first test was conducted with 150 lb of 1- by 1/2-inch limestone. The continuous operation was conducted for about 4-1/2 hours on the first day and for about 5-1/2 hours on the following day. Approximately 700 gal of raw water, pH 5.8 and ferrous iron content of 70 ppm, at a temperature of 12° to 13° C was treated. The equilibrium pH varied from 7.80 to 7.55. The ferrous iron concentration of the reactor discharge in the settling basin and the clarified effluent was determined at intervals throughout the test. Ferrous iron concentration in the treated water did not exceed 3 ppm.

The second test was conducted with 150 lb of 1/2- by 1/4-inch limestone at an initial raw water feed rate of 2.5 gpm, with pH of 5.6 and ferrous iron content of 90 ppm. A pH of 7.15 was obtained in the reactor and 7.35 in the settling basin. An additional 117 lb was added to the reactor. The pH rose slightly to 7.40, but considerable ferrous iron, about 50 ppm, was still present. The test was run for approximately 30 min. The temperature of the raw water in this test was 6° C (43° F).

The third test consisted of 300 lb of 1/2- by 1/4-inch limestone with a raw water feed rate of 2-3/4 gpm. After 30 min of operation, the pH steadied at 7.6. The ferrous iron content in the treated water was 22 to 28 ppm. The raw water feed was reduced to 2 gpm with a resulting pH of 7.8, but the iron content remained at 22 ppm. The temperature of this water was 6° C (43° F).

TEST RESULTS

pH Increase With Limestone Treatment

Figures 2 through 7 show the change in pH with time as the reaction progressed for all waters tested. The points on the curve indicate the time a sample of the water was withdrawn from the reactor and the pH determined electrometrically. The total reaction time was arbitrarily set at 20 min, with several tests prolonged beyond that.

Ferrous Iron Depletion With Limestone Treatment

Figure 8 shows the concentrations of dissolved ferrous iron (Fe^{++}) as the reaction progressed. The ferrous iron determination was made from the same sample that was withdrawn for pH measurement. Relatively few ferrous iron determinations were obtained. The ferrous iron concentration is dependent on

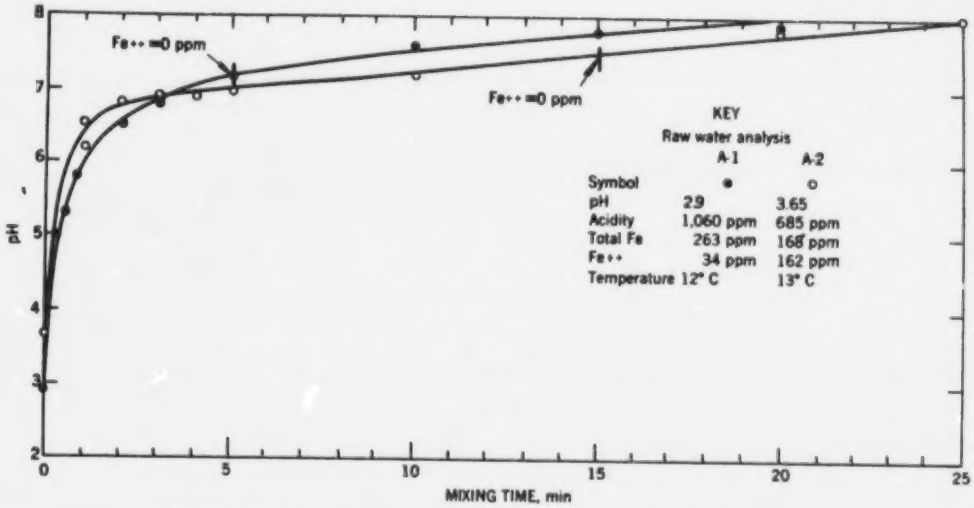

FIGURE 2. - Limestone Neutralization of A-1 and A-2 Mine Waters.

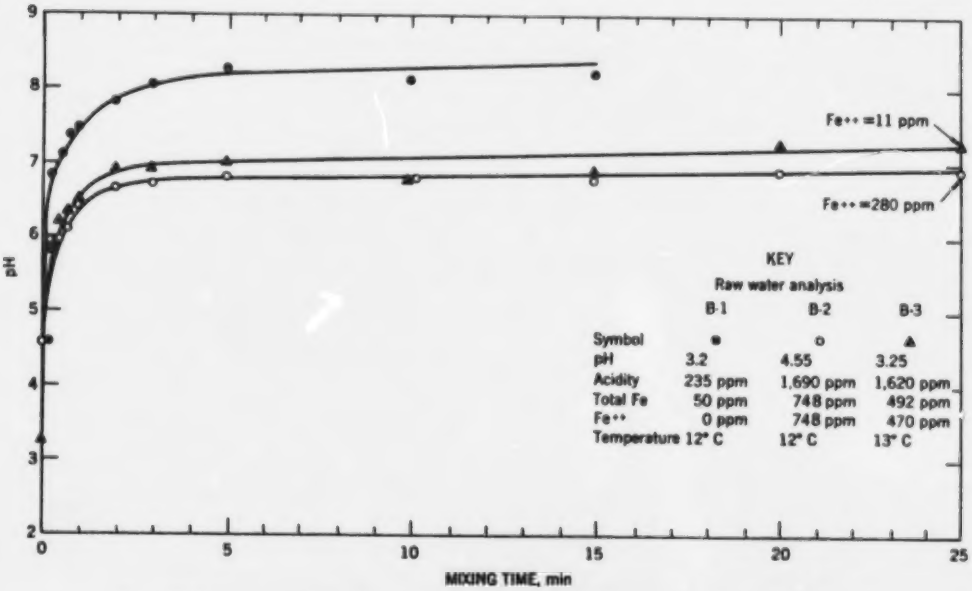

FIGURE 3. - Limestone Neutralization of B-1, B-2, and B-3 Mine Waters.

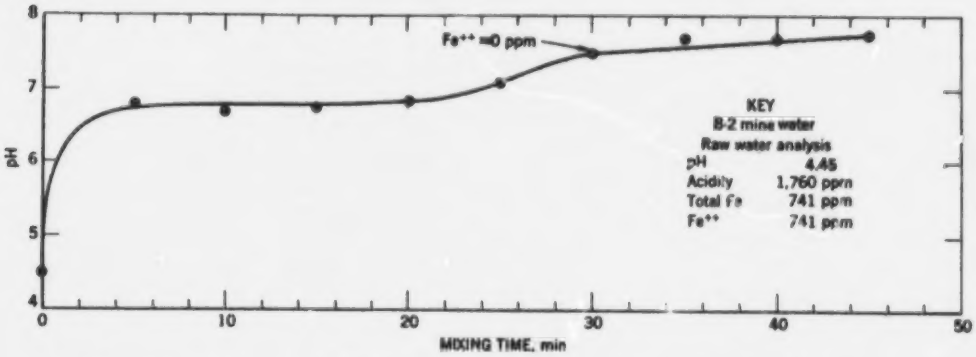

FIGURE 4. - Limestone Neutralization of B-2 Mine Water With 250 lb Limestone.

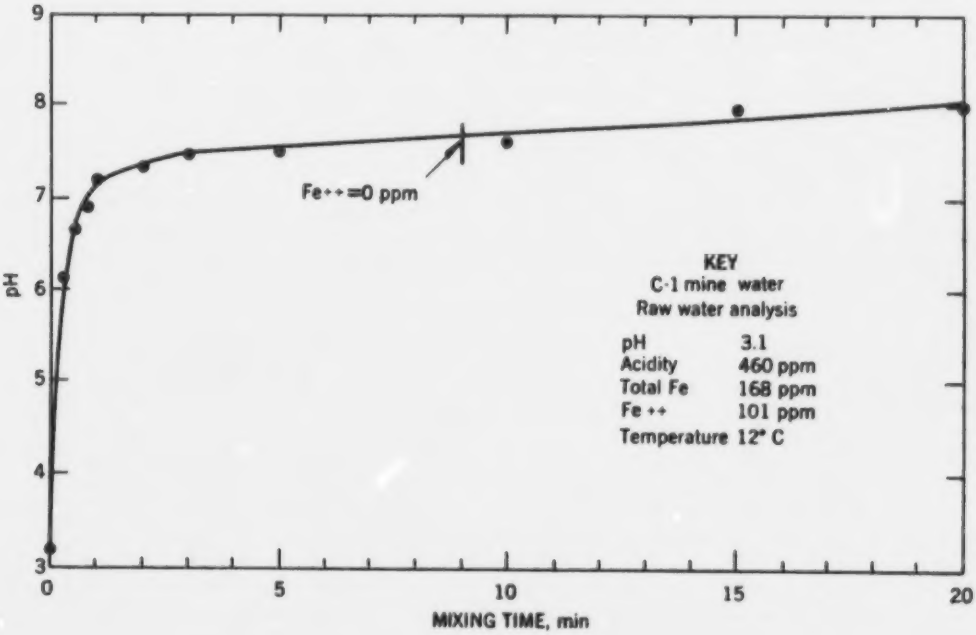

FIGURE 5. - Limestone Neutralization of C-1 Mine Water.

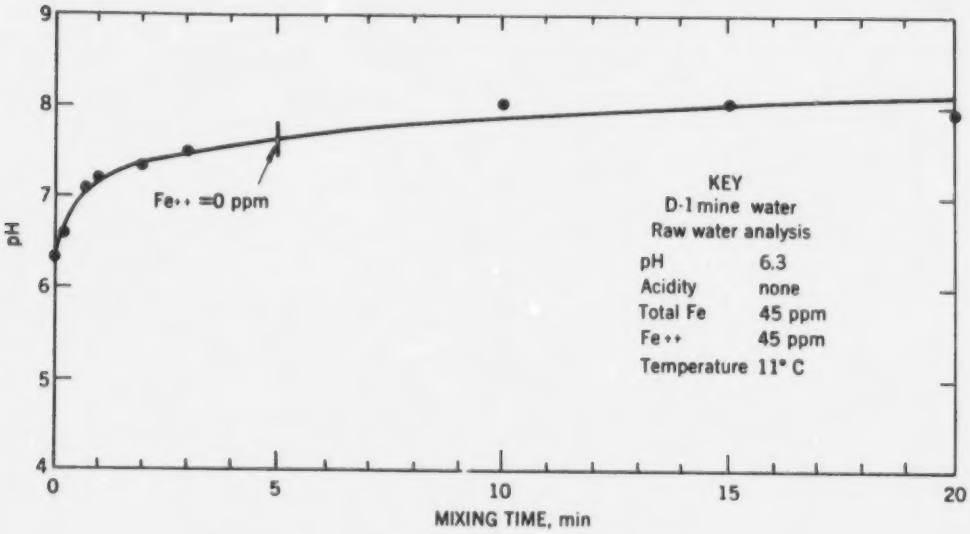

FIGURE 6. - Limestone Neutralization of D-1 Mine Water.

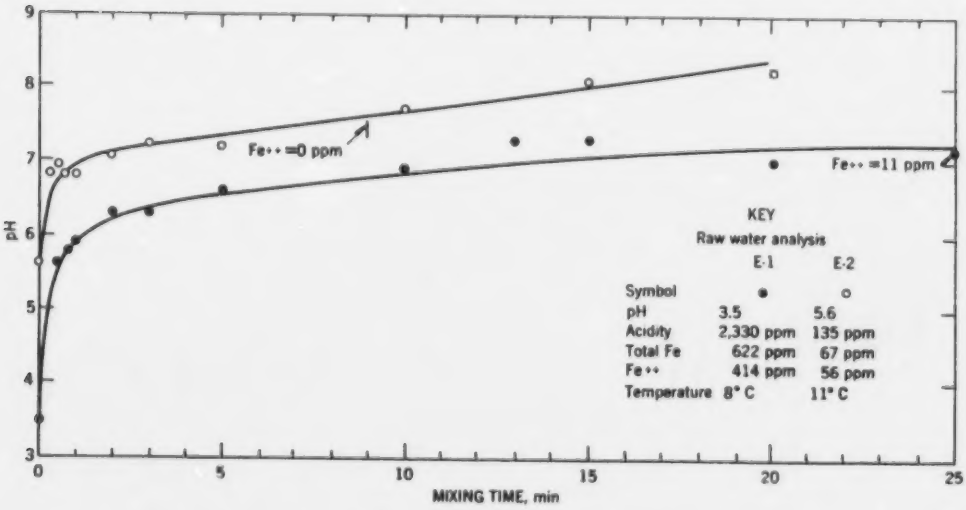

FIGURE 7. - Limestone Neutralization of E-1 and E-2 Mine Waters.

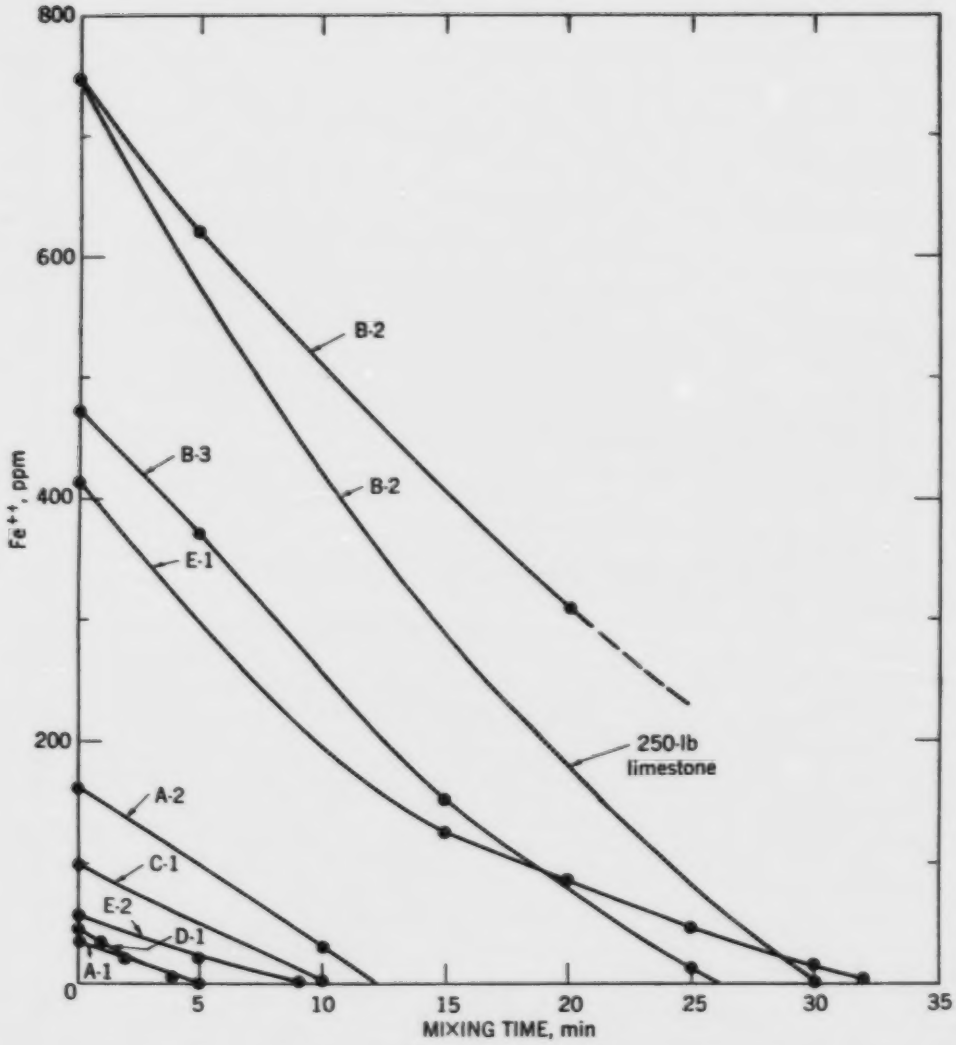

FIGURE 8. - Ferrous Iron Depletion With Limestone Treatment of Various Mine Waters.

reaction time, but the determination itself is time consuming; therefore, reactor samples could not be saved for later analysis.

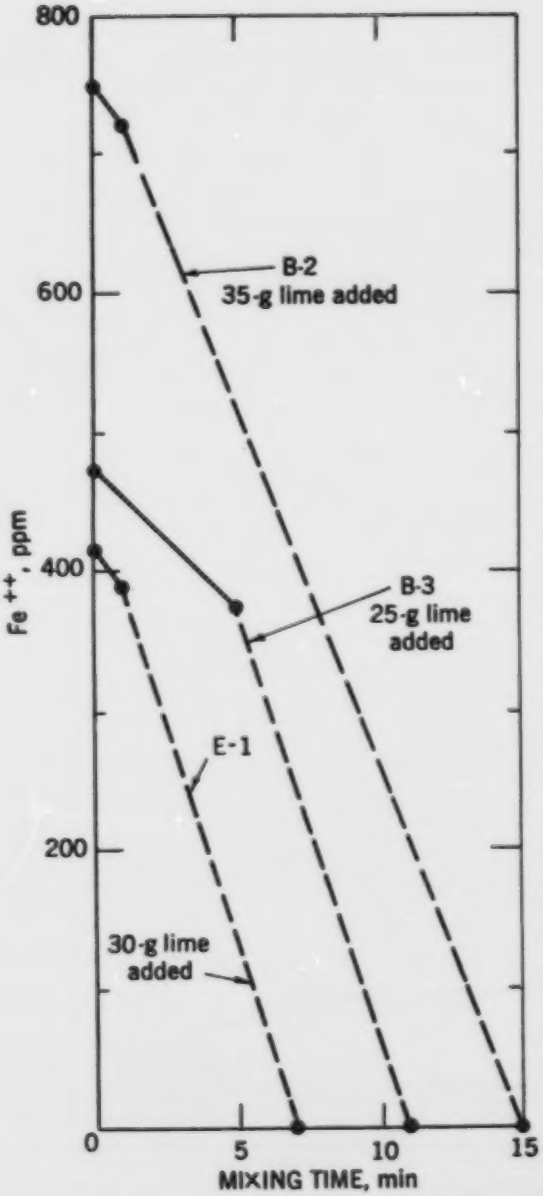

FIGURE 9. - Ferrous Iron Depletion With Limestone-Lime Mixed Treatment.

Ferrous Iron Depletion With Limestone-Lime Treatment

Figure 9 shows the ferrous iron depletion trend of several mine waters high in ferrous iron with a primary limestone treatment of 1 to 5 min, and with indicated amounts of hydrated lime added and mixed for the remaining time.

Sludge Settling Rates and Sludge Volumes

As soon as the neutralization process was completed, portions of the treated water were placed in 1-liter graduated cylinders for settling rate and sludge volume determinations. The results of these tests are shown in figures 10 through 18. Well-defined interfaces between settled solids and supernate were observed where there were high solids concentrations; dilute solids concentrations, especially those formed with lime, showed poorly defined interfaces in the early stages of settling.

These settling rate curves show that wherever limestone is used for neutralization treatment, either alone or with lime, the settling rates and volumes of compacted solids indicate more favorable conditions for solids-liquid separation than when lime alone is used.

It is obvious that the more rapid settling rates and high degree of compaction for limestone-treated water are due, in part, to the excess limestone abraded during the mixing action. This, of course, can be minimized but it is expected that the favorable influence of limestone on settling and

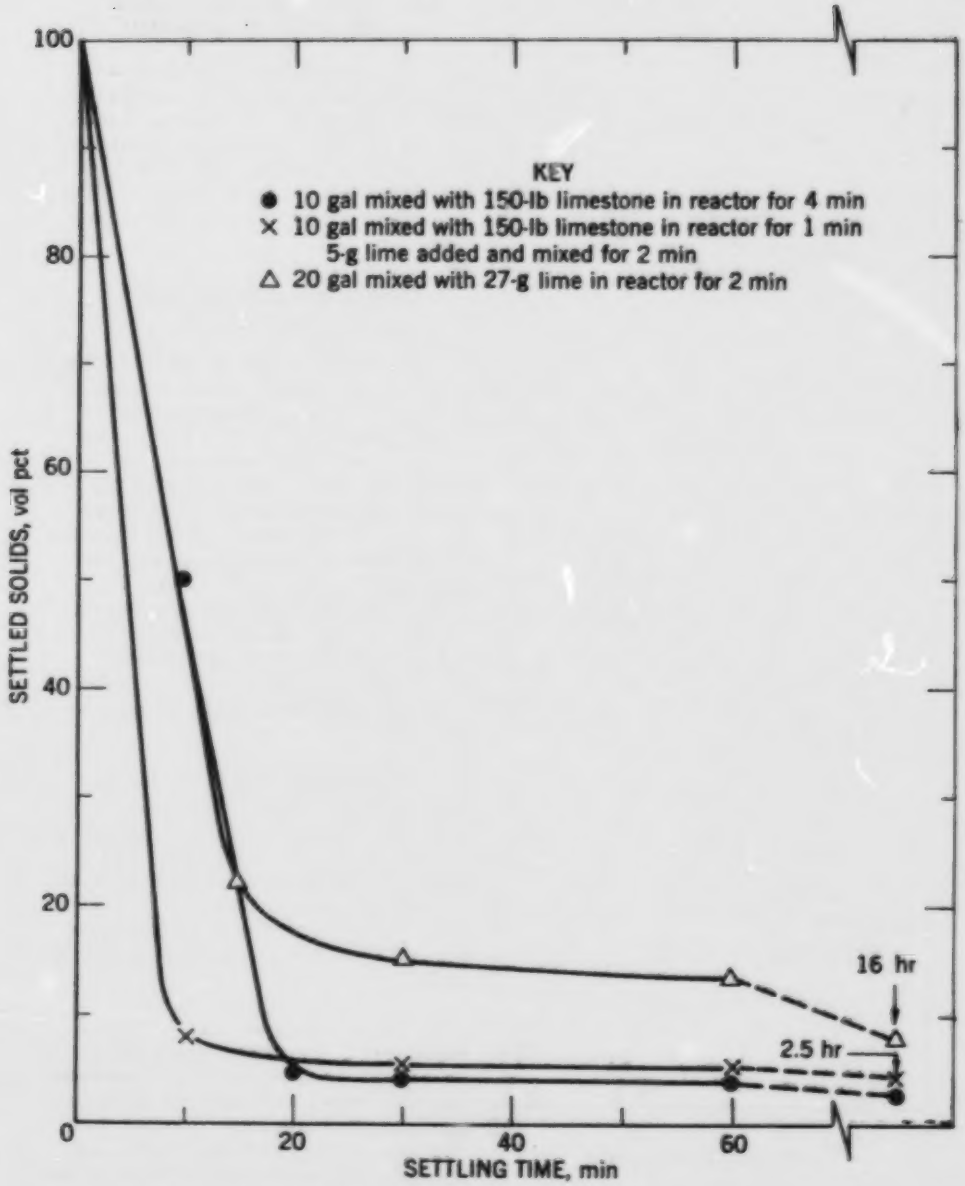

FIGURE 10. - Settling Rate of Sludges From A-1 Treated Water.

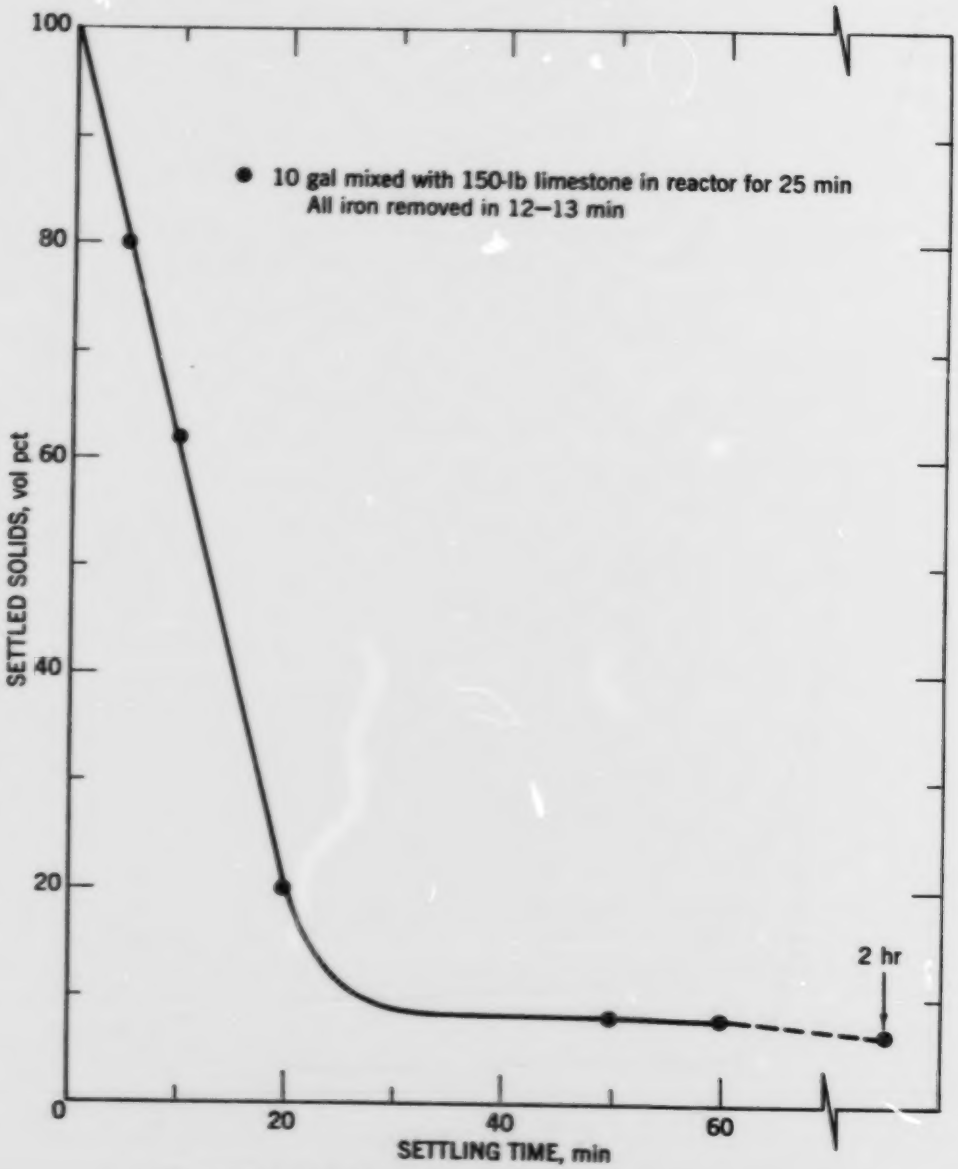

FIGURE 11. - Settling Rate of Sludge From A-2 Treated Water.

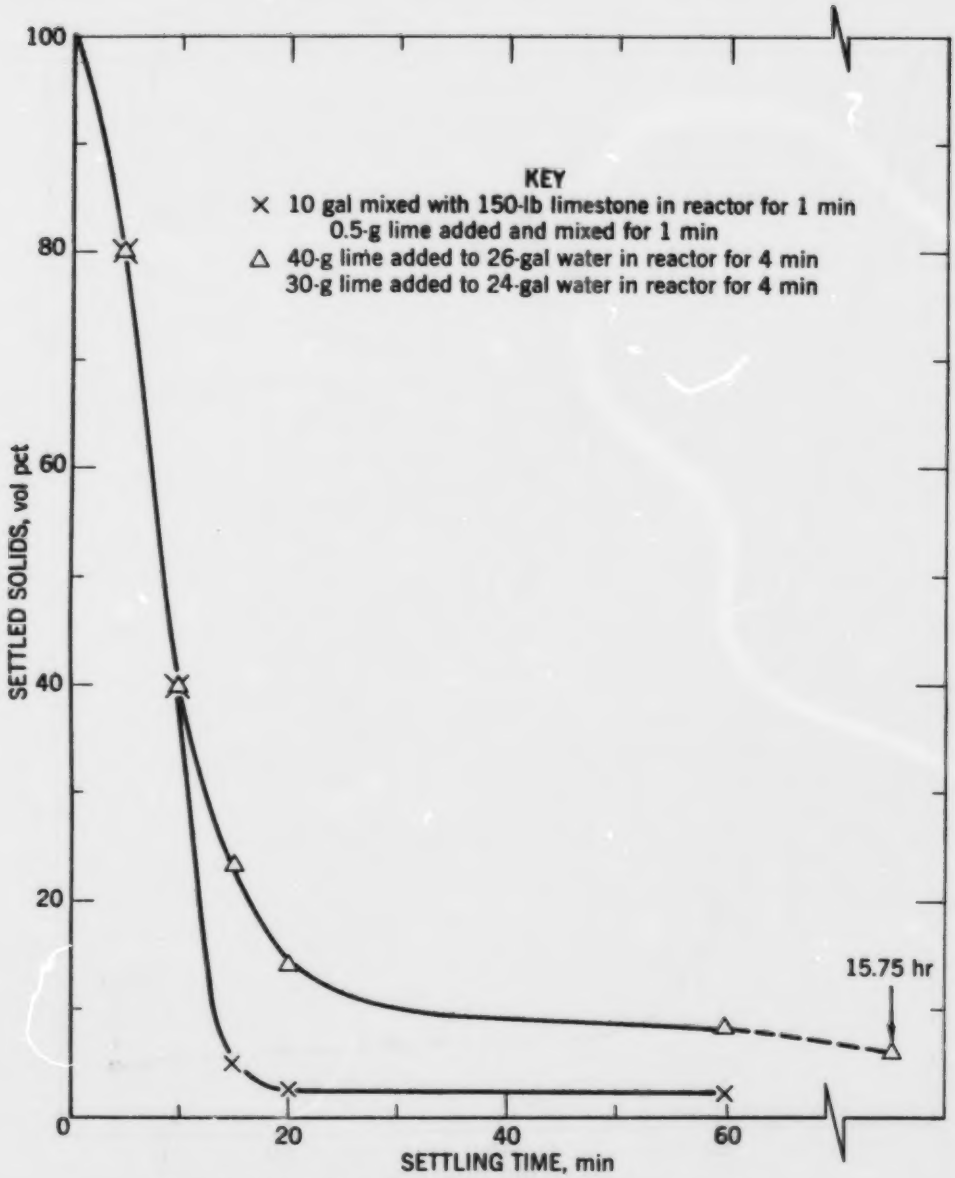

FIGURE 12. - Settling Rate of Sludges From B-1 Treated Water.

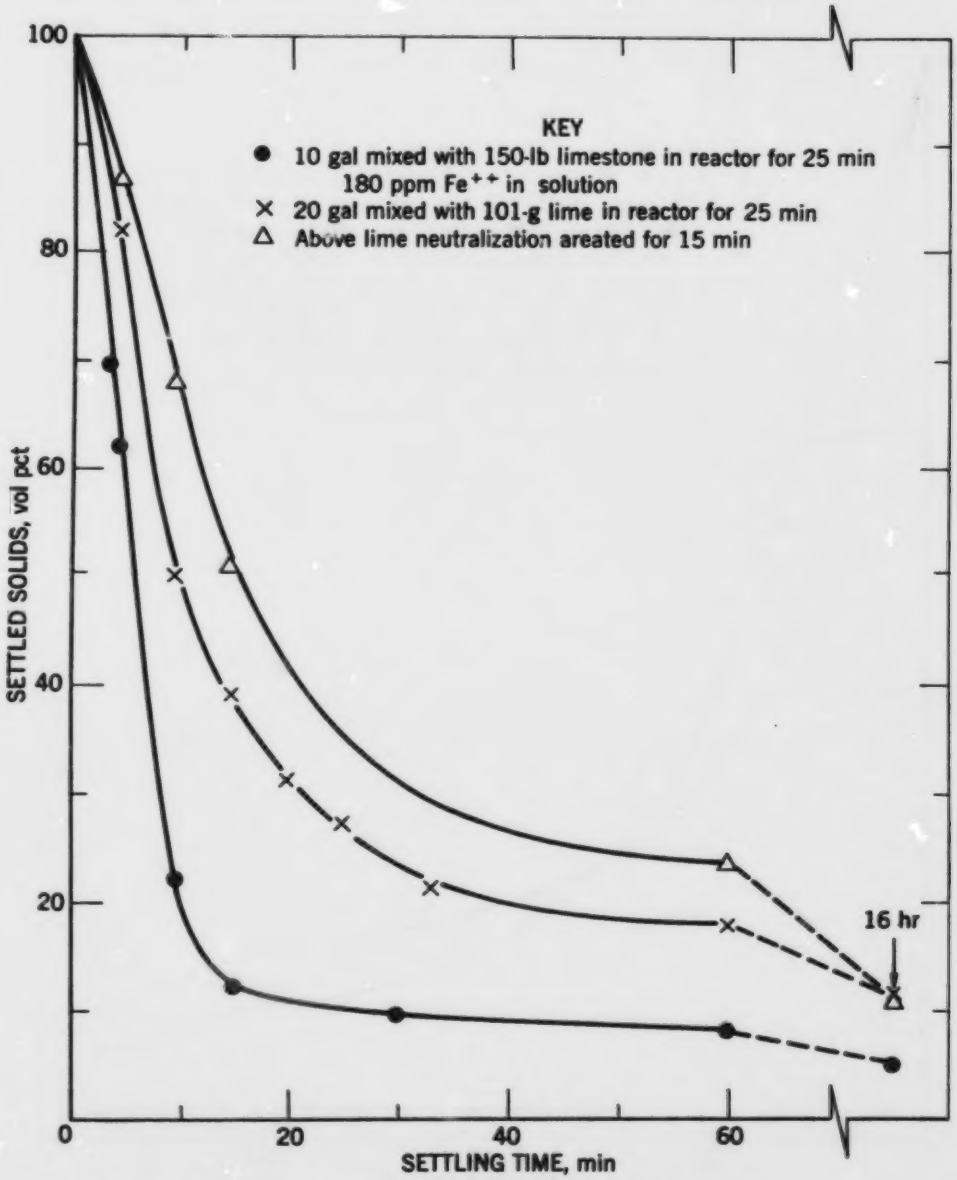

FIGURE 13. - Settling Rate of Sludges From B-2 Treated Water.

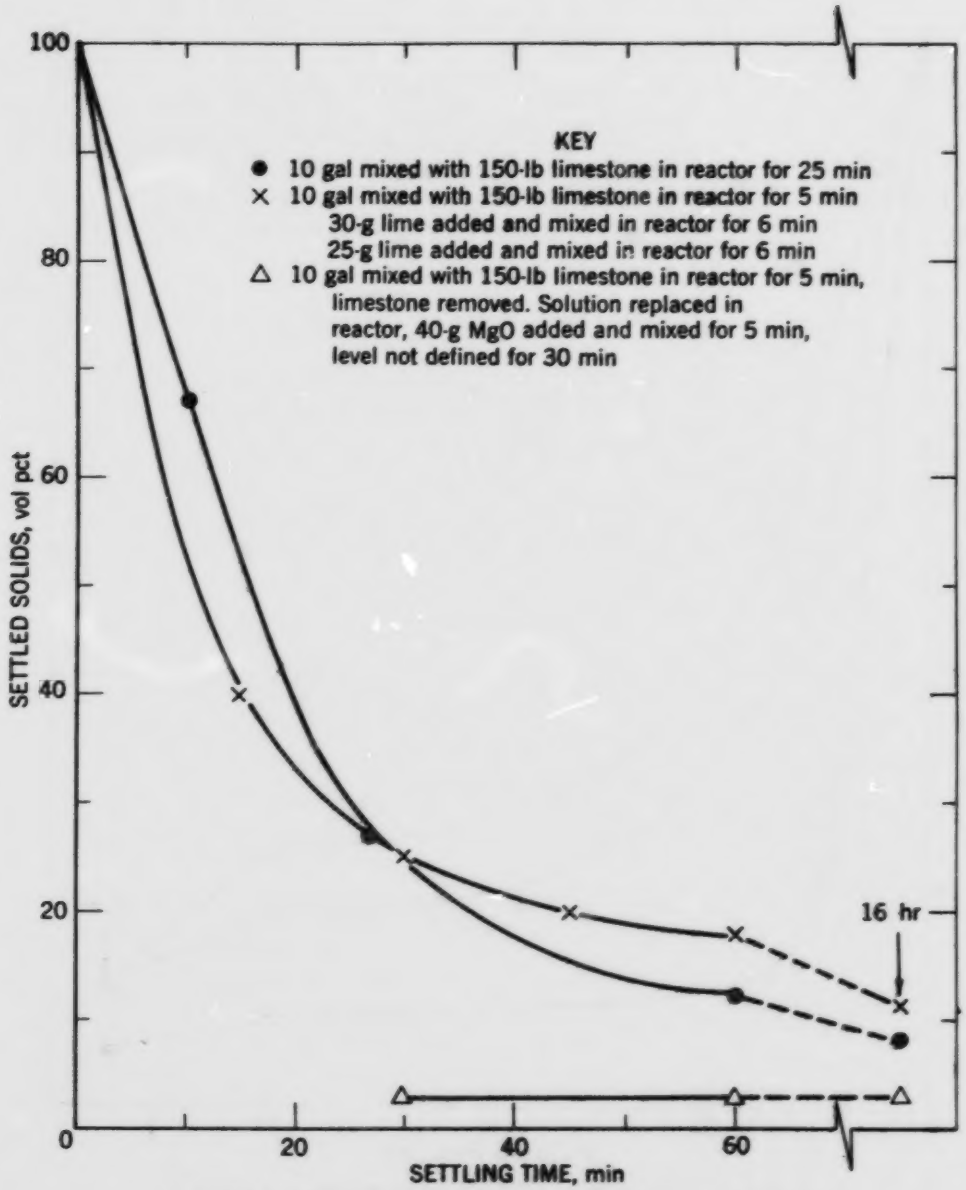

FIGURE 14. - Settling Rate of Sludges From B-3 Treated Water.

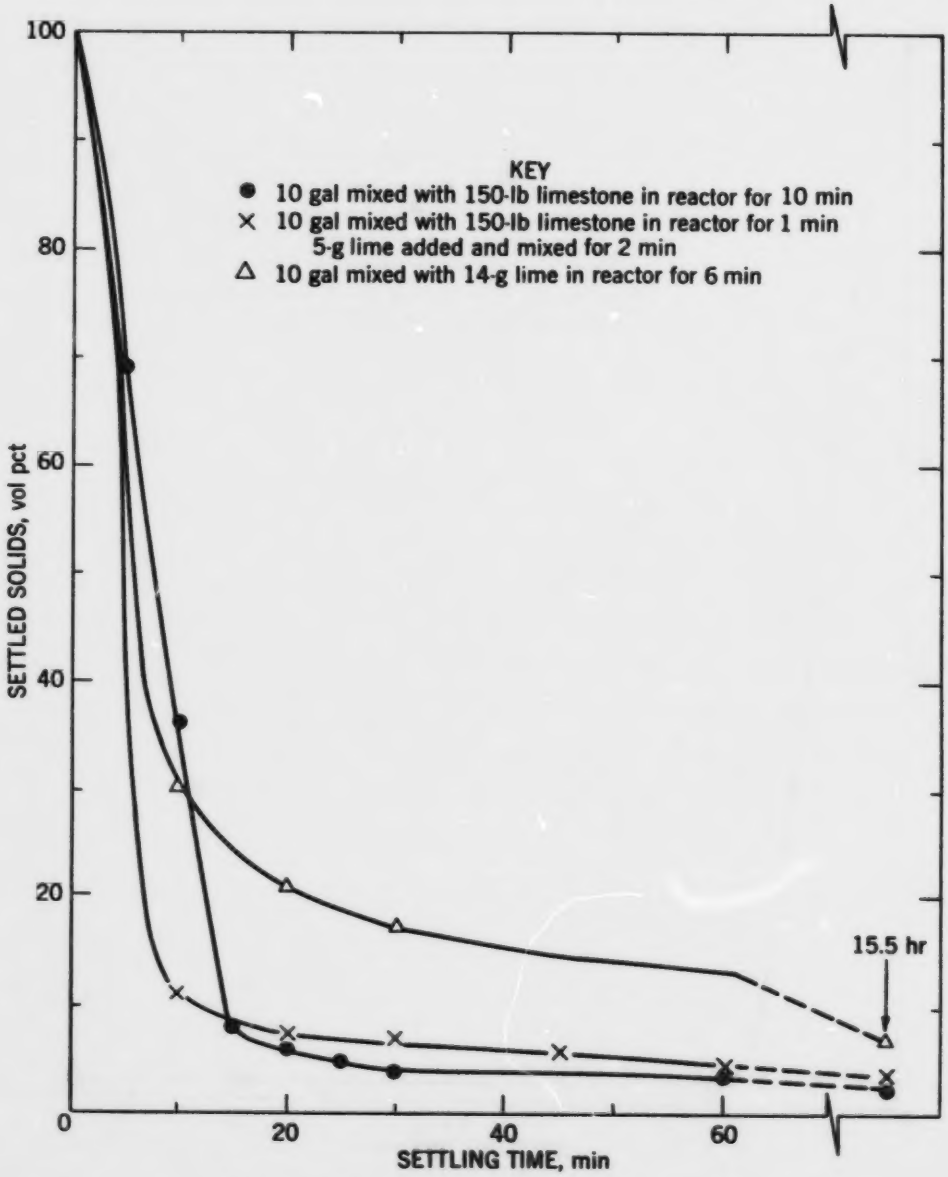

FIGURE 15. - Settling Rate of Sludges From C-1 Treated Water.

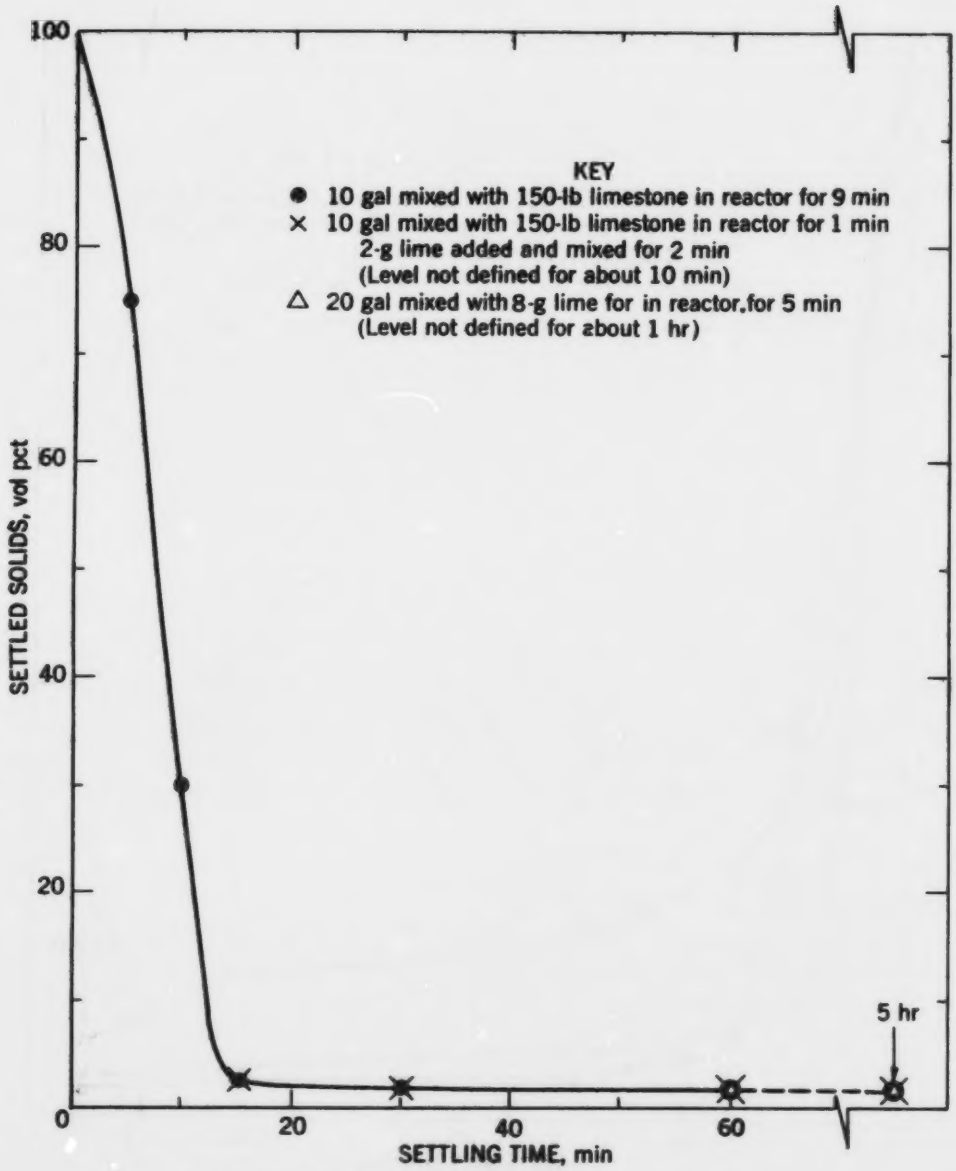

FIGURE 16. - Settling Rate of Sludges From D-1 Treated Water.

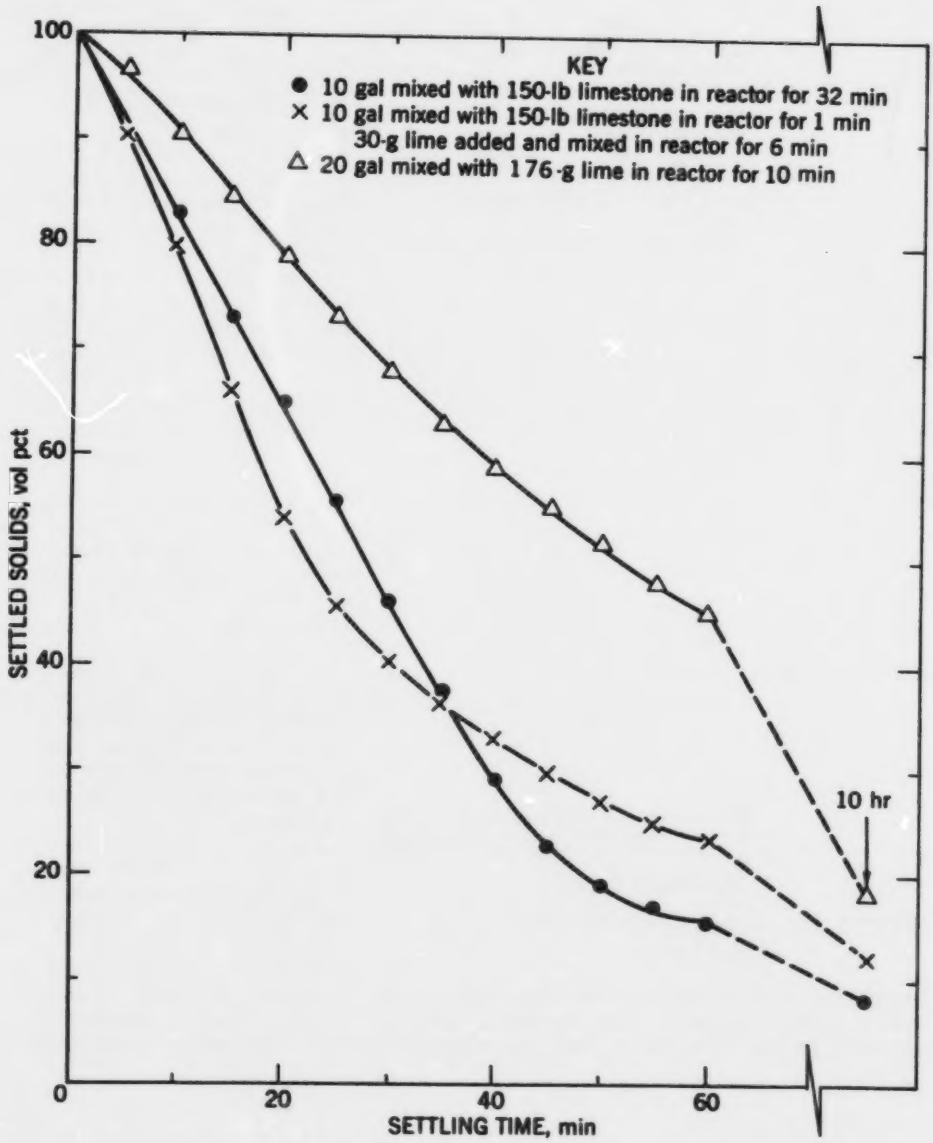

FIGURE 17. - Settling Rate of Sludges From E-1 Treated Water.

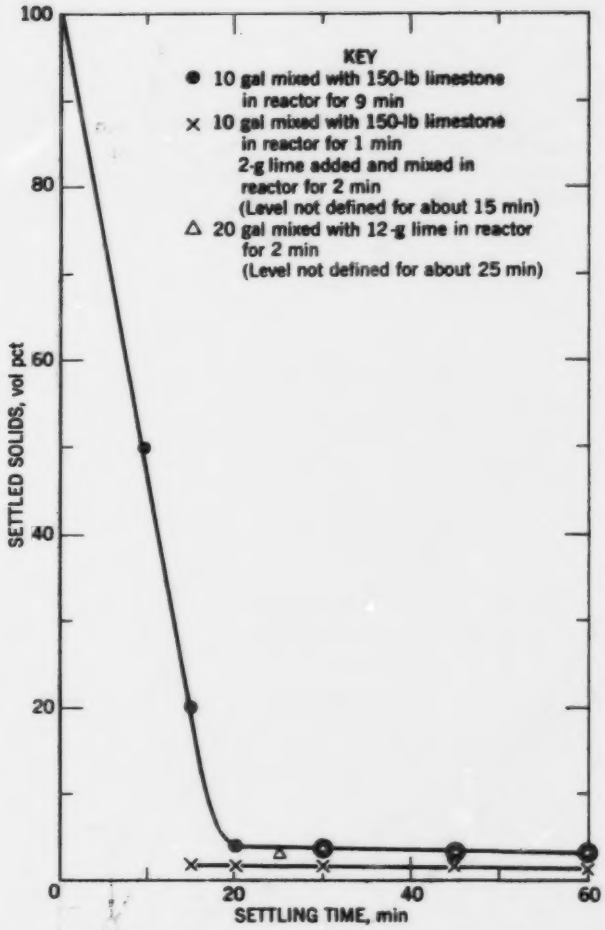

FIGURE 18. - Settling Rate of Sludges From E-2 Treated Water.

compaction characteristics will remain. The discussion of this effect will be deferred to a later report.

Summary of Batch Test Results

The analyses of the waters treated in the field and the results of all the batch neutralization tests are summarized in table 3. Also included are the volumes and weights of settled solids from the batch tests.

Continuous Treatment With Limestone and Ferrous Iron Depletion

Continuous limestone neutralization tests were conducted on the E-2 mine water using 1/2- by 1-inch and 1/4- by 1/2-inch limestones.

With low flow rates of about 1 gpm, the reactor operated satisfactorily; however, with higher flow rates, an effluent quality meeting minimum standards could not be attained. Thus, it appears that the reactor, as used for batch neutralization, was operating efficiently. The reactor functions as both a neutralizer and oxidizer; consequently, it was not possible to separate the reactions for rate studies of each separate process. Continuous neutralization could not be studied effectively at the flow rates used and under variable temperature conditions.

TABLE 3. - Composition of waters treated, batch test results, and volume and weight of solids after 1 hour settling

Mine water	Raw water analysis					Mine water treatment											Volume and weight of solids, 1 hour settling, pct					
						Limestone[1]			Limestone-lime[2]				Lime[3]				Limestone		Limestone-lime		Lime	
	Temperature, °C	pH	Acidity (as $CaCO_3$), ppm	Total Fe, ppm	Fe^{++}, ppm	Final pH	Time, min	Fe^{++}, ppm	Final pH	Time, min	Fe, ppm	Lime, g	Final pH	Time, min	Fe^{++}, ppm	Lime, g	Vol	Wt	Vol	Wt	Vol	Wt
A-1	12	2.90	1,060	263	34	7.35	5	0	7.00	3	6	5	8.20	2	0	27	5.5	-	10.0	-	13.0	-
A-2	13	3.65	-	168	162	7.70	15	0	-	-	-	-	-	-	-	-	8.0	-	-	-	-	-
B-1	12	3.20	235	50	0	8.05	3	0	8.60	2	0	.5	8.50	4	0	14	-	-	2.0	-	8.0	-
B-2	12	4.50	1,725	748	748	6.85	20	280	7.80	15	0	35	9.10	25	0	101	7.5	-	17.5	-	20.0	-
B-2[4]	-	4.45	1,760	741	741	[4]7.50	[4]30	[4]0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B-3	13	3.25	1,620	492	470	7.20	25	11	8.60	6	0	25	-	-	-	-	-	-	-	-	-	-
C-1	12	3.15	460	168	101	7.30	10	0	8.50	3	0	5	9.15	6	0	28	3.5	1.43	5.0	0.38	13.5	0.06
D-1	11	6.30	-	45	45	7.60	5	0	7.75	3	0	2	7.55	5	0	8	1.5	.72	1.5	.26	1.5	.01
E-1	8	3.50	2,330	622	414	7.70	32	6	7.85	7	0	30	9.05	10	0	176	15.5	2.59	23.5	.86	45.0	.62
E-2	11	5.60	135	67	56	7.70	9	0	7.80	3	0	2	9.15	2	0	12	3.0	.80	1.0	.30	3.0	.04

[1]10 gal of mine water added to 150 lb of limestone (1- by 1/2-inch) in reactor at 22 rpm.
[2]10 gal of mine water added to 150 lb of limestone, after 1 min in reactor, lime added and mixed.
[3]20 gal of mine water; lime added and mixed in reactor at 22 rpm.
[4]10 gal of mine water added to 250 lb limestone (1- by 1/2-inch) in reactor at 22 rpm.

DISCUSSION

As mentioned in the Introduction, the use of limestone as a neutralizing agent in the treatment of mine water promises several important advantages. Lime is the most commonly used acid neutralizing agent and iron precipitant; consequently, the technology of lime neutralization is highly developed in water treatment and neutralization of pickle liquor from steel processing plants. Although there have been many attempts at using limestone for pickle liquor neutralization, none have been successful. Results of experiments described in this report indicate that the benefits to be derived from the use of limestone are greater than merely from the use of a cheaper reagent.

Mine waters have a much lower iron and acid sulfate concentration than pickle liquor, but the volume of water that may require treatment is many times greater and it must be recognized that, despite the general similarities, the differences are large.

Lime neutralization of acid mine waters yields a highly flocculent iron hydrate precipitate which does not compact well. In contrast, limestone neutralized mine waters do not yield a hydrophilic floc; the precipitated material is crystalline gypsum with coprecipitated iron oxide. A complete study of these contrasting reactions is being conducted as part of the continuing long range research program of the Bureau on the chemistry of mine waters.

The use of coarse limestone, with abrasive agitation, to provide a large surface of air-water-limestone interfaces appears to be the key to making limestone neutralization work. Fixed bed, coarse limestone and finely pulverized limestone reactions have failed in the past because surface coatings of neutralization products have hindered further reaction. Only in a dynamic system are reactive surfaces continuously renewed.

The oxidation of ferrous iron is highly temperature dependent.[5] This was demonstrated in limestone neutralization tests where a temperature drop of 5° C resulted in high ferrous iron concentration remaining in treated waters at a pH of about 7.5, in contrast with ferrous iron concentration less than 7 ppm achieved at pH 7.5 at 11° C.

For very high ferrous iron concentrations, the reaction time with limestone alone may be excessive. Yet with lime alone, the precipitated sludge would be extremely difficult to concentrate to a high solids concentration. The best effects of both reactions can be achieved by first neutralizing with limestone to a pH near 7, and using lime to complete the precipitation of the remaining iron. This is especially significant because the rate of lime neutralization of highly ferruginous acid waters is not well established. This too is being investigated as part of our long-range program.

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[5]Barthauer, G. L. Mine Drainage Treatment: Fact and Fiction. Coal Age, June 1966, pp. 79-82.

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WATERWHEEL LIMESTONE TUMBLER

A semi-passive limestone neutralization system for AMD treatment has been developed by the Pennsylvania Bureau of Abandoned Mine Reclamation. Their system places large limestone crushed rock into a cage on a shaft which is connected to a waterwheel. AMD is discharged so that it powers the waterwheel to turn the cage so that the limestone particles are constantly abraded. The water then flows over the limestone in the cage and into a settling pond. This system was not inspected, but it was confirmed that a large demonstration unit was installed to treat acid mine drainage at the Quakake Tunnel southwest of Wilkes-Barre, Pennsylvania. The major advantages of using crushed limestone rather than lime for AMD treatment are listed as follows:

- Low reagent cost (about one sixth the cost of lime).
- Low sludge volume and dense, easily dewatered sludge.
- The impossibility of overtreatment reduces process control costs.
- Safer reagent handling with minimal storage problems.
- Potentially simpler process design with reduced capital and operating and maintenance costs.

On the basis of this demonstration plant, it is believed that a full-scale demonstration plant will be installed at the headwaters of Little Tobie Creek in Elk County, Pennsylvania, again funded by the state.

A description of the large Quakake Tunnel Demonstration Project-Limestone Neutralization of Acid Mine Drainage in Carbon County, Pennsylvania, is described by a report for the Pennsylvania Dept. of Environmental Resources, prepared by:

GEO-TECHNICAL SERVICES, INC.
Consulting Engineers and Geologists
Harrisburg, PA

Additional information on the Quakake Tunnel Mine Drainage Pollution Abatement Study is contained in a detailed report for the Pennsylvania Dept. of Environmental Resources and from their office that managed the program:

NORMAN S. BATCHELER
Chief, Susquehanna River Basin
Abandoned Mine Section
Division of Mine Hazards
Commonwealth of Pennsylvania
Dept. of Environmental Resources
Post Office Box 1467
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Division of Field Operations
Bureau of Abandoned Mine Reclamation
Third and Reilly Streets
Harrisburg, PA 17120
(717) 783-2267

Crushed limestone for AMD treatment may be considered where the main aim is to bring pH into the range, say 6-6.5, and where iron and other metal loadings are low.

The Quakake Tunnel Project was tested several design procedures based on theoretical derivations and emperical data obtained from laboratory experiments and reported by PEARSON and McDONNELL (1975, 1975a, and 1978) of Pennsylvania State University.

BUREAU OF MINES

Information Circular 8905

ACID MINE DRAINAGE: CONTROL AND ABATEMENT RESEARCH

By Ann G. Kim,[1] Bernice S. Heisey,[2] Robert L. P. Kleinmann,[3] and Maurice Deul[4]

ABSTRACT

Acid drainage from underground coal mines and coal refuse piles is one of the most persistent industrial pollution problems in the United States: This Bureau of Mines report reviews the acid mine drainage problem generally and describes research currently underway to combat it.

INTRODUCTION

In the last 15 years there has been little improvement in the number of streams adversely affected by acid mine drainage. The Bureau of Mines has developed a comprehensive program of acid mine drainage research oriented toward both active and abandoned mines. It includes improved prediction of acid potential, improved mine planning, at-source control of acid formation, improved reclamation, improved water treatment techniques, and assessment of ground water contamination in major mining districts.

Controlling the acid at its source by limiting pyrite oxidation is a major objective of the program. The Bureau of Mines is investigating methods of slowing reaction kinetics by limiting oxygen, inhibiting iron-oxidizing bacteria, or otherwise influencing reaction chemistry. The Bureau has recently developed and field-tested a practical method of bacterial inhibition which is effective in reducing acid drainage from coal refuse piles. Since this technique is probably not applicable to abandoned underground mines, improved methods of mine sealing are required.

Bureau of Mines research into treatment of acid mine drainage is oriented toward improving water treatment efficiency and developing low-maintenance treatment systems. Current areas of investigation include improved iron oxidation efficiency, limestone neutralization, disposal of acid mine drainage sludge, and development of an artificial bog treatment system.

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THE ACID MINE DRAINAGE PROBLEM

Acid drainage from underground coal mines and coal refuse piles is one of the most persistent industrial pollution problems in the United States. Pyrite in the coal and overlying strata, when exposed to air and water, oxidizes, producing ferrous ions and sulfuric acid. The ferrous ions are oxidized and produce an hydrated iron oxide (yellowboy) and more acidity. The acid lowers the pH of the water, making it corrosive and unable to support many forms of aquatic life. The iron oxide forms an unsightly coating on the bottom of streams, and further limits the ability of aquatic life to survive in streams affected by acid mine drainage.

Before coal is mined, very little of the pyrite is exposed to the conditions necessary to produce acid drainage. The mining and coal cleaning process exposes the pyrite to surface or ground waters and allows pyrite oxidation to occur. A ton of coal containing 1 pct pyritic sulfur has the potential of producing 33 pounds of yellowboy and over 60 pounds of sulfuric acid. However, the rate of acid production varies, and abandoned mines and refuse piles can produce acid drainage for more than 50 years. The drainage, if discharged into surface streams or ponds, constitutes an extensive, expensive, and persistent

FIGURE 1. - Ground water percolating through pyritic material produces sulfuric acid and iron compounds which are eventually discharged into surface streams.

environmental problem (fig. 1). Federal law (37)[5] now requires that water discharge from active coal mines have a pH between 6 and 9 and places limits on the total iron, manganese, and suspended solids. Controlling acid mine drainage from active mines usually requires expensive water treatment and the necessity of handling very large volumes of water. Controlling drainage from abandoned mines is even more difficult due to location, water volume, and the general limitation on public funds available for work in this area. The Bureau of Mines research program in acid mine drainage addresses the problems of both active and abandoned mines.

In 1936, it was estimated (17) that more than 9 million tons of sulfuric acid were discharged annually from coal mines into the streams of Pennsylvania. Now, although Federal and State regulations specify water quality standards for coal mine discharges, acid mine drainage remains a problem. The most comprehensive survey of the extent of acid mine drainage pollution was conducted by the Federal Water Pollution Control Administration in 1967 (2, 8). Drainage basins throughout the Appalachian Region, in Pennsylvania, West Virginia, Maryland, Ohio, Kentucky, Virginia, Tennessee, Alabama, and Georgia, were sampled for various water quality parameters including acidity, to determine the extent of water pollution caused by coal mine drainage. At that time, 10,500 miles of streams were significantly degraded by coal mine drainage, and further analysis of the data showed that approximately half, or 5,740 miles was affected by acid mine drainage (11).

Since that time, no Federal agency has undertaken a survey of this scale; current mine drainage assessments are restricted to statewide estimates. Direct comparisons between current State data and those collected in the 1967 study cannot be made, because of differences in the intensity of sampling and variation in the criteria used to classify a stream as degraded. However, current water quality data, obtained from State environmental agencies of the Appalachian Region, do indicate that there has been little overall improvement in streams affected by acid mine drainage.

In Pennsylvania, which annually produces approximately 82 million tons of coal (22), there are 2,795 miles of major streams that fail to meet current water quality standards (32). Drainage from abandoned mines contributes to at least 70 pct of the total. Although projected figures for 1983 indicate a slight decrease in stream miles that will not meet water quality standards, no decrease in the drainage pollution related to mining is expected.

In Ohio, where annual coal production was nearly 42 million tons (22), a 1979 study conducted by the Ohio Environmental Protection Agency indicates that acid mine drainage affects 1,075 miles of streams (30). In Maryland, where annual coal production was just over 2-1/2 million tons (22), the Maryland Bureau of Mines currently estimates that 450 miles of streams are affected by acid mine drainage (9), much of it related to mining in neighboring States. In Tennessee, where annual coal production is nearly 11-1/2 million tons (22), acid mine drainage was estimated to affect 994 miles of streams, according to the Division of Water Quality Control of the Tennessee Department of Public Health (35). In Kentucky, the Department for Natural Resources and Environmental Protection, Division of Abandoned Lands, has compiled data for 1978-80 which show that of a total of more than 2,100 miles of streams within the Eastern Coalfield affected by coal mine drainage, only 77 miles are acid (12). The low proportion of acid streams in this area of Kentucky is apparently related to the abundance of limestone in the coal-bearing rocks.

Although rigorous comparisons cannot be made, the more recent data indicate that the extent of acid mine drainage

[5]Numbers in parentheses refer to items in the list of references at the end of this report.

pollution is of the same order of magnitude as that measured in the 1967 study. Government regulation has done much to upgrade the quality of discharges from active mining operations, but most acid mine drainage comes from abandoned mines, which are not regulated. In spite of increased efforts to control it, acid mine drainage continues to be a major problem.

Present regulations stipulate that acid drainage from active mines and refuse piles must be chemically treated for as long as it is discharged from the mine or pile. These mandatory standards have generated research needs in the following areas: More efficient treatment methods, the disposal of sludge produced by treatment, engineering methods to reduce acid formation and other at-source methods of control, control of acid formation and erosion from spoil piles, and improved water management techniques. In addition, there is no systematic, cost-effective method of reducing the acid load from mines already abandoned and from mines to be abandoned in the future, although an estimated 80 pct of acid mine water comes from abandoned mines and spoil piles. This area particularly requires a concentrated research effort if there is to be significant improvement in the quality of many streams.

CHEMISTRY OF FORMATION AND CONTROL

Prevention and/or control of acid mine water depends on an understanding of the chemical, biological, and geological factors that influence its formation, which is best described as a series of chemical reactions. Acid mine water is produced by the oxidation of the pyrite (FeS_2) normally present in coal and the adjacent rock strata. The oxidation of pyrite is usually described by the reaction below in which pyrite, oxygen, and water form sulfuric acid and ferrous sulfate:

$$2Fe_2 + 7O_2 + 2H_2O = 4H^+ + 2Fe^{2+} + 4SO_4^{2-}.$$

Oxidation of the ferrous iron produces ferric ions according to the following reaction:

$$2Fe^{2+} + 1/2\ O_2 + 2H^+ = 2Fe^{3+} + H_2O.$$

When the ferric ion hydrolyzes, it produces an insoluble ferric hydroxide (yellowboy) and more acid:

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+.$$

Although this summary is correct at pH above about 4.0, it is only one of three different reactions systems, which vary in significance with pH (14). Also significant in the oxidation of pyrite is a bacterium, Thiobacillus ferrooxidans.

At near-neutral pH (stage 1), the rates of oxidation by air and by T. ferrooxidans are comparable. This stage is typical of freshly exposed coal or refuse. Despite the high concentration of pyrite, the rate of oxidation either by oxygen or by T. ferrooxidans is relatively low, and the natural alkalinity of ground water may effectively neutralize the acid formed at this stage.

When the neutralizing capacity of the environment is exceeded, acid begins to accumulate and the pH decreases (stage 2). As the pH decreases, the rate of iron oxidation by oxygen also decreases. But at the lower pH of stage 2, the rate of iron oxidation by T. ferrooxidans increases. The action of the bacteria causes increased acid production, which serves to further lower pH (fig. 2).

As the pH in the immediate vicinity of the pyrite falls to less than 3, the increased solubility of iron and the decreased rate of $Fe(OH)_3$ precipitation affect the overall rate of acid production (stage 3). At this point, ferrous

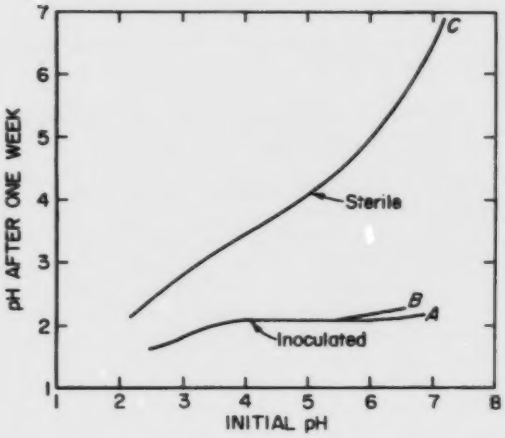

FIGURE 2. - In solutions inoculated with 0.2 ml of T. ferrooxidans (*A*) and 0.1 ml each of T. ferrooxidans and Metallogenium (*B*), the decrease in pH is greater than in sterile controls (*C*).

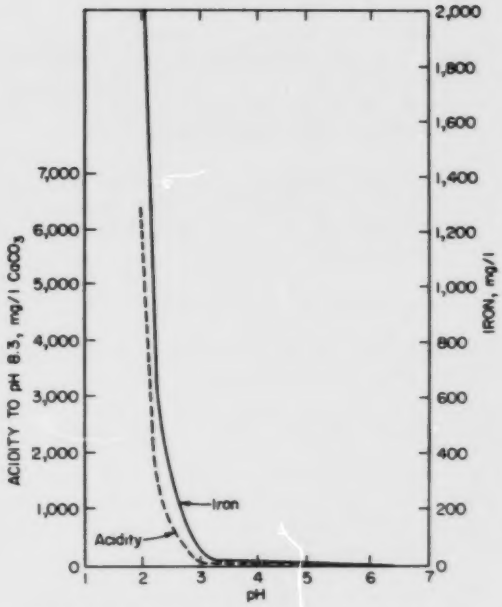

FIGURE 3. - Plot of acidity and total dissolved iron versus pH measured in laboratory simulations of a coal refuse pile shows the rapid production of acid and iron at low pH.

iron is oxidized by T. ferrooxidans and the ferric ion in turn oxidizes the pyrite:

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + SO_4^{2-} + 16H^+.$$

In this third stage, the rate of acid production is high (fig. 3) and is limited by the concentration of ferric ions. Inhibition of T. ferrooxidans would prevent ferric oxidation of pyrite and should therefore reduce acid production by at least 75 pct.

When untreated acid mine drainage is mixed with surface waters, it has a deleterious effect upon the receiving stream, usually making it unsightly and inhospitable to most forms of aquatic life. Most organisms cannot tolerate an acid environment. Also, the ferrous iron in acid mine drainage consumes the oxygen in a stream, and the precipitated ferric hydroxide covers the streambed, limiting the oxygen available to benthic organisms. The acidity and total solids adversely affect aquatic life, and heavy metal ions present in some mine waters have an increased toxicity in acid solutions (6). In streams severely polluted with acid mine drainage, there are usually no complex aquatic plants, no fish, few if any benthic invertebrates, and only a few species of algae. In some cases, the invertebrates and algae that can survive grow to nuisance proportions.

When acid mine drainage is produced in an active mine, environmental laws require that it meet minimum standards before it is discharged into surface streams. According to the Federal Water Pollution Control Act, water from coal mines must have a pH between 6 and 9 and must contain no more than an average of 3.5 ppm and a maximum of 7 ppm iron, no more than an average of 2 ppm and a maximum of 4 ppm manganese, and no more than 70 ppm total suspended solids.

Standard acid mine drainage treatment methods involve neutralization of the acid by the addition of a base, oxidation

of ferrous iron in an aeration tank or pond, and precipitation of iron compounds in a settling pond. Manganese, unless present in high concentrations, is usually removed with the iron.

The chemistry of the basic treatment method is relatively straightforward. Neutralization is the reaction of the acid with a base:

$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O.$$

If limestone is used as the neutralizing agent, the reaction is

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2.$$

To remove the ferrous iron, the neutralized water is aerated to produce ferric ions, which react with the base to form insoluble ferric hydroxides:

$$Fe_2(SO_4)_3 + Ca(OH)_2 = Fe(OH)_3 + CaSO_4.$$

With limestone as the neutralizing agent, the reaction is

$$Fe_2(SO_4)_3 + 3CaCO_3 + 3H_2O = 2Fe(OH)_3 + 3CaSO_4 + 3CO_2.$$

Other alkaline agents can be used, but because of cost, ease of handling, or other environmental effects, lime is most commonly used. Other methods that have been suggested for treating acid mine drainage include reverse osmosis, ion exchange, and flash distillation. However, these are not treatment methods per se, but methods for producing potable water that were suggested for acid mine drainage only where there is no alternative source of potable water. With these methods a concentrated acid brine or sludge must be disposed of, and because of technical problems and high cost, processes like these are not commonly considered as reasonable alternatives to neutralization.

BUREAU OF MINES ACID MINE DRAINAGE RESEARCH

Methods to reduce the pollution from ferruginous acid water from coal mines and spoil banks usually involve either reducing the rate of acid formation or increasing the efficiency of mine water treatment. Although acid mine drainage has been a problem for many years, there have been few significant innovations in its prevention and control. The Bureau of Mines was involved in much of the acid mine drainage research conducted before 1970 (17, 20, 26). The Bureau performed analytical studies to determine the acidity, composition, and corrosivity of acid mine water. Sources of and variations in acid mine drainage, the effect of pyrite content, rock dusting, and chemical neutralization also were investigated. In addition, the Bureau of Mines was a major contributor to the development of mine seals during the 1930's.

During the 1970's the Bureau of Mines had only a limited acid mine drainage program as other Federal agencies, such as the Environmental Protection Agency (EPA), assumed primary responsibility for water pollution research. Because of the continuing problems in acid mine drainage control, the Bureau of Mines has recently developed a comprehensive program of acid mine drainage research. This program is directed toward several areas, including improved prediction of acid potential, improved mine planning, at-source control of acid formation, improved reclamation, improved water treatment, techniques to control acid drainage at abandoned mines and waste piles, and assessment of ground water contamination in major mining districts.

MINE SEALING

In 1928 it was reported that mines sealed by natural caving produced less acid than unsealed mines in the same locality (19). It was assumed that limiting the amount of air and water entering the mine reduced the rate of acid formation. After a 1-year field study, an extensive mine sealing program was undertaken in 1933 through the Works Progress Administration and the Civil Works Administration. Records indicate that sealing did produce favorable results in

West Virginia, Ohio, and Pennsylvania (36). However, the Federal sealing programs were short term and did not provide funds for maintaining the seals. Lack of maintenance, natural deterioration, vandalism, and subsequent mining combined to reduce the long-term effectiveness of the mine sealing program.

Despite the lack of long-term monitoring, mine sealing is considered a standard method for reducing acid formation from coal mines (27, 29). In mines located below drainage, natural flooding is used to cover the pyritic material and exclude air (fig. 4). When the air supply is eliminated, it is assumed that the pyrite is no longer oxidized. If the water pool is stable and the additional hydraulic pressure creates no downdip drainage problems, flooding is considered adequate.

This effect is currently being observed in the Northern Field of the Pennsylvania Anthracite Region (7), where flooded workings underlie approximately 43,000 acres. The Bureau of Mines is currently studying the hydrology and geochemistry of this large mine pool complex because the pool is well established, having started to form over 30 years ago. Owing to its size and flow characteristics, water draining from the mines remained acid until only a few years ago, casting some doubt on the effectiveness of flooding. However, our study has shown that the water in the mine pools has now recovered and is in fact slightly alkaline.

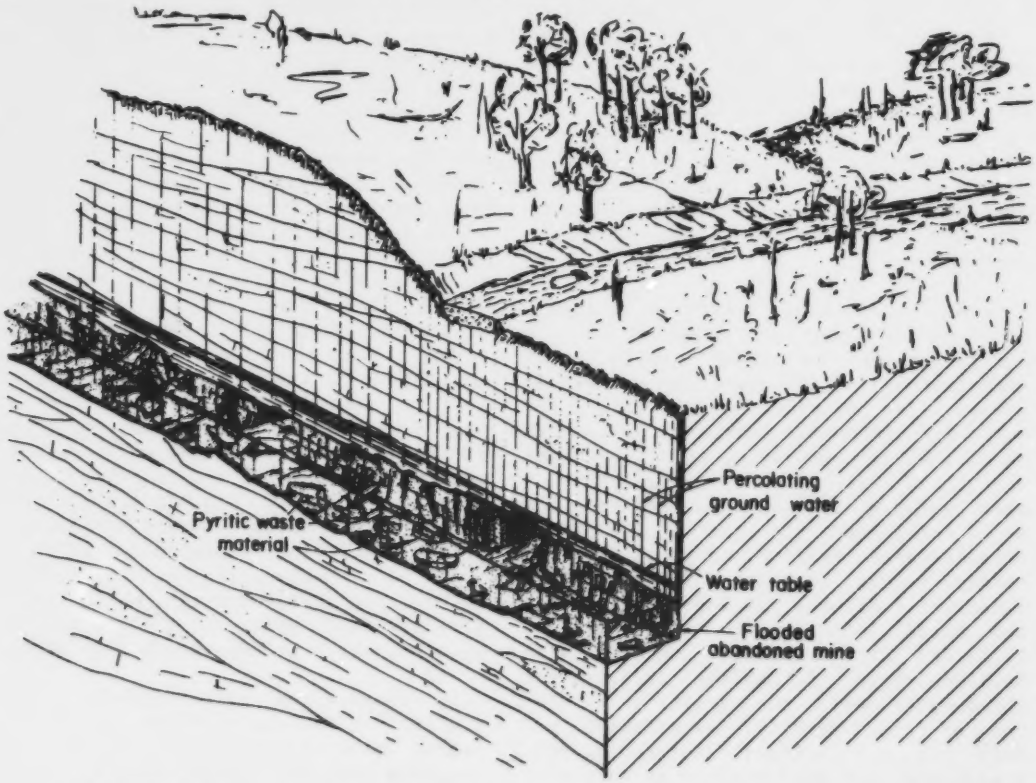

FIGURE 4. - In abandoned mines below drainage, natural flooding can be used to exclude air, limiting pyrite oxidation.

In deep mines above drainage, flooding is generally ineffective owing to seepage through surface fractures and the tendency of the water to migrate to other discharge points. In such mines, conventional seals are airtight and/or watertight masonry walls hitched into the roof, bottom, and ribs of mine openings (fig. 5). Subsidence fractures that extend from the mine through the caved overburden to the surface serve as open pathways for the migration of air and the drainage of surface water (fig. 6). To effectively seal these mines, it is also necessary to backfill and grade all fractures that extend from the mine to the surface. Although aerial photography and infrared scanning can be used to locate zones of high permeability, this process is expensive and not sensitive enough to delineate relatively small subsidence fractures. Indiscernible joints and subsidence fractures can affect the overall effectiveness of a mine sealing project by allowing a mine to "breathe" (fig. 7). Monitoring by the Bureau of Mines has shown a general correlation between the oxygen level in the mine, the differential pressure across mine seals, and changes in the barometric pressure (28).

Because most mine sealing evaluations are based on short-term observation, the Bureau is now evaluating the long-term effectiveness of mine sealing in several areas. For example, at Moraine State Park grouted double bulkhead seals were used in an area where an artificial lake was built over 10 years ago. In this area, water discharged from sealed areas has a total mean acid load of 206 lb/day 10 years after sealing, compared with 540 lb/day before sealing. The discharge rate varies between 250 and 500 gpm, and the total iron has a mean value of 53 lb/day at present, compared with 46 lb/day prior to sealing (21). Over the 10-year period the variation in discharge rate, acidity, alkalinity, and total iron has declined, indicating that a mine pool has been created as a result of sealing. In the Highland Fuel Mine area (Butler County, Pa.) water samples are obtained from discharge points and from observation holes behind the seals. The discharge from the sealed area varies from 25 to 80 gpm, and the pH of the water is approximately 4. Total iron in the discharge averages 12 to 14 ppm. Water samples from the mine pool behind the seals have an average pH above 6 and a higher total iron content.

Recent inspection of wet, dry, and hydraulic and/or bulkhead seals constructed 13 years ago in abandoned mines near Elkins, W. Va., has shown that five of the clay seals have deteriorated, allowing acid seepage to kill vegetation on the slopes below the seal. Yellowboy precipitate has restricted the drainage opening of one wet masonry block seal. Water quality in at least one stream receiving discharge from the sealed mines has not improved significantly since the mines were sealed.

The Bureau's evaluation of mine seals installed approximately 10 or more years ago has indicated several serious problems with conventionally constructed seals. First, completely sealing a mine above drainage is very difficult and may be very expensive. Complete sealing requires that all zones of high permeability be located and sealed. The usual procedure is to locate subsidence fractures, cover the area with a compacted clay blanket, and regrade it. To be effective, this procedure requires that all fractures be located and that no further subsidence occur. The evidence indicates that surface sealing is rarely effective for long periods. Another problem with mine sealing is that masonry seals require continued maintenance. Even if seals are adequately built and maintained, the improvement in water quality directly attributable to the sealing process has not been adequately determined.

To improve the effectiveness of mine sealing, the Bureau of Mines is studying sealed mines to determine factors controlling changes in water quality and is developing techniques to build more efficient, less expensive seals. In

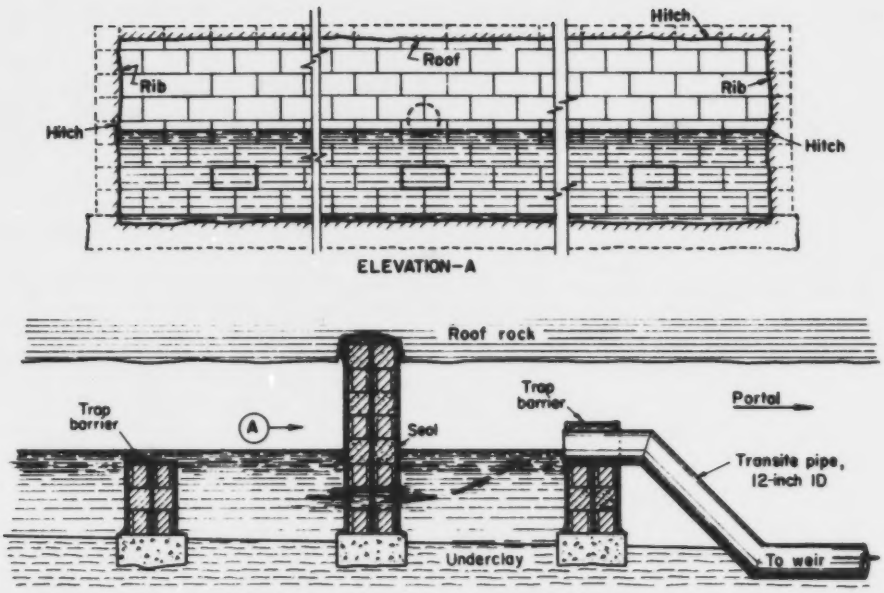

FIGURE 5. - A wet seal with an air trap allows water to leave the mine while preventing air from entering.

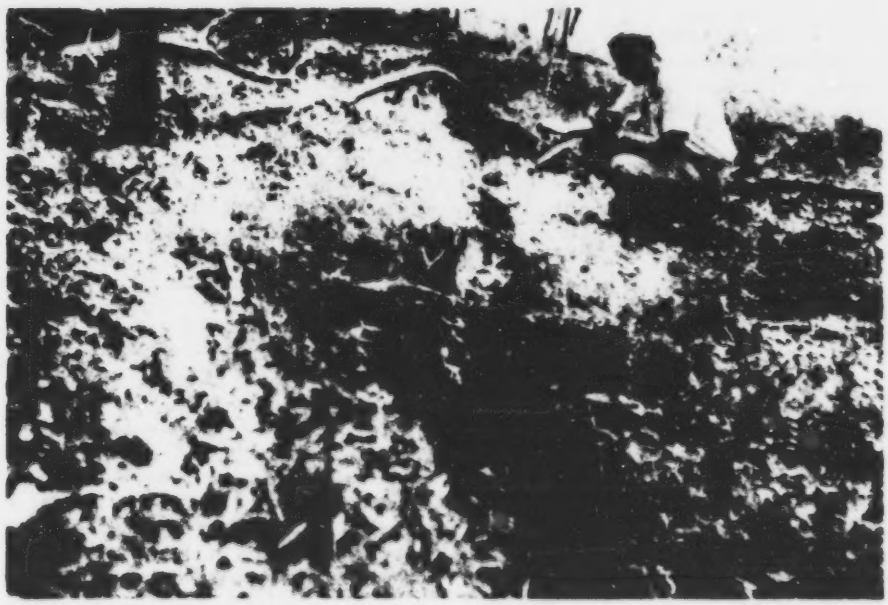

FIGURE 6. - Subsidence cracks over an underground mine may allow surface water and air to enter a sealed mine.

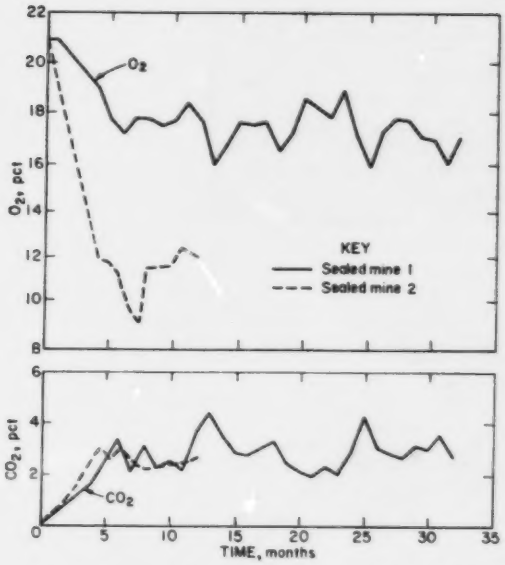

FIGURE 7. - Although the oxygen level in a sealed mine may be lower than that of normal air, it may be sufficient to support oxidation for long periods of time.

addition to monitoring discharge rates and water quality parameters, at some sites drawdown testing will be used to determine aquifer capacity and water level fluctuations. Subsidence areas will be surveyed during and after drawdown testing. The collection of rainfall data and the use of fluorescent dye to determine the direction and velocity of ground water flow in the mine pool will also be used to determine the factors that affect water quality when mines are sealed conventionally.

The Bureau also is involved in a demonstration of pneumatic stowing of limestone as a method of producing more effective mine seals at a cost equal to or less than that of conventional seals. Observations of mine seals to date indicate that seals constructed of cement block and grout do not substantially improve water quality, may not effectively contain impounded water, and are subject to failure and/or leakage. The construction of a competent seal requires that it be permanently attached to the roof, ribs, and floor. Frequently the failure of conventional seals is due to collapse of weak strata over the seal. Pneumatic stowing produces a highly compacted limestone plug which supports roof and ribs. Movement of surrounding strata will cause further compaction of the limestone. Concrete or other additives to the limestone can be used to produce a stronger seal. If appropriate, the limestone seal can be constructed to allow low flows of mine water. If the water is only slightly acid, passage through the limestone can effectively neutralize it. In a field trial of pneumatic stowing, the limestone seals were found to be satisfactory in terms of the safety of construction, the strength of the seal, and the cost. Long-term monitoring of these seals is planned to determine their effect on water quality.

In deep mines, the construction of mine seals limits the water discharge rate and creates a mine pool covering some or all of the pyritic material. If inundation is to be an effective method of controlling acid drainage, outcrop barrier pillars must be capable of withstanding the hydrostatic head created by the impounded water. In general, Federal and State regulations on mine closure do not deal directly with criteria for outcrop barriers used to flood the mine. A Bureau of Mines contract report (31) details the factors that affect the competency and stability of outcrop barriers. According to the study, an outcrop barrier should be wide enough to prevent seepage, have sufficient overburden to prevent a blowout, and provide a stable slope. Curtain grouting, compartmentalized barriers, and relief wells can be used to reinforce outcrop barriers.

In mines that have been successfully inundated, water quality is often good in the mine pool but generally acid after seeping through the barrier. Use of a relief well system, as suggested in the contract report (31), would remove water from the mine pool prior to its exposure to pyrite-bearing coal and would also limit the hydrostatic head that the outcrop barrier would have to withstand. Properly designed outcrop barriers could

reduce acid formation in abandoned mines and allow maximum coal removal.

Oxygen may also be a limiting factor in coal refuse piles and some surface mines. The Bureau of Mines is currently using soil gas probes to study oxygen diffusion characteristics in coal refuse piles; preliminary results indicate that pyrite oxidation is limited to a near-surface layer. A similar study will soon be initiated in an abandoned surface mine. Followup research will concentrate on current reclamation methods to determine if any reduce oxygen diffusion or result in the consumption of oxygen, thus limiting acid formation.

ACID MINE DRAINAGE TREATMENT

Many factors influence the quantity and quality of water handled by a mining operation, but it is not unusual for a single mine to treat 1 million gallons of acid water per day. Water from coal mines is usually treated by chemical neutralization. At present, lime is the most commonly used neutralizing agent. Generally, a small volume of mine water is added to powdered lime to produce a slurry which, added to the raw mine water, raises the pH to between 7 and 9. The water is aerated to oxidize the ferrous iron and is then transferred to a settling pond for precipitation of the iron compounds (fig. 8). Although commonly used, lime neutralization has several inherent problems. Lime is a caustic material and can produce water with an unacceptably high pH. Lime treatment produces a flocculant precipitate that does not form a dense, easily handled sludge. Research by EPA failed to produce any economical improvement in sludge disposal methods. The Bureau is evaluating the technology and economics of current sludge disposal practices to determine the most promising area of research. Sludge disposal problems, and high cost (fig. 9) are the principal reasons for seeking improved acid mine drainage treatment methods.

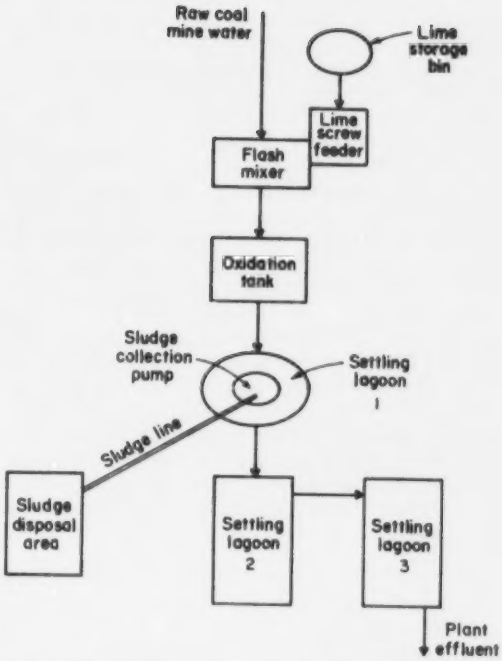

FIGURE 8. - Flow diagram of hydrated lime treatment process for acid mine drainage (34).

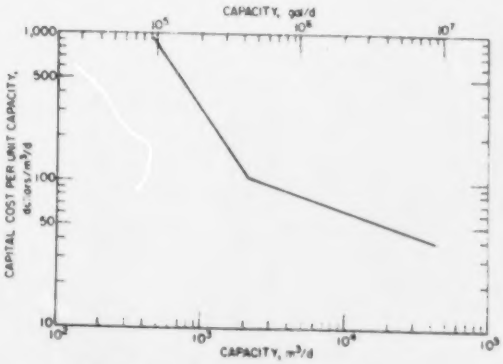

FIGURE 9. - Although the unit cost decreases with capacity, the total capital costs may range between $500,000 and $2 million for a conventional treatment process (34).

As an alternative treatment method, the Bureau has developed a neutralization process using limestone instead of lime (4, 6, 14, 17, 24-25). Limestone is readily available and costs less than lime, and limestone treatment produces a dense crystalline sludge (fig. 10). In the Bureau treatment process, very fine (5 to 10 μm) limestone is produced by wet autogenous grinding in a tube mill. The limestone slurry is mixed with the acid mine drainage, and the drainage is aerated to remove carbon dioxide and to oxidize the ferrous iron (fig. 11). The gypsum-iron oxide sludge separates from the drainage in settling ponds. Although limestone treatment has the advantages of lower material costs, simplicity of plant design and operation, the use of a less hazardous material, and a denser sludge, its use is limited by the rate at which ferrous iron is oxidized. With limestone neutralization, the pH of the treated drainage is between 6.8 and 8.0 and the iron oxidation rate ranges from 10 to 25 ppm/min (fig. 12).

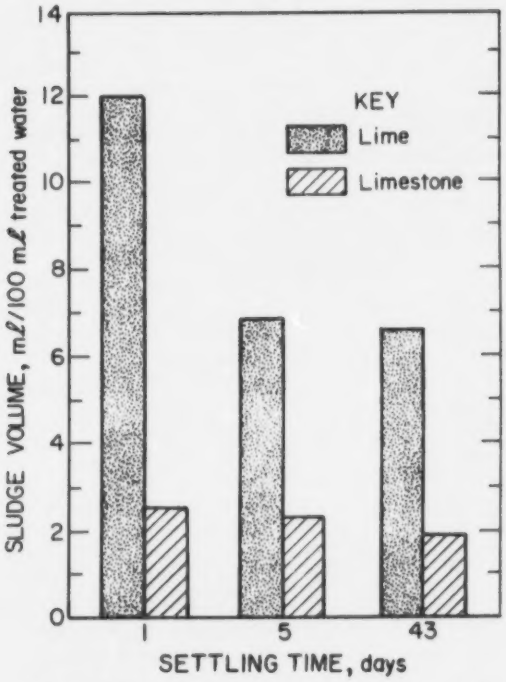

FIGURE 10. - Limestone treatment produces a denser sludge in 1 day than lime neutralization produces in 43 days.

To minimize the power and land requirements for aeration, the Bureau is investigating the use of catalysts to increase the rate of ferrous iron oxidation at low pH. A laboratory study by the Bureau of Mines indicated that activated carbon was an effective catalyst in the oxidation of ferrous iron (23). In batch tests, the ferrous iron content of acid mine drainage flowing through an aspirated column of activated carbon was reduced from over 700 ppm to less than 10 ppm in approximately 1 minute. In these tests, approximately 5,000 ml of the acid drainage was passed through the 200 grams of activated carbon before the catalytic effect was noted. During this period the pH of the effluent was higher than that of the mine drainage feed. Since the increase in iron oxidation rate was observed after the pH of the drainage showed substantially no change, the onset of the catalytic effect was attributed to acid conditioning the carbon.

A pilot-scale field study was conducted (33) to study the effect of activated carbon on the ferrous iron oxidation rate using a three-stage continuously stirred reactor. Continuous agitation of the carbon in the mine water provided more efficient water-carbon contact and prevented channeling and/or fouling. A weir device at the top of the reactor controlled carbon loss. In this system the ferrous iron oxidation rates were not as high as those reported in the previous laboratory study. Acid conditioning the carbon did not significantly affect the iron oxidation rate. When the pH of the influent water was adjusted to 5, the rate of iron oxidation increased, but not to the levels reported in the laboratory study. When comparing the rate data from the field and laboratory studies, it was considered possible that the high iron oxidation rate reported was due to the growth of iron-oxidizing bacteria on the carbon rather than to direct catalysis by the carbon. T. ferrooxidans is an aerobic bacterium which derives energy from

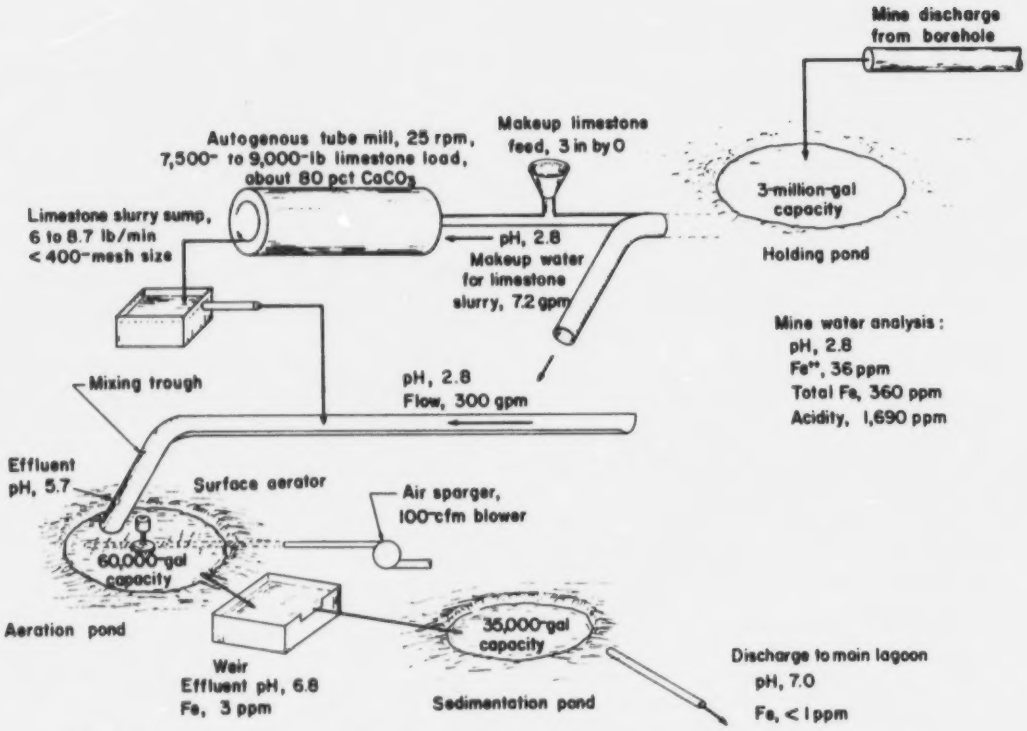

FIGURE 11. - Limestone treatment, which includes neutralization, aeration, and settling, is less expensive and produces a dense crystalline sludge.

the oxidation of ferrous iron in acid mine drainage. It is possible that the activated carbon provides a substrate to which the bacteria adhered. However, recent laboratory tests showed no significant bacterial activity or catalytic action.

The Bureau is also funding an investigation of the growth of iron-oxidizing bacteria on clay particles (5,000 mg/l) in a sequencing batch reactor. In this test bacteria are grown on clay particles in a ferrous sulfate solution containing appropriate inorganic nutrients. The reactor, a system of fill, aerate, settle, and discharge cycles (fig. 13), is designed to produce an effluent with a Fe^{2+} concentration of less than 10 mg/l. The retention of bacteria on the clay particles is dependent upon the ferrous iron content. If the Fe^{2+} content of the system decreases to 5 mg/l, the bacteria are desorbed from the clay and removed from the reactor in the discharge cycle. Using the sequencing batch reactor, a ferrous iron oxidation rate of approximately 290 mg/l/hr has been reported for estimated bacterial populations of approximately 5×10^7 cells/ml.

The disposal of sludge produced by neutralization of acid mine drainage is expensive and potentially one of the most persistent problems in its treatment. As a preliminary step, the current sludge disposal practices of 33 treatment plants were assessed to determine the magnitude of sludge production, current disposal practices, and constraints on their usage (1). The primary sludge disposal problem involves the large volume of sludge generated and the scarcity of approved disposal sites. The four most commonly used

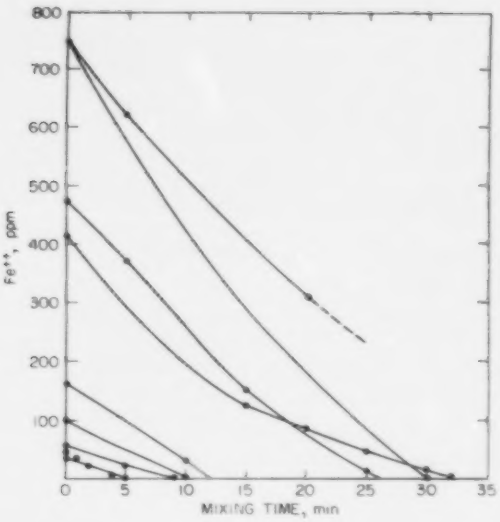

FIGURE 12. - In acid mine drainage neutralized with limestone, the rate of ferrous iron oxidation is 10 to 25 ppm/min.

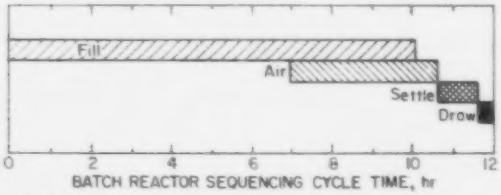

FIGURE 13. - The sequencing batch reactor incorporates fill, aerate, settle, and discharge cycles to optimize the rate of ferrous iron oxidation by bacteria.

methods of sludge disposal are deep mine disposal, retention in ponds, incorporation in coal refuse piles, and surface burial. The amount of land required for disposal is usually the determining factor in the overall cost, although transportation, equipment, maintenance, and labor are also significant (fig. 14). The development of methods to efficiently and economically increase the density of the sludge would substantially reduce the cost of sludge disposal.

Although there are other methods potentially applicable to acid mine drainage

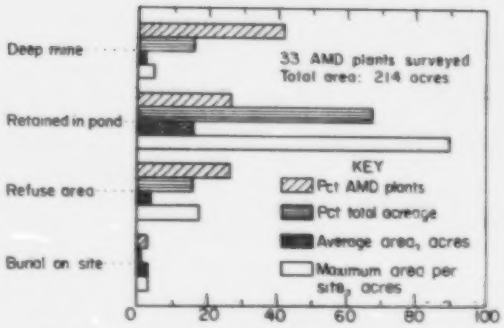

FIGURE 14. - Most sludge from acid mine drainage (AMD) treatment is retained in ponds, pumped into abandoned sections of deep mines, or dumped in refuse areas.

treatment, such as ion exchange, reverse osmosis, and flash distillation, the Bureau is not currently investigating these. Most of these processes are high in cost, have high power requirements, and produce a highly concentrated toxic brine or sludge which is more difficult to dispose of than the original sludge. The Bureau's research program in treating acid drainage from active mines is directed toward development and demonstration of a complete limestone treatment system, including a suitable catalyst for rapid oxidation of ferrous iron and sludge disposal.

The Bureau is also investigating a low-cost, low-maintenance treatment system for small streams contaminated by acid drainage from abandoned mines. Conventional treatment is not applicable because of the low flow rate and the remote rural location. It has been observed that bogs containing sphagnum moss and/or cattails remove iron by ion exchange and precipitation (10). Subsequent neutralization at limestone outcrops completes an effective natural treatment system. Artificial duplication of this natural process could improve water quality in many small streams.

The Bureau will test the practicality of duplicating this natural treatment system at a low-flow acid drainage discharge point in Northern Appalachia.

The system will include an artificial sphagnum moss bog followed by limestone rubble. The system is designed so that the drainage will pool in the moss, but will not raise the upstream water level enough to allow the water to flow around the treatment system. Monitoring the pH, Eh, temperature, iron and sulfate concentrations, and total acidity of the stream above and below the artificial bog will determine its effect on water quality. The monitoring will extend over at least 6 months so that the effect of uncontrollable parameters such as ambient temperature, rainfall, and stream flow rate can be determined. If this low-cost, low-maintenance system proves to be effective, it could be used to restore many small streams in rural areas.

AT-SOURCE CONTROL OF ACID MINE DRAINAGE

Of the millions of dollars spent on acid mine drainage each year, the major portion is spent on treatment. But treatment is not the best solution to most acid mine drainage problems. Treatment has the disadvantage of being necessary for as long as the acid discharge continues and thus requires manpower, surface facilities, and a sludge disposal area indefinitely.

Since acid drainage results from the oxidation of pyrite associated with coal and overburden strata, limiting the rate of pyrite oxidation would reduce the amount of acid formed. T. ferrooxidans normally catalyzes the pyrite oxidation and accelerates the initial acidification of freshly exposed coal and overburden. Inhibiting bacterial activity, therefore, would limit the rate of acid production and, in combination with proper reclamation, would reduce substantially the total amount of acid produced. Of the multitude of potential bactericidal agents, certain biodegradable anionic surfactants (detergents) have been found to control T. ferrooxidans in an economical and environmentally safe manner (15).

Field tests were recently conducted by the Bureau of Mines on both active and abandoned coal refuse piles in West Virginia (16). Sodium lauryl sulfate was applied at rates of 20 to 55 gal of 30-pct solution per acre, with a dilution range between 1:100 and 1:1000. Application rates were based on laboratory adsorption tests; dilution rates were dictated by site characteristics. At each site, drainage pH rose from approximately 2.5 to 5.5 or higher, with similarly dramatic decreases in acidity, iron, and sulfates.

One disadvantage of the detergents is that their effectiveness is limited; repopulation of the bacteria typically occurs in 3 to 4 months. To provide long-term control, the surfactants have been incorporated into rubber pellets (16) which can be applied early to a refuse pile or pyrite mine spoil. These pellets gradually release the surfactant into infiltrating rain water. In laboratory studies (fig. 15) and pilot-scale tests (fig. 16), controlled release of sodium lauryl sulfate reduced acid production 50 to 95 pct (14). Full-scale field tests are now in progress.

Another potential approach to at-source control of acid production requires the establishment of an alkaline environment. As already discussed, pyrite oxidation is

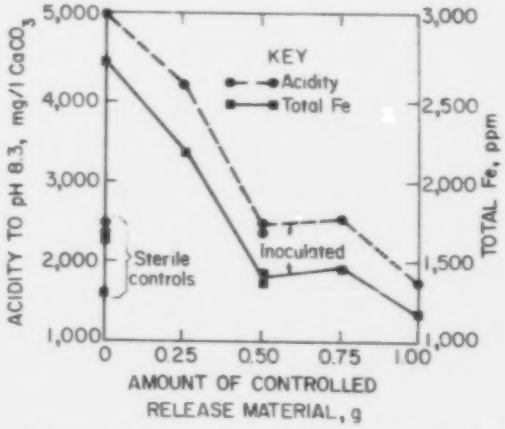

FIGURE 15. - The rate of acid production was approximately that of sterile controls when detergent was used to limit bacterial activity in a laboratory study.

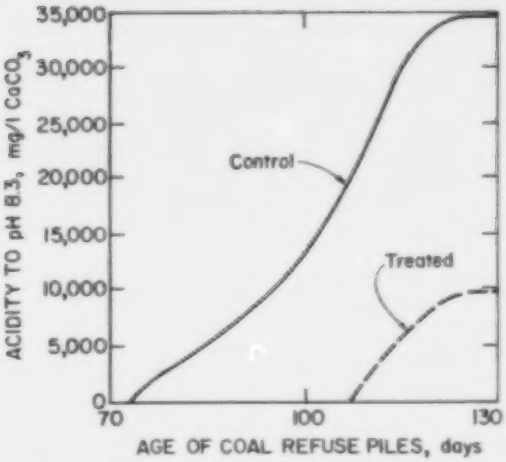

FIGURE 16. - Controlled release of detergents can be used to reduce acid production from spoil piles by 50 to 95 pct compared with an untreated control.

slow at near-neutral pH. A source of alkalinity such as lime, if added to recently exposed pyritic material, will retard or prevent acidification. The Bureau of Mines is currently investigating the possibility of reestablishing a radically alkaline environment, albeit temporarily, to determine if this will slow pyrite oxidation to the point where limestone will be sufficient to maintain near-neutral pH.

Water handling procedures for underground coal mines generally combine gravity flow and collection with pumping from sumps to surface treatment and/or disposal areas. To minimize the formation of acid water, properly placed sumps and pumping systems can reduce the time the water is in contact with pyritic materials. The size and location of sumps is also governed by the ability to discharge water on the surface with minimum power. Since on the average it requires 0.5 kwhr to pump 1,000 gal of water against a 100-ft head, gravity drainage and an efficient pump are most cost effective. The capacity of water treatment facilities depends upon flow rate and the concentration of pollutants. In designing a treatment system, using infiltration control and efficient water handling to reduce the amount of water flowing through the mine and minimize the amount of acid formed can result in substantial savings in water treatment costs.

A recent Bureau of Mines contract study examined current state-of-the-art methods of water diversion and overburden dewatering in Appalachian bituminous coalfields (3). It was found that most water enters underground mines either through water-bearing strata in contact with the coal seam, from surface seepage, through faults and fractures, or from abandoned workings. If surface water is the source, runoff diversion, regrading, soil sealing, and streambed modifications are possible control methods. The influx of ground water may be controlled by reducing the permeability of overlying strata, sealing abandoned mines, and well dewatering in advance of mining. Although all of these methods have been tried to some extent (table 1), their successful application depends largely upon geologic and hydrologic conditions. In general, the standard approach to handling the influx of water into underground mines consists of collecting the water and pumping it back to the surface. At present it appears that water diversion and overburden dewatering are, at best, supplements to traditional water handling procedures. Such methods have the advantages of helping to control large influxes of water that could affect production and reducing the cost of water treatment.

TABLE 1. - Water control practices (2)

Water control practice	Application	Limits of control	Field experience
	SURFACE WATER CONTROLS		
Runoff diversion...	Prevents infiltration into soil, mine openings, outcrops, rock fissures, strippings, cave-ins, surface cracks, and subsidence areas.	Effective if mine inflow is due to infiltration. May increase stream flow.	Used with varying success.
Surface regrading..	Eliminates ponding and improves drainage. Applicable near surface mines or other large land disturbances.	Depends on drainage area, annual precipitation, rate of infiltration into soil. May increase stream flow.	Used at strip mine sites. Can be very effective if mine water is due to ponding of water over mine.
Soil sealing.....	Prevents infiltration into soil by reducing permeability.	Prevents infiltration into soil only. Not effective in sealing fractures or other flow conduits.	Limited success.
Stream channeling..	Prevents inflow to mines from streams, especially in areas of vertical fractures, subsidence, or high permeability.	Can prevent large quantities of water from entering a mine.	Very effective.
	GROUND WATER CONTROLS		
Grouting and/or grouting curtains.	Reduces permeability of overlying strata by sealing fissures, fractures, and permeable formations.	Effective in limiting inflow via direct conduits.	Effective in curtailing water inflow during shaft sinking. Also used to cement localized areas of water inflow such as faults and joints.
Borehole sealing...	Prevents inflow to mines through boreholes from surface water sources and/or overlying aquifers.	Sealing ineffective after roof collapses.	Effective in reducing inflow through boreholes.
Subsurface soil sealing.	Prevents infiltration through the soil by reducing permeability.	Sealing efficiency reduced if area fractured. Most sealants are uneconomical.	No demonstrations of this technique.
Mine sealing.....	Prevents water from escaping an abandoned mine and infiltrating active workings.	Seals may lose effectiveness with time, depending on construction method and strata changes. Seals may cause ground water levels to rise, causing surface damage. Breached seals may prove hazardous to adjacent operating mines.	Effective in reducing or eliminating flow from abandoned mines into active mines.
Well dewatering....	Intercepts aquifers and controls the movement and discharge of groundwater.	Requires favorable geologic conditions.	Limited success. Used in reducing water handling requirements in mine.

In coal mines where fracture-dominated inflow is localized, intercepting water entering through faults and fractures may be feasible. Water flowing through such fracture zones is essentially surface water and would not normally require treatment. The Bureau has awarded a contract to conduct a pilot study on controlling fracture-dominated inflow. The study will develop design criteria for, and determine the cost effectiveness of, intercepting nonacid water flowing through localized fractures and transporting it to the surface. Economic and engineering analysis of this process should determine if it would reduce the cost of treatment substantially.

Coal storage piles and refuse piles may also be sources of ground water contamination (38). Rainfall percolating through such piles may leach acid and/or other toxic ions and carry them into ground water. The Bureau has awarded a contract to assess the extent of ground and surface water contamination from coal storage piles. Methods to prevent contamination of ground water include surface collection, impoundment, and treatment of runoff water. Preliminary cost estimates and a discussion of beneficial and adverse effects will be included.

Another area of concern is the effect of large-scale lignite mining in western Tennessee on ground water resources. At present there are few data available on the effects of mining upon ground water in the alluvial plain, in both shallow and deep aquifers. To gather data, four wells and two pits have been dug to determine ground water levels, movement, and chemistry. A contract report will assess the hydrologic impact of lignite mining.

SUMMARY AND RECOMMENDATIONS

The Federal Water Pollution Control Act of 1972 set effluent standards for coal mines, requiring treatment for acid mine drainage. Although these standards have been in effect for almost a decade, there has not been significant improvement in the water quality of many streams affected by mine drainage. This lack of improvement is related to the amount of acid drainage flowing from abandoned mines.

It has been known for years that air, water, bacteria, and pyrite are essential elements in acid production, yet at present there is no standard method or program for limiting the formation of acid mine drainage. Controlled release of anionic surfactants appears to be applicable to near-surface sources of acid production but not to long-term treatment of underground mines. Mine sealing, which is supposed to limit acid production in abandoned mines, has been only marginally successful (table 2). Bureau of Mines studies indicate that surface reclamation and seals at mine openings do not retard the passage of air into a mine. In many cases, seals used to flood a mine or the surrounding strata cannot withstand the continuous hydraulic pressure, resulting in failure of the seal or seepage around it. The Bureau is now evaluating mine seals in several areas in order to determine relevant chemical, geological, and engineering parameters and to determine the long-term effect of mine sealing on water quality.

Mine sealing is relevant not only to abandoned mines, but also to operating mines that will close in the future. At the present, mines must eliminate acid production or treat acid drainage indefinitely. It is possible that bond forfeiture may become a realistic economic alternative to the long-term cost of water treatment. In this area, there is need for development of low-cost seals that will maintain their integrity indefinitely. Other methods such as controlled roof collapse, water diversion, bacterial inhibition, and improved drainage should be investigated to determine their usefulness in reducing the formation of acid in mines that are no longer operating.

TABLE 2. - Variation in composition of mine effluent before and after sealing

	Mine 1				Mine 2			
	Before		After		Before		After	
	Low	High	Low	High	Low	High	Low	High
pH	2.9	3.2	3.0	5.5	2.3	3.2	2.85	3.70
Total acidity (as $CaCO_3$)[1] ppm	75	1,290	45	490	80	1,210	20	1,170
Sulfate (as SO_4) ppm	655	2,260	356	1,180	349	2,520	152	2,375
Calcium (as $CaCO_3$) ppm	203	1,242	36	625	125	760	70	725
Magnesium (as $MgCO_3$) ppm	109	520	76	336	76	530	7	502
Total iron (as Fe_2O_3) ppm	13	508	5	160	33	670	23	720

[1]End point = pH 8.2 at 60° C.

Improved prediction of acid drainage potential is being investigated in order to eliminate or minimize the formation of acid mine drainage. At present, core samples are analyzed for total sulfur and potential alkalinity, or tested with slow leaching methods. These procedures have not been correlated with acidity measurements in the field, and they are generally acknowledged as only an approximation of potential acid problems. Available techniques will be tested at sites where the extent of acid production is known, to determine their accuracy and possibly develop modifications. Rapid-leaching tests will also be examined for their applicability to the determination of acid potential. Accurate methods of predicting acid potential of coal and overburden will allow better permitting by State agencies, improved mine planning, and improved reclamation.

In operating mines, the need to treat large volumes of acid drainage is a problem. Currently, lime neutralization with aeration is the standard method of treating acid mine drainage. This method is relatively expensive, requires handling a caustic substance, and produces a sludge with poor settling characteristics. The Bureau has developed and is now improving a treatment system using limestone. Limestone treatment is less expensive, uses a noncaustic material, and produces a denser sludge. Routine use of the system requires the rapid oxidation of ferrous iron at acid or neutral pH. In an initial field study, activated carbon did not have the anticipated catalytic effect on the iron oxidation rate. Presently, studies are underway to determine if iron-oxidizing bacteria grown on activated carbon can increase the rate of iron oxidation in acid mine drainage. A study using bacteria grown on clay particles in a sequencing batch reactor has the same purpose. The develop-ment of an effective oxidation step will allow full-scale testing of the limestone treatment process. At present, other methods of treating acid mine drainage are not economically or technically practical. Limestone treatment seems to be one alternative that could be technically feasible and economically superior to lime treatment, although at present it is primarily applicable to waters with a low ferrous iron content. It also has the advantage of being readily adaptable to reclaiming streams affected by drainage from abandoned mines. A passive system using sphagnum moss and limestone will be tested as a means of improving water quality in low-flow streams.

It is apparent that 10 years of mandated water treatment have not produced a significant improvement in overall water quality. Although treatment of acid drainage from active mines prevents further deterioration, the majority of mine water pollution originates from abandoned mines. At present there is a need to develop methods for reclaiming polluted streams and for at-source control of acid production. Research is needed to

develop limestone treatment into a practical alternative to lime neutralization. To address these and other acid mine drainage pollution problems, the Bureau of Mines is conducting research in bacterial inhibition to control acid generation, improved water handling to reduce acid load, development of improved mine seals, rapid biological oxidation of ferrous iron, improved sludge disposal practices, low-maintenance treatment of small streams, reclamation techniques to reduce acid drainage formation, and limestone treatment of acid drainage (table 3).

Work in these research areas comprises a comprehensive approach to solving many of the longstanding problems associated with acid mine drainage. Improved treatment methods, at-source control methods, and stream reclamation methods resulting from the Bureau's research program will make a significant contribution to upgrading water quality in mining areas.

TABLE 3. - Bureau of Mines conservation and development program--acid mine drainage

Research area	Proposed time frame, fiscal years
Prediction of acid mine drainage:	
Prediction of acid potential	1981-85
Prediction of water infiltration	1981-84
Integration of predictive technology and premine planning	1984-86
At-source control technology:	
Inhibition of acid-forming bacteria:	
Surface mines and refuse piles	1981-83
Tailings piles	1983-84
Extension of bacterial inhibition to underground mines where applicable	1983-86
Alkaline treatment of coal refuse	1982-83
Placement of phritic overburden	1982-85
Water handling procedures, including diversion and dewatering	1981-85
At-source control technology for inactive or abandoned mines:	
Daylighting	1982-85
Effect of flooding on acid production, limiting parameters	1982-85
Improved mine seals	1981-86
Feasibility study--underground disposal mine refuse in a flooded mine	1982-83
Demonstration of above if feasible	1984-85
Reclamation of acid seeps (burnout) on revegetated mine sites	1982-85
Water treatment:	
Enhanced oxidation of iron	1981-86
Limestone neutralization	1984-86
Improved sludge disposal	1982-84
Assessment studies:	
Ground water contamination by acid-producing metal ore mines and tailings ponds	1982-86
Economic analysis--recovery of metals from tailings or streams	1983-85
Manuals:	
Premine planning to minimize acid drainage	1985-86
At-source control of acid drainage	1985-86

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QUAKAKE TUNNEL DEMONSTRATION PROJECT
LIMESTONE NEUTRALIZATION OF AMD

At some point in time, under very selective circumstances, construction and operation of an AMD treatment plant might be unavoidable. When either active or abandoned mining has been developed to a stage where the groundwater is a vast polluted mine pool and the surface waters are contaminated beyond use, treatment of AMD will be required to meet clean water needs. Treatment may not be the whole solution, but it will be a costly part of the solution.

The Pennsylvania Department of Environmental Resources has constructed five major AMD treatment plants between 1970 and 1979 at a total cost of $14 million. These plants were funded by the State's $500 million environmental bond issue of 1967. Today, only two plants are operating (one only part of the year) at an annual operating cost of $535,000. All of these plants have been of the conventional wastewater treatment design utilizing either hydrated or pebble lime for neutralization.

We can sum up our experiences as follows:

1. Very high capital costs.
2. Very high annual operating cost.
3. Constant maintenance problems.
4. Very poor initial design.
5. Labor intensive operations.
6. Hydraulically undersized for peak flow conditions.
7. Sludge removal and disposal problems.
8. Low factor reliability.

In the mid-1970's the Department initiated a state-of-the-art search for limestone neutralization technology. We found much fragmented research and development completed. A demonstration project was then developed to test, refine, and compare current technology. The Quakake drainage tunnel from the abandoned deep mines of the Jeansville Basin in the middle anthracite coal fields was the selected site.

Our ultimate purpose was to develop design and operating criteria at the Quakake pilot plant for application to full scale plants. The object was to use existing research and technologies for the project development.

Various neutralization processes were designed upon theories developed and presented by Dr. F. Pearson's and Dr. A. McDonnell's "Use of Crushed Limestone to Neutralize Acid Waters." Static limestone beds of varying stone size, length, and energy gradients were tested. Vertical beds contained in columns, where hydraulic suspension of the bed for cleaning was possible, were tested. Also, an autogenous mill, which was a simple water wheel and rotating drum, was operated at various flow rates with different size and quality of limestone.

Our findings are that limestone neutralization is feasible, economical and the reliable treatment process. Limestone facilities will have a lower capital cost, lower reagent cost and be less labor intensive to operate. The handling and long-term storage of reagent, as well as reliability of a simple process control are built-in benefits. Sludge settling and dewatering characteristics are excellent to allow for landfill disposal of a solid cake.

Pennsylvania is developing plans to construct a full scale limestone pilot plant in the headwaters of Little Toby Creek, Elk County. This pilot plant will be operated and evaluated to prove the findings of the Quakake demonstration project. The results of its operation and evaluation will be the basis to determine if limestone neutralization will play a major role in the control of acid mine drainage in Pennsylvania.

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Harrisburg, PA 17120

Dear Mr. Friedrich:

You contacted us sometime ago about the self-feeding limestone drum acid water neutralization system. This is an update on the testing of the proto-type station.

We had hoped to have testing completed this spring, but a number of small problems developed that will require another six months or so of testing. Enclosed is a performance report that will give you the current status of the project.

The testing scheduled for this winter and next spring will concentrate on maximizing production rates of $CaCO_3$ fines from the drum. Results may require some minor changes in blueprints and specifications for drum manufacture.

You will be contacted again next year and given the project status.

Sincerely yours,

Peter E. Zurbuch

Peter E. Zurbuch
Assistant Chief
Wildlife Resources Division

PEZ:ll

Enclosure

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DESIGN OF AN ECONOMIC AND EFFICIENT TREATMENT STATION FOR ACIDIC STREAMS

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ABSTRACT

This paper deals with the design of a treatment station for acidic streams using a self-feeding rotary limestone tumbling drum activated by the stream flow. It can operate unattended for seven to ten days while being supplied continuously at the required rate from a storage bin. Unique features of the self-feeding mechanism are presented here with experimental data that can be used in the design of high efficiency drums.

INTRODUCTION

The West Virginia Department of Natural Resources (WV DNR) pioneered the successful use of crushed limestone to neutralize lightly buffered acid streams [1]. The high-calcium limestone was tumbled within drums, equipped with water vanes, that were powered by stream flow. The drums were batch-loaded with 1,800 pounds of stone which was used up within four days at the maximum operating flow of 4.0 cfs. Each drum abraded an average of 20 pounds per hour of limestone fines into the stream at that flow. A treatment station of four such drums was operated from 1964 to 1979 on the headwaters of Otter Creek, a small mountain stream in the Monongahela National Forest of West Virginia. Neutralization of the streams acid flow permitted the establishment of a native brook trout (Salvelinus fontinalis) sport fishery [2].

In the 1970's West Virginia began to have increasing problems in stocking trout in some major trout streams because of spring acid conditions. Many of these waters were in watersheds that had no coal mining thus discounting acid mine drainage as a possible cause. Acidification appeared instead to be associated with acid precipitation. The decline in these fisheries approximated the increase in acid precipitation for eastern North America [3].

Treatment of the affected waters is beyond the capabilities of the batch-loaded "limestone drums". Previous experiments with the drums indicated their efficiency in producing limestone fines could be increased if they were operated partially filled. To be feasible for use in stream neutralization, operating a partially filled drum would require external stone storage and a method to feed the stone into the rotating drum. It was felt that this type system would have the advantages of increasing the amount of limestone fines being produced while reducing the servicing requirements.

A test of this hypothesis was conducted by the WV DNR in 1980. A batch-loaded drum was tested containing only 10 percent of its capacity of stone. At one-half intervals the drum was stopped and a small amount of stone added. The test showed a dramatic increase in the amount of limestone fines being dissolved into the stream. It also indicated the drum would stabilize itself so that the rate of limestone was equaled the rate of stone being fed into the drum. A research project was then initiated to develop a second generation limestone drum system that would be self-feeding. The WV DNR entered into a cooperative research endeavor with the Mechanical and Aerospace Engineering Department at West Virginia University to design and test such a system. This paper presents the results of this effort.

1. SELF-FEEDING WATER POWERED LIMESTONE DRUM SYSTEM

In Figure 1 the principal components of the self-feeding water powered limestone drum system are shown. The system consists of a rotating drum with waterwheel blades that is activated by falling water through an opening at the bottom of the sluice. The limestone aggregates that are stored in a 10-ton gravity bin and hopper are fed to the rotating drum through the action of a reciprocating feeder at the bottom of the storage bin. After falling through a chute they are transported in a hollow shaft with internal helical blades acting as a screw feeder. A flexible drive shaft is used to convey directly power from the rotating drum shaft to the reciprocating feeder through two speed control units. A calibrated opening in the reciprocating feeder acts as a metering device to control the amount of aggregates that can be fed to the chute after each stroke of the feeder.

With this arrangement the feed mechanism can be compared to a feedback control system providing the exact amount of aggregate to the drum for any flow rate of the stream. When the rate is high the drum turns faster, the number of strokes of the reciprocating feeder per unit time increases, and hence more aggregate is supplied to the drum. The opposite happens when the stream flow is low and less amount of aggregate is needed in the drum. Metering the flow of limestone to the drum in this way, at the exact pre-determined rate for the corresponding flow rate of the stream, keeps the desired value of the pH level constant in the water, regardless of flow conditions.

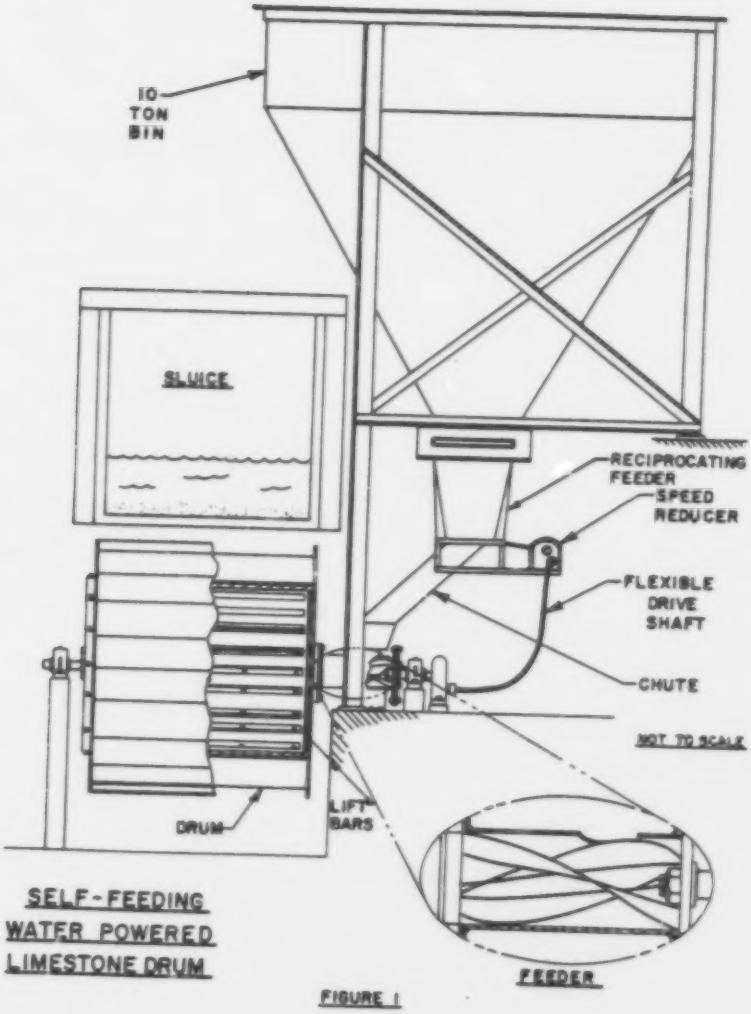
The action of the limestone aggregates in the revolving drum is a wet autogeneous process. Falling water through sluice opening enters the drum on top through small holes in the shell of the drum between the water wheel blades, and after mixing with (-400) mesh limestone particles already generated through the tumbling process in the drum, leaves it through the same holes at the bottom position where it is discharged to the stream for acid neutralization.

1.1 Main Features of Principle Components

All components of this neutralization station are designed with the primary objective of providing trouble-free operation requiring very little supervision and operator assistance.

1.1.1 10-Ton Storage Bin

The square pyramidal bin with 60 degree hopper angles can store a one week supply of limestone of 1¼ in. size for acid stream treatment. The bin provides continuous gravity flow of limestone particles at the rate of 120 lb/hr. to the reciprocating feeder through a 15 in. square opening. The bin geometry was determined after considering the flow characteristics of limestone aggregate



SELF-FEEDING
WATER POWERED
LIMESTONE DRUM

FIGURE 1

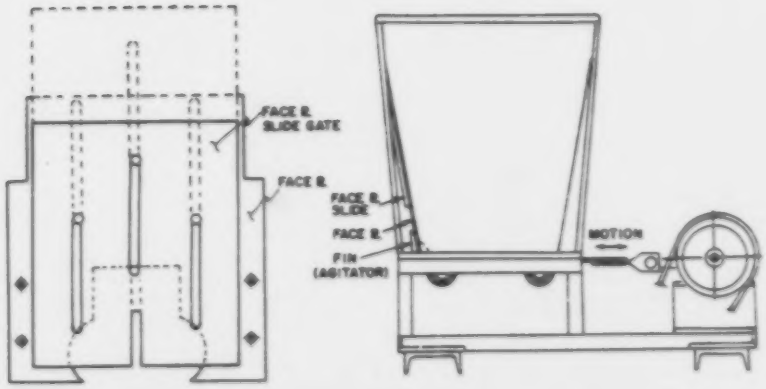
in the bin, its density, angle of repose, and possible resultant loads on the reciprocating feeder. Also of prime importance was the height of the bin which was desired to be kept at minimum for the required capacity. This height is within the reach of a front loader that can be used by an operator to load the bin once a week most economically.

1.1.2 Reciprocating Feeder

Main features of the reciprocating plate feeder in this application consist of the feeder rate control gate and the agitator as shown in Figure 2.

An adjustable limestone feed rate control gate was incorporated in this design on the face of the feeder hopper to manually regulate and set the flow of the limestone particles out of the feeder in accordance with stream flow and the RPM of the drum.

The purpose of the agitator is to provide a continuous flow of the limestone particles toward the control gate in the feeder by breaking any arches that may form in the hopper and overload the drive system.



RECIPROCATING LIMESTONE FEEDER

FIGURE 2

1.1.3 Inverted Screw Feeder

Limestone is fed continuously to the rotating drum through a 6-inch diameter hole cut into its feed side where a 6-inch hollow shaft made of schedule 40-pipe is attached to the drum. A 2-inch solid shaft coupled to the hollow shaft extends on the other side to rest on a pillow block to support the rotating drum. A 4-inch diameter hole in the surface of the hollow shaft receives the limestone particles falling through the chute, and the helical fins in the hollow shaft act as an inverted screw feeder to transport the limestones until they fall inside the drum. A casing surrounds the hollow shaft, and it includes a small hopper to funnel the aggregates into the 4-inch hole on the hollow shaft.

1.1.4 Flexible Drive Shaft

In order to provide the necessary feed rate of the aggregate to the drum for various flow rates of the stream the reciprocating feeder must discharge the proper amount of limestone during each operating stroke. A flexible drive shaft supplying power to the reciprocating feeder from the drum shaft was found to be the most suitable possibility for such an arrangement. When the flow rate in the stream is high, the drum turns faster and more aggregates are made available for grinding. The opposite happens when the stream flow is slowed down. This way, after properly adjusting the feed gate on the feeder, the pH level of the stream can be kept constant at any desire value.

For smooth operation of the reciprocating feeder, two speed control units were placed at each end of the flexible shaft. The one attached to the drum shaft increases the input RPM from 35 to 900 at the flexible shaft, and the other having the same velocity reduction ratio delivers 35 RPM to the reciprocating feeder drive shaft. This way torque variations in the shaft are kept at a minimum level when the aggregates in the feeder hopper are jammed, and the agitator is applying pressure to break limestone arches impeding the flow in the hopper.

1.1.5 Rotating Drum

The design of water powered tumbling drums loaded with crushed limestone is critical when hydraulic and grinding efficiencies are considered. The hydraulic efficiency is defined as the ratio of power consumed by the drum to the power supplied by the water in the sluice, and the grinding efficiency is measured by the capacity of drum to deliver the amount of fine limestone particles per unit time, (lbs/hour). The hydraulic efficiency is only a function of the geometry of the drum, and it depends mainly on the water wheel diameter, and drum diameter. The grinding efficiency for an autogenous wet process is more complex and it is mainly affected for a given aggregate material, on the aggregate size, inside drum geometry (diameter, length), drum speed, percent volume of the tumbling aggregate to the volume of the drum, and lift bar configuration. This last item includes number of lift bars, their geometry and their spacing and positioning around the periphery inside the drum.

Some of the experimental work dealing with the above-mentioned parameters will be presented in more detail in the following section of this paper.

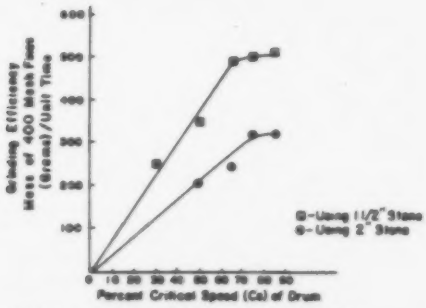
For 4 ft^3/sec. of water flow at the pilot treatment station, the final design of the drum included a drum diameter of 36 in., with 44 in. length, and an outside water wheel diameter of 32 in. This drum also contains 22 water wheel blades (vanes) on the outside and 22 lift bars in the inside equally spaced around the circumference of the unit. Life bars made of standard angles,

1½ in. x 1½ in. x ¼ in., are placed along the length of the drum parallel to the axis of rotation, Figure 1.

2. EXPERIMENTAL WORK

To determine the effect of principal parameters on the grinding efficiency of tumbling drum a 12 in. diameter and 8 in. long model was built and powered by a variable speed motor. All tests were run with limestone aggregates in dry condition. It is a generally well known fact that in comminution processes the grinding efficiencies are always higher in wet conditions than the dry ones for similar conditions. However, the relative influence of each parameter as a variable affecting the grinding efficiency remains the same whether the process is wet or dry. It is for this reason that dry grinding was selected in this investigation since it also simplified the laboratory equipment and technique required for the present tests.

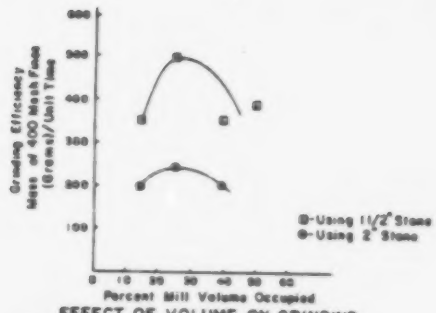
Figure 3 shows that for any given aggregate size there is a drum speed at which the grinding efficiency is maximum. For 1½ in. and 2 in. limestone size this was found to be between 65%-75% of the critical speed when the load in the drum occupied 25% of the total volume. The critical speed (Cs) is defined as the minimum speed at which the media in the drum are held against the shell by centrifugal force, i.e., the speed at which the centrifugal force is just balanced by the weight of the media. These values are in agreement with suggested values in the literature for similar cases.



EFFECT OF DRUM SPEED ON GRINDING EFFICIENCY AT 25% OCCUPIED VOLUME

FIGURE 3

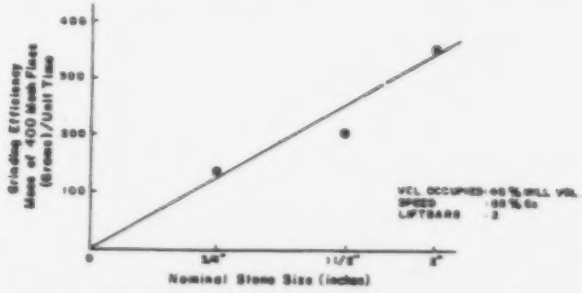
The grinding efficiency was found to be maximum for a given aggregate size when the charge in the drum occupied about 25% of the total volume as shown in Figure 4. This can be explained by the fact that there must be enough aggregate mass present in the drum to produce fines but there must also be enough space for particles to collide with minimal impedence from the drum walls. The level of material must be kept as low as possible to prevent larger stones impacts from being cushioned by too high aggregate level. [4]



EFFECT OF VOLUME ON GRINDIND
EFFICIENCY AT 65 % CRITICAL SPEED

FIGURE 4

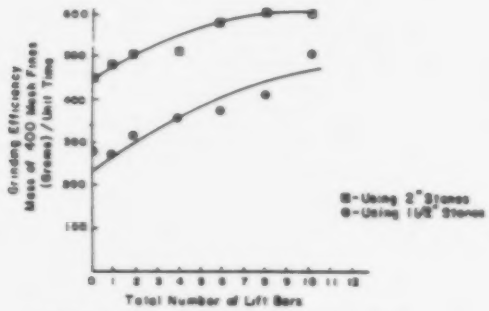
Figure 5 shows the effect of aggregate size in grinding efficiency. The efficiency is directly proportional to the aggregate size of the tumbling charge in the drum within the limit of this investigation. This is probably due to the fact that increased masses in this case provide additional impact forces which facilitate the breakage process. Once the smaller particles are generated in the charge, the overall available rough surface area in contact in the drum is increased. This increase in the total friction surface in the media results in more fines being produced in the process.



EFFECT OF AGGREGATE SIZE ON GRINDING EFFICIENCY

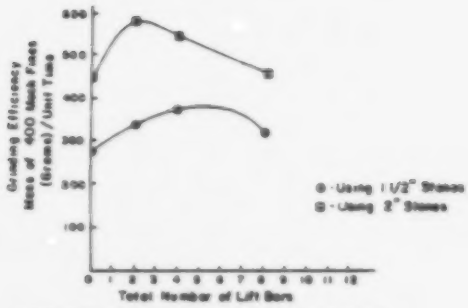
FIGURE 5

Figures 6 and 7 show the variations of the grinding efficiency with the size and the total number of lift bars in the drum for two different aggregate sizes. The grinding efficiency increases with the number of lift bars (1 in. size) until the spacing between bars reaches a size where particles can lodge there and impede the grinding process. This usually happens when this space is about less than three to four times the aggregate size in the drum.



GRINDING EFFICIENCY WITH 1" LIFT BARS

FIGURE 6



GRINDING EFFICIENCY WITH 2" LIFT BARS

FIGURE 7

The lift bars affect output through two ways; one, by providing a mixing action so that the aggregates will move about and abraise each other, and two, by providing an aid to crushing and chipping, similar to impact action of a continuous anvil. Mixing is important, but if the lift bars are too high and too great in number, stones will be retained excessively between bars and only part of the stones above the bars will be permitted to tumble in a normal cascading fashion in the drum. This can explain the decreasing value of the grinding efficiency in Figure 7 with the increase of the number of bars.

In conclusion it can be said for the lift bars that they serve two purposes, mainly breakage, and mixing of the aggregates. They should protrude above the fines in contact with the drum lining and not confine many stones between their walls. For a given size of aggregate there is a bar height and bar spacing which will produce the maximum grinding efficiency.

As mentioned previously all the tests were done in dry running conditions. Following the completion of the pilot station, similar tests will be performed in actual wet operating conditions in the next phase of this investigation and validity of some of the assumptions will be checked.

A further parameter affecting the grinding efficiency is the amount of water present in the drum during the wet tumbling process. It was, of course, impossible to investigate this parameter within present test conditions. This effect will be studied in in-site testing by varying the number of access holes on the drum shell for water inlet and outlet during the operation of the pilot station.

CONCLUSION

Recent investigations have shown that crushed limestone can be used effectively and most economically to neutralize acidic streams. Water powered tumbling drums loaded with limestone aggregate can make effective use of the energy inherent in the streams and can supply the necessary fines to control the pH level of the water. A self-feeding treatment station requiring very little supervision presents the most economical solution to this problem since it reduces to a minimum level the cost of extensive manual labor otherwise needed in this operation. The main features of such a treatment station consist of a storage bin and hopper, a feeding mechanism which can vary with the flow and acid level requirements of the stream, and some means of metering and transporting the limestone aggregates from the storage unit to the tumbling drum. The solution presented here has the capability of performing all these tasks using only as the sole power source the energy available in the stream. Such a system tested at one pilot treatment station at Otter Creek, West Virginia, was found to be 600 percent more effective than the batch-loaded drum while requiring only one-sixth of its water flow requirements.

The proper design (geometry, configuration and components) of the tumbling drum requires careful considerations. Among them are principally, the rate of flow and acid level of the stream, the aggregate feed rate and size, and the RPM of the drum. Experimental data included in this paper show that the output of fines produced in a drum can be maximized with the selection of proper values of relevant parameters in the final design of a tumbling drum.

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NEUTRALIZATION OF ACIDIFIED STREAMS IN WEST VIRGINIA

Peter E. Zurbuch

ABSTRACT

The West Virginia Department of Natural Resources has 25 years of experience in neutralization of acidified streams. Early efforts were on lightly buffered waters that gained most of their acid content from watershed geologic conditions. Research led to a method of treating acid stream flow with limestone aggregate contained in water powered rotating drums (Limestone Drum System). Increased acidification of West Virginia streams by acid precipitation has rekindled research efforts on a problem of larger proportions than that experienced in the late 1950s and 1960s. This paper reviews work on treatment of acidity in natural streams—particularly that dealing with use of the Limestone Drum System. It reports on recent development of a second generation drum that is self-feeding from streamside stored aggregate. The new system's efficiency may permit its application to large streams affected by acid precipitation.

West Virginia has relatively few impounded waters. As a result, fisheries management in the state has focused on stream environments. Many streams in the north central and western parts of the state have been severely impacted by acid mine drainage (AMD). A number of others, especially in the eastern mountains, are lightly buffered and small amounts of acid, from mining or acid precipitation, cause severe problems for fisheries. Mining reclamation and treatment of AMD have greatly improved water quality in the state and good fisheries exist where there had been none for 40 years or more. In the lightly buffered waters, including much of West Virginia's trout habitat, the advent of acid precipitation is reversing these gains. The control of acid production from mining of coal is being offset by increased acid deposition from burning of it.

Peter Zurbuch

THE AUTHOR: Peter E. Zurbuch received a B.S. in forestry from West Virginia University and an M.S. in fisheries from the University of Michigan. He has been employed by the Wildlife Resources Division of the West Virginia Department of Natural Resources since 1956. His initial employment was as a D-J Project Leader for Fisheries Investigations of the Ohio River and its tributary streams. In 1957, he was placed in charge of the states' hatcheries and trout research program. During this period he started research efforts in neutralization of lightly buffered acid streams. He became chief of the Wildlife Resources Division in 1966 and served in that position until 1971. He then moved back into research and has headed wildlife research and special projects working out of the Department's Operation Center in Elkins, West Virginia.

Acid mine drainage that has not been contained by mine reclamation is commonly being treated by the mining industry in the state. Generally, these treatment stations involve the use of hydrated lime ($Ca(OH)_2$) or quicklime (CaO). Recently, some success has been achieved with the combined use of hydrated lime and limestone ($CaCO_3$). AMD neutralization techniques provide valuable information to fishery managers on methods of applying neutralization reagents to acidified waters, problems commonly encountered, and give insight into costs involved. Data cannot, however, be directly applied to lakes and streams being adversely affected by acid precipitation. Significant differences exist. AMD usually has a much higher concentration of solids and flows are small and regulated. Waters impacted by acid precipitation have very low solid concentrations, many near distilled water, and natural flows are large and unregulated. AMD treatment stations are usually near road access, utilities, and a labor force for operation and maintenance. Lakes and streams impacted by acid precipitation are often remote and not readily accessible.

Research on treatment of lightly buffered acid streams was initiated by the West Virginia Department of Natural Resources (DNR) in the late 1950s. The first attempts involved placement of bags of hydrated lime in small tributaries, hoping that a slow dissolution of the material would neutralize acid loads in the main stream. The impracticality of this approach was soon evident, and more sophisticated treatment systems were developed. Four techniques are presented below: hydrated lime/aglime ($CaCO_3$ fines) feeders, streambed limestone, rotary drums, and self-feeding rotary drums.

HYDRATED LIME/AGLIME FEEDERS

Effective stream neutralization requires a slow release of base, ideally with the rate of release regulated by stream flow and acidity. To at least partially fulfill these needs, the DNR initially designed and tested (in the late 1950s) a mechanical feeder powered by stream flow and constructed to dispense calcium hydroxide gradually into the stream. While the original treatment station was crude in construction compared to present

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day systems, the problems encountered then still plague modern counterparts, i.e., the daily maintenance of the feeder to keep the feed free flowing and regulated to stream requirements, and dry storage of large amounts of the reagent.

More recently (1971–1972), the U.S. Forest Service tested a stream powered aglime feeder on Dogway Fork, a tributary of Cranberry River, for about a year. The project experienced many stoppages and neutralization effects varied considerably. The Forest Service concluded the system was not applicable to stream requirements and stopped treatment.

The West Virginia DNR, in cooperation with Trout Unlimited has also experimented with a modification of the mechanical feeder system, feeding aglime or hydrated lime into a mixing vat prior to dispensing into the stream. Power for the feeder and vat agitation is from water piped into the station from an upstream inlet. While effective for a short-term (24-hour) operation, the system has unresolved problems similar to the direct dry feed systems. Because of the numerous inlet and outlet pipes, the system is also subject to freeze up during cold weather.

STREAMBED LIMESTONE

After initial attempts with hydrated lime feeders were nonproductive, much simpler procedures were proposed. Placement of bags of hydrated lime in streams had provided inadequate contact between the base and the water and thus inadequate neutralization. To improve this interaction, limestone aggregate was spread along the streambed. Although effective initially, the benefits of this treatment are often short-lived, as the stone becomes unreactive due to silting and coating with precipitate.

In 1974 a West Virginia chapter of Trout Unlimited treated a small tributary of Dogway Fork of the Cranberry River. Thirty-six tonnes of 2 to 2.5 cm limestone aggregate were spread over a 183 m segment of streambed. At first water quality was improved, raising the stream pH from 4.1 above the stone to a maximum of 6.1 below the treated segment. The reactivity of the stone, however, gradually decreased. Eventually, passage over the limestone aggregate had no significant effect on streamwater pH. Neutralization lasted through the spring and summer months following application. The lowest pH recorded during that period was 5.4.

The full benefits of streambed limestone may not be entirely evident from chemical data alone. In Otter Creek, a stream treated with limestone fines (a waste product from rotary drum operations), residual benefits have continued long after treatment ceased. Native brook trout (*Salvelinus fontinalis*) are now able to inhabit sections of the stream where they were not present before treatment. Size of the aggregate or fines may be important. If stream movement of the bottom material is able to keep a portion of the limestone surfaces reactive, water quality may be improved sufficiently for fish populations to survive.

Similar results have since been noted by a number of researchers (Fraser and Britt 1982). Namely, treatment results in a slight improvement in pH followed by a decline to the original pH. The apparent benefits for fish populations, however, suggest that streambed application of limestone has potential value and should be further researched.

ROTARY DRUM

Problems with coating of limestone aggregate and reduction of the neutralization reaction in streambed applications led to development of the rotary drum system. In order to keep the limestone from coating, agitation of the aggregate in a water-powered rotary drum was proposed as a solution. The first drum was constructed by hatchery personnel using a 151-liter oil drum. The drum was fitted with an axle and house guttering welded to it for water cups so that it would be turned by stream flow. Holes were punched in the drum to permit water to enter and exit. Testing of the drum indicated that, besides keeping the stone from coating, reaction rates were increased as a result of abrasion and production of fine particles of $CaCO_3$ that readily dissolved in the stream flow.

Following this initial success, two manufactured drums were installed in Condon Run (Figure 1), a tributary of Otter Creek, in the Monongahela National Forest near Elkins, West Virginia. These were tested from 1960 to 1962 and showed that the system could be used to treat lightly buffered acid stream flow (Zurbuch 1963).

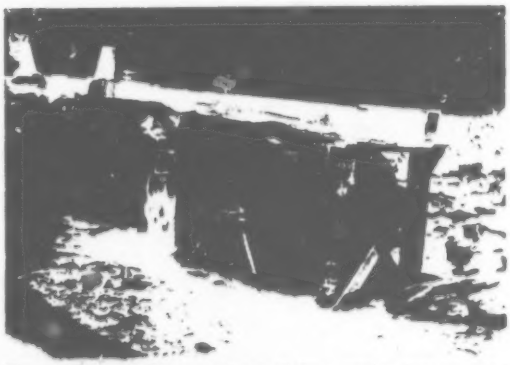

Figure 1. Condon Run experimental drum station that operated 1960 to 1962.

A federal aid project (Dingell-Johnson) was approved in 1963 to apply the rotary limestone drum system in continuous treatment. Two systems were designed. One, a four-drum station at the head of Otter Creek was intended to neutralize the entire 16 km stream, and to sustain a native brook trout fishery. The second, a four-drum station was installed on a tributary stream of Sherwood Lake, a 67 ha infertile soft-water lake; with the objective to increase productivity of the warm water fishery of the lake.

The Sherwood Lake installation was operated from 1964 through 1969 and its effects were reported by Sumner (1970). While there was an overall increase in the standing crop of fish, it could not be directly attributed to treatment. The lake was changed from a very soft water lake (0–400 μeg/L alkalinity) to a soft water lake (420–800 μeg/L alkalinity). It also shifted from a slightly acidic environment (mean pH 6.6) to a slightly alkaline one (mean pH 7.1). Dissolved calcium remained low during the first two years of treatment, never exceeding 80 μeg/L. In the third year (1967) the concentration reached 140 μeg/L. In 1968, the fourth year of treatment, there was a dramatic increase in calcium concentrations, with levels ranging from 180 to 340 μeg/L. Sumner (1970) postulated that much of the $CaCO_3$ initially dissolved into the lake water was absorbed in the mud of the lake bottom. Further, once the mud was neutralized the chemistry of the lake water improved, and if treatment were continued even more significant

increases in dissolved calcium, alkalinity, and pH would have been achieved.

The drum installation was within 1 km of the lake and stream dissolution of the limestone was probably not complete by the time it reached the lake. Within the stream, pH was normally raised two full units above vs. below the treatment, from 6.6 to 8.6, and total alkalinity from 136 μeg/L to 300 μeg/L.

The Otter Creek installation (Figure 2) was operated for 15 years from 1964 to 1979. Research results for the period 1964–1968 have been reported by Menendez (1974). A native brook trout population was established for about half of the length of the treated stream. The population was still expanding when the last survey was made in 1970. Subsequent to this the area below the treatment station was designated a wilderness area, thus, limiting additional fish surveys. The annual neutralization of acid load was in excess of 83% at the treatment site. Downstream, at the stream mouth the reduction varied from 33% to 50%. Alkalinity immediately below treatment increased from a pretreatment of 60 μeg/L to around 200 μeg/L. Alkalinities at the stream mouth were increased by only 20 to 40 μeg/L. The pH values below the drum site were usually kept above 6.0 and reached a high of 7.3. In the lower stream, effects on pH were not as discernible.

Construction of the Otter Creek station cost $17,761 and the Sherwood Lake station $13,479 (1963 dollars). For the period 1964–1969 the Otter Creek station required an average 60 man-days per year for maintenance and operation and 53.2 tonnes of limestone aggregate per year. The Sherwood Lake station required 42.4 man-days annually and averaged 44.8 tonnes of limestone consumption per year. Maintenance and operation included stockpiling of limestone, hand-loading the drums, and maintenance of the drums, sluice, dam, and grounds. It was felt that the drums operated satisfactorily and at a reasonable cost. Very few mechanical problems were encountered.

Beaver (*Castor canadensis*) control on treated streams is an important consideration. Considerable effort was spent at both sites to keep beaver cuttings out of the sluice area. At Sherwood Lake the entire dam area was eventually fenced, while live trapping and removal alleviated the problem at Otter Creek.

Extremely cold weather did not freeze up the drums if there was sufficient operating flow. If flows decreased below operational levels (0.014 m^3/s), and the drums froze, stopping rotation, they would resume operation within a few hours of increased stream flow. It was not uncommon to break an 8 to 15 cm cacoon of ice surrounding an operating drum to permit loading it with stone. Otter Creek winter temperatures were frequently −10°C or below, with a low recorded at −28°C.

A coal company attempted to use the drum system to neutralize a stream draining a large strip mining operation. They installed a treatment station on Beaver Creek, a tributary of the Blackwater River near Davis, West Virginia. The acid load requiring neutralization, however, was more than the capability of the drums, and neutralization was only about 20% effective. During one sampling period, stream flow was 0.03 m^3/s and pH above the treatment station was 4.0 with a total acidity of 1760 μeg/L. Immediately below the drums, acidity was reduced to 1500 μeg/L; and to 1440 μeg/L 3 km downstream at the mouth of the stream. The pH remained at 4.0 at both

Figure 2. Otter Creek four-drum continuous neutralization station that operated 1964 to 1979. See cover photo.

downstream sites. The treatment station was operated sporadically for a few years and then abandoned.

The U.S. Forest Service installed a one-drum treatment on Bear Run, a tributary of the North Fork of Cherry River near Richwood, West Virginia. The stream is polluted with AMD and the drum successfully neutralized enough acid to permit trout stocking in the headwaters of the North Fork. Data are available for years 1970 to 1973. Stream flow fluctuated between 0.014 m^3/s and 0.034 m^3/s and the drum was refilled every two weeks. The pH of the untreated water ranged from 4.0 to 5.5 and conductivity from 52 to 110 μmhos/cm. At the mouth of the stream, about 1 km downstream from treatment, the pH was raised 1.0 to 1.5 units.

The Pennsylvania Department of Environmental Resources (PADER) recently released a comprehensive report evaluating techniques that use limestone in neutralization of AMD (PA DER 1982). Static barriers, downflow beds, upflow beds, alternating flow beds, an autogenous cleaning mill, and rotary drums were evaluated. The report concluded that crushed limestone is a feasible alternative to lime or other base treatments for treating AMD. Further, they recommended use of the rotary drums for final treatment of effluent that is pretreated using a filter bed of limestone having backwashing cleansing capabilities. The pretreatment bed's purpose is to remove metals (Al, Fe). The report is an excellent reference for fishery scientists studying use of limestone to neutralize acidified streams.

SELF-FEEDING ROTARY DRUM

In the mid-1970s the DNR became aware of the impact of acid precipitation on some of the major trout streams of the state. Streams that had once been stocked with trout from January through June were now unable to accept fish until late April or early May because of low pH. A study was made of the feasibility of treating these streams using the rotary drum system developed at Otter Creek. Hand-loaded drums, as used at Otter Creek, however, were impractical. For example, it was estimated that over 70 drums would be required to handle flows and acid loads for Cranberry River—formerly one of the premier trout streams in West Virginia.

During the original development of the Otter Creek drums it was apparent that at small drum loads, 25% or less of drum volume, the limestone reaction rate was much higher. It was believed that if a drum could be developed that maintained a light load, and fed itself from a storage bin, a more efficient treatment system was possible. To test this hypothesis, the Otter Creek station was repaired in 1980 so that one drum could be put into operation. It was hand-loaded at 0.5 hour intervals in order to maintain a 91 kg to 114 kg load of stone. These tests indicated that it might be possible to increase the drum output by 600% if a self-feeding drum could be designed and successfully tested.

A cooperative project was entered into in 1981 between the DNR and the College of Engineering at West Virginia University (WVU) to design and construct a self-feeding rotary drum and attendant storage bin. Design goals were: (1) development of a self-feeding drum powered by stream flow; (2) production of up to 54 kg/h of limestone fines (90% with 38 μm diameter or less) at an operating flow of 0.113 m^3/s; (3) unattended operation with minimum maintenance; and (4) bin storage of a week's supply of stone (9.1 tonnes). The Otter Creek station was repaired, a new sluice installed, and a self-feeding drum station placed into operation in March 1983 (Figures 3 and 4).

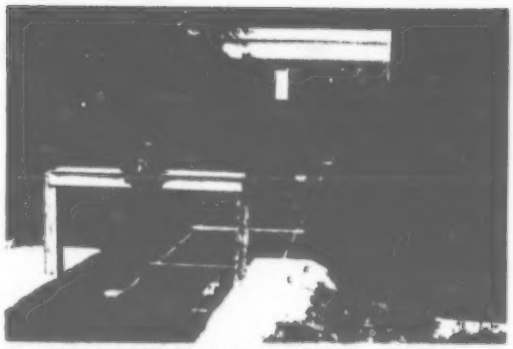

Figure 3. Experimental self-feeding rotary drum limestone neutralization station installed at Otter Creek in 1983. Photo shows sluice and sluice gate; building enclosing drum apparatus, storage bin, and limestone stockpile.

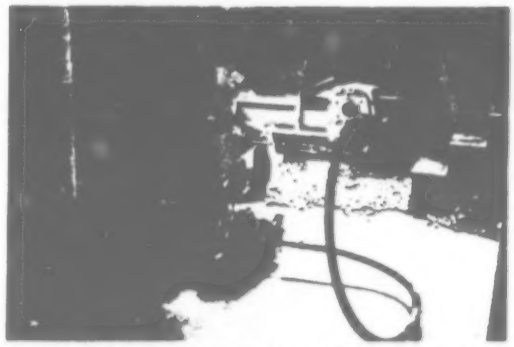

Figure 4. Self-feeding limestone drum apparatus. Photo shows water powered drum, drum feed, flexible drive shaft, reciprocal feeder and bottom of 9.1 tonne bin.

In preliminary testing (March–May 1983) the self-feeding drum performed well. In excess of 36 tonnes of 3.8 cm limestone were consumed during testing. The system operated continuously for three weeks during one test period without mechanical problems or feed stoppages. In one previous 24-hour test, the self-feeding drum produced fines at a rate of 57 kg/h into a stream flow of 0.184 m^3/s. Above treatment the pH was 4.7, total acidity 108 μeg/L, and alkalinity 30 μeg/L. After treatment, and downstream 0.4 km, pH was raised to 8.4, alkalinity to 680 μeg/L and the acid load completely neutralized. The self-feeding drum design and its mechanical operation are presented in more detail in Gencsoy et al. (1982).

Laboratory research indicates that an even more efficient drum may be possible with variations in drum design and stone size. At the present output, the system can produce six times the neutralization of the hand-loaded drum (54.4 kg/h vs. 9.1 kg/h at an operating flow of 0.113 m^3/s). The feeder can be adjusted to produce any desired treatment rate lower than the maximum rate. The design of a neutralization station would be similar to the hand-loaded drums. A series of self-feeding

drums would be powered by the stream flow channeled over the drums by a common sluice. As flow increased or decreased, more or fewer drums would be automatically placed in operation. A necessary addition to the new installation is a storage building to keep limestone dry during winter operation. A new system will be tested this fall, winter, and spring, and a report is expected next summer (1984).

As reported by Zurbuch (1963), fines that are not dissolved provide additional buffering action when drum treatment is stopped. Four days after treatment had stopped, following a 30-hour test, residual limestone fines were still neutralizing about 37% of the acid load. Six days after treatment 25% was being neutralized. One of the questions that will be investigated in future studies is how $CaCO_3$ fines that build up in the streambed compliment the fines dissolved in the flow during neutralization.

Construction costs of an eight-drum treatment station were originally estimated at $250,000 (Zurbuch 1981). Otter Creek construction of the three-drum station shows this estimate to have been fairly close. The present estimated cost of a three-drum installation is $150,000. Prorating the costs per drum would amount to about $50,000 each. Such a station should efficiently operate on flows from 0.028 m^3/s to 0.34 m^3/s. Maximum station production of $CaCO_3$ fines at the higher flow would be 163.2 kg/h or 3.92 tonnes/d.

The costs of construction of rotary drum facilities can be roughly compared to those for aglime and hydrated lime silos. The PADER estimates today's cost of a 27.2 tonne capacity hydrated lime silo to be $84,000 with treatment capability of up to 0.242 m^3/s of flow and feed rates of 9.4 kg/h to 45 kg/h. Sweden (Fraser and Britt 1982) reports that a silo that adds 200 tonnes of aglime annually to a treated stream costs $20,000 (1981 dollars). The annual application converts to an average rate of 22.8 kg/h. One self-feeding rotary drum should produce 54 kg/h of $CaCO_3$ fines into a flow of 0.113 m^3/s. Thus, one drum appears equivalent to two Swedish silos in application rate, and station construction costs would be about the same ($50,000 vs. $40,000). Two of the drums are equivalent to one Pennsylvania silo in flow capacity, and construction costs are again about the same ($100,000 vs. $84,000). The two drums would have the capacity to more than double the maximum output of the Pennsylvania silo—108 kg $CaCO_3$ fines/h vs. 45 kg $Ca(OH)_2$/h. Savings in operation costs by using the rotary drums could result from reduced labor, better neutralization efficiency of drum $CaCO_3$ fines to aglime, and the lower cost of limestone aggregate relative to both aglime and hydrated lime. It is stressed that the above calculations are rough and preliminary. Firm data will be available when testing is completed at the Otter Creek station and a final report prepared.

RELATED STUDIES

While the emphasis of this report is on stream neutralization, there have been two long-term lake liming projects in West Virginia. Spruce Knob Lake is a 10.5 ha impoundment located near the highest elevation in the state (1,483 m). The impoundment was opened to fishing in 1953. In 1958 fish kills occurred that were related to acidification with pH readings of 5.2 to 5.6. In April of 1958, 9.1 tonnes of agricultural limestone ($CaCO_3$-aglime) were applied by boat to the lake. The pH was raised to a range of 6.0 to 6.8. In October 1958 the watershed was treated with 95.3 tonnes of aglime. The watershed was similarly treated in 1971 with 30.8 tonnes and in 1978 with 61.7 tonnes. Generally, the pH of the lake has stayed above 6.0 since the initial treatment. There has been no additional reported mortality of rainbow trout (*Salmo gairdneri*) or other species related to acid water during this period. Studies have not been made to determine the cause of the acidification of the lake, nor have there been any in-depth chemical analyses of the effect of the neutralization treatments.

The other treated impoundment is Summit Lake, a 17.4 ha impoundment, located some 90 km southwest of Spruce Knob Lake, but still in the mountainous area of West Virginia. The impoundment has had acid water problems since its construction in 1956. Aglime has been used to neutralize the acid with amounts ranging from 1.4 tonnes in 1965 to 9.1 tonnes in 1958. For the last 10 years 0.3 tonne of hydrated lime ($Ca(OH)_2$) has been applied annually together with 4.5 tonnes of aglime. The lake pH is usually less than 6.0 before treatment and has been as low as 5.2. Following treatment in March or April, pH ranges from 6.0 to 6.8. On several occasions fish kills have occurred following treatment. Species involved have included stocked rainbow trout and resident smallmouth bass (*Micropterus dolomieui*) and green sunfish (*Lepomis cyanellus*). While some investigations have been made to determine the cause of these kills, no definitive answers have been obtained. In 1973 the lake was drained for repair and 91 tonnes of aglime were spread on the lake bottom. This apparently had little lasting effect on water quality as the lake required treatment the following spring.

Other related studies involve measurements of water quality and precipitation chemistry for streams in West Virginia potentially sensitive to acid deposition. Flow and stream chemistry data have been collected weekly since 1981 in Otter Creek at a station above the treatment site. Relative to similar data collected in 1964 through 1968, average annual values for pH and free acidity have not changed significantly over time. Using only measurements for winter months (January–March), however, free acidity has increased significantly from a mean of 6.3 μeq/L in 1964–1968 to 15.6 μeq/L in 1981–1982 (Table 1). Bedrock geology appears to be responsible for much of the free acidity in Otter Creek, but cannot account for the increase in H^+ since 1964–1968.

Table 1. Change in free acidity levels in Otter Creek during winter months (Jan–Mar) over the period 1964 to 1982.

Year	Free acidity* (μeq/L)	
1964	6.2	
1965	6.5	*Periods*
1966	6.5	1964 to 1968 $\bar{x}$ = 6.3
1967	7.2	1981 to 1982 $\bar{x}$ = 15.6
1968	7.3	
1981	11.4	
1982	12.2	

* Free acidity is estimated from ambient pH. The mean free acidities for the winter months from 1964 to 1982 are based on regression analysis (r^2 = 0.36 and p = <0.05), while the period means are calculated from weekly data.

Similar flow and chemistry data are collected biweekly at eight stations in Cranberry River (pH 5.6 to 5.8 at the mouth). These data in conjunction with long-term daily flow records collected by the U.S. Geological Service are being used to develop a computer model to determine if self-feeding rotary drum stations, installed in the headwaters of the Cranberry, could add enough alkaline material to permit a trout fishery to exist downstream 48 km to the river mouth. The first run of the simulation model indicated that two six-drum stations could neutralize enough of the acid to provide suitable water quality even with worse case conditions—the wettest year and highest daily flow. An estimated 1,800 tonnes of limestone would be consumed at each station over each year. The model is still in development and the above conclusions are tentative.

In 1983 a survey of streams in West Virginia potentially impacted by acid deposition was initiated. Some 90 streams have been selected to be sampled twice a year—spring and fall. Data will be used to categorize streams based on buffering capacity, effects of acid deposition, and watershed geology and soils. This study should give us information on water quality trends and a good appraisal of the effect acid deposition is having on the fisheries of West Virginia.

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PERFORMANCE REPORT

STATE: West Virginia PROJECT NUMBER: F-24-R-3

PROJECT TITLE: Acid Water Studies

PERIOD COVERED: March 1, 1983 through June 30, 1984

Study Objective: To (1) gather background data on two acid impacted trout streams to determine feasibility of neutralizing acidity; (2) test a self-feeding limestone drum; and (3) survey acid impacted streams in West Virginia.

(1) Job Number and Title: I-2 Testing Second Generation Limestone Drums

Job Objective: To field test a proto-type self-feeding limestone drum, and determine the feasibility of constructing acid treatment stations on the Cranberry River.

(a) Activity: A self-feeding drum system, attendant water sluice and limestone storage building, were installed at the site of the old Otter Creek treatment station. Three drums were tested during the project segment. One drum was a modified model of the original hand-loaded one and the others newly designed ones. Tests were conducted through a range of flows, climate conditions and drum design modifications.

Some 300 tons of limestone aggregate of uniform size and quality were obtained for test purposes. Efficiency of the treatment was based on continuous operation, automatic adjustment to flow change, minimal maintenance, and production rate of fines dissolving into the stream flow. The latter was measured by feed/use rate of stone in pounds per hour. Water chemistry and measurement of $CaCO_3$ dissolution were taken at sample sites below the treatment station.

(b) Target date for achievement: June 30, 1988

(c) Status of progress: On schedule

(d) Significant deviations: None

(e) Recommendations:

It is recommended that testing continue on the self-feeding drum through the next fall, winter and spring. Testing will concentrate on the optimizing of the drum production of limestone fines (use rate). When this has been achieved, various size screening will be installed in the drum to determine effect on drum output and downstream chemistry. Following these tests the drum will be operated continuously over the winter and spring months. Effects on downstream chemistry and limestone fines sedimentation will be studied weekly during continuous operation. Finally, in the late spring (1985), other types of limestone will be tested. These will vary in hardness and chemical constituents. Effects will be measured on drum output and changes in stream chemistry.

It is anticipated that a final report will be prepared early next summer. This report will cover effectiveness of the treatment system, and economic

advantages when compared to other treatment methods. Data will be analysed in conjunction with those gathered in Job 1 to determine if the method can be applied to the Cranberry River.

(f) Cost:

Total	State	Federal
$10,000	$2,500	$7,500

(g) Remarks:

General

A history of the limestone drum treatment system leading to the present work is appended (Zurbuch 1984). The design of the self-feeding system has been reported by Gencsoy et al (1982) and is also appended.

Drums Tested

Three drums were tested during this segment. The B model is a modified drum from the original hand-loaded drums (A model) used to treat Otter Creek from 1964 to 1979. Model C is based on specifications derived in a research contract with the College of Engineering, West Virginia University (WVU). Model D is a recently constructed drum of the same design as Model C, but of lighter materials to reduce its weight by some 1,000 pounds. Very little testing of this drum was accomplished during this segment.

Major design characteristics of each drum are:

Model B—Fifty-inch diameter overall with 34-inch inside drum diameter, 18 water vanes (cups), empty weight 790 pounds (without feed cylinder attached).

Model C—Fifty-two inch diameter overall with 36-inch inside drum diameter, 22 water vanes (cups), empty weight 2,100 pounds (without feed cylinder attached).

Model D—Same design as Model C, but constructed of lighter materials, empty weight 1,010 pounds (without feed cylinder attached).

During testing various internal drum configurations were used. These involved number of lift bars, size and shape of lift bars, number, size and shape of water holes, and various types of hole screening.

Limestone Used

Care was taken to use the same size and quality limestone aggregate throughout the tests. Stone was obtained from the Germany Valley, West Virginia quarry. The quarry operators stockpiled a special lot of the desired size stone that was mined from the same quarry site. Three random samples, taken from the quarry stockpile, of stone were analysed for hardness and chemical content (Table 1).

The size of the stone used was AASHO Number 57. The percentages by weight passing square openings of this size stone are: 1.5-inch 100%, 1-inch 95-100%, 0.5-inch 25-60%, smaller openings 0-10%.

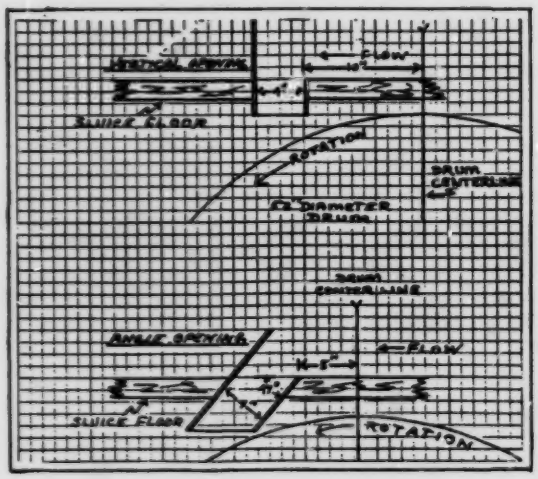
Table 1. Germany Valley, West Virginia, high calcium limestone used in 1983-84 Otter Creek testing.

	Sample 1	2	3
Chemical Composition % Weight			
Calcium Carbonate $CaCO_3$	95.22	94.32	96.72
Magnesium Carbonate $MgCO_3$	0.29	0.29	0.59
Silica SiO_2	1.16	1.17	0.87
Aluminum Oxide Al_2O_3	0.06	0.06	0.06
Iron Oxide Fe_2O_2	0.11	0.11	0.11
L. A. Abrasion %	34.16	34.06	33.82

Sluice Opening

Tests were made to compare two type sluice openings to direct water onto the drums. One was a vertical sided slot and the other an angled slot (Figure 1). The angled slot directed flow into the drum vanes at approximately vane-angle after passing the top midline of the rotation. The devices were constructed to permit changing their position relative to the horizontal position over the drum. Model B and Model C drums were used to evaluate the two type slots.

Figure 1. Sluice water openings tested.



All tests shown in Table 2 were run with same weight of stone (400 lbs) and same flow (5.0 cfs). Location of the slot refers to the most efficient location of the rear (upstream) edge of the slot opening in inches downstream from the vertical center line of the drum.

Table 2. Comparison of efficiency of water power of a vertical slot opening to an angled slot opening in operation of two limestone drum models.

	Vertical slot		Angled slot	
Drum model	max. rpm	location	max. rpm	location
B	23.0	8.0 in.	15.0	0.0 in.
C	18.5	10.0 in.	15.5	5.0 in.

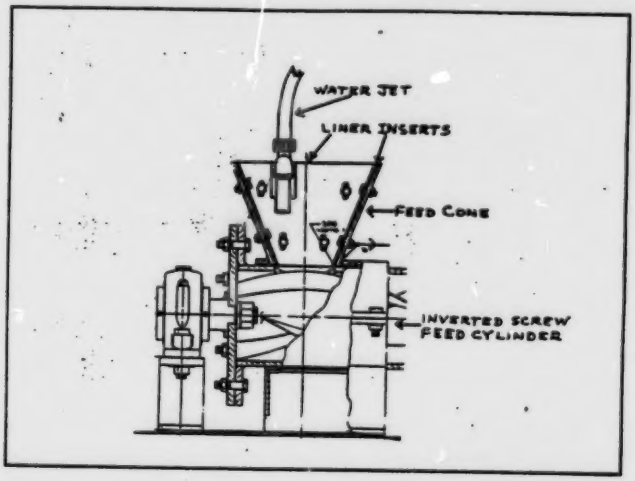
There did not appear to be any change in drum rpm by changing the closeness of the drum to the bottom of the sluice between one and three inches. Experiments by the Pennsylvania Department of Environmental Resources (PA DER) (1982) indicated a significant increase in hydraulic efficiency with a drum using a one-inch water drop to a drum with a six-inch water drop. Additional testing will be conducted at Otter Creek to confirm the data above.

In summary, testing indicated a vertical slot design to be the most efficient method of directing water power to the rotating drums. This design was used in constructing an adjustable opening slot. This adjustable slot will be important in calibrating correct flows to a series of drums and to shut off flow to an individual drum for repair and maintenance.

Water Jet

The reciprocal feeder delivers a small amount of limestone dust and fines along with the coarse aggregate to the feeder cone. After a few days operation this material will cake in the inverted screw feeder cylinder and not permit stone to enter it. Stone continues to drop from the reciprocal feeder and, not being able to enter the cone, piles up on the floor on each side of it. To over-come the caking, a small jet of water was introduced into the cone that effectively kept it clean (Figure 2). The water is taken from the side of the sluice upstream from the drum. A one-inch hose conducts the water by gravity flow to a pipe welded to the inside of the feed cone. The water jet operated throughout the test period when protected from sub-zero freezing (discussed later). During summer flows, the perforated plate covering the water takeoff on the side of the sluice must be brushed weekly to remove alage accumulation. The water jet provides an effective and economical means of preventing caking of limestone fines and dust in the inverted screw feeder.

Figure 2. Water jet and feed cone adjustable liners.



Feed Cone Liners

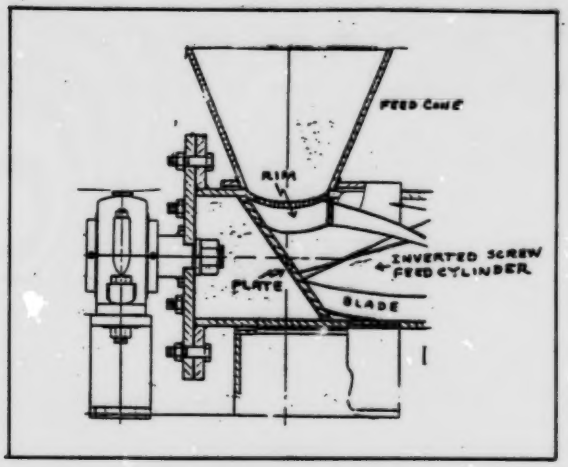
The inverted screw feed cylinder turns inside the feed cone assembly. Stone drops into the cone and is held there until the access hole to the screw feed rotates to the up-vertical position permitting the stone to drop inside. In the manufacturing process there is an allowable space of one-fourth inch between the outer circumference of the screw feed and the inner circumference of the feed cone assembly. This permits small pieces of aggregate chips (one-eighth inch or less in diameter) to be pulled by the rotation of the screw cylinder in between these two surfaces. These stone pieces produce a braking resistance and reduce the hydraulic efficiency of the drum.

To overcome this problem adjustable metal liners were placed on the inside of the cone on three of its four sides (Figure 2). The upstream side does not need one since rotation of the cylinder does not let aggregate enter the space between the two surfaces. The liners are adjusted as close as possible to the rotating feed cylinder. This system keeps the small aggregate chips from getting between the two surfaces and holds them in the cone until they are washed into the inverted screw cylinder. The front and rear liners are made of one-eighth inch thick carbon or low alloy steel. The downstream liner must be made of one-fourth inch thick stainless steel. This is because occasionally a piece of aggregate will be crunched between the edge of the liner and the rotating rear edge of the access hole of the screw cylinder.

Screw Cylinder Modification

Another way small aggregate chips entered the space between the cone assembly and the screw cylinder was by dropping out of the cylinder when the access hole was in the full down position. This was overcome by modification of the interior of the screw cylinder (Figure 3). A slanting plate was placed under the access hole to carry stone and stone particles beyond the hole with assistance from the water jet. An inner rim to the access hole was constructed to keep stone particles from rolling out of the hole when it rotated to the full down position.

Figure 3. Modified inverted screw feed cylinder.

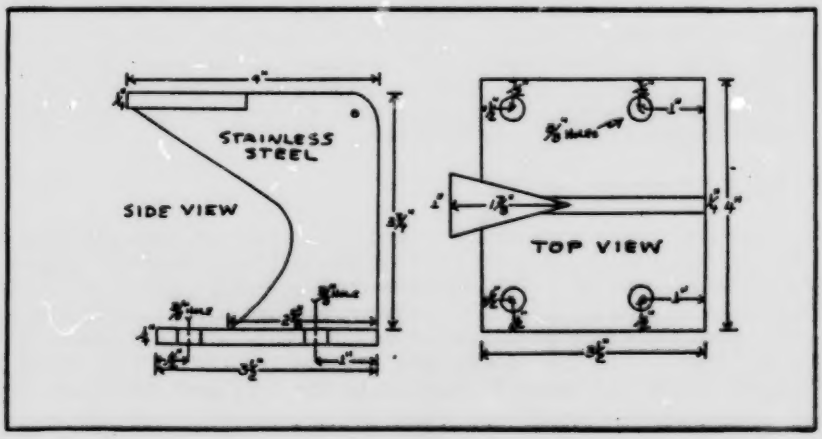


Modifications of the screw cylinder and liners for the cone assembly solved a major design problem and were incorporated in blueprints and specifications of the treatment system. These modifications, along with the washing action of the water jet, kept the feed cylinder running smoothly and overcame the breaking problems from small aggregate chips getting between the surfaces of the cone assembly and the feed cylinder. It is important that in the construction specifications the maximum allowable eccentricity of the inverted screw feed cylinder be one-eighth inch or less. If it is more than one-eighth inch the usefullness of the adjustable cone liners is reduced.

Reciprocal Feeder Agitator

The original design of the reciprocal feeder agitator did not keep the stone from bridging in the hopper and stopping delivery to the drum. A number of designs were tested that led to the present one (Figure 4). This design keeps the stone free flowing and some 200 tons of stone have been fed through the feeder without stoppages due to its operation.

Figure 4. Agitator for reciprocal feeder.



The agitator receives considerable stress from crunching of stone within the hopper. To withstand this stress it is made from one-fourth inch thick stainless steel. The welding of the vertical section to the attachment plate must be carefully done to specifications. If this weld is weak, the vertical section can break loose and fall into the feed cone. Because of this possibility, a safety wire should be attached to the vertical section of the agitator to keep it from entering the cone assembly should it break loose. This will prevent damage to the inverted screw feed cylinder.

Drum Adjustment to Flow Changes

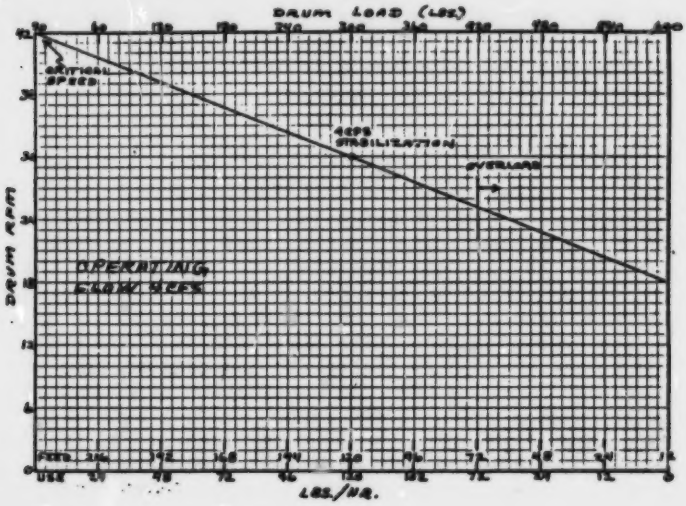
To understand the operation of the self-feeding drum, some terms need defining. The drum uses "autogenous" grinding which is a grinding process using the aggregate itself for abrasion. The "feed rate" is the input into the drum of the aggregate expressed in pounds per hour. The "use rate" is the output of the drum of fines from the grinding process in pounds per hour. A "stabilized" drum is when the "use rate" equals the "feed rate" and the turning speed of the drum in rpm remains constant for a given operating flow. The feed rate is a function of the rpm of the drum imparted to the reciprocal feeder and the gate setting on the feeder. Stabilization of the drum occurs when the combination of amount of stone in the drum and its rpm produces a grinding efficiency or "use rate" equal to the feed rate. Before this point is reached the drum is either: (1) increasing its loading with slowing rpm as grinding efficiency improves and feed rate slows; (2) decreasing its loading with accelerating rpm as grinding efficiency declines and feed rate increases; or (3) "overloading" because the drum's load has exceeded the point of additional grinding efficiency with additional load and the feed rate is more than the use rate. Overloading is the result of opening the reciprocal feeder gate too far so that more stone is delivered for each revolution than the drum is capable of grinding in a stabilized state.

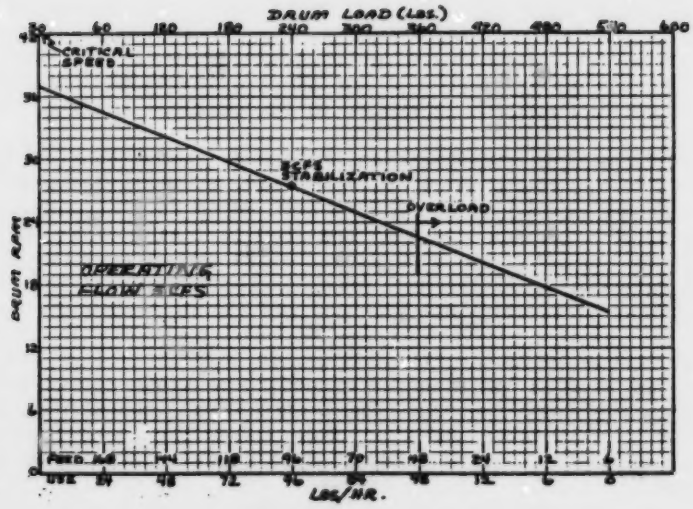
"Critical speed" is when the rpm of the drum is high enough to hold the stone load to the outer surface by centrifugal force. At this speed there is very little grinding action. With the drums tested this speed was 42 rpm. When the self-feeding drum is started empty it will not start grinding action until enough stone is fed into it so that rpm are decreased to the critical speed or below.

Examples of the drum stabilization process are shown in Figures 5 and 6. In these examples, if the operating flow of 4 cfs of a stabilized drum were reduced to 3 cfs, the drum's rpm would be reduced from 30 to 25. This would be because the drum load of 300 pounds would stay the same initially, and with less water power (3 cfs), the rotation would be slower. The use rate, however, is higher than the feed rate (84 vs 70 lbs/hr), thus, the drum will lighten until it reaches 240 lbs, stabilizes at 27 rpm, and the feed and use rates are the same at 96 lbs/hr.

In actual stream operation, the changes in operating flows are gradual and, thus, the changes in drum rpm (and corresponding feed/use rates) are not as noticeable as in the example given. The process described permits individual drums to adjust to changes in operating flow. When the first drum in a series approaches its maximum output, the second drum starts operating as excess flow passes over the first drum's sluice opening. Thus, the treatment stations ability to adjust treatment to changes in stream flow is the result of both the individual drum's ability to adjust to changes in its operating flow and the changing of more or fewer drums in operation based on more or less sluice (stream) flow.

Figures 5 and 6. Examples of drum stabilization at operating flows of 4 cfs and 3 cfs.

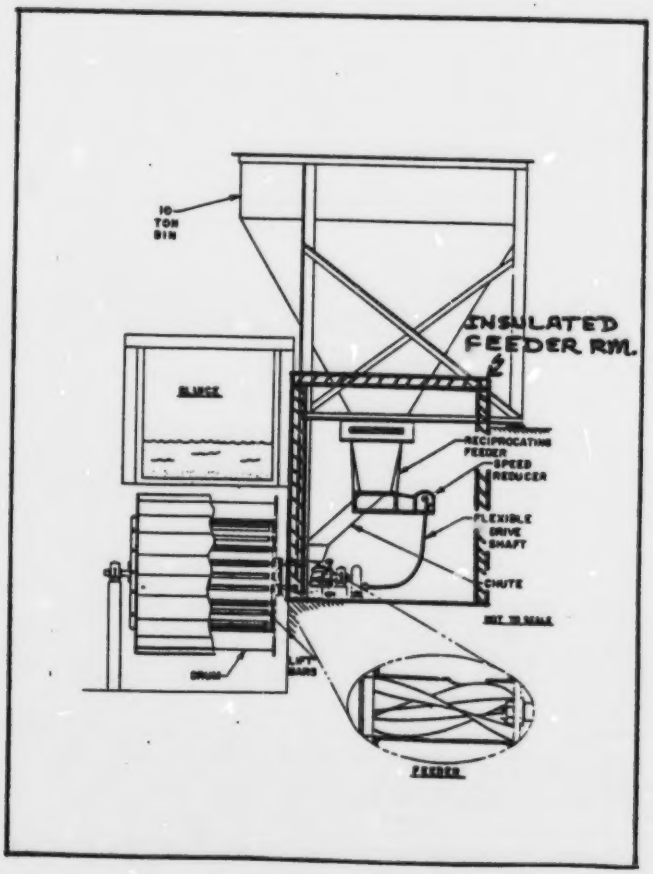




10-Ton Storage Bin

Under a contract with the DNR, The College of Engineering at West Virginia University designed the 10-ton bin and the feeder system (Clites 1982). Engineers at WVU were concerned that the 10-ton storage bin and/or the reciprocal feeder hopper were potentially problem areas that could cause stone bridging and stop the free flow of aggregate to the reciprocal feeder. The bin and hopper (Figure 7) did not bridge once in over an 18-month test period and with some 300 tons of stone passing through them. The stone flowed freely in all cases; whether it was loaded dry, wet or with frozen clumps of aggregate. The wet or frozen stone did cause problems of bridging in the area of the agitator of the feeder and this will be discussed later.

Figure 7. Self-feeding water powered limestone drum acid water neutralization system.

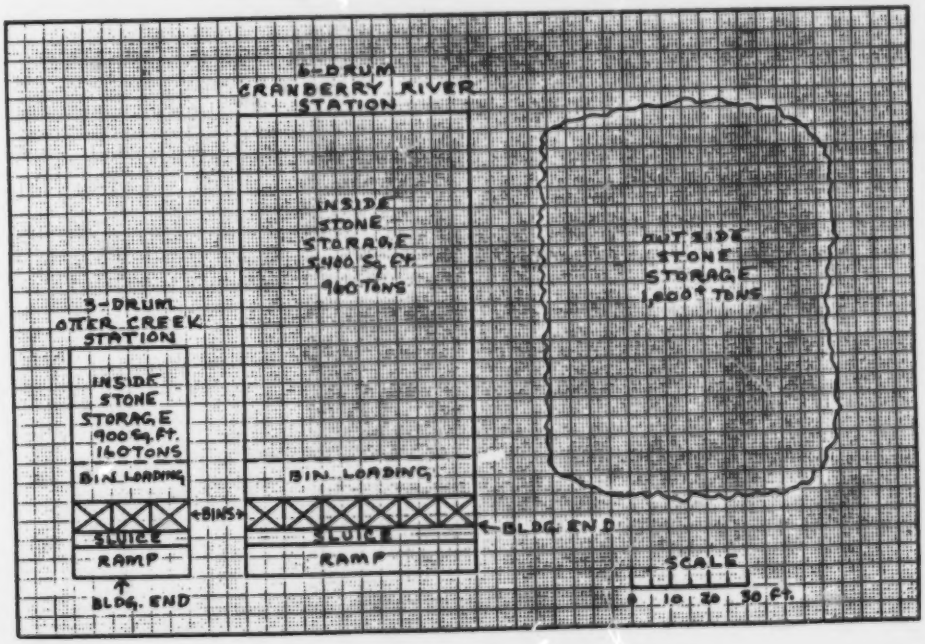


Stone Storage and Handling

As was experienced in previous testing, stone should be loaded into the bins in a dry condition. A portion of the station's yearly stockpile needs to be stored in a building enclosing the bins. This is the amount estimated that would be used by the treatment station during the period of extreme winter conditions. In West Virginia this would be a four-month period from November through February. Before or after this period, weather conditions are such that stone can periodically be replenished in building storage from that stored outside. In treatment of the Cranberry River, it is estimated that a year of maximum treatment would require use of 1,700 tons at each of two six-drum stations. About one-half of this would be stored inside and one-half outside. The storage building must be designed then to have an area large enough to store the amount necessary. This storage area is dependent on how high the stone can be piled using the end loader that is also used to load the 10-ton bins.

At Otter Creek stone was stockpiled to an average height of five feet. An area of 900 square feet was able to accommodate 160 tons of stone. This would supply one drum for four months of operation running at a maximum output of 120 pounds per hour or 10 tons per week. A six-drum station would require 5,400 square feet of storage area for 960 tons of aggregate. Figure 8 shows the relationship between the Otter Creek storage building and that proposed for a six-drum station on the Cranberry River.

Figure 8. Relationship of stone storage of the Otter Creek station to proposed Cranberry River station.



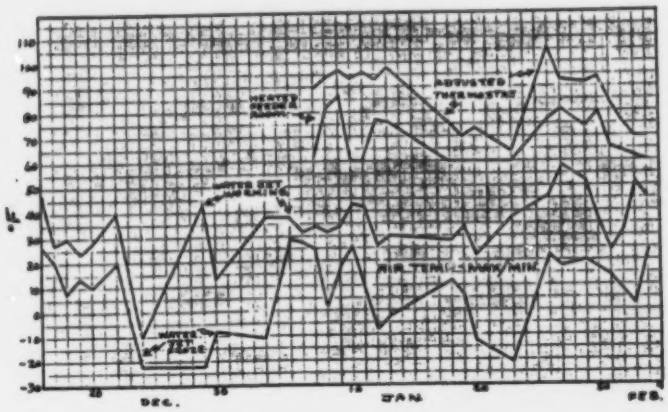
Movement of stone from outside storage and in bin loading is important in economy of time and effort. A John Deere JD24-A end loader was used at Otter Creek for movement of stone and loading the 10-ton bin. This loader is a small wheeled vehicle with a 0.39 cubic yard bucket. The bucket's average load of stone was 800 pounds (0.4 ton). An operator could easily pick up a load from inside storage, move it to the 10-ton bin, and return to the stockpile in one minute. To completely fill an empty 10-ton bin required 25 minutes. In a six-drum station, to completely fill six empty bins would require 2.5 hours. In once-a-week servicing of the station, a crew would have ample time for travel, replenishing stone in bins and other maintenance in a normal 8-hour work day.

Movement of stone from outside storage to inside storage averaged two minutes per round trip. Moving 960 tons (a four-month supply for a six-drum station) would require 80 hours or 16 days (five hours moving stone, one hour maintenance, and two hours travel each day). This may be excessive. The movement time could be reduced to one week by using a larger loader with a 1.25 cubic yard bucket. This will be studied further. It may be best to have a small loader at each station for loading bins and a larger loader, transportable between stations, for moving stone from outside to inside storage. The larger loader could substitute for a smaller one if it were inoperative. If the larger loader could pile stone higher in the storage building, the size of the building may be reduced.

Winter Operation

Successful winter operation of the treatment station was one of the major objectives in this project segment. Addition of the water jet in the feed cone, previously discussed (Figure 2), required modification of the treatment station to include a small, heavily insulated, heated room around the feed mechanism as shown in Figure 7. This was required when testing showed the hose to the jet would freeze solid at temperatures below 0° F. Temperatures experienced at the station are given in Figure 9 for the middle of December 1983 through the first

Figure 9. Maximum/minimum outside air temperature and feeder room temperature at the Otter Creek station, December 1983 through February 1984.



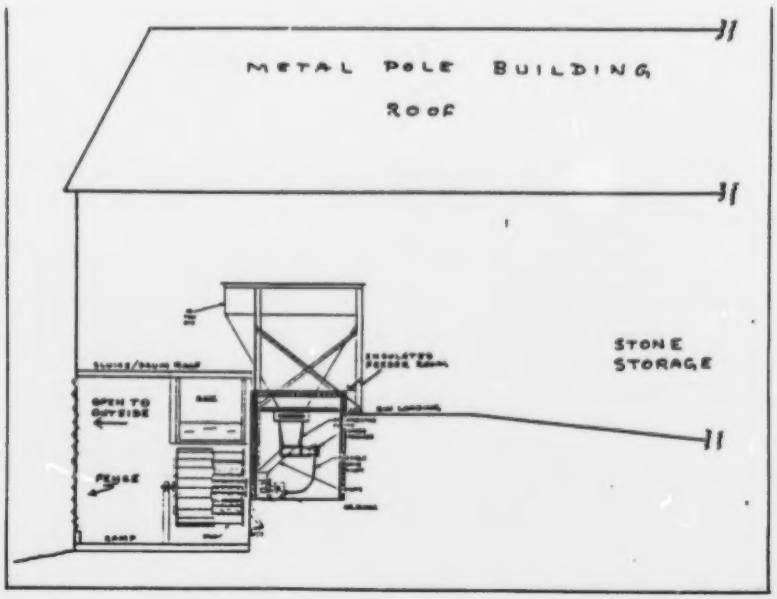
of February 1984. The room was kept as small as possible to conserve fuel and still provide sufficient work space. It was heated using a 30,000 BTU LP gas stove. The stove had a thermostat and could be adjusted for any desired room temperature. A 1,000 gallon capacity LP gas tank was positioned outside the storage building. The heated feeder room eliminated all freezing problems with the water jet. It was also found that heat from the room was funneled up through the 10-ton bin. Stone that was placed in the bin wet or frozen was dried out by this heat. The heated room could be kept in the 60-70° F. range for operation of the feed mechanism. If wet stone were placed in the storage bins, the heat could be increased to 80-90° F. to dry the stone. In one case, frozen clumps of stone were placed in the bin and the heat increased in the feeder room. The clumps were thawed and the wet stone dried in three days.

Using the heated feeder room, it is felt that the treatment system can be kept working at below 0° F. outside air temperatures without any problems. Operation of the station requires sufficient flow to power the drums. At very low temperatures the Otter Creek's water sources become frozen and stream flow can be reduced below that necessary for drum operation. Within a few hours of thaw conditions, the sluice flow increases, the drum(s) thaw loose and start operating again.

Storage Building Design

The Otter Creek storage building was built enclosing the sluice and drums as shown in Figure 10. The building is of the pole design using metal and Fiberglass sheathing. During cold periods the water from the sluice and drum operation produced moisture that condensed on the inside of the storage building.

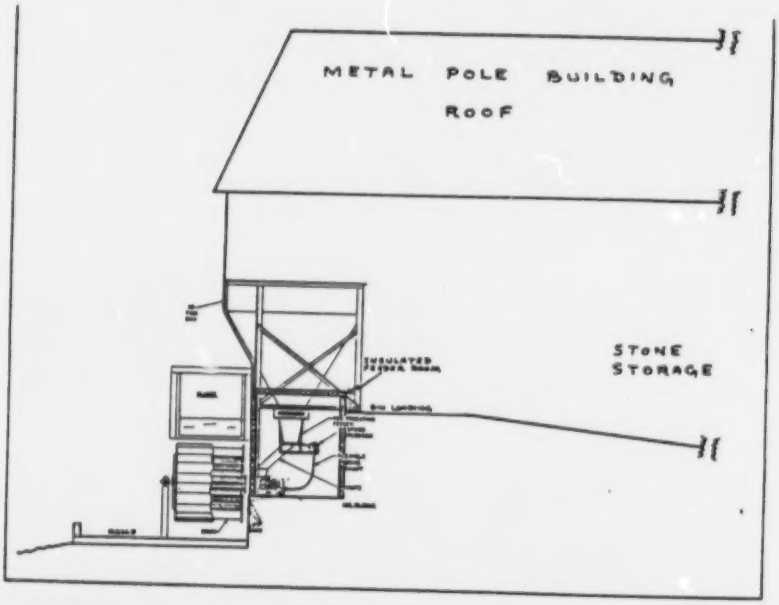
Figure 10. Otter Creek experimental treatment station.



This would drip on the stone loaded in the 10-ton bin and stored on the floor. To overcome this, a roof was constructed over the sluice and drum ramp separating this area from the rest of the building (Figure 10). This effectively eliminated the problem.

In future storage building designs the sluice and drum ramp will be placed outside the building as shown in Figure 11. Besides eliminating moisture condensation, the size of the building will be reduced.

Figure 11. Proposed change in treatment station building design.



Comparison of Models B, C and D Drums

Under a contract with the DNR, the College of Engineering at WVU designed a self-feeding rotary drum system. The drum itself was designed using data collected in lab tests at the University (Pappajohn 1983), from that gained in use of the hand-loaded drums at Otter Creek (Zurbuch 1963), and from an analysis of drum design by Pearson and McDonnell 1978.

In the initial testing of the new drum (Model C) its performance did not meet expectations. In fact, its efficiency for grinding was less than that experienced with the modified hand-loaded drum (Model B). Because of this, much of the project segment was used in comparison testing of the two drums and trying to duplicate dry grinding lab data with wet grinding under actual stream treatment conditions. Results of this testing are summarized as follows:

A. Effect of Drum Weight—The new drum (Model C—2,100 lbs) was constructed of much heavier materials and, thus, weighed considerably more than the older drum (Model B—790 lbs). It was slightly larger in diameter, 36 inches vs 34 inches for Model B, with an overall diameter of 52 inches vs 50 inches. Model C contains 22 water cups while Model B has 18. Model C had 22 lift bars while Model B had 9. The additional number of lift bars and water cups should have increased Model C's grinding efficiency. It was felt that drum weight may be a significant factor and the reason for the poor performance of the new drum. To test this, both models were run in identical tests to measure maximum rpm through a range of flows with the drums empty and with the same stone loading.

The recently acquired Model D drum was run through the same tests. This model is the same design as Model C, but constructed of lighter material with a weight of 1,010 pounds. Figure 12 shows the results of the tests and indicates drum weight is a significant factor in determining the maximum rpm obtained at various operating flows. Another analysis was made comparing operating loads and rpm of Models B and C at 4 and 5 cfs flow. These data, Figure 13, further substantiate that a lighter drum is more efficient than a heavier one.

Figure 12. Hydraulic efficiency of light weight drums (Models B and D) to heavy drum (Model C).

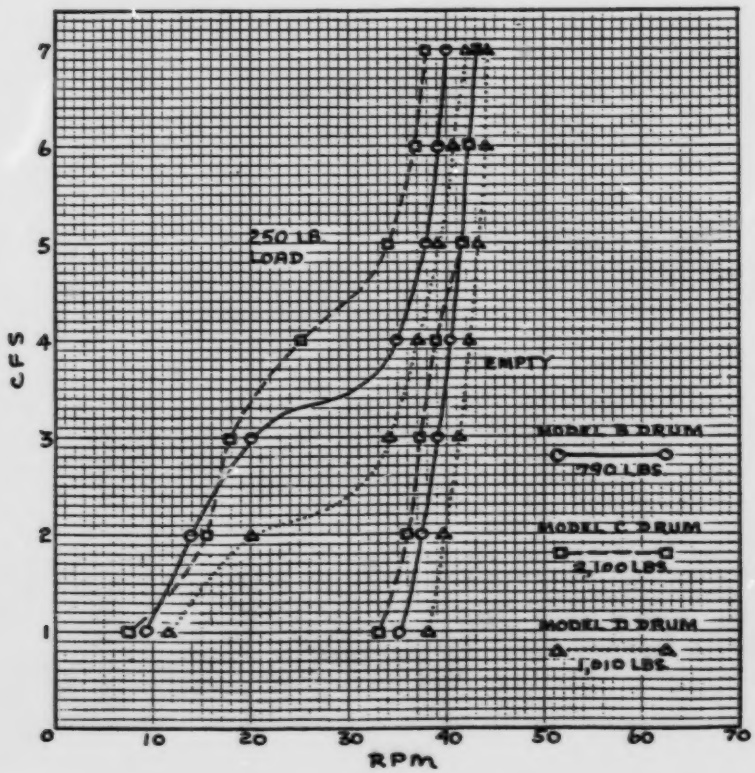
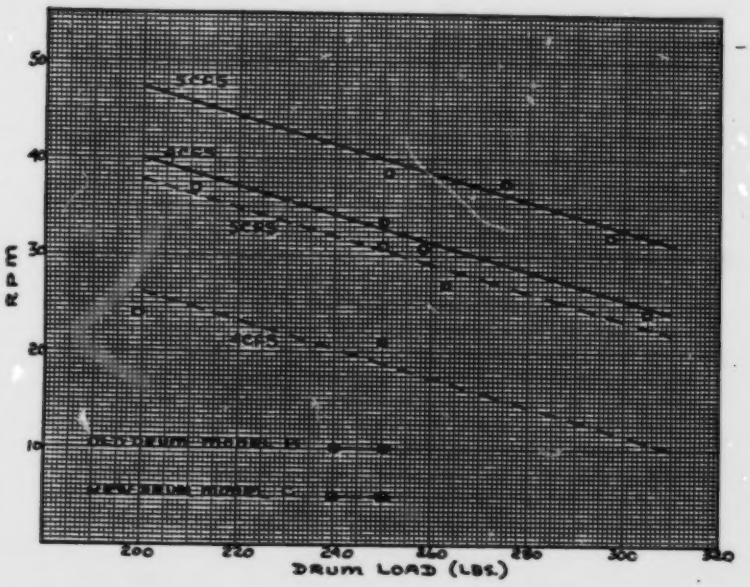


Figure 13. Drum loads of Models B and C and resulting rpm at flows of 4 and 5 cfs.

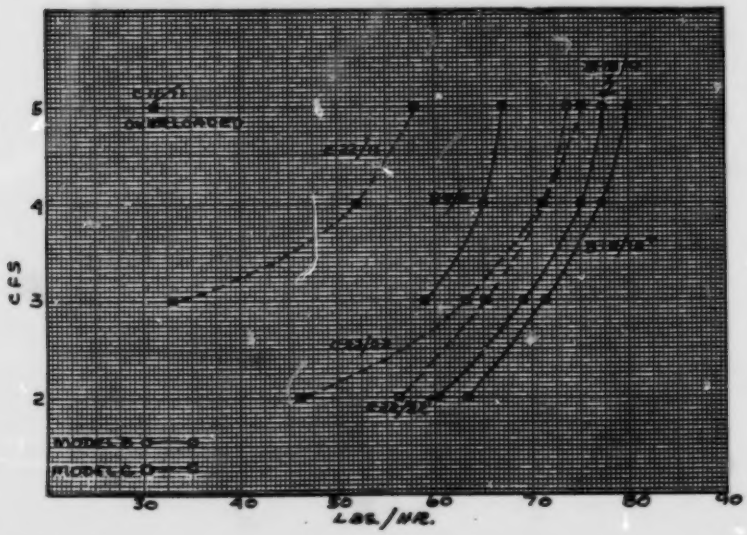


The heavier drum probably increases friction resistance in the pillow block bearings causing it to turn slower and carry less stone than the lighter drum. Both the slower rpm and smaller stone load would decrease the drum's grinding efficiency. Indication of the effect of bearing friction was shown during greasing of the bearings. In one instance the rpm of an operating drum was increased from 22 to 24 rpm by greasing the outer bearing. To provide constant greasing, automatic greasers were added to the pillow blocks.

B. Effect of Number of Lift Bars—WVU lab data indicated addition of lift bars would increase grinding efficiency of a drum. Modifications of the number of lift bars in both models showed this to be true (Figure 14). All tests were conducted at the same reciprocal feeder gate opening (4.0 cm). Test drums were run overnight at each flow to permit stabilization of the grinding rate. The curve labeled C 22/11 refers to the Model C drum with 22 lift bars, 11 of which have water access holes. The point labeled C 11/11 is the Model C drum in which 11 of the lift bars were removed. Reduced grinding efficiency caused it to overload with stone at the maximum (5 cfs) operating flow. The curve labeled B 9/9 refers to the Model B drum containing 9 lift bars, each with water access holes. This drum's performance shows the greater efficiency of the lighter drum. When the number of lift bars were doubled, curve labeled B 18/9, efficiency was substantially improved.

The question remains of how efficient the Model D drum will be with weight reduced some 1,000 pounds from Model C's weight. These tests will be conducted in the next project segment.

Figure 14. Stabilized use rate of Model B and Model C drums at various flows and configurations (reciprocal feeder gate opening of 4.0 cm).



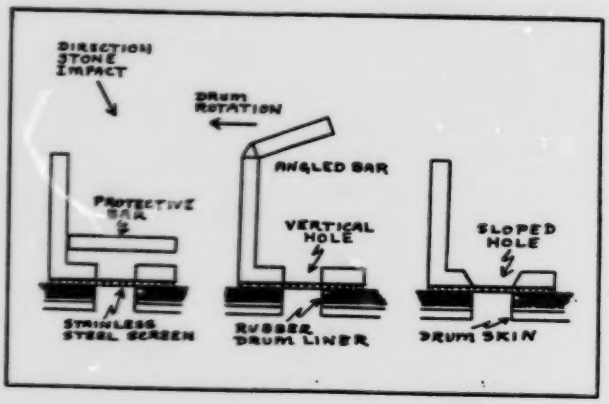
C. Effect of Area of Water Access Holes—The amount of area for water to enter and leave the drum is dependent on number of holes, size of holes, size of screening covering holes, and occlusion of holes by stones and stone fines. The effect of varying hole area is difficult to measure due to variables associated with the grinding process. Figure 14 shows that in short periods of operation (12-24 hours), addition of more water access area improved performance of both Model B and Model C drums. Model C drum performance (curve C 22/11), substantially improved when all of the lift bars contained access holes (curve C 22/22). Some additional efficiency was obtained when the holes were increased in size from 7/16-inch diameter to 5/8-inch diameter as shown by the curve C 22/22^{+}. Model B shows a similar, but less dramatic increase in efficiency when all 18 lift bars had water access holes and drilled to the 5/8-inch diameter (curve B 18/9 vs curve B 18/18^{+}).

Literature on industrial application of wet grinding processes indicated that reduction of the water content of a tumbling drum could increase the grinding efficiency. Considerable effort was made in testing the drums with varying reductions in water access area. No successful tests were made that sustained a higher drum output by reduction of drum water access. However, increasing the access area, as shown in Figure 14, did significantly improve performance.

It was also observed in the operation of the heavier drum (Model C), that a feed rate and operating flow that gave rpm in the range of 29 to 34, the drum would not stabilize, but would periodically surge between a high and a low rpm. It was felt that this probably was the result of changes in the water content of the drum. When the area of access holes was doubled (curve C22/22), the surging problem was minimized.

D. Occlusion of Water Access Area—After three weeks of operation of the Model C drum, with protective bars over the water access holes (Figure 15), fines were being retained by collecting under the bars, and stopping up a large portion of the water access hole area. This occlusion reduced drum grinding efficiency. The protective bars were removed and the drum operated to see if the stainless steel screening could withstand the action of the tumbling stone load. After 15 days the drum was taken back to the shop for inspection. The stainless steel screening was little affected, but 223 of the 418 holes (53%) were occluded by stones becoming stuck in them. The Model B drum was then installed and operated for 7 days without protective bars over access holes. During this operation 162 of 378 holes (43%) were blocked by stones.

Figure 15. Experimental lift bars and water access holes.



Two modifications of the lift bar design were then tested to reduce occlusion of the drum water access holes. These are shown in Figure 15. Tests are not complete, but preliminary results show that both the angled bar and the tapered hole design will probably work with the open bar and tapered holes the probable best choice. This design will probably keep the greater percentage of the hole area open. The tapered holes give the minimum contact between the stone and the metal, thus, prohibiting them from becoming stuck as in holes with vertical sides.

The reduced efficiency of the hand-loaded Otter Creek drums over extended operation (1964-1979) was probably the result of water access holes being blocked by stones. This blockage resulted in additional water containment in the drum and reduced grinding efficiency by slowing rpm and lubrication of the stone.

E. Effect of Increasing Size of Aggregate—WVU lab tests using dry grinding showed a 75 percent increase in grinding efficiency when two-inch stone was substituted for one and one-half-inch stone. In the Otter Creek wet grinding process, if the larger stone were more efficient in grinding, addition of two-inch stone at the same stabilized feed rate of the one and one-half-inch stone should cause the drum to lighten and increase its rpm. If the feed rate of the two-inch stone were then increased, the drum load would increase, slowing rpm back toward its original speed, but grinding stone at a higher use rate. Two tests were conducted on a stabilized drum by hand feeding two-inch stone in place of one and one-half-inch stone. The predicted reaction of changes in drum rpm and grinding

were observed and are shown in Figures 16 and 17. These tests indicate that using two-inch stone the wet grinding efficiency would be some 40 percent better than using one and one-half-inch stone.

Figure 16. Effect of changing stone size on drum use rate (Test No. 1, feed gate setting 4.3 cm, flow 4.9 cfs).

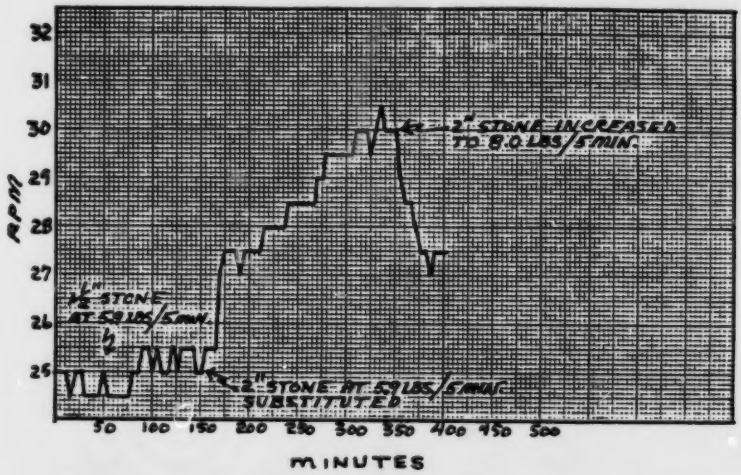
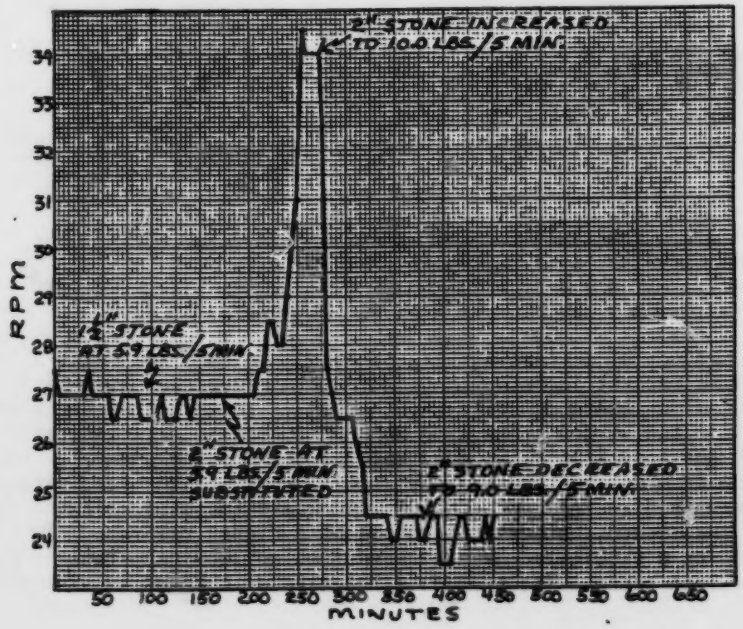


Figure 17. Effect of changing stone size on drum use rate (Test No. 2, feed gate setting 4.3 cm, flow 4.9 cfs).



Use of larger aggregate would require design changes in the reciprocal feeder. This may be done if the desired efficiency (120 pounds per hour at 4 cfs) cannot be achieved by the Model D drum.

Grinding Efficiency

A design goal for the self-feeding drum was a grinding efficiency that would produce 120 pounds per hour of limestone fines (90 percent 38 µm diameter or less) at an operating flow of 4 cfs. The maximum sustainable production achieved during this project segment, using the Model B drum, was 90.8 pounds per hour at an operating flow of 4.6 cfs. It is anticipated that the Model D drum will substantially improve output without the need for use of a larger size aggregate. The larger stone (2-inch) tests showed a 40 percent increase in grinding efficiency (Figures 16 and 17). Use of the larger stones, however, would require redesign of the reciprocal feeder and inverted feed cylinder and the opening of the 10-ton bin.

Samples of effluent from the drum have shown the grinding efficiency exceeding 90 percent 38 µm diameter or less. Tests during this segment used screening having 1.0 mm openings. After maximum production has been achieved with the Model D drum, screens with larger and smaller openings will be tested.

It may be beneficial in stream treatment to have neutralization from stream bottom fines. In treatment of a lake tributary stream, the smaller screen openings may be more desirable so that as much of the $CaCO_3$ as possible dissolves in the lake and little or none settles out in the lake bottom. The relationship of screen opening size, fine size production and stream bottom fines neutralization will be further studied.

Stream Chemistry

During this project segment the effect of the treatment has been studied to develop a methodology that would adequately correlate the following: (1) use rate of the drum; (2) size of fines produced; (3) ratio of dissolved, suspended and settled out $CaCO_3$; (4) changes in pH, alkalinity and acid loads of flows of sluice and stream at the treatment site and at various stations downstream; and (5) amount and effect of streambed settling out of $CaCO_3$ fines.

Optimum efficiency of the self-feeding limestone drum's grinding process has not yet been attained. The drum's present operation is sufficient to maintain pH 6.0 or above for the entire length of Otter Creek. It is felt that a two or three-drum treatment station will be adequate to treat the acid conditions of Otter Creek and maintain a native brook trout fishery. The goal of 120 pounds per hour at 4 cfs drum output should be achieved in the next project segment testing. Data gathered and analysed in Job 1 indicates the Otter Creek self-feeding drum system will effectively and economically treat the acid conditions of the Cranberry River. A more in-depth analysis will be presented in the next segment's report.

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PENNSYLVANIA DEPARTMENT OF ENVIRONMENTAL RESOURCES

PETER S. DUNCAN

SECRETARY OF ENVIRONMENTAL RESOURCES

QUAKAKE TUNNEL DEMONSTRATION PROJECT
LIMESTONE NEUTRALIZATION OF ACID MINE DRAINAGE
CARBON COUNTY, PA.
PROJECT NO. SL 135-10
DECEMBER 1982

PREPARED BY:

GEO-TECHNICAL SERVICES, INC.

Consulting Engineers and Geologists

HARRISBURG, PENNSYLVANIA

1501

TABLE 7.1

DISSOLVED CARBONATE EQUILIBRIUM DEFINITIONS

(after Stumm and Morgan)

Species:

CO_2 (aq), $H_2CO_3^*$, HCO_3^-, CO_3^{--}, H^+, OH^-

$H_2CO_3 = H_2CO_3^* + CO_2(aq)$

H_2CO_3 = "true" H_2CO_3

Equilibrium Constants:

$k_1 = [H^+]\,[HCO_3^-] \,/\, [H_2CO_3]$ $(10^{-6.46}$ @ $10^oC)$

$k = [H^+]\,[CO_3^{--}] \,/\, [HCO_3^-]$ $(10^{-10.49}$ @ $10^oC)$

$k_w = [H^+]\,[OH^-]$ (10^{-14})

Concentration Conditions:

$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{--}]$

Ionization Fractions:

$\alpha_0 C_T = [H_2CO_3]$

$\alpha_1 C_T = [HCO_3^-]$

$\alpha_2 C_T = [CO_3^{--}]$

$\alpha_0 = (1 + k_1/[H^+] + k_1k_2/[H^+]^2)^{-1}$

$\alpha_1 = (1 + [H^+]/k_1 + k_2/[H^+])^{-1}$

$\alpha_2 = (1 + [H^+]/k_2 + [H^+]^2/k_1/k_2)^{-1}$

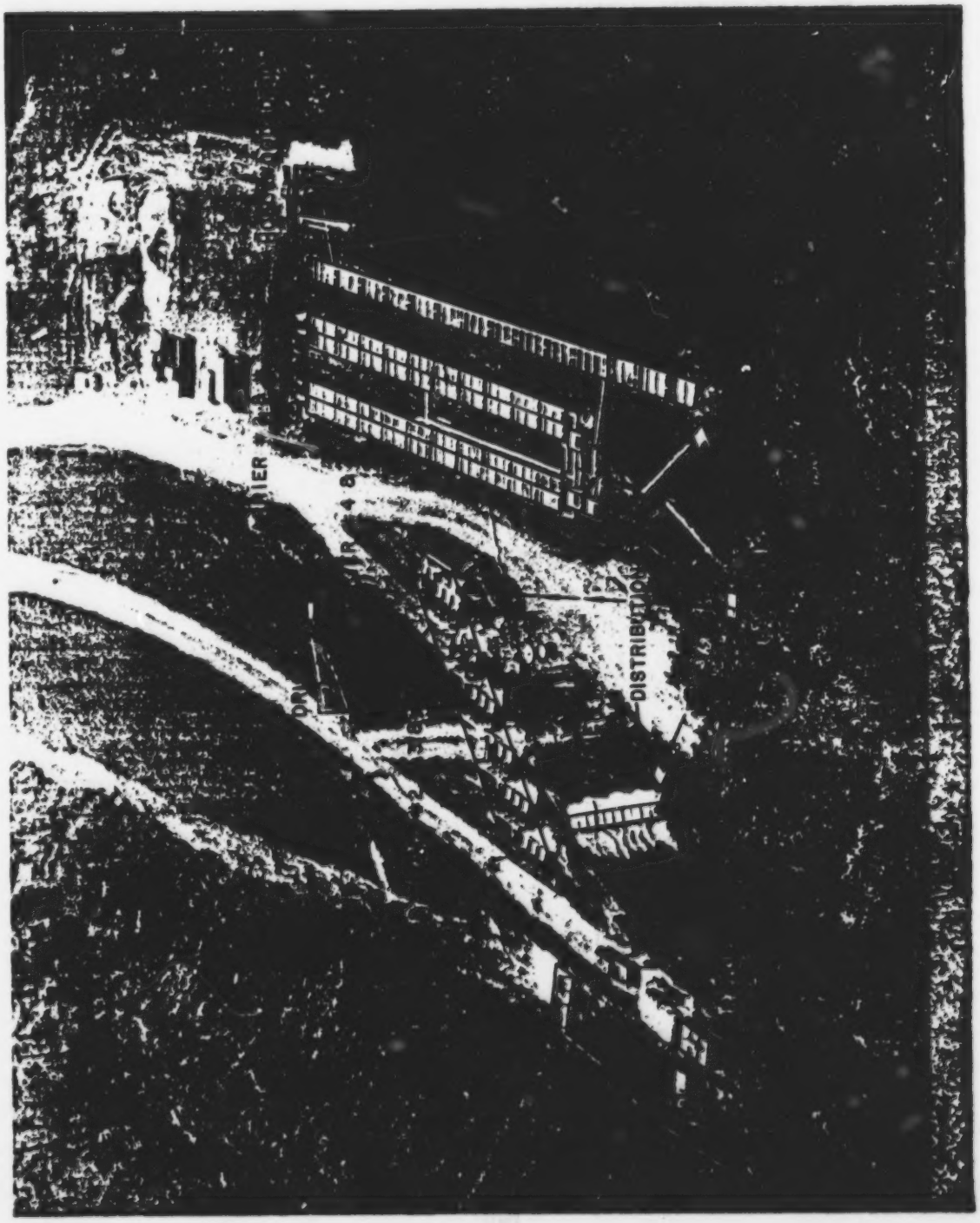
Alkalimetric Titration:

$f = C_B/C_T = \alpha_1 + 2\alpha_2 + ([OH^-] - [H^+]) / C_T$

$[alk] = C_T(\alpha_1 + 2\alpha_2) + [OH^-] - [H^+]$

Buffering Intensity:

$\beta = 2.3\,([H^+] + [OH^-] + C_T\,[(\alpha_1\alpha_0 + \alpha_1\alpha_2) + 4\alpha_2\alpha_0])$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2. QUAKAKE TUNNEL WATER QUALITY

Initial Investigations - 1973/1974: Prior to the design of the prototype installations, the tunnel discharge was sampled and flows were measured twice monthly from March 10, 1973 to May 29, 1974. Six monitoring stations were established at the locations shown in Appendix "A". The monitoring station at the tunnel portal was equipped with a Leupold Stevens Type F continuous water level recorder. Flow measurements were obtained using a propeller type "Ott" current meter. Water samples were collected in plastic bottles and shipped to the commercial water quality laboratories then under contract with the Department of Environmental Resources.

Monitoring stations downstream of the Tunnel were established to provide data on the impact of the Tunnel discharge on the receiving stream. Comparison of flows and water quality, taken on the same day, allowed an evaluation of the dilution effect from the unpolluted watersheds. Water quality monitoring results, tunnel discharge hydrographs and mass curves and precipitation data are presented in Appendix "A". A summary of the tunnel flow and quality data for the 1973/1974 samplings is presented in Table 2.1. This data formed the basis for the design of the demonstration prototypes.

Prototype Operation 1979/1980: Additional samples of the Quakake AMD discharge were collected and tested during the operation of the prototype facilities between July 10, 1979 and May 21, 1980. During this period, 238 untreated water samples were analyzed. A statistical summary of the various AMD parameters for this time period is presented in Table 2.1 for comparison with the initial test data.

Figure 2.1 presents the acidity, sulfate and metals concentration, grouped according to pH range showing that higher pollutant loadings are generally associated with decreasing pH.

TABLE 2.1 - FLOW AND QUALITY DATA FOR THE QUAKAKE DISCHARGE

Parameter and Unit	1973 - 74			1979 - 80			
	Ave.	Min.	Max.	Ave.	SD	Min.	Max.
Flow, cfs	21.2	10.1	33.6	-	-	-	-
Field pH	3.6	3.2	3.9	3.9	0.2	3.4	4.6
Lab pH	3.4	3.0	3.8	3.7	0.1	3.6	4.6
Free Acidity, mg/L	25	0	75	22	8	8	70
Total Acidity, mg/L	145	100	190	80	8	66	110
Iron (total, mg/L	2.3	0.7	3.7	0.83	0.47	0.18	0.97
Aluminum, mg/L	16.6	6	24	9.8	1.5	5.5	17.0
Calcium, mg/L	12.6	1	24	14.1	3.9	6.0	39.8
Sulfate, mg/L	237	100	460	144	21	80	200
Temperature, ^{o}C	9	9	10	9	-	-	-

SD - Standard Deviation

3. PRE-DESIGN INVESTIGATIONS

Literature Review: A survey of recent literature pertinent to the treatment of acidic waters with crushed limestone was conducted prior to the formulation of the design process.

Early significant literature was concerned with the neutralization by crushed limestone of such acidic industrial wastes as nitrocellulose manufacturing wastes (6) and steel pickling liquors (7, 8). This work led to recommendations for the design of processes to treat these particular wastes. However, the applicability of the results of these methods to the treatment of acid wastes other than those studied is uncertain. Moreover, no reported use of these processes in the neutralization of acid mine drainage was found.

It is reported (9) that there had been a number of previous attempts to use crushed limestone as static beds placed in flumes to neutralize mine drainage. However, these processes were abandoned when coating of the limestone surface by metal hydroxides severely reduced the degree of AMD neutralization obtained within a short time after starting the process.

Autogeneous mills filled with crushed limestone have been successfully used in the neturalization of acidic water in pilot installations by Mihok (10) and others. The continuous abrasion caused by the tumbling movement of the pieces of crushed limestone over each other produced very fine particles (400 mesh grain size). The surface area to particle weight ratio is larger for fine particles than for coarsely crushed stone. Consequently, as AMD flows through the drum, the presence of fine particles increases the reaction rate and accelerates the neutralization process. Also, the continuous abrasion of the crushed limestone exposes fresh surfaces over the crushed limestone and reduces the effects of stone coating phenomenon.

Lovells (21) work at the Hollywood experimental station of the Pennsylvania State University indicates that complete neutralization of AMD can be achieved by a revolving drum. In the Hollywood Plant, an autogeneous mill filled with crushed limestone and driven by a 25 horsepower motor was used to neutralize AMD flow at a rate of 0.5 cfs.

Frequently quoted is Hill and Wilmoth's (11) state of the art paper on the use of limestone to neutralize acid mine drainage, in which the observation is made that grinding of limestone to increase its reactivity, may raise its cost above that for lime.

Progress toward rationalization of the chemical and hydraulic processes occurring in the limestone neutralization processes has been made by a number of independent investigations at the Pennsylvania State University. In one such investigation (12), crushed limestone or discs cut from limestone were exposed to acidic water under a variety of conditions and the temperature coefficient and effect of flow velocity evaluated. Another investigation was conducted to evaluate the kinetics of exsolution of carbon dioxide as a function of temperature, ionic strength, and water turbulence (13). Jarret and Kountz (14) investigated the principle reaction between sulfuric acid and limestone and formulated a barrier design procedure.

Based on the results of laboratory studies, the Pennsylvania Department of Mines and Mineral Industries constructed six limestone barriers during 1970/71 in streams of the Trough Creek watershed (15). The barriers were installed to alleviate the acid-

pollution of the streams caused by coal mining in the watershed. In June 1972, high streamflows resulting from the Hurricane Agnes damaged or demolished five of the barriers. Three barriers were reconstructed and completed in November 1972. Stream water quality was monitored prior to and after construction of the barriers under a joint federal/state program. Another monitoring program was initiated by the Land and Water Research Institute of the Pennsylvania State University to evaluate the mechanisms that operate in limestone barriers and to provide for a more rational design (17).

These studies included a pilot-plant scale evaluation of the joint influence of the two rate-limiting chemical reactions on the overall performance of the process. These reactions are, first, the attack of limestone by acidic water and, second, the exsolution of carbon dioxide that is generated by the limestone dissolution.

Reaction rates are expressed per unit area of reacting surface (e.g. stone surface area) and are related to such environmental conditions as temperature, ionic strength, and flow turbulence. Differential equations expressing rates of the two limiting reactions are solved simultaneously to describe the overall neutralization process for comparison with data obtained from operation of the pilot plant (16).

The mathematical model developed for the limestone neutralization process from the pilot plant operating data was applied to predict the performance of the prototype limestone barriers operating in Trough Creek. Results showed that when the interstices within crushed limestone became clogged by silt or by iron or aluminum hydroxide, the limestone became inactivated as the acidic water had no access to the reactive surfaces. In free flowing streams, where no such clogging occurred, the reactivity of the limestone was 20 percent of the reactivity of clean stone as a result of the inhibitory effects of the coatings that formed on the stone. At lower concentrations of metallic ions no iron or aluminum hydroxide coatings accumulated, but a coating of clay-like material developed on the stone. As a result of this work, design procedures for limestone neutralization processes were developed (2).

The exsolution of carbon dioxide has an increased effect on the performance of the process as the final pH of the water rises above 5.0. Downstream of the limestone neutralization process the pH will continue to rise as carbon dioxide is lost from the water. Stumm and Morgan (18) deal with many of the chemical equilibria that pertain to the neutralization process. Their formulations provide a basis for estimating water quality after the carbon dioxide reaches equilibrium with the atmosphere.

Successful neutralization of a lightly buffered acidic stream by the use of crushed limestone filled drums was reported by Zurbuch (19, 20). The method was demonstrated at the Otter Creek installation in the Monongahela National Forest, West Virginia. The neutralization of Otter Creek raised the pH values from less than 5.1 to over 7 and sustained fish life in 12 miles of stream. This project was unique in that the power for grinding the limestone is obtained from the acid water itself. The drums were fitted with vanes and operated as overshot water wheels, utilizing the power of the stream for self-neutralization. Each drum was 44 inches wide and 50 inches in diameter. The inner drum containing the limestone was 34 inches in diameter. A minimum flow of 0.5 cfs was required to rotate a drum and agitate the crushed limestone. Flows exceeding 4 cfs were diverted to a second drum. The success of the Otter Creek installation encouraged Pearson and McDonnell to investigate the hydraulic, mechanical and chemical process design of the drums (3).

Of the literature reviewed, only Pearson and McDonnell (1, 2, 3) proposed rational and comprehensive design procedure based on both empirical and theoretical considerations. Accordingly, theoretical design of the chemical processes was determined in accordance with their proposed procedures.

Pre-design Chemical Testing: A limited number of laboratory and field tests using the Quakake AMD and limestone were conducted prior to the design. The tests were made to confirm that the behavior of the proposed prototype would be at least partially predictable by the theoretical methods used for design. The tests consisted of bench (laboratory) tests and field tests. In the bench tests, a known weight of limestone was placed in a known volume of AMD and the rate of change of pH with time was recorded. The experimental data generally confirmed the order of magnitude of the limestone loading required to produce a final pH of 6.

In order to evaluate the chemical coating which forms on the limestone particles field tests were made. These tests were made by submerging limestone chips in the tunnel discharge until the coatings developed. The limestone and coating were examined at the Pennsylvania State University by X-Ray diffraction techniques and scanning electron microscopy. These analyses indicated that the chips have three coatings:

(a) An overall coating of recrystallized calcite which is relatively porous;

(b) A brown coating rich in iron, which is not as porous and flakes off when dry;

(c) An off-white coating similar to (b), rich in aluminum and sulfur.

The exact chemical composition of the compounds in (b) and (c) could not be determined.

In general, the chemical tests indicated that the proposed design methods were reasonable and prototype design proceeded on that basis. A summary of the test methods and results is presented in Appendix "B".

4. PRINCIPLES OF AMD NEUTRALIZATION BY CRUSHED LIMESTONE

The following outlines of the chemical principles involved in the neutralization process are presented to facilitate an understanding of conventions used to evaluate the data obtained at the Quakake Tunnel.

Chemical Reactions: The neutralization of acidity by crushed limestone is controlled by the following chemical reactions:

$$CaCO_3\,(s) + H^+ = Ca^{++} + HCO_3 \qquad \text{(Limestone Dissolution)} \qquad (4.1)$$

$$HCO_3^- + H^+ = H_2CO_3 \qquad \text{(Carbonate Equilibrium)} \qquad (4.2)$$

$$H_2CO_3 = H_2O + CO_2\,(g)\uparrow \qquad \text{(Carbon Dioxide Exsolution)} \qquad (4.3)$$

Where H_2CO_3 = Dissolved Carbon Dioxide

HCO_3^- = Bicarbonate

Because the first reaction upsets the equilibrium between the bicarbonate and dissolved carbon dioxide, part of the bicarbonate formed reacts with hydrogen ions to form dissolved carbon dioxide. The formation of dissolved carbon dioxide by the second reaction in turn upsets the natural equilibrium between dissolved carbon dioxide and the level of carbon dioxide in the atmosphere. As a result, there is a chemical driving force for dissolved carbon dioxide to transfer from water to air, as represented by the third reaction.

Reaction Rates: Reactions involving only one phase (solid, liquid or gas) are usually faster than multi-phase reactions that are limited by rates of transfer of materials across the surface separating the phases. Thus, the reactions of Eq. 4.1 and Eq. 4.3 which occur across the liquid-solid limestone surface and across the liquid-gas water surface respectively, are much slower than the rate of Eq. 4.2 that occurs in the liquid phase and is instantaneous for all practical purposes.

The rates of Eqs. 4.1 and 4.3 depend on the rate constant and order of each reaction, the limestone surface area per unit flow for Eq. 4.1 and the water surface area per unit flow for Eq. 4.3. The reaction rates are influenced by temperature, ionic strength and the intensity of turbulence, but the range of their effects is minor and invariant. Consequently values for average conditions can be assumed for practical design procedures. Equations 4.1 and 4.3 have been found experimentally to be first order with respect to the concentrations of reactants (14). This means the reaction rate in Eq. 4.1 is directly proportional to the concentration of mineral acidity (hydrogen ions) in the AMD. Similarly the reaction rate in Eq. 4.3 varies directly with the concentration of dissolved carbon dioxide. Equations 4.4 and 4.5 define the change of mineral acidity and carbonic acidity with respect to the limestone surface area and the free water surface:

$$-\frac{d[H^+]}{d\alpha} = k_1[H^+] \qquad (4.4)$$

$$-\frac{d[H_2CO_3]}{d\beta} = k_3[H_2CO_3] \qquad (4.5)$$

in which:

[ ] = Concentration - moles
α = Surface area of crushed limestone per unit flow of AMD, sec-m^{-1};*
β = Free water surface area per unit flow, sec-m^{-1};
k_1 = Proton effective diffusion rate constant
k_3 = Carbon dioxide diffusion rate constant

* (area in m^2)/(Flow in m^3/sec) = sec-m^{-1}

Pilot scale investigations (16) under laboratory conditions have shown that the rates of Eqs. 4.1 and 4.3 under standardized conditions of no turbulence, 10°C temperature and an ionic strength of 0.001 kg mole-m^{-3} are:

k_1 = 0.0055 m-sec^{-1}
k_3 = 0.00058 m-sec^{-1}

Acidity and Alkalinity: The alkalinity of a water is the capacity of that water to accept protons (e.g. hydrogen ions - - [H^+]). Conversely the acidity of a water is the capacity of that water to donate protons. Alkalinity and acidity are measured by the procedures specified in "Standard Methods" (22). Acidity is measured by titrating the water to a pH of 8.3 where the concentrations of acid, base and carbonate are equal. The proton condition of a pure carbonate solution at the pH = 8.3 end point is:

$$[H_2CO_3] + [H^+] = [CO_3^{2-}] + [OH^-] \tag{4.6}$$

At low pH values the solution contains strong acids such as H_2SO_4. In this case the solution is said to contain mineral acidity or free acidity. The concentration of mineral acidity is commonly measured by titrating the solution to the methyl orange acidity end point of pH = 4.5. The proton condition of a pure solution at this end point is:

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \tag{4.7}$$

When the initial pH of a solution is greater than 4.5 the solution is titrated with a strong acid to the methyl orange end point. The concentration of acid required to accomplish the titration is termed alkalinity.

Alkalinity and acidity are formulated as follows:

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{4.8}$$

$$[Acy] = [H_2CO_3] - [CO_3^{2-}] - [OH] + [H^+]$$

in which:

[Alk] = alkalinity in kg mole-m^{-3}

[Acy] = acidity in kg mole-m^{-3}

[H^+] = is interpreted to include protons released by hydrolysis of metals and by dissociation of non-carbonic weak acids, as well as from mineral acidity

Alkalinity Change as a Measure of Neutralization: The change in alkalinity is a measure of proton consumption as the reaction proceeds. The value of alkalinity as described by eq. 4.8 can be computed for the controlling chemical reactions; Eq. 4.1, 4.2 and 4.3.

The first reaction removes one proton from solution thereby increasing the alkalinity by one unit. It also adds a bi-carbonate ion resulting in a net alkalinity increase of 2 units. The remaining two reactions do not affect the alkalinity concentration as shown below:

$$CaCO_3\,(0) + H^+\,(-1) = Ca^{++}(0) + HCO_3^-\,(+1) \qquad Alk = +2 \qquad (4.1)$$

$$HCO_3^-\,(+1) + H^+\,(-1) = H_2CO_{3(0)} \qquad Alk = 0 \qquad (4.2)$$

$$H_2CO_3\,(0) = H_2O\,(0) + CO_2\,(0) \qquad Alk = 0 \qquad (4.3)$$

($\pm$) = Positive or negative alkalinity unit

Equating the incremental decrease in proton concentration by Eq. 4.1 to the incremental increase in alkalinity:

$$d[H^+] = 0.5\ d[Alk] \qquad (4.10)$$

Eq. 4.4 can then be transformed to reflect the alkalinity change throughout the neutralization process:

$$0.5\ \frac{d[Alk]}{d\alpha} = k_1[H^+] \qquad (4.11)$$

The value of [Alk] is dependent on the concentration of carbonate and protons in the solution as described by Eq. 4.8. The total concentration of carbonate in solution is described by:

$$C_t = H_2CO_3 + HCO_3^- + CO_3^{--} \qquad (4.12)$$

and if Eqs. 4.8 and 4.9 are combined, we find:

$$C_t = [Alk] + [Acy]$$

Where C_t = the total concentration of carbonate, kg-mole-m^{-3}

Alkalinity can be formulated in terms of C_T and H^+ as follows:

$$[Alk] = \frac{C_t}{1 + [H^+]/K_1} - [H^+] \qquad (4.13)$$

Where K_1 is the first dissociation constant for carbonic acid.

Eq. 4.13 disregards the $[OH^-]$ and $[CO_3^{--}]$ concentrations as they are very small in the pH range of interest. Table 7.1 presents a complete description of the carbonate equilibrium system.

A numerically soluble expression describing the neutralization process can be obtained by calculating the derivative of Eq. 4.13 with respect to $[H^+]$;

$$\frac{d[H^+]}{d\alpha} = \frac{2k_1[H^+]}{(1 + K_1C_t/(K_1 + [H^+])^2)} \qquad (4.14)$$

Roughly translated, Eq. 4.14 states that the change in protron concentration with respect to the neutralization opportunity (i.e., stone surface area, AMD volume, contact time) is a function of the concentrations of protolized ions (e.g. H^+, Al^{++}, Fe^{+++}) and the inorganic carbon (i.e., Acidity + Alkalinity).

Inorganic Carbon Balance: The solution of Eq. 4.14 is complicated by changes in concentration of inorganic carbon concentration during the neutralization process. During neutralization, the carbonate concentration is increased in the AMD at a rate equal to the rate of dissolution of limestone, according to Eq. 4.1. This increase in inorganic carbon concentration is offset by a decrease due to the expulsion of carbon dioxide from solution. The rate of carbon dioxide exsolution is proportional to the concentration of carbon dioxide present in solution, as Eq. 4.5 shows. The total incremental change in concentration of inorganic carbon is expressed by the differential:

$$dC_t = K_1 [H^+] d\alpha - k_3 \frac{C_t}{1+K_1/[H^+]} d\beta \qquad (4.15)$$

which may be written:

$$\frac{dC_t}{d\alpha} = k_1[H^+] - k_3 \frac{C_t}{1+K_1/[H^+]} \frac{d\beta}{d\alpha} \qquad (4.16)$$

The linked differential Equations 4.13 and 4.16 can be solved by numerical methods. The solution mathematically models the neutralization process for given initial concentrations of protons and C_T and for given treatment conditions. The treatment conditions being the limestone and free water surfaces provided per unit flow.

Limestone Characteristics: The neutralization characteristics of crushed limestone depend on both the physical and chemical properties of the stone. Particle size and shape control both the hydraulics of flow through the crushed stone and the surface area of $CaCO_3$ available for reaction with the acid water. Hardness of the stone determines the rate of abrasion and chemical dissolution of the stone, which is related to the Magnesium Carbonate ($MgCO_3$) content of the stone.

The hardness of the limestone was measured by the Los Angeles Abrasion Test (ASTM C-131) which consists of rotating an aggregate sample in a 28-inch diameter drum at a speed of 30 to 33 RPM for 500 revolutions. The fine material ground from the original sample is discarded and the difference between the original weight and the final weight, expressed as a percentage, is reported as the percent L.A. Abrasion wear. Zurbuch (20) found that this abrasion test method correlated well with observed limestone use rates in revolving drums.

The rate of dissolution of limestone is dependent on its magnesium carbonate content. It appears that the rate of dissolution of a limestone is inversely proportional to its $MgCO_3$ percentage. Pearson (16) derived this relationship from data presented by Hoak, Lewis and Hodge (8).

Shape Factor: The shape factor of the crushed limestone particles is required to determine for the the surface area per volume of stone and computations of flow through the beds of crushed limestone. The shape factor is defined as:

$$\frac{V}{A} = \frac{SD}{6} \qquad (4.17)$$

where:

S = Shape factor
D = Nominal particle diameter, equal to the diameter of a sphere of the same volume
V = Volume of the particle
A = Surface area of the particle

This equation defines the shape factor as the ratio of the surface area of a sphere with the same volume as the particle, to the surface area of the particle. Previous investigators (23) estimated the shape factor-surface area relationship by individual measurements on more than one ton of crushed limestone. For 1,218 stones, the mean shape factor was 0.76 with a standard deviation of 0.04 and a range of 0.59 to 0.89. Accordingly, a shape factor of 0.76 was used for design of the prototypes and evaluation of the operating data.

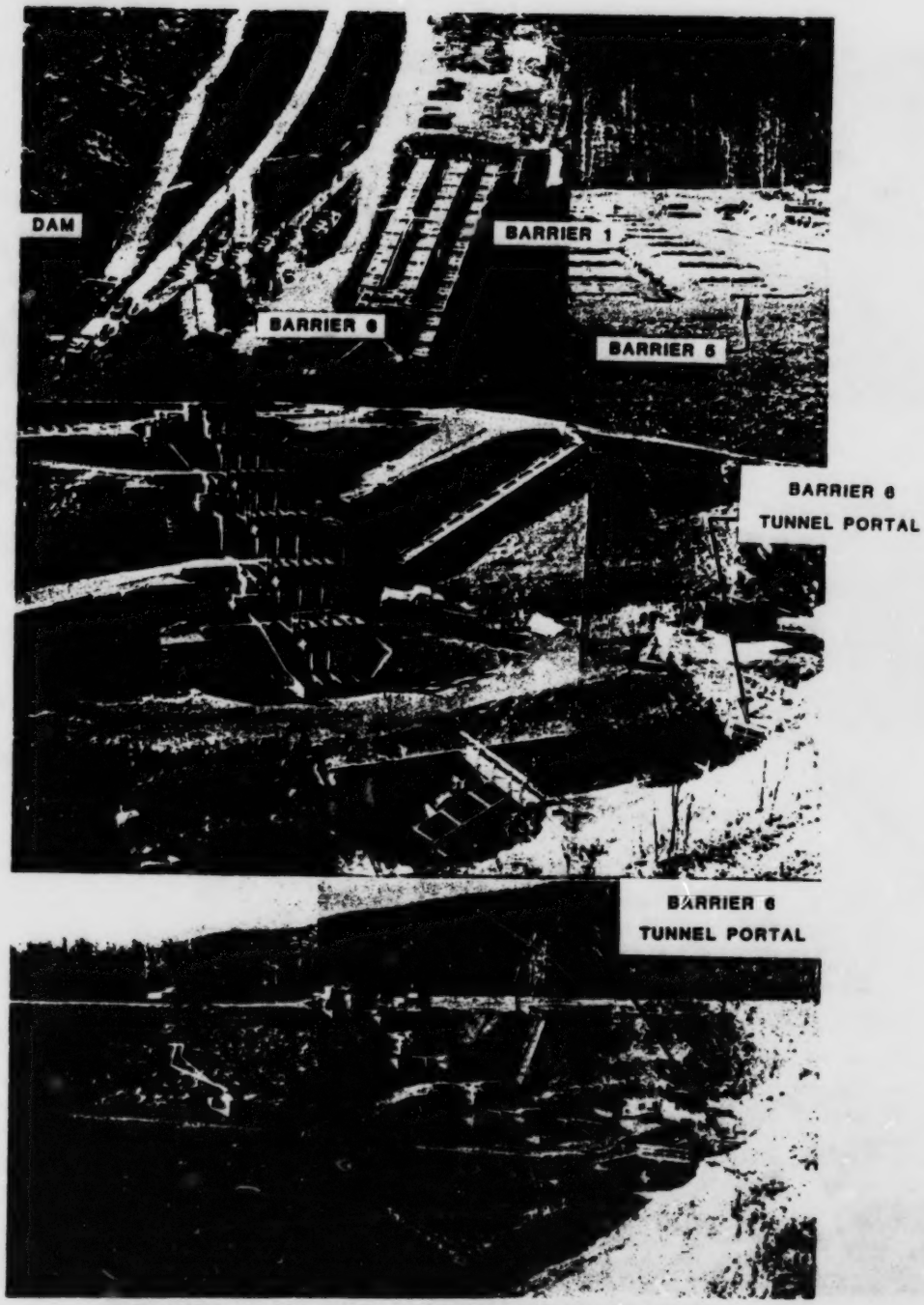
Reactivity Coefficient: The rate constant for the dissolution of limestone by AMD was determined experimentally for clean limestone in the laboratory. But, it has been observed that limestone placed in natural streams carrying AMD develops a surface coating of sediment, aquatic organisms and/or heavy metal oxyhydrates, depending on the chemical make up of the AMD. Comparisons between observed and predicted performances of four limestone barriers in the Trough Creek Watershed, Pennsylvania (17), indicate that both sediment/biological coatings, and the heavy metal oxyhydrate coatings reduced the reactivity of the limestone. At Trough Creek, the reactivity of the limestone was found to be 20 percent of the reactivity obtained for clean limestone under laboratory conditions. This factor of 20 percent has been termed the reactivity coefficient, and describes the effect of the thin film that forms on the stone surface which inhibits the neutralization process. It does not account for those surfaces of the limestone which are unsubmerged in AMD or blanketed by sediment, nor does the factor account for the deposit of metal oxyhydrates in the pores between the stones.

Load Factor: For design purposes, it is convenient to express the ratio of reactive limestone surfaces to AMD volume (α in Eq. 4.4) in terms of commonly used stone and flow measurements. Therefore α (in $sec\text{-}m^{-1}$) is converted to Load Factor (LF) in terms of tons of limestone per cfs of AMD per inch of stone size.

$$LF = \frac{Wr\ (TONS)}{pSQD(in)(cfs)} \qquad (4.18)$$

in which:

W = mass of crushed limestone, tons;
D = diameter of crushed limestone, inches;
Q = AMD flow, $ft^3\ sec^{-1}$;
S = stone shape factor
r = limestone reactivity coefficient; and
p = percentage magnesium carbonate in limestone (1.0 for limestone containing 1% $MgCO_3$, or less)



OVERVIEWS OF THE QUAKAKE DEMONSTRATION PROJECT

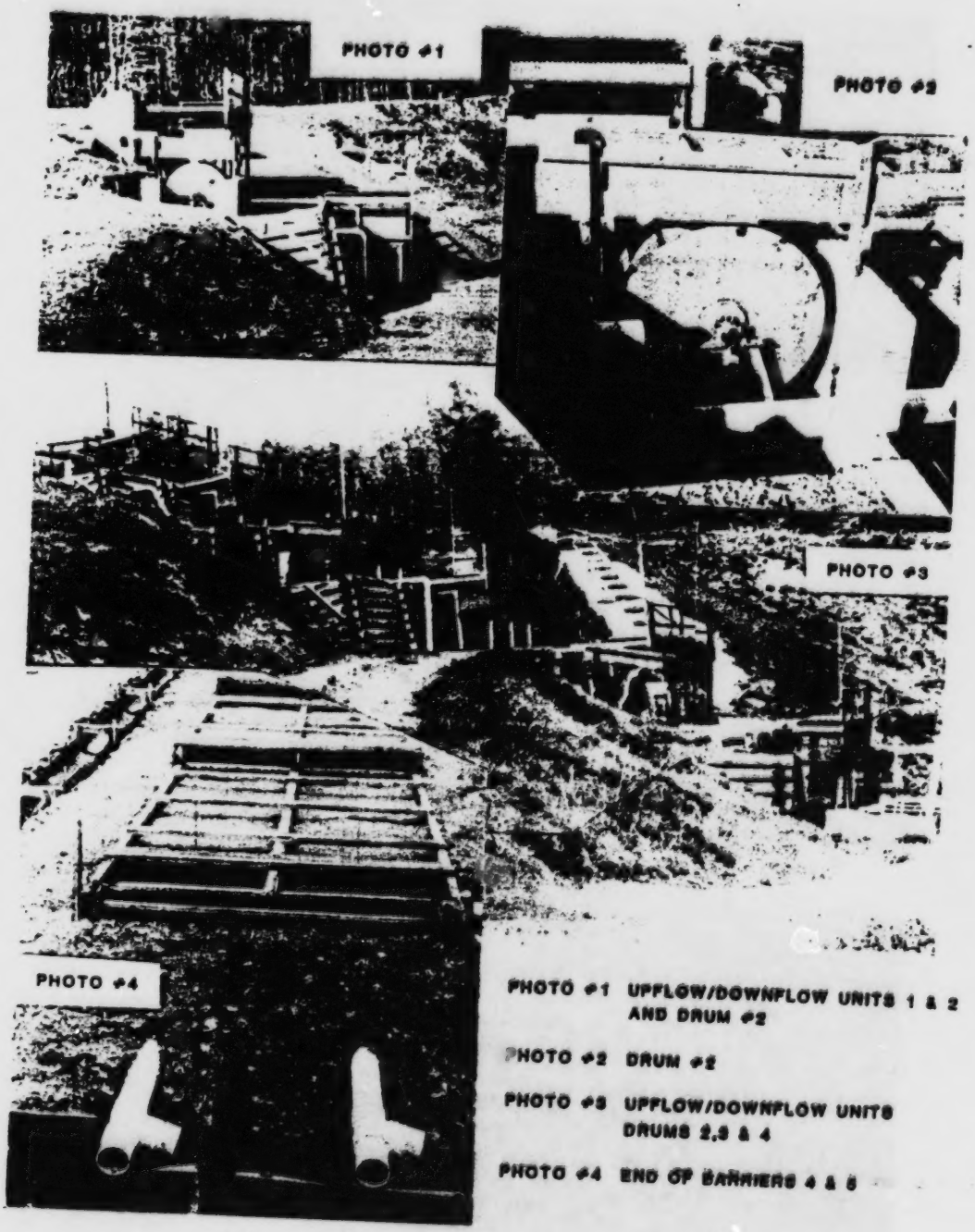


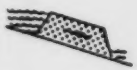
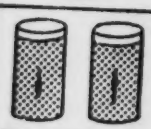
PHOTO #1 UPFLOW/DOWNFLOW UNITS 1 & 2 AND DRUM #2

PHOTO #2 DRUM #2

PHOTO #3 UPFLOW/DOWNFLOW UNITS DRUMS 2,3 & 4

PHOTO #4 END OF BARRIERS 4 & 5

TABLE 6.1 PROTOTYPE PROCESS CHARACTERISTICS

PROCESS TYPE		SCHEMATIC CONFIGURATION	NO. OF UNITS AT QUAKAKE	STONE SIZE (mm)	DESIGN FLOW (RANGE, cfs)	NEUTRILIZATION PROCESS MECHANISM
STATIC BARRIER			6	5, 13, 20	1/2	LIMESTONE DISSOLVES IN AMD. EXCESS TREATMENT CAPACITY PROVIDED TO OFFSET SEDIMENT AND CHEMICAL COATING.
FILTER TYPE UNITS	DOWNFLOW BED		6	5	1/4 TO 3/8	LIMESTONE DISSOLVES IN AMD. STONE CLEANED BY PERIODIC MANUAL BACKWASH.
	ALTERNATING FLOW BED		6	5	1/4 TO 3/8	LIMESTONE DISSOLVES IN AMD. MINOR ABRASIONS OF FINES. STONE CLEANED BY FREQUENT AUTOMATIC BACKWASH.
	UPFLOW FLUIDIZED BED		6	5	1/4 TO 3/8	LIMESTONE DISSOLVES IN AMD. FINES ABRADED BY FLUIDIZED OPERATION SELF CLEANING.
AUTOGENOUS MILL			1	5	1/4 TO 1/2	LIMESTONE DISSOLVES IN AMD. BED CLEANED BY PERIODIC REVOLUTION OF DRUM.
TUMBLING DRUM			5	20	1/2 TO 1	CONTINUOUS ABRASION OF LIMESTONE. AMD NEUTRILIZED BY FINES PRODUCED.

5. PROTOTYPE DESIGN AND CONSTRUCTION

The Quakake Tunnel prototype installations were designed and constructed during 1978 and 1979. A total of 30 individual process units representing variations of 4 basic design processes were installed. All the units employed crushed limestone for neutralization of AMD. The installed processes included both static and abrasive processes and are characterized in Table 5.1. The combined treatment capacity of the prototypes was 3 cfs. Flow was delivered to the units by a turbine pump capable of delivering 1800 GPM at a 50 foot head. A schematic layout of the project is presented in Figure 5.1 and aerial views are shown in the frontispiece.

Pumping of a portion of the AMD to the treatment units was employed for the prototype demonstration rather than gravity flow which is envisaged for a permanent project. Pumping was used to minimize site work and disturbance of adjacent woodlands as the use of the land for the project was obtained through gratis easements. It is intended that a permanent treatment facility would not require outside power sources to operate the treatment units.

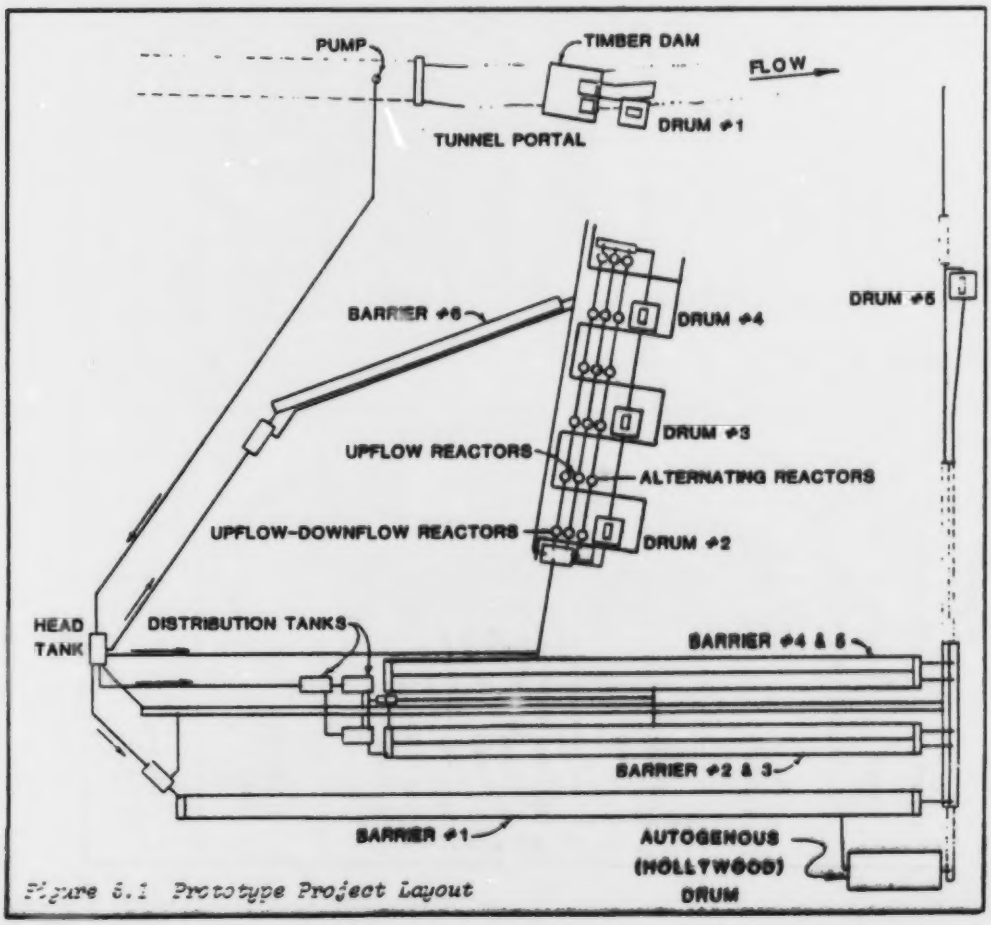


Figure 5.1 Prototype Project Layout

Limestone: Crushed limestone for the demonstration project was obtained from two sources. A high calcium limestone from the Bethlehem Mines Millard Quarry in Annville, PA, was selected for use in all the prototypes. In addition, a high magnesium limestone was obtained from local sources for comparative use in the tumbling drums. Three sizes of the high calcium stone were used. The chemical and physical properties for both limestones are as shown below.

TABLE 5.2 - CHEMICAL AND PHYSICAL CHARACTERISTICS OF PROCESS LIMESTONES

Characteristic	High Calcium Limestone			High Magnesium Limestone		
	Mean	Min.	Max.	Mean	Min.	Max.
Chemical Composition % Wt.						
Calcium Carbonate $CaCO_3$	97.0	96.9	97.2	62.2	59.5	66.2
Magnesium Carbonate $MgCO_3$	1.12	0.92	1.28	34.3	30.2	36.8
Silica SiO_2	0.98	0.76	1.29	2.64	2.46	2.73
Aluminum Oxide Al_2O_3	0.76	0.68	0.87	0.85	0.82	0.89
Iron Oxide Fe_2O_2	0.22	0.20	0.27	0.41	0.39	0.43
L.A. Abrasion %	43	39	45	25	-	-
Specific Gravity	2.72	2.72	2.73			
Bulk Density, Pcf						
Loose 5mm Stone (1/4")	88.6	88.1	90.1			
Rodded 5mm Stone	96.9	96.5	97.8			
Loose 13mm Stone (1/2")	83.7	81.7	85.2			
Rodded 13mm Stone	92.2	90.6	94.6			

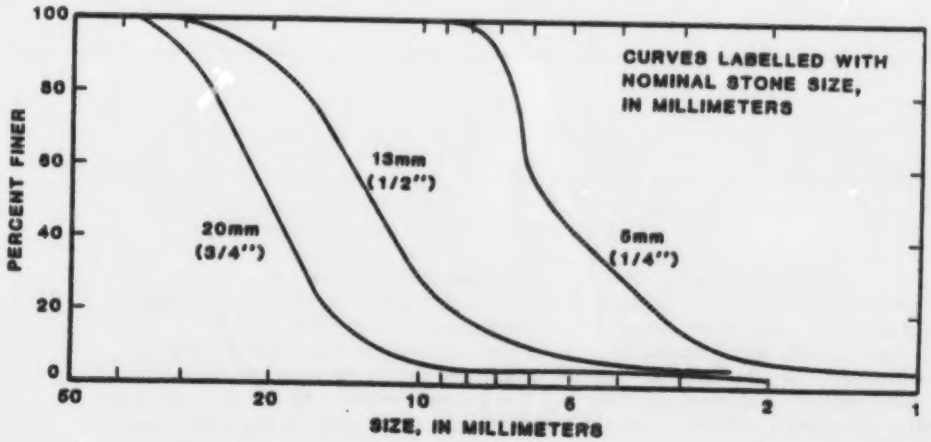
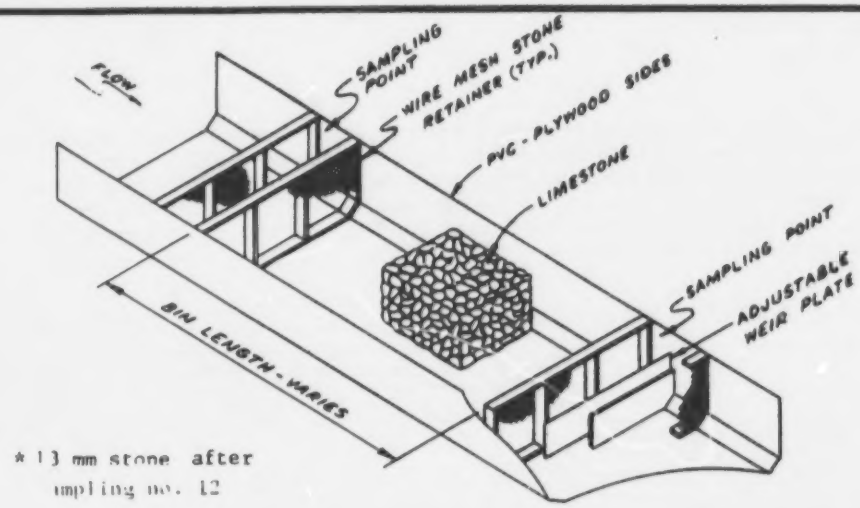


Figure 5.2 Grain Size Curves of Process Limestones



* 13 mm stone after
ampling no. 12

CONSTRUCTION DETAIL	BARRIER NO. 1	BARRIERS 2 THRU 5	BARRIER NO. 6
STONE SIZE (mm)	20	5 *	5 *
TOTAL LENGTH (ft.)	199	143	86.7
BIN LENGTH (ft.)	12	10	6
WIDTH (ft.)	6	4	3
STONE DEPTH (ft.)	2'-4"	2'-4"	3'-6"
NUMBER OF BINS	14	10	10
STONE (tons per bin)	6.8	4.5	3.1
BED SLOPE	-5.00%	-1.00%	-30.00%

Figure 5.3 Limestone Static Barrier Construction

Static Barriers: Ideally, the problem of neutralizing an acid stream might be solved by the simple method of placing a sufficient amount of limestone as a bed or barrier, directly in the stream. However, during previous attempts to implement this method, the limestone became coated with metal complexes and the stone became clogged by stream sediments. These problems could have been partially the result of design deficiencies since both laboratory studies and evaluation of the Trough Creek Limestone Barrier Project (14, 15, 17) indicated that the use of instream barriers was feasible under certain conditions. The conditions which favor the use of limestone beds are low stream discharge variations, low sediment load and low iron content. These criteria were used in the selection of the Quakake Tunnel Project site. Also, the diversion of a constant amount of flow to the prototypes in the demonstration project eliminated flow variations. Standard sanitary septic tanks were used as combination diversion/sedimentation tanks. They were designed to remove sediment sizes greater than the sizes which would theoretically be carried through the stone voids by the flowing water.

Previous research identified the parameters considered to govern the neutralization process. They include the following:

Stone and AMD composition,
Available Limestone Surface (stone size and shape),
Contact time, Streamflow and Temperature,
Water Turbulence - Hydraulic Shear Forces, and
CO_2 Exsolution Subsequent to Neutralization.

The prototype limestone barriers were designed to explore the response of the process to variations in stone size and hydraulic characteristics. Prior studies indicated that under barrier conditions of near constant flow and low iron and sediment loads, the reduction in reactivity due to fouling of the limestone surfaces did not fall below 20% of that for fresh clean stone. Accordingly, all the barriers were sized to provide 5 times the limestone surface area per unit flow of AMD (Load Factor) above that required by theory to achieve the desired degree of neutralization using clean crushed stone.

Each barrier was subdivided into individual units, (bins) within which limestone was placed. This provided convenient sampling points along the treatment path and allowed adjustment of hydraulic gradient through the barrier. The use of adjustable weir plates between the bins provided control of stone submergence and hydraulic gradient through the stone. The limestone barriers were constructed in plywood channels lined with 20 mil. PVC. Divisions were created within the barriers by using wooden frames covered with heavy diamond wire mesh and 1/4 inch hardware cloth. Figure 5.3 shows construction details of the six barriers. The flow to the inlet of each barrier was measured using a 90° v-notch with a plywood stilling box. The dissipation of flow energy into the stilling boxes was accomplished by using slotted PVC pipes fitted with end caps.

Filter-Type Units: The filter-type processes consisted of the installation of three parallel sets of six filter units. The units were designed to operate in three modes; downflow, upflow and alternating downflow-upflow. Construction details are illustrated in Figure 5.4.

An upflow method of operating was reported to have been successful in the treatment of steel pickling liquors (7,8). In upflow process, abrasion of the limestone particles is created by maintaining the bed in a constant fluidized condition. In the downflow design, the beds act as a static barrier but they have the capability of being backwashed to remove the buildup of sediments and coatings. Backwashing is initiated by closing the bottom gate valves and operating the units in the fluidized upflow mode. The alternating flow units were designed as downflow units with automatic backwashing capabilities.

Downflow operation was achieved by opening the bottom gate valve allowing AMD to percolate downward through the stone and through the gate valve to the next unit. By closing the bottom gate valve, the operation converted to the upflow mode, wherein AMD entered the bottom chamber, flowed upward to fluidize the stone, and then passed through the slotted control valve to the base of the next unit downstream. For operation in the alternating flow mode the slotted control valve was replaced by a siphon. The bottom gate valves were partially operated and the unit operated in a down flow mode. The siphon discharged to the base of the next downstream unit causing an upflow flushing of the downstream unit.

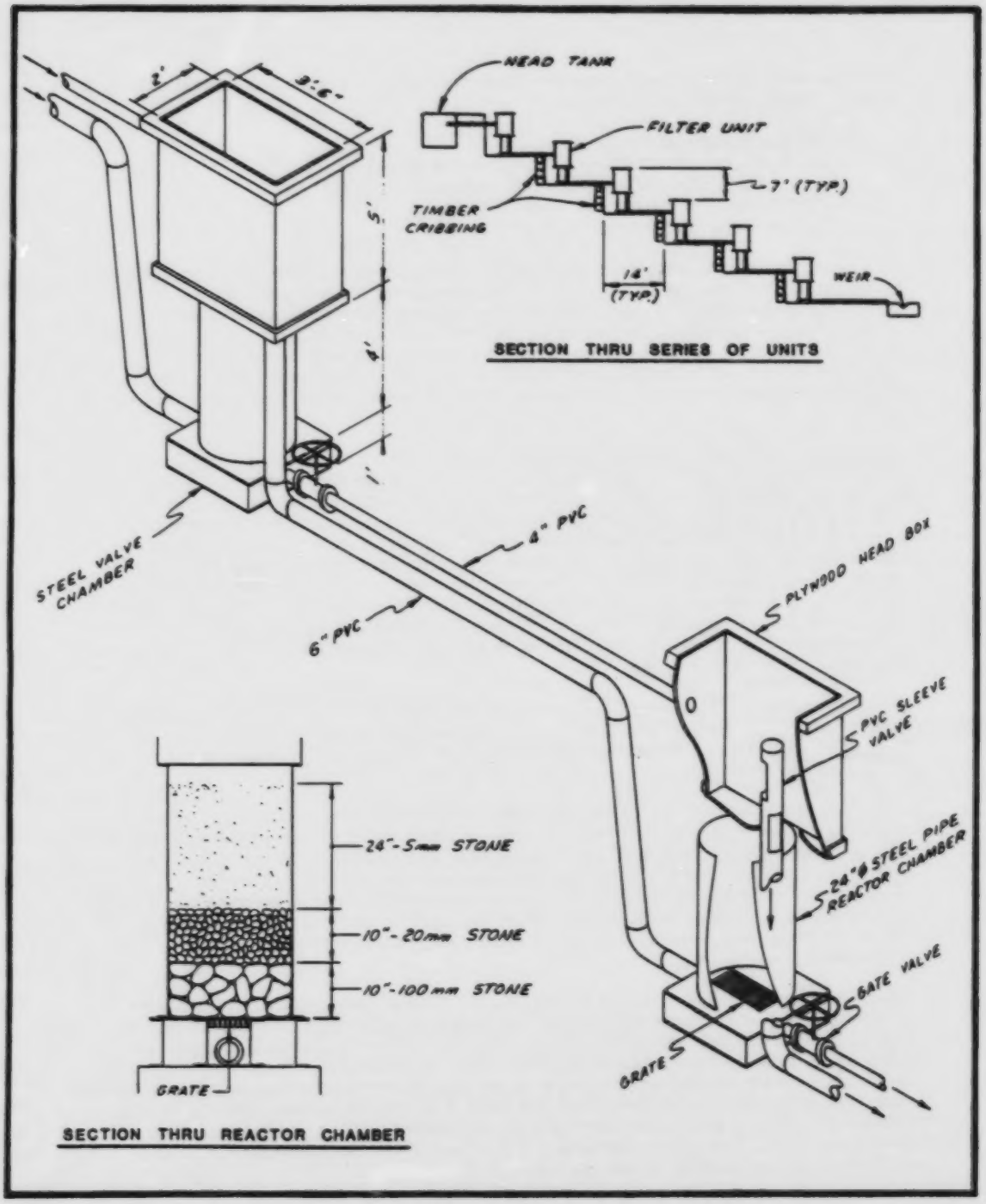


Figure 6.4 Construction Details of Filter-Type Units

Tumbling Drums: Rotating drums containing crushed limestone act as grinding mills to produce fine limestone particles which are highly reactive with AMD. Motor powered tube mills and limestone filled water wheels for neutralization of AMD and slightly acid streams have been successfully demonstrated (10, 19, 20, 21). The success of the unique drums demonstrated by Zurbuch, coupled with the subsequent analysis of the chemical and hydraulic/mechanical processes of the drums by Pearson and McDonnell led to the design and installation of similar units at the Quakake Tunnel site.

Of the five drums installed at Quakake, three drums (Drums 2, 3 and 4) were installed in series as an integrated treatment unit. One drum (No. 5) placed separately to treat the effluent from the static barriers provided data on combining the two methods. The remaining drum (No. 1) located in the stream channel, below the diversion dam, provided information on flows exceeding the capacity that could be delivered through the pumped distribution system (1± cfs). A typical drum installation is illustrated in Figure 5.5.

The five drum installations were constructed identically. Drum bays were constructed of 6 inch cinder block walls placed on 6 feet, 8 inch square by 8 inch thick concrete pads. The front bay walls were erected 4 feet high for splash containment. The bay side walls were 2 feet high in order to facilitate loading and unloading and periodic checks of the drum contents.

The drum shell was constructed from 3/8 inch thick steel pipe with an inside diameter of 3 feet and a length of 18 inches. Welded to both ends were 3/8 inch thick, 4 feet 8 inch diameter end plates. Welded between each end plate were sixteen curved water wheel vanes, having a 10 inch radius, which functioned as water containing buckets. The curved metal vanes were cut from standard steel pipe. Half-inch diameter holes were drilled through the inner drum at the base of each bucket to allow water to enter the drum and wash out the limestone fines generated by the tumbling stone in the drums. Baffles of 1/4 inch thick by 2 inch angle iron were bolted to the inside of the drum surface at the base of each vane to prevent slippage of the stone mass. A hinged door, bolted shut during operation, allowed loading of limestone into the drum. The drums were supported by 2 inch steel axles seated in pillow blocks with sealed ball bearings which rested on structural steel angle tripods.

Lovell (21) noted that noise is a drawback associated with operation of the drums. Zurbuch (19) significantly reduced this problem by lining his drums with a steel reinforced rubber mat. The Quakake drums were provided with a similar liner. Consequently noise levels created by the drums were not objectionable.

Autogenous Mill: The method of passing AMD through motorized rotating tubes partly filled with crushed limestone has been used to neutralize AMD. One such installation was transferred from its original Hollywood, Pennsylvania location to the Quakake Tunnel site prior to the third sampling period. The mill, shown in Figure 5.6, is a steel drum 5 feet in diameter and 20 feet long. The drum which rests on idlers is rotated by a 25 HP electric motor. The operation of this unit as an autogenous mill has been previously reported (21).

The mill was used at Quakake to investigate the concept of mechanically cleaning a static bed. The drum was used as a stationary limestone bed with periodic revolutions to achieve stone cleaning, rather than the production of fines. The bed was turned through two revolutions every four or eight hours. The drum was filled approximately one-half of its capacity with 5mm (1/4 inch) limestone.

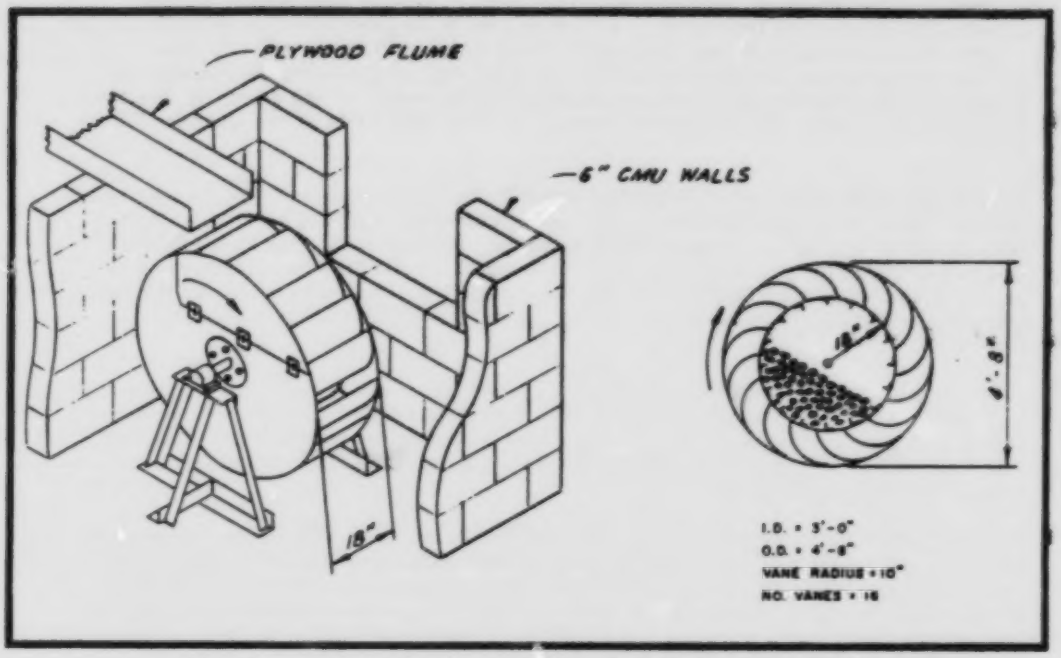


Figure 5.5 Construction Details of Tumbling Drum Units

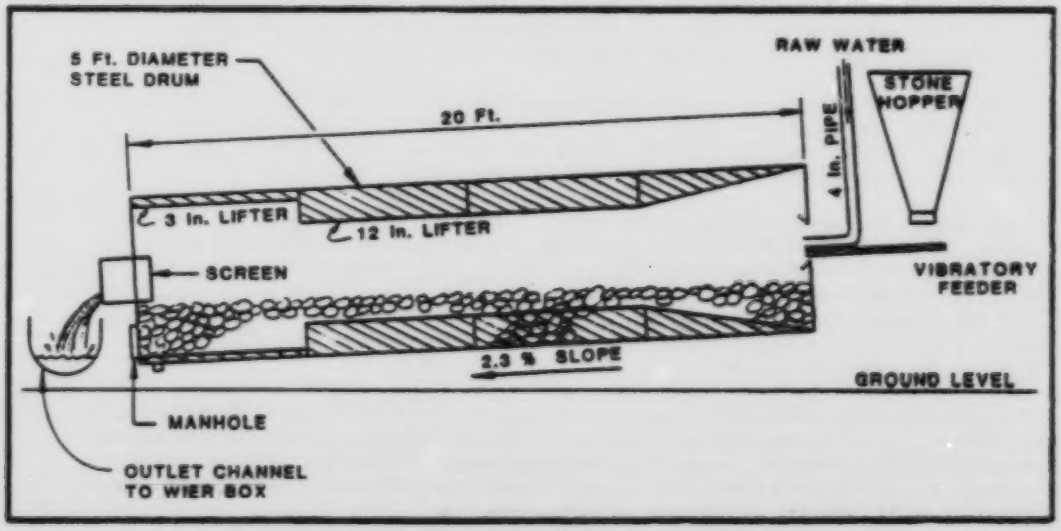
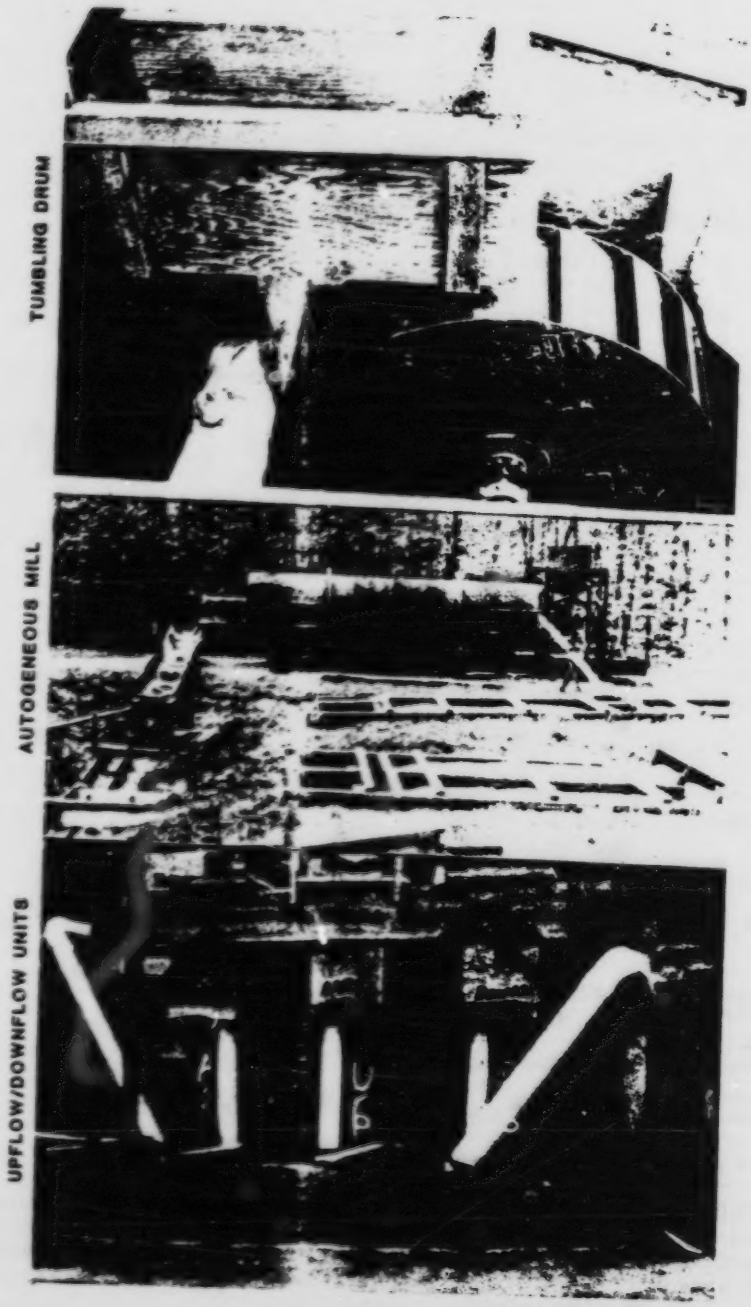


Figure 5.6 Section Through The Autogenous Mill


UPFLOW/DOWNFLOW UNITS
AUTOGENEOUS MILL
TUMBLING DRUM

6. PROTOTYPE OPERATION

The Quakake Tunnel prototypes were operated periodically over a 2-year period. The facility was operated for four separate sampling periods (runs) as follows:

Run No.	Sampling No.	Begin-End Dates
1	1 thru 12	7/10 - 10/4/79
2	13 thru 39	11/12 - 11/21/79
3	40 thru 65	5/19 - 5/21/80
4	66 thru 83	7/20 - 7/25/81

The non-operating periods were used for the chemical analysis of samples, evaluations of results, planning subsequent runs, and modification or repair of the plant.

Monitoring and Analytical Procedures: For samplings 1 thru 65, a 500 mL sample and a 125 mL acidified sample were taken at each sampling point. Bottles were rinsed before filling, capped underwater and stored at 9°C until shipping to the laboratory in ice-packed containers. Chemical analyses were performed at the Harrisburg Laboratory of the Pennsylvania Department of Environmental Resources. All samples were tested for the following parameters:

pH;
free acidity
total acidity;
alkalinity;
iron (total and ferrous);
sulfate;
aluminum;
calcium.

Occasional determinations were also made of:

manganese;
magnesium;
sodium;
potassium;
silica;
chloride;
solids (total and suspended).

The following field measurements were also made at each sampling:

pH;
temperature (water and air);
flow rate (by weirs);
hydraulic head; and
stone load and RPM for tumbling drums

During Run No. 4, the pH, alkalinity and acidity were determined on site.

Results of the monitoring program are presented in Appendix "C".

Run No. 1: Initially, the plan of operation for the demonstration project anticipated a 6-month operating period with twice-weekly samplings. This procedure was followed for samplings 2 through 12. Sampling No. 1 was a false start as the project operation was halted by a malfunction of the generator which supplied power to the pump. Figure 6.1 shows the operation schedule for Run No. 1.

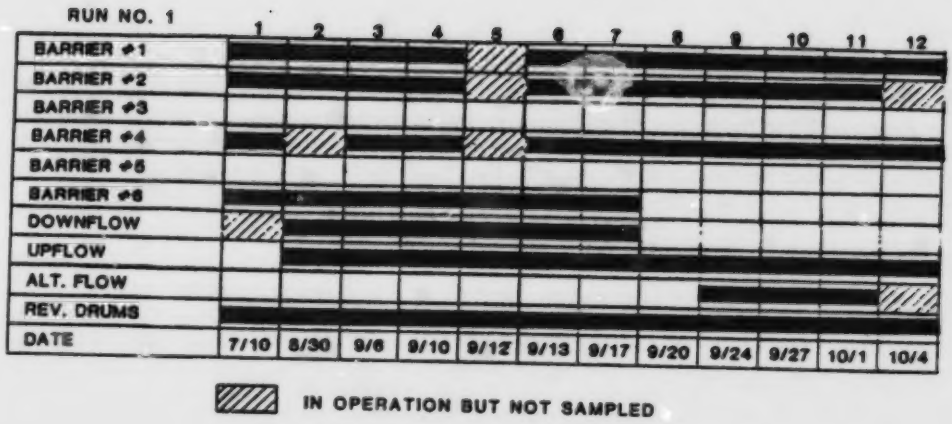


Figure 6.1 Operation Schedule - Run No. 1

During Run No. 1, several problems developed which required correction. The siphon units in the alternating filter units did not function because they were unable to develop sufficient head to purge the air in the pipes between the units. To correct the situation, the siphon in the upper unit was replaced with a mechanical flusher, while the siphon in the third unit was replaced by a commercial sanitary siphon with non-pressure discharge. Both modifications worked satisfactorily, although the modification of the backwashing equipment required the removal of some of the stone, thereby reducing neutralization capability. Having demonstrated the feasibility of automatic backwashing on some of the units, the remaining filter-type units were backwashed manually.

Major problems were encountered in the units containing the 5mm (1/4") stone. The rate at which the limestone fouled was much greater than had been originally anticipated. The front face of the stone beds of barriers 2, 4a and 6 became clogged which reduced the permeability of the stone bed to the point that the AMD ran over the tops of the beds rather than through them. This was particularly problematic in barrier No. 6 which was on a 30% slope.

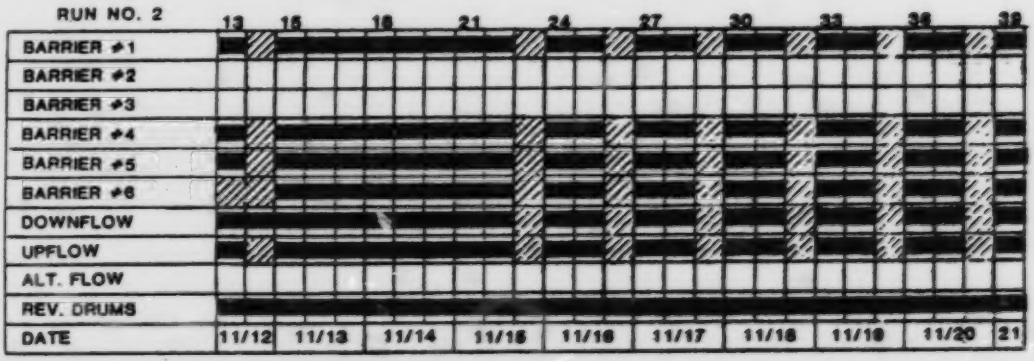
The permeability of the filter units was also seriously reduced by clogging. The original design of these units used an 1/8-inch screen to retain the stone at the base of each bin. These screens became almost totally clogged after 3 weeks of operation. In several instances, the upper one foot of the downflow units was actually "cemented" by the fouling coat and could not be backwashed. Mechanical prodding was necessary to break the "cemented" layer so that the stone could be cleaned. After sampling No. 8, the stone and screens were removed from the upflow and downflow units and a graded filter was placed in lieu of the screening. Also the monitoring of barrier No. 6 was halted at this time.

Evaluation of the results from the first sampling run indicated that the monitoring procedures would have to be revised in order to adequately investigate the rate of limestone consumption and fouling. It was clear that an increased sampling rate would be required because the rate at which the stone reactivity decreased necessitated hourly rather than daily measurements as had been originally anticipated. Similarly, the filter units required more frequent backwashing to maintain reactive limestone surfaces. In addition, the three to four day sampling intervals did not allow gathering

of sufficient data to describe the short term oeprations of the tumbling drums. The refilling cycle for the drums coincided with the sampling frequency approximately 3 to 4 days. As a result, the data gathered was primarily for freshly filled or nearly empty drums. Another problem associated with the drum operations noted during this run was that the detention time provided by the units was insufficient. It was observed that the AMD leaving the process units was milky colored, indicating that the reaction of the limestone fines with the AMD was not complete.

Run No. 2: The operation of the units during Run No. 2 was planned in a manner which would supplement the data gathered during Run No. 1 by utilizing shorter sampling intervals. The monitoring frequency was increased to 3 samplings per day with continuous 24-hour operation of the units.

Run No. 2, consisting of samplings 13 through 39, started on November 12, 1979. Figure 6.2 shows the operation schedule for Run No. 2.



IN OPERATION BUT NOT SAMPLED.
DRUM STONE LEVELS CHECKED.

Figure 6.2 Operation Schedule - Run No. 2

On completion of the laboratory testing of samples for Run No. 2, the monitoring results were evaluated with respect to the design theories. At this point, more than 2000 samples and measurements had been collected. Analysis of the data indicated that although design processes could be described emperically, the results did not correlate with the initial theoretical derivations. Part of this problem is related to the random nature of the data itself which is illustrated in Table 2.1 by the wide chemical variations of the AMD influent itself. The lack of agreement between the theoretical and experimental results was related to buffering effects observed in the pH 4.5 to 6.0 range. Additional correlation problems were encountered while trying to relate the measured drum operation parameters - RPM, flow and stone load, to the observed neutralization process.

As a result of the evaluations of Runs 1 and 2, the following measures were taken in preparation for Run 3:

Fresh 5 mm (1/4") limestone was placed in the filter type units after removal of the used stone.

The 5 mm (1/4") limestone in barriers 5 and 6 was replaced with 13 mm (1/2") limestone.

Facilities were added to provide detention of a portion of the effluent from the drum series 2, 3, and 4. This was achieved by diversion of 1 to 3 gallons per minute into two 55 gallon drums, providing up to 1 hour detention time for the process to continue.

Run No. 3: The third sampling run concentrated on the operation of the downflow units and revolving drums. The operation schedule is shown in Figure 6.3. The evaluation of the data from Runs 1 and 2 indicated that these processes were the most promising treatment methods. As it was felt at this time that the likely cause of the buffering problem was the carbon dioxide being generated by the neutralization process, aeration equipment was provided for the drum detention units. The autogenous mill from the Hollywood Plant was also installed at this time.

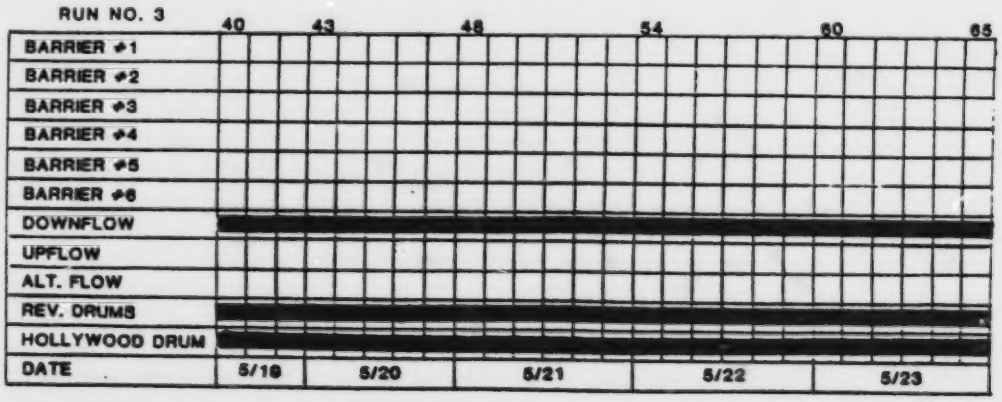


Figure 6.3 Operation Schedule - Run No. 3

Following the evaluation of Run No. 3, a draft report was prepared and tentative design procedures were proposed. The design procedures were based almost entirely on empirical data as the relationships between the observed neutralization processes and theory were not established. A fourth run was proposed in an attempt to establish this link. Marked differences between laboratory pHs and field pHs were noted in all the samplings as illustrated in Figure 6.4. The pH, acidity and alkalinity relationships are fundamental descriptors of the chemical processes in the reactions. It was questionable if the values obtained in the laboratory adequately describing the chemical process at the site. For example, the carbon dioxide content of the process effluent could not be determined in the laboratory. It was decided to attempt to solve these problems by testing the acidity and alkalinity on fresh samples in the field during a fourth run.

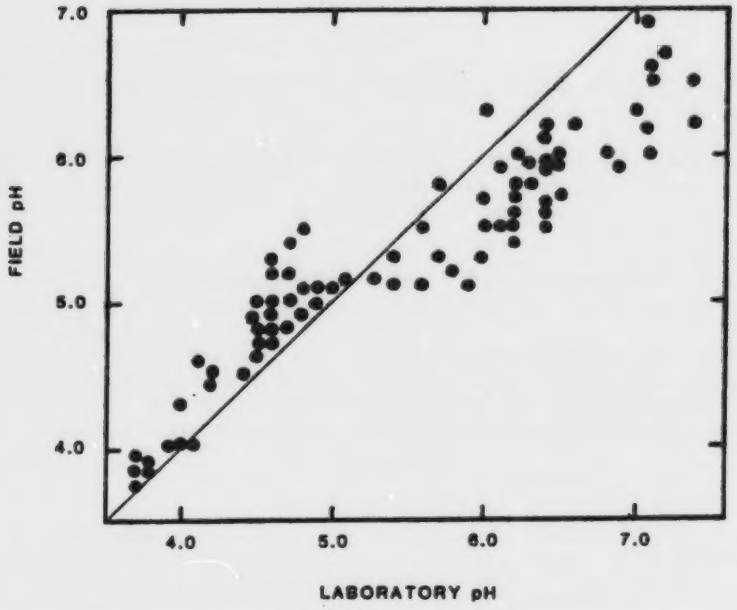


Figure 6.4 Field pH Determinations Compared with Lab pH The differences between lab and field values are consistant with pH levels. This suggests the chemistry of the sample has been altered between testing periods. Loss of CO_2 and continued $CaCO_3$ dissolution could contribute to these changes.

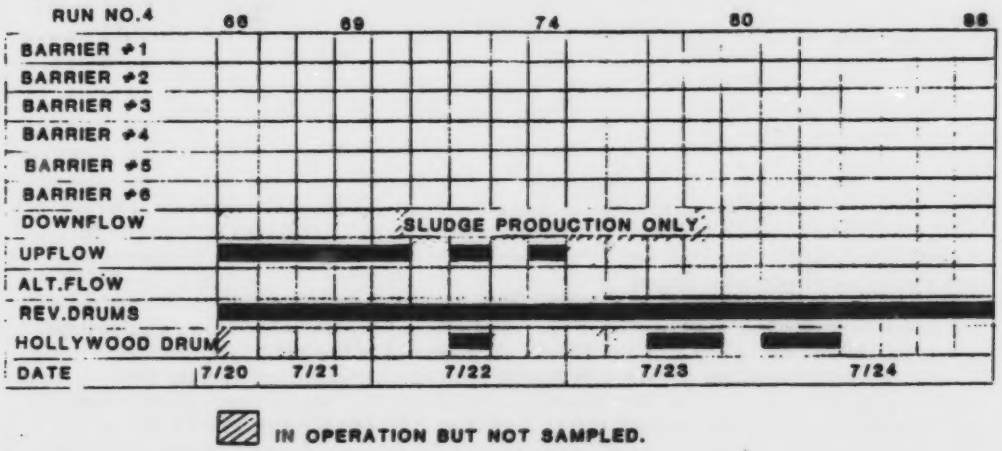


Figure 6.5 Operation Schedule - Run No. 4

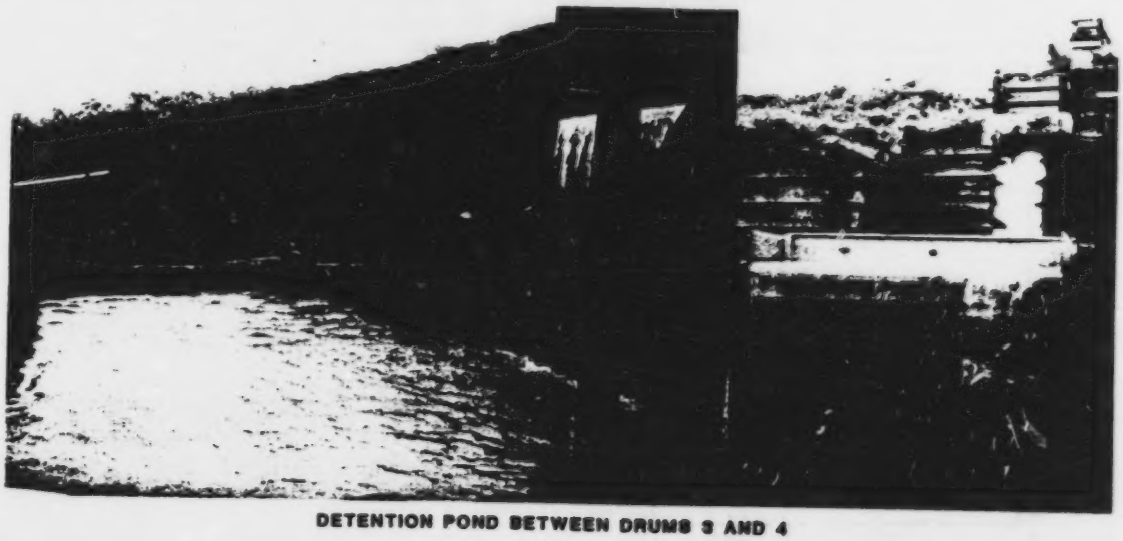
Run No. 4: Run No. 4 consisted of intense sampling of the drums and upflow units for one week as shown on Figure 6.5. A laboratory trailer was provided by the Department and the chemical tests for pH, acidity and alkalinity were performed onsite on fresh samples. In addition to the standard test for hot acidity, titrations on cold unoxidized samples were made. Comparison of the oxidized titrations with the unoxidized titrations allowed a rough estimate of the carbon dioxide to be made. Intermediate readings were taken during the tests to allow comparison of the entire titration curves.

Additional objectives of Run No. 4 were the gathering of additional data on carbon dioxide stripping by aeration, sludge production in the downflow units, and the effects of increased detention time on drum process series.

Two 500 gallon tanks with aeration equipment were installed for carbon dioxide stripping tests on the tumbling drum effluent. Both flow through and batch stripping tests were made.

An additional 200 gallon tank was used to settle sludge from the downflow backwash water. Dewatering tests were performed on the settled sludge. The tests were for the rapid sludge dewatering system of U.S. Environmental Products Inc. and the results are presented in Appendix "E."

A 2,500 gallon shallow detention pond was constructed between Drum No. 3 and Drum No. 4 in order to evaluate the effect of maintaining the ground limestone fines within the process. Partial aeration was provided by a seven feet high drop into the pond with a steel edged 8 feet long weir maintaining sheet flow.



DETENTION POND BETWEEN DRUMS 3 AND 4

7. NEUTRALIZATION PERFORMANCE EVALUATION

The performance of the limestone neutralization process is evaluated in terms of the degree of decreased acidity and corresponding increased alkalinity and pH which are inter-related by chemical equilibria conditions. The original design procedures were based on neutralization kinetics observed in the laboratory and the assumption that equilibrium conditions for a pure carbonate solution would control the process. pH was assumed as the master variable.

The original design assumptions appear to be substantially correct. In Figure 7.1, observed pH values obtained in the initial run of Barrier 5 are plotted against their appropriate load factors. Theoretical curves derived by the initial design procedures are also superimposed on this figure. The two theoretical curves represent the two extreme cases of carbon dioxide exsolution (i.e., all CO_2 is retained in solution or is completely exsolved). In practice, neither of these states will be achieved and the actual results will plot between the theoretical derivations. As seen on Figure 7.1, the field results do plot within the theoretical limits. These results suggest that if suitable values for CO_2 exsolution and for the reactivity coefficient can be obtained, the design process is valid. However, when the observed alkalinity and acidity values were examined along with the pH values in terms of chemical equilibria, there appeared to be some major inconsistencies. The observed pH values are lower than the values computed by carbonate equilibria criteria computed for the alkalinity and acidity test values. Average observed pH values and pH values computed from the acidity-alkalinity test values are plotted against alkalinity in Figure 7.2. Some variations between field results and laboratory values can be expected as there is an opportunity for continued reaction within the sample bottles. However, if the basic equilibria assumptions are correct, there should not be any discrepancies between the laboratory pH, acidity and alkalinity values. The computed pH values, field pH values and the average alkalinity and acidity values used for this comparison are plotted against laboratory pH in Figure 7.3. These values are mean values for all tests taken prior to Run No. 4.

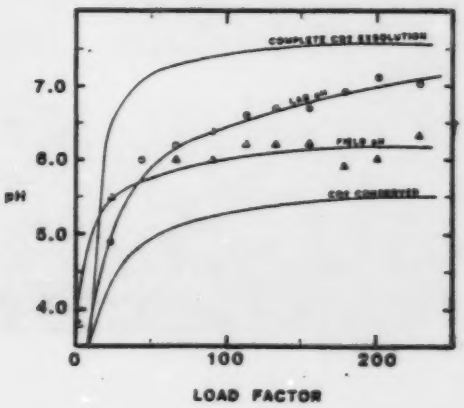


Figure 7.1 Observed pH - Load Factor Relationships. The upper and lower curves are computed values for the limiting CO_2 cases is

1. All the CO_2 generated is driven off.

2. None of the CO_2 generated by the dissolution of limestone is lost. The observed values fall between these two extreme cases.

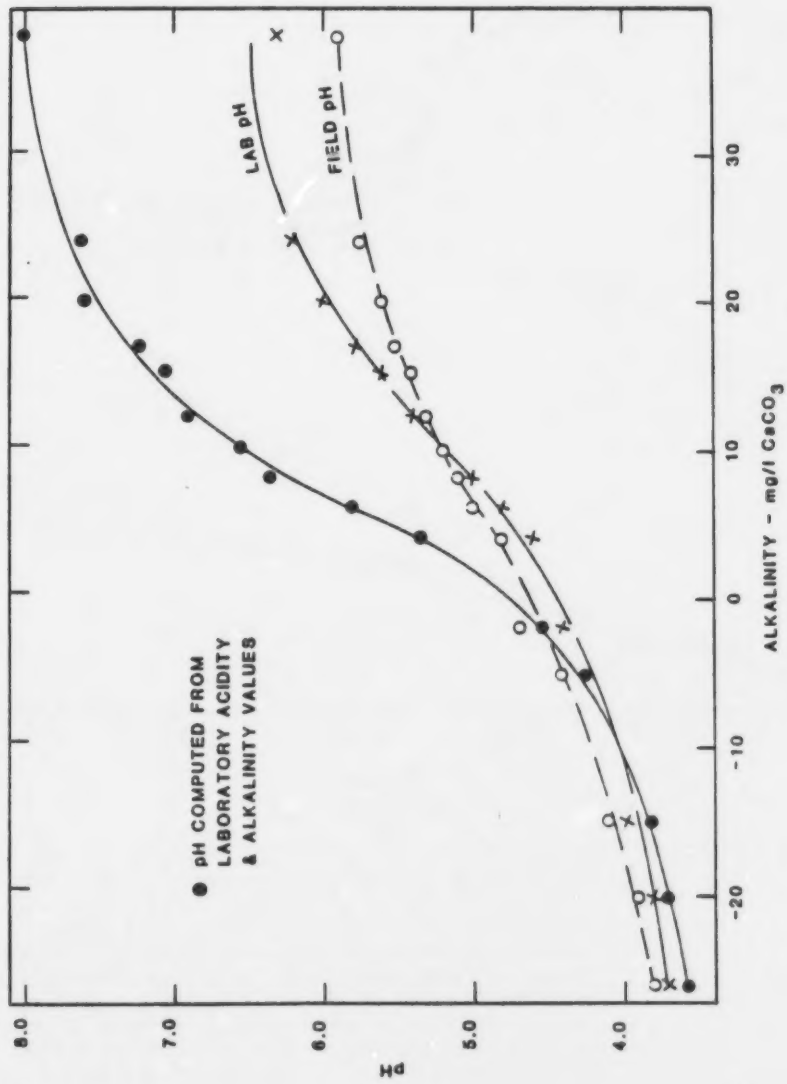


Figure 7.2 pH Variations Compared with Alkalinity

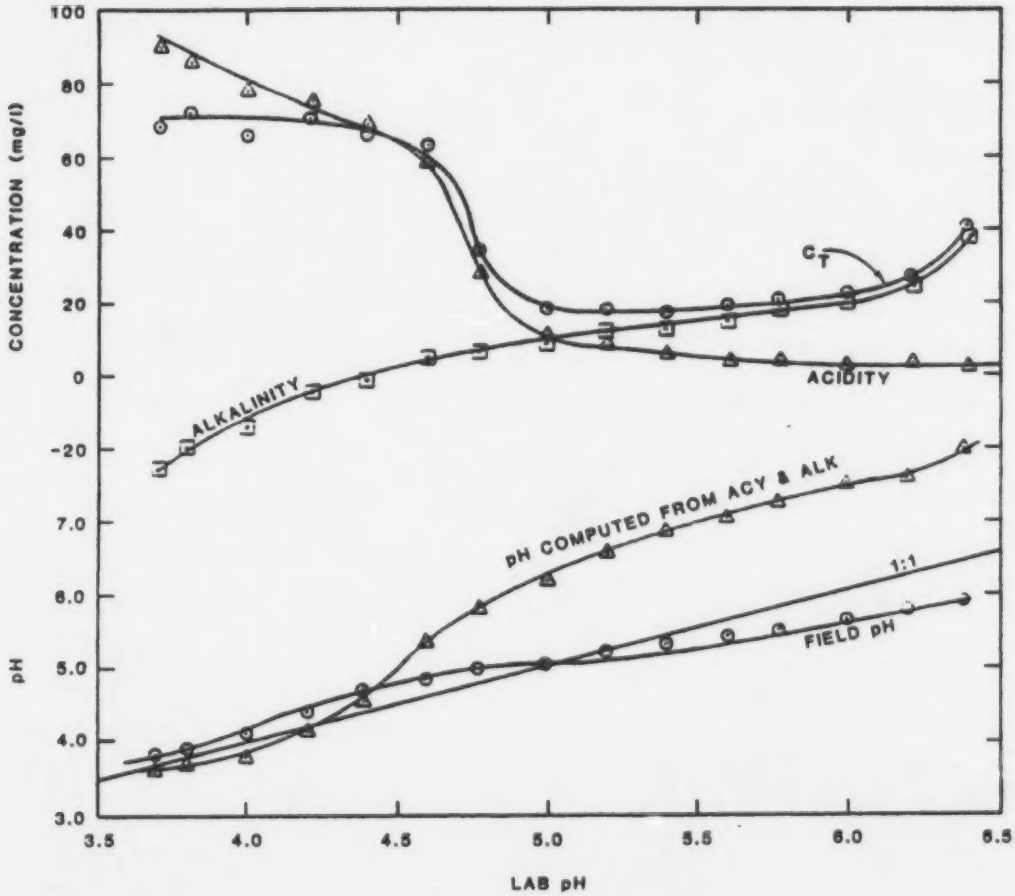


Figure 7.3 *pH and Carbonate Parameters Compared with Lab pH These values are mean values for all tests taken prior to Run No. 4. Figures 7.2 and 7.3 were prepared to illustrate the marked differences between the pH values measured in the field and in the lab and theoretical pH values computed from the results of the Acidity and Alkalinity tests. Resolution of the cause of these differences is necessary so that the test data can be evaluated in terms of chemical equilibrium.*

Carbonate System Equilibria: The relationships between pH, acidity and alkalinity are described by carbonate systems equilibria. Table 7.1 and Figure 7.4 identify the governing species and their relationship to one another in the carbonate equilibrium system. The alkalinity and acidity in the reactions are measured by titrating the water samples with an acid or base to the appropriate end point. The titration end points correspond to the equivalence points, x, y and z in Figure 7.4 The equivalence points define the Acid or Base Neutralization Capacity (ANC or BNC).

The equations in Table 7.1 define the theoretical acid-base neutralization capacities of the carbonate systems. Alkalinity and acidity are measures of the proton excess or deficiency of a solution with respect to a reference proton level (C_t). Titrations taken to the equivalence points f = 0 and f = 1 give the alkalinity and acidity values of a sample from which C_t is obtained as the difference in the titration values between the two equivalence points.

Point y on Figure 7.4 is the phenolphthalein end point. It represents the point at which the solution's ANC is capable of neutralizing an acid concentration equal to the C_t of the solution. Point x represents the end point of the alkalinity determination by "Standard Methods" (22). At this point the solution has no acid neutralization capacity. A negative ANC is common for AMD. The amount of base required to bring the solution to f = 0 (End Point x) is termed the mineral acidity, or, equivalently, free acidity or negative alkalinity. In this range, the solution is highly ionized and H^+ added will remain disassociated; a characteristic of a "Strong Acid". In contrast, a "weak" acid is only partially ionized. Aqueous CO_2 (H_2CO_3) acts like a weak acid and the resulting acid concentration is governed by the equilibrium constants given in Table 7.1.

The relationship of concentrations of alkalinity, acidity and total carbonate species (C_t) are independent of temperature, pressure and some selected changes in the solutions chemical composition. Graphs of pH contours can be constructed using these concentrations (C_t, Alk, Acy) which can be used to investigate equilibrium conditions. On Figure 7.5 Alkalinity is plotted as a function of C_t as derived from the equations in Table 7.1. Similarly, Figure 7.6 is a plot of C_t versus Acidity. On these graphs, the addition or removal of base, acid, CO_2, $CaCO_3$ or dilutions of the solution is a vector quantity.

The problems of reconciling the test data with equilibrium theory can be illustrated by plotting a typical neutralization result on Figures 7.5 and 7.6. For example, for a lab pH of 6.0 on Figure 7.3, we obtain the following average test results:

Alkalinity	=	20 mgl
Acidity	=	2 mgl
C_T	=	22 mgl

However, when alkalinity is plotted against C_t on Figure 7.5 (point A) and acidity against C_t on Figure 7.6, a pH value of 7.5 is obtained rather than the actual test value of 6.0. In order to move the plotted Point A from the 7.5 contour to the test 6.0 contour, the addition of an acid or CO_2 concentration is required in accordance with the vector diagrams on the graphs. In the case of our example a vertical translation of the axis by 15 mgl is necessary to reconcile the test values. This indicates that the solution contains an acid other than that derived from the H^+ ion and its presence is not being detected by the acid and alkalinity test values when they are related to the pH test value.

The discrepancy between the lab test values themselves and with neutralization theory created difficulty in analyzing the results of the first 3 runs. In order to resolve this problem, an expanded testing program was proposed, which included field testing for alkalinity and acidity.

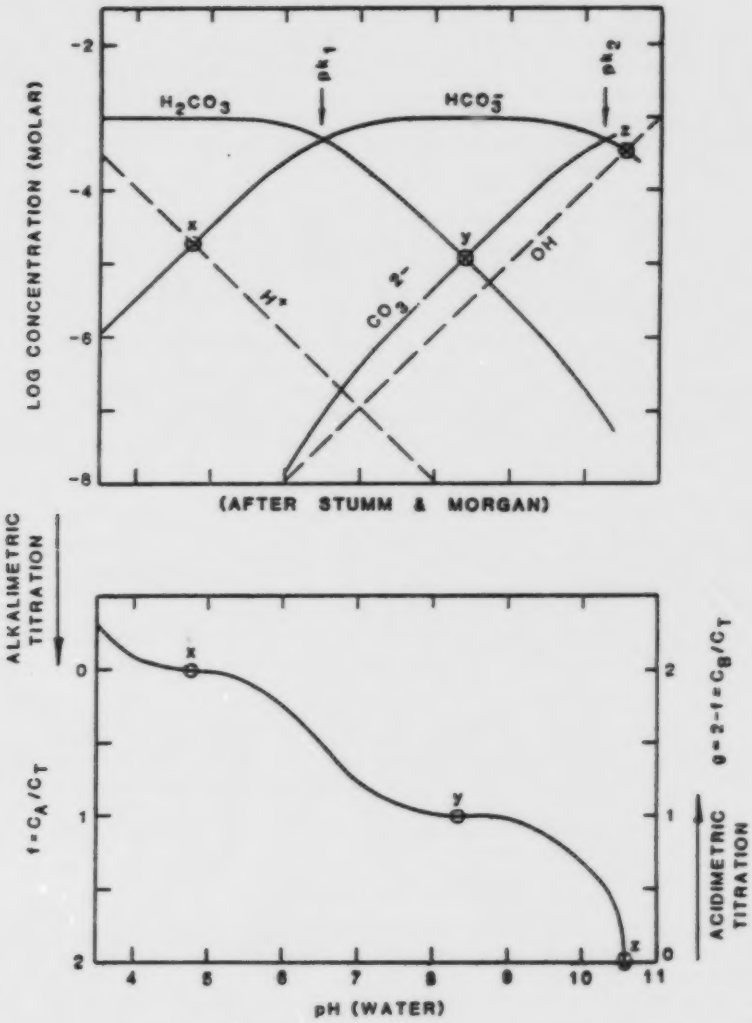


Figure 7.4 Carbonate Equilibrium Relationships
The equivalance points x,y,z correspond to pure solutions (C_TMolar) of H_2CO_3, $NaHCO_3$ and Na_2CO_3. pk is the negative logarithim of the first dissassociation constant. At this point H_2CO_3=HCO_3^-.

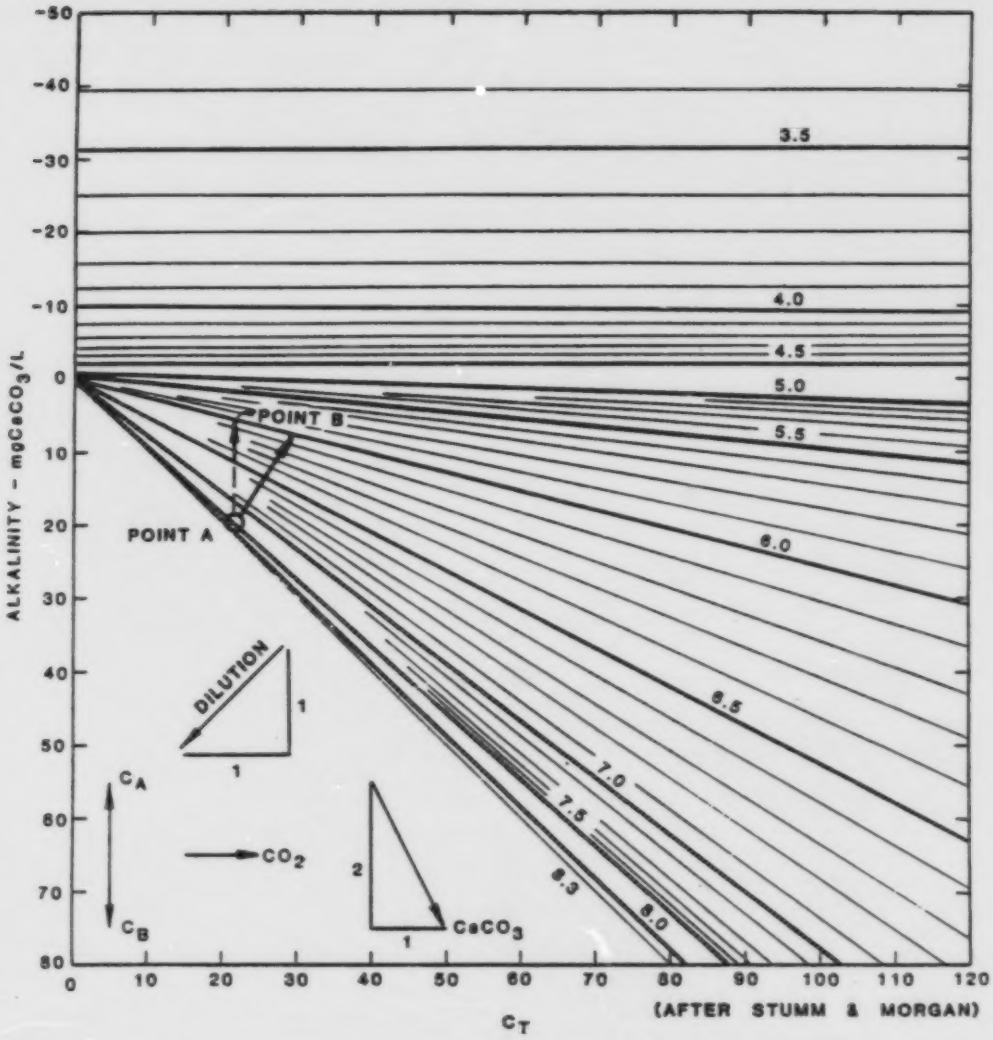


Figure 7.5 Theoretical Total Carbonate, pH and Alkalinity Relationship The usefullness of these graphs is based on the fact that changes in the carbonate solution can be represented as a vector. Adding a strong acid or base moves the point representing the initial solution composition vertically. Vertical lines would therefore represent titration curves. Note that changes in C_T do not affect alkalinity values In solutions that contain bases and acids other than H^+, OH^- and carbonate species, the contours in the diagrams will be displaced vertically. Therefore, if the solution represented by point A contained 15 mgl of acid caused by iron or aluminum, it would plot at point B on the 6.0 pH contour line.

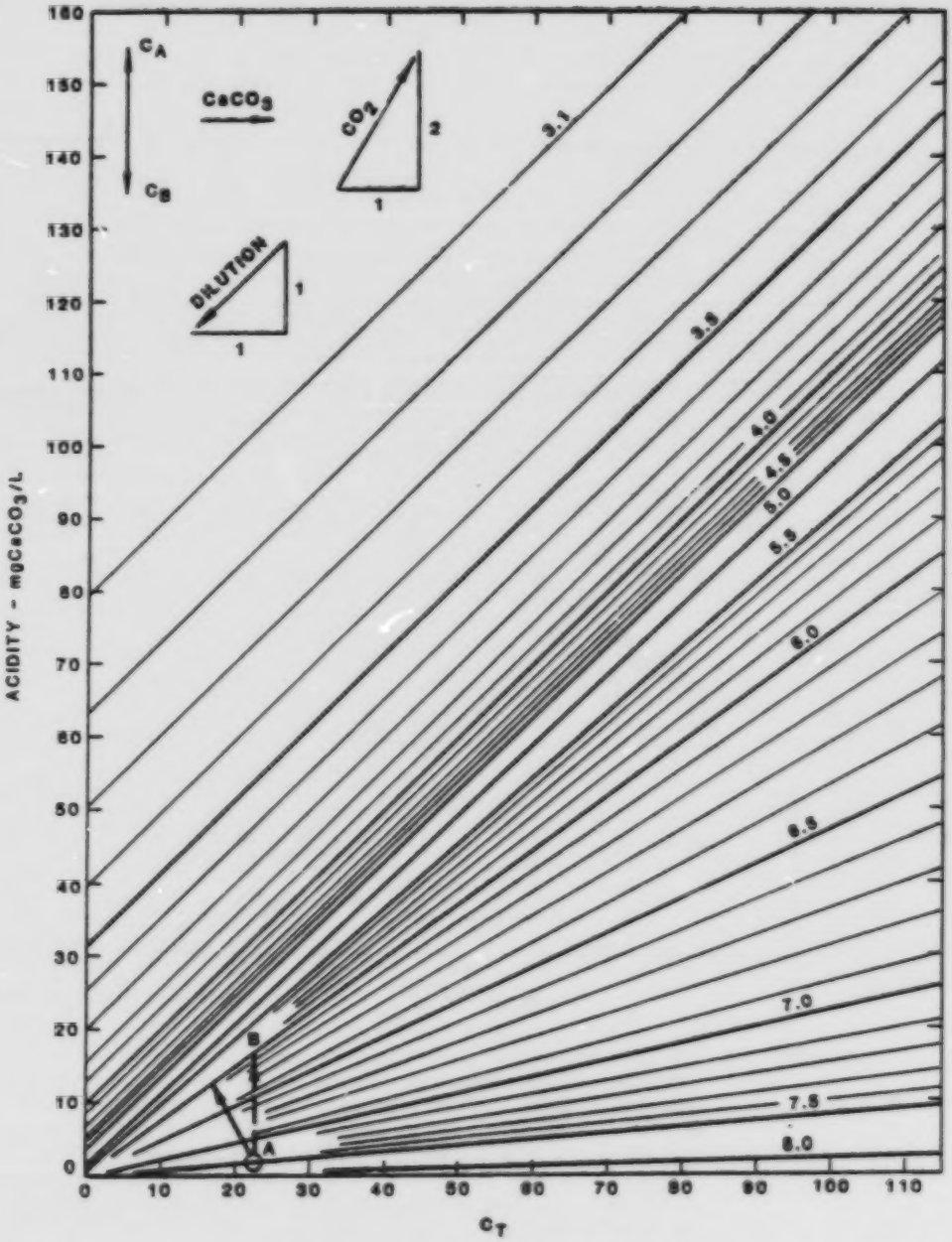


Figure 7.6 Theoretical Total Carbonate, pH and Acidity Relationship Note that the addition of $CaCO_3$ to the solution does not decrease the amount of acid in solution, but adds a base.

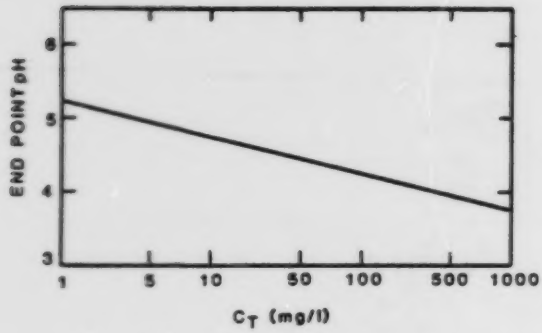


Figure 7.7 Alkalinity Endpoint Compared to Carbonate Concentration The Alkalinity endpoint is dependant on the total carbonate content.

Field Titration Results: All the field titration tests were performed immediately after the samples were obtained. Care was taken to minimize CO_2 losses caused by over-handling and mixing. Two types of titration were performed. First, a sample was titrated before the AMD could change temperature ("Cold" titration). A second sample was boiled ("Hot" titration) in accordance with Standard Methods (phenolphthalein acidity at boiling temperature). The boiling drives off all the free carbon dioxide and promotes the hydrolysis of iron and aluminum compounds. A relative measure of the carbon dioxide content is obtained from the difference between the hot and cold acidity titrations (amounts).

Plots of the "Hot" and "Cold" titration results are presented in Figure 7.8. As expected, the "Cold" acidity values were much higher than the "Hot" values due to the aqueous carbon dioxide. However, the alkalinity titrations were not expected to show a large increase in mineral acidity. The high "Hot" acidity levels at pH's greater than 5.0 were unexpected as well.

A typical set of titration curves, presented in Figure 7.9, illustrates the effects of the carbon dioxide content and mineral acidity. The increase in mineral acidity is attributed to aluminum hydrolysis since iron levels, generally 1.0± mg/l, could not have caused the increased mineral acidity through ferrous-ferric oxidation. The "Hot" acidity values for Run No. 4 are compared with the acidity curve computed for 13 mgl of aluminum in Figure 7.10. As can be seen from this, the acidity beyond the strong (mineral) acid range is caused primarily by partially disassociated aluminum species acting as a weak acid.

Figure 7.11 suggests why the acidity caused by the aluminum species was not identified prior to Run No. 4. The low laboratory acidity values, beyond pH = 5, led to the assumption that, once the mineral acidity was neutralized, the remaining acidity would be predominately CO_2 acidity. It was also assumed that the iron and aluminum contributed primarily mineral acidity which was largely converted to a precipitate beyond pH = 5.5. The results of the field titrations in Run No. 4 show these assumptions to be incorrect, indicating that the chemical evaluation of the neutralization process is more complex than previously assumed.

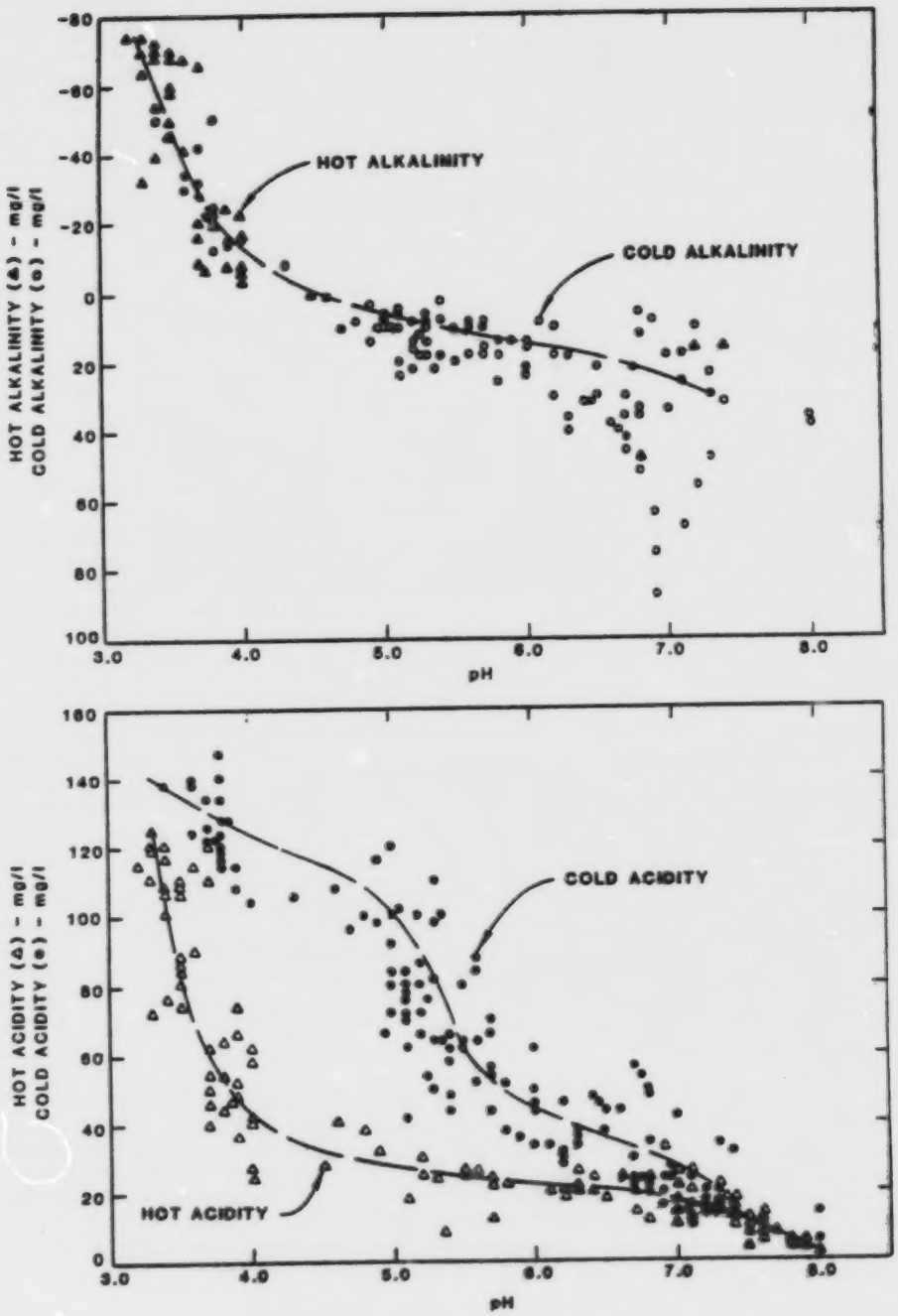


Figure 7.8 Comparison of Hot & Cold Acidity - Alkalinity Tests

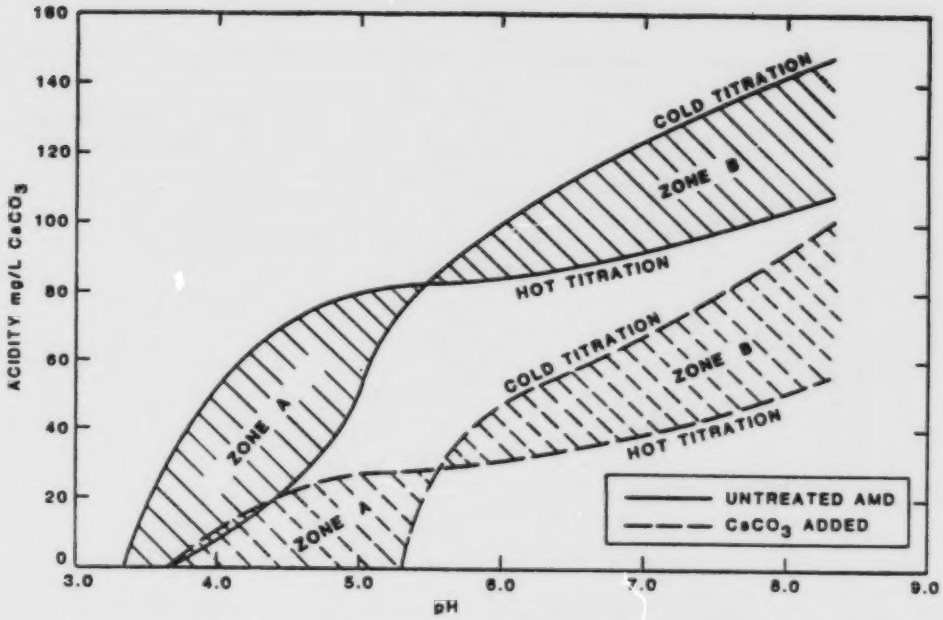


Figure 7.9 Typical Field Titration Test Results
The differences causing Zone A are attributed to mineral acid formation by oxidation while Zone B represents the differences in CO_2 concentrations.

Neutralization Computations: The numerical model of the neutralization process was modified since the previous model considered only carbonate alkalinity and buffering. As previously shown, the addition of terms for the aluminum species would have been sufficient to adequately model the Quakake AMD, but in order for the procedure to have a more general application, the acidity due to ferric and ferrous iron species was included. Consequently, the alkalinity term was redefined as:

$$
\begin{aligned}
[Alk] = \; & [HCO_3^-] - [H^+] - [HSO_4^-] \\
-3 \; & [Al^{+3}] - 2[Al(OH)^{+2}] - [Al(OH)_2^+] \\
-3 \; & [Fe^{+3}] - 2[Fe(OH)^{+2}] - [Fe(OH)_2^+] \\
-2 \; & [Fe^{+2}] - [Fe(OH^+)]
\end{aligned}
$$

The strength of the acidity contributed to the solution is computed in terms of ionization fractions by procedures similar to those used for the carbonic system. The expressions representing all species become extremely cumbersome as the Iron and Aluminum ions are polyprotic (i.e. able to donate more than one proton). Therefore, the species included were limited to those species having the greatest effect on the system (i.e. those with an equilibrium constant within or close to the (H^+) concentrations representing the range of pH under consideration; A pH = 3.0 to 8.3). Even with these limitations, the governing equations are lengthy. A detailed description and derivation of the computation procedures are presented in Appendix "D." The relative importance of the various acid forming elements are shown in terms of acidity (Figure 7.12) and buffering intensity (Figure 7.13). Buffering intensity represents the resistance to pH change provided by a particular element of the AMD system.

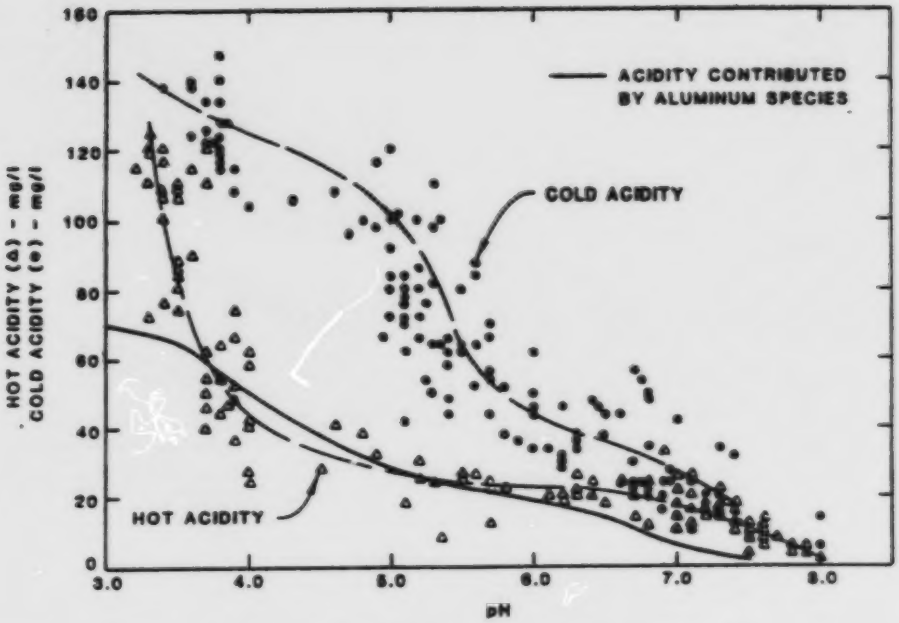


Figure 7.10 Theoretical Acidity from Al^{+++} Compared with Field Tests

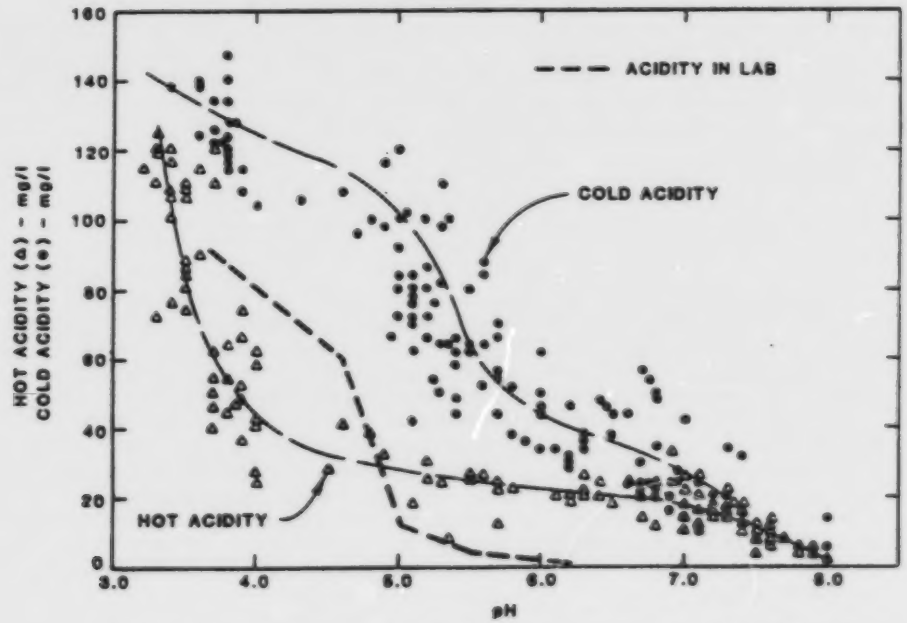


Figure 7.11 Laboratory Acidity Tests Compared with Field Tests

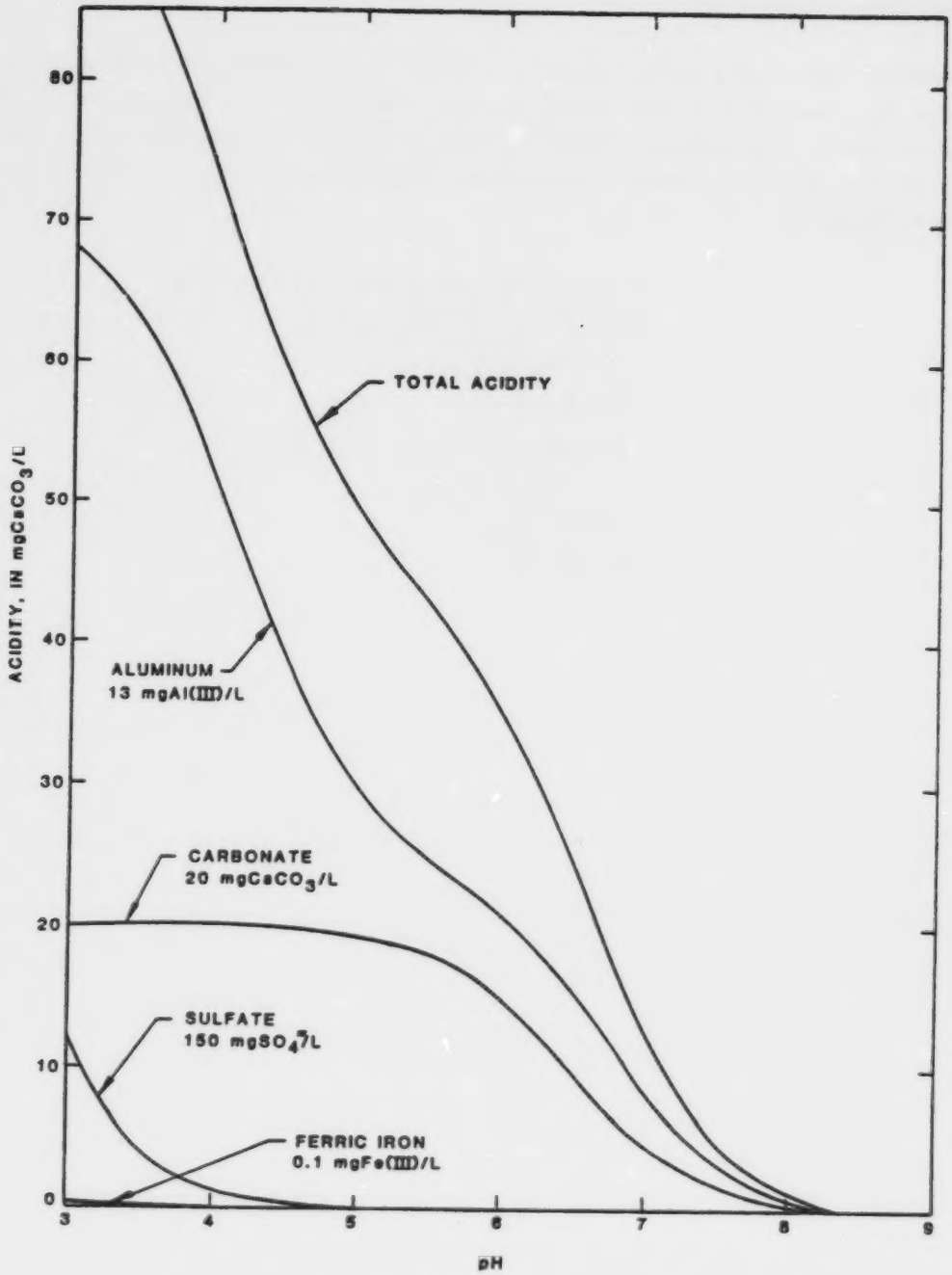


Figure 7.12 Computed Acidity of the Quakake Tunnel AMD

LIMESTONE COLUMN TEST

A limestone AMD neutralization column was tested at a Canadian mine-mill complex. An excerpt from the report on these tests provides some insight into some further aspects of limestone use for this purpose. Further details on the use of a limestone column might be available from one of the NORANDA employees involved who is now a consultant, or from Noranda Research.

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Telex: 05-268-745
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NORANDA RESEARCH CENTRE
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FURTHER LABORATORY STUDIES

Introduction

Although the pilot plant studies had indicated no positive advantage of limestone neutralization for the strong [redacted] drainage, it was felt that the process might be successful with weaker minewaters. It was hoped to include a period of limestone neutralization in the final demonstration run with the weaker [redacted] drainage. It was recognized, however, that a comprehensive laboratory evaluation was required to define as closely as possible the performance to be expected from the pilot column. In the light of previous experience, long laboratory runs were planned and in the first phase a synthetic minewater was used which corresponded closely to the actual Heath Steele drainage. In the second phase, conducted at the pilot plant, actual minewater and local limestone were used. Thus any difference between the pilot and laboratory results could be attributed to scale-up effects.

Operations

The column used in these laboratory studies was 2.44 m (8 ft.) high, 3.81 cm (1.5 in.) in inside diameter and was constructed of transparent acrylic material. All column joints were sealed with rubber gaskets. The minewater was pumped upwards through the column and the effluent was carried from the top of the column through a length of Tygon tubing. A 1.22 m (4 ft.) bed of crushed limestone was supported by a distribution plate with 2.4 mm (0.094 in.) diameter holes on 1.27 cm (0.5 in) centers. The particle size range of the limestone was from 1.68 mm (0.067 in.) to 1.0 mm (0.039 in.). The bed was pulsed with air by an electrically controlled solenoid valve, using the standard cycle of 2 seconds "on" and 3 seconds "off".

In the first phase, two 4-hr. runs were conducted at each of three flow rates: 4.54 lpm/m^2 (0.11 U.S. gpm/ft^2) 9.1 lpm/m^2

TABLE 2-33

[redacted] Drainage

Limestone/Lime Run (January 18 - March 29, 1974)

Clarifier Overflow Metal Levels

		Lead (Pb)				Zinc (Zn)				Copper (Cu)				Iron (Fe)			
		AV*	SD	CV	RG	AV	SD	CV	RG	AV	SD	CV	RG	AV	SD	CV	RG
Period		mg/l	mg/l	%	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	%	mg/l
1	D+	0.18	0.05	30.5	0.10-0.30	0.32	0.12	36.1	0.16-0.70	0.03	0.01	26.5	0.02-0.04	0.18	0.08	43.6	0.07-0.4[illegible]
	E	0.21	0.06	27.0	0.10-0.30	0.50	0.23	45.2	0.28-1.16	0.04	0.01	36.2	0.02-0.08	0.29	0.17	55.7	0.10-0.[illegible]4
2	D	0.16	0.05	31.0	0.09-0.25	0.26	0.12	46.9	0.13-0.47	0.03	0.01	20.8	0.02-0.04	0.20	0.09	46.0	0.08-0.3[illegible]
	E	0.18	0.07	39.9	0.03-0.24	0.30	0.13	43.5	0.12-0.53	0.03	0.01	13.7	0.03-0.04	0.28	0.14	51.6	0.12-0.52
3	D	0.18	0.04	23.1	0.10-0.25	0.15	0.15	95.2	0.06-0.75	0.03	0.01	28.3	0.01-0.04	0.23	0.17	75.3	0.08-0.91
	E	0.21	0.06	27.9	0.13-0.34	0.43	0.41	96.5	0.13-1.59	0.03	0.01	25.8	0.01-0.04	0.60	0.46	76.7	0.13-1.75
Overall	D	0.17	0.05	27.2	0.09-0.30	0.24	0.15	62.9	0.06-0.75	0.03	0.01	26.4	0.01-0.04	0.21	0.13	62.7	0.07-0.91
	E	0.21	0.06	29.2	0.03-0.34	0.43	0.32	73.6	0.12-1.59	0.03	0.01	33.1	0.01-0.08	0.42	0.36	84.5	0.10-1.75

NOTE: * AV - Arithmetic Mean
SD - Standard Deviation
CV - Coefficient of Variation
RG - range

+ D - Dissolved metal level
E - Extractable metal level

TABLE 2-34

[redacted]. [redacted] Drainage

Limestone/Lime Run (January 18 - March 29, 1974)

Effluent Polishing Results

Extractable Metal Levels

	Lead (Pb)				Zinc (Zn)				Copper (Cu)				Iron (Fe)			
Period	AV*	SD	CV	RG	AV	SD	CV	RG	AV	SD	CV	RG	AV	SD	CV	RG
	mg/l	mg/l	%	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	%	mg/l
								Sand Filtration								
1*	0.19	0.08	43.2	0.01-0.30	0.27	0.14	49.8	0.10-0.50	0.03	0.01	27.1	0.02-0.04	0.13	0.07	53.8	0.07-0.30
2*	0.16	0.05	29.2	0.07-0.26	0.09	0.03	33.3	0.06-0.17	0.03	0.01	29.8	0.01-0.04	0.17	0.07	42.3	0.08-0.34
Overall	0.17	0.06	35.7	0.01-0.30	0.15	0.12	79.4	0.06-0.50	0.03	0.01	28.7	0.01-0.04	0.15	0.07	45.8	0.07-0.34
Clarifier Overflow	0.22	0.07	32.4	0.03-0.34	0.35	0.22	63.1	0.01-1.16	0.03	0.01	24.9	0.01-0.05	0.44	0.38	85.7	0.12-1.75
								Bucket Settling								
Overall	0.11	0.06	55.6	0.01-0.17	0.25	0.17	67.2	0.05-0.45	0.02	0.01	22.0	0.02-0.03	0.10	0.04	40.8	0.05-0.17
Clarifier Overflow	0.17	0.04	25.5	0.10-0.22	0.46	0.19	41.6	0.30-0.83	0.04	0.01	33.7	0.02-0.06	0.21	0.12	55.5	0.10-0.43

NOTE: * AV - arithmetic mean
SD - standard deviation
CV - coefficient of variation
RG - range

* Period 1 - filtrate backwashed
Period 2 - cleanwater backwashed

surface as would happen if slugging were occurring. A definite cause of the poor performance of the pilot scale limestone column with Brunswick No. 12 drainage could not be assigned, because of the effects of the various factors could not be separated without conducting further laboratory studies. These were not considered justifiable in view of the poor pilot plant performance. However, the experience showed the need for more comprehensive laboratory evaluation if limestone neutralization were to be considered for other minewaters.

Effluent Levels The analyses of the metal levels in the clarifier overflow (both extractable and dissolved) based on the three periods of operation, as well as on the overall run, are shown in Table 2-33. These results indicate that the clarifier overflow levels were independent not only on the height of the limestone column but also of the flowrate of the pulsing air, and the column feedrate. In addition, there was no difference in performance between a pulse cycle of 2 seconds on/3 seconds off and one of 1 second on/2 seconds off.

Table 2-34 presents the analyses of the effluent polishing results, both sand filtration and 24 hour bucket settled. Besides the results based on all the tests, sand filtration results were also analysed on the basis of the backwash used (Period 1 using a filtrate backwash, Period 2 using freshwater backwash) as indicated in Table 2-34. The analyses of the extractable metal levels in the clarifier overflow based on the different times during which the effluent polishing tests were performed are also shown in Table 2-34 for comparison purposes. Both polishing methods effectively reduced the clarifier effluent metal levels. No significant differences were noted between the results obtained by either technique. Sand filtration using freshwater backwash resulted in lower metal levels compared to operation with filtrate backwash. Filtrate backwashing resulted in gypsum precipitation in, and fouling of, the sand filters giving rise to poorer performance.

Sludge Characteristics Even though the sludge produced during this run contained some carbonate as a result of the initial limestone treatment, its characteristics would not be expected to differ too much from a sludge produced during lime only treatment since gypsum would be the

ferrous ion. The ratio of ferrous/total iron increased from 0.77 to 0.97 on passing through the limestone column reflecting the relative solubilities of the iron carbonates (or hydroxy-carbonate complexes) at the pH's encountered in the column.

An attempt was made to identify the factors responsible for the poorer-than-anticipated performance of the limestone column. Mechanical failures could not be blamed entirely, as poor results had occurred even when the actual operation of the column had been satisfactory. Three factors were considered to be primarily responsible: inadequate length of laboratory tests, differences between synthetic and actual minewater and scale-up effects (particularly, the reduced "slugging" effect and lower abrasion of the solids was obtained in the larger column). The use of a different limestone was not considered to be important, since both were classified as "high calcium". In laboratory tests, it was assumed that equilibrium had been reached when a constant effluent pH was achieved for 1 or 2 hours operation. However, this may not have been the true equilibrium. The synthetic minewater used in the laboratory tests contained very large concentrations of sulphates (17,000 mg/l) and sodium hydroxide, which had been added to raise the initial pH. Cursory measurements made during the laboratory trials indicated greater than 60 percent neutralization of acidity through the column at an effluent pH of 5.2 - 5.5. It is suspected that there was a significant difference between pH response and buffering capacity of the synthetic and of the real minewater. In the synthetic minewater, all the iron was in the ferrous form, whereas in the actual minewater a large portion of it was initially in the ferric state. Since studies have indicated that coating of the limestone is associated with the formation of ferric hydroxy complexes in the pH range 2 to 3, the actual minewater would be expected to coat the limestone more. The abrasion in the large column was likely inferior to that in the small one because of the absence of true slugging action. To achieve slugging, the bubble diameter must be at least as great as the column diameter. Although the actual movement of the limestone could not be seen in the large column, observation of the liquid surface above the limestone showed an upwelling in the centre of the column, rather than upward movement of the entire

TABLE 2-32

Analyses of Limestone Column Overflow

Limestone/Lime Run (January 18 - March 29, 1974)

Parameter	Arithmetic Mean	Standard Deviation	Coefficient Of Variation	Range
	mg/l	mg/l	%	mg/l
		Overall		
Lead+ (Pb)	0.93	0.36	38.7	0.41 - 2.0
Zinc (Zn)	898.0	68.3	7.6	700 - 990
Copper (Cu)	5.64	1.43	25.3	2.65 - 8.90
Iron (Fe* - Total)	752.0	122.0	16.2	400 - 966
Sulphates ($SO_4^{=}$)	7,749.8	682.3	8.9	6288 - 9816
Acidity	4,200.3	437.9	10.4	3170 - 5395
Period		Periods		
1 Sulphates	7,394.8	435.2	5.9	6288 - 8064
Acidity	3,994.7	361.8	9.1	3170 - 4750
2 Sulphates	8,336.0	805.7	9.7	7776 - 9816
Acidity	4,504.0	520.5	11.6	3950 - 5395
3 Sulphates	8,202.0	503.1	6.1	7680 - 8664
Acidity	4,341.0	371.2	8.6	3905 - 4820

NOTE *Fe^{++}/Fe (Total = 0.97 (by weight)

+All metals are extractable values

Operation of the limestone column proved fairly straightforward. No difficulties were encountered in feeding, charging or cleaning the column. In addition, the bed showed no tendency to bind due to calcium sulphate precipitation as long as the unit was pulsed with air (rather than continuously air fed). For most of the run, a two second on, three second off air pulse at a rate of 707 lpm (25 cfm) was used; however, between January 25 to February 5 difficulties were encountered with the solenoid timing valve and air was fed continuously during this period.

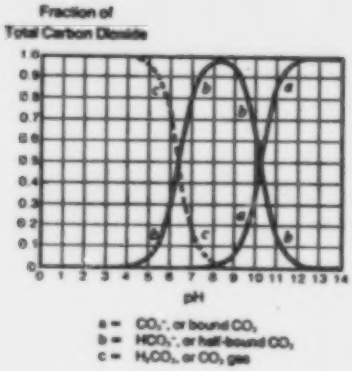
Results

Limestone Column Analyses of the limestone column effluent parameters based on the entire run and on the periods of operation are given in Table 2-32. Metal analyses based on the entire run are given also. Overall, only about 22% of the acidity of the acid mine drainage was removed by the limestone column. Acidity removals for the three operational periods were 25%, 16% and 19% respectively. The actual height of the limestone column had little effect on acidity removal. The increase in acidity reduction over Period 1 was due at least in part to the recharging of the bed. A short period of poor performance during this period (due to timer problems) caused substantial deposition of iron hydroxide on the limestone and the reactor had to be recharged with fresh limestone. The removal of acidity by the limestone column was much less than anticipated.

The limestone column caused a decrease in the sulphate content of the influent. Mean influent sulphate values of 7,680 mg/l, 8,548 mg/l and 8,778 mg/l for the three operational periods decreased to corresponding effluent values of 7,395, 8,336 mg/l and 8,202 mg/l.

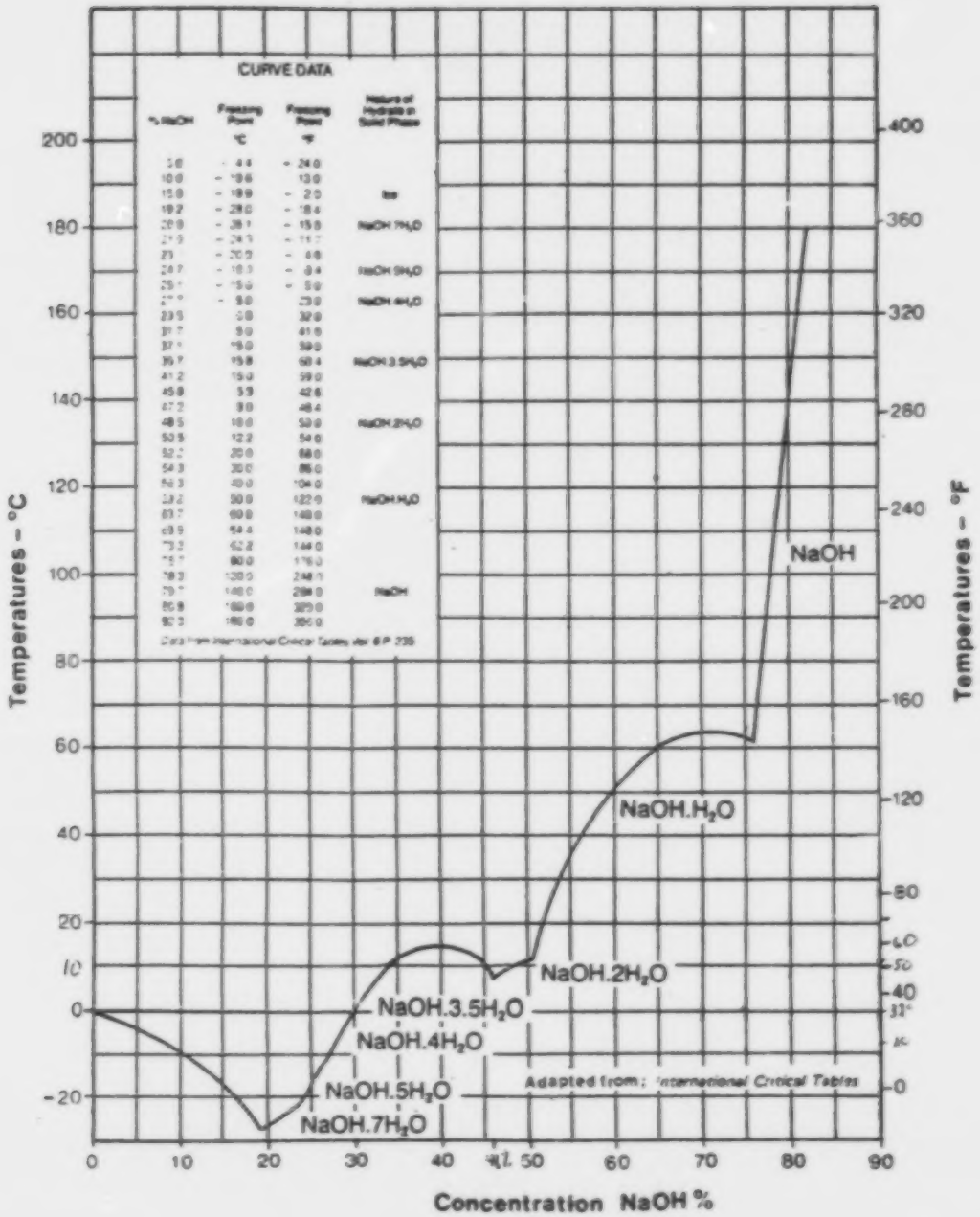
The limestone column also effected the removal from solution of heavy metals by precipitation. Based on mean dissolved values determined by the overall run, zinc, copper, total iron and lead removals were 1.5, 11.0, 34.0 and 61.0% by weight respectively. This trend in metals removal reflects the relative difficulty in removing the various heavy metals from solution in the pH range 4-6. The column also caused the precipitation of most of the ferric ion but little of Fe^{++}

Effect of changing pH on distribution of different CO_2 related ions in solution.



PEARSON, et al. (1982) present a theory on the decarbonation process and design procedures for CO_2 removal from limestone-treated mine wastewaters and provided equations and nomographs for the stripping of CO_2 from wastewater by air.

Freezing Points of Caustic Soda Solution



NAOH NEUTRALIZATION OF AMD

Use of NaOH for AMD treatment would normally not be considered economically attractive. NaOH, although consumed stoichiometrically, costs much more than lime. One advantage of NaOH, especially where solutions must be recycled many times, is that no gypsum builds up with its related scale problems.

For small installations which do not justify the capital cost of an HDS plant or even an agitated lime reactor, lime addition system, flocculant makeup system, thickener, etc., the much simpler equipment needed for NaOH addition may prove to be cost effective after all. The small additional cost of reagent will be more than justified by capital cost savings.

Three interesting applications of NaOH were observed for AMD treatment.

- Falconbridge Onaping Minewater, Ontario

Water pumped from the Onaping mine amounts to a small flowrate (about 103,000 Igpd or 470 m^3/d) but required neutralization nonetheless to precipitate dissolved nickel and to raise the pH high enough to precipitate nickel at pH10. The minewater, while the mine is in operation, runs pH 9-12. Because the volume is small and minor pH adjustment is only sometimes needed, this was achieved using a 50% NaOH solution metered directly from drums. Only 15 gpd was needed.

When the mine shut down temporarily, however, pH of AMD dropped back to 7 because cemented backfill was no longer being pumped underground, and the advantages of NaOH over lime were less apparent.

The neutralized minewater drains by gravity to a small settling pond fitted with a floating plastic boom curtain to increase the residence time. Metal hydroxides, mainly of nickel and iron, precipitated and sank to the bottom of this pond leaving a clear supernatant to discharge.

Two interesting phenomena should be taken into account. First, in cold conditions great care must be taken when using liquid NaOH solutions as they have very high freezing temperatures as shown on the following graph. 50% NaOH freezes around 54°F. The second phenomenon has to do with the discharge of sewage from the mine into this settling pond. Sludges settled to the bottom as well, where, because of warm conditions in summer in the shallow pond, bacterial action generated gases which attached themselves as minute bubbles to precipitate sludge particles on the floor of the pond. This occured to an extent that the sludges containing 6% Ni were floating to the surface and discharging to the greater lake water system. Not much of this precipitate needs to get into a water sample to get a very high reading.

More can be learned about this phenomenon from:

FALCONBRIDGE NICKEL MINES LTD.
Onaping, Ontario P0M 2R0
(705) 966-3411
Mark Wiseman

Quotations on NaOH supply can be obtained from:

CIL CHEMICALS LTD.
90 Sheppard Avenue East
Willowdale, Ontario M2N 6H2
(416) 229-7000

IN-LINE AERATON FOR ACID MINE DRAINAGE

The U.S. Bureau of Mines IN Pittsburgh, Pennsylvania, has developed a simple low capital cost device to treat AMD using NaOH as a neutralizing reagent. Their system is described by ACKMAN and KLEINMANN (1984).

The basis for the system is to use a jet pump to inject air and caustic soda into the system which subjects the water to be treated to instantaneous rapid pH change. After mixing in the jet pump, a static mixer is used. These flocs settle well to yield a normal sludge density of 2-3%.

Of interest is the fact that the precipitate settles as a green ferric hydroxide sludge which oxidizes as it ages to a red ferric hydroxide of a day or two.

One amazing feature is the behavior of manganese. When an AMD solution containing 70 ppm Mn was tested, about 50% of the Mn precipitated and settled at pH 4-5 and almost quantitatively at pH 7-9.

In the case of a West Virginia coal mine, AMD containing 900-1000 ppm Fe^{2+}, all the iron could not be precipitated at once, and two in-line systems were needed in series, each associated with a separate settling pond. Decant solutions meeting the regulatory discharge levels were very easily achieved.

The advantage of the in-line system is that it has no moving parts and is designed to fit on the end of the pipeline delivering the AMD from underground.

The system consists of a venturi jet pump with a mixing chamber and an internally spiralled static mixer. The small scale unit could achieve the same result as a conventional lime-aeration device costing over a million dollars.

Normally, solutions containing 500 ppm Fe^{2+} and 10-20 ppm Mn can be handled in one pass. One solution containing 70 ppm Mn was tested, and it achieved a 30 ppm Mn effluent in one pass. The portable unit was to be tested on more sites during the summer of 1984.

There is a fair degree of oxidation of Fe^{2+} to Fe^{3+} even without adding alkali to the system. For example one solution containing 20 ppm Fe^{2+} was treated at pH 5.5-6, and the iron in the ILS effluent was dropped to below 1 ppm without alkali addition.

Further tests are in progress using lime and pulverized limestone and by the 1985 Technology Transfer meeting anticipated by the AMD Group at the USBM Bruceton Laboratories; they hope to have design data.

Several design observations have been made:

- The higher the water pressure, the more air is drawn into the system.
- 20% caustic solution is a convenient way to add NaOH together with the air flow.
- A 4"Ø trash pump from suppliers like Homelite give only 20 psi and, using the jets alone without static mixer, only 14% of the iron was oxidized.
- Larger pumps are prefered as these give 40 psi, but without a static mixer, only 14-15% of the iron oxidizes.
- To accommodate larger flows, several jet pumps can be mounted in parallel.
- 1500 gpm has been handled through three jets in parallel. A maximum of 200 psi is recommended.

THE USBM ESTIMATES THAT OVER $1 MILLION/DAY IS SPENT BY THE MINING INDUSTRY ON ACID NEUTRALIZATION, AND OVER 5000 MILES OF STREAMS ARE ADVERSELY AFFECTED BY AMD THAT HAS NOT BEEN TREATED.

FEATURES OF THE IN-LINE AERATOR SYSTEM (ILS)

1) Simultaneous aeration and neutralization.
2) Extremely rapid oxidation of ferrous ions.
3) Low capital cost of equipment.
4) Low maintenance equipment.
5) Reduced space requirements.

Meanwhile, it is known that at least two companies are working on commercial applications of this sort for jet pumps.

A 6" aquaflow hydraulic submersible trash pump was used with some success in conjunction with the ILS test rig. These are available from among others:

MARK PLACE
Post Office Box 10926
Pittsburgh, PA 15236
(412) 892-2000

Feed to the pump should be screened to keep the ¼" holes in the jet from clogging.

A 12"Ø Helix or static mixer is used as supplied by Polcon Sales Ltd.

The system has been demonstrated at a flow rates of 300-1500 U.S. gpm.

Interesting pH phenomema have been observed. For example, pH could likely be at 6-9 at the exit point of the air jet but have dropped at the end of the day in the pond to pH 4-6. By the following day, pH in the pond has dropped further to pH 3-4. This no doubt is due to the oxidation of ferrous to ferric hydroxide in the precipitates.

The ILS treatment method has been tested and applied by the U.S. Bureau of Mines. One location where it is used is:

KITT ENERGY COMPANY
BCNR Mining Division
Meadowland, PA
(412) 228-8400
Tom Simonetti

The Bureau of Mines uses the Penberthy jet pump; the supplier's address is shown below:

The best source of design parameters for this system is:

BUREAU OF MINES
U.S. Dept. of the Interior
Bruceton Research Laboratories
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Terry E. Ackman

Penberthy jet pumps are available in PVC up to the 3" model which costs $812 each. Larger units in iron cost much more--for example, the least expensive 6" unit in iron costs $1,812 per jet. These are designed to provide aeration and mixing for relatively low pressure flows.

PENBERTHY DIVISION
Houdaille Industries, Inc.
Prophetstown, IL 61277
(815) 537-2311
Telex: 25-7339
Ken Bowman

The Pittsburgh agents for the Penberthy jet pump are:

M. S. JACOBS AND ASSOCIATES, INC.
810 Noblestown Road
Pittsburgh, PA 15205
(412) 923-2090
Kenny Aquadro

BARRETT, HAENTJENS AND CO.
225 North Cedar Street
Hazelton, PA
(717) 455-7711
John R. Ackerman

Barrett, Haentjens & Co. have developed an improved jet pump for turbulent mixing of dry reagents, water, and air in the same reactor placed in line with a pump.

The patented Turbojet system has multiple jacket chambers in the jet pump for mixing and multiple nozzles up to 24 or 48. The units are available in three sizes, the largest of which is priced at $16,000. They are made of 316 stainless steel.

The three sizes are:

100- 300 gpm
300- 600 gpm
600-1000 gpm

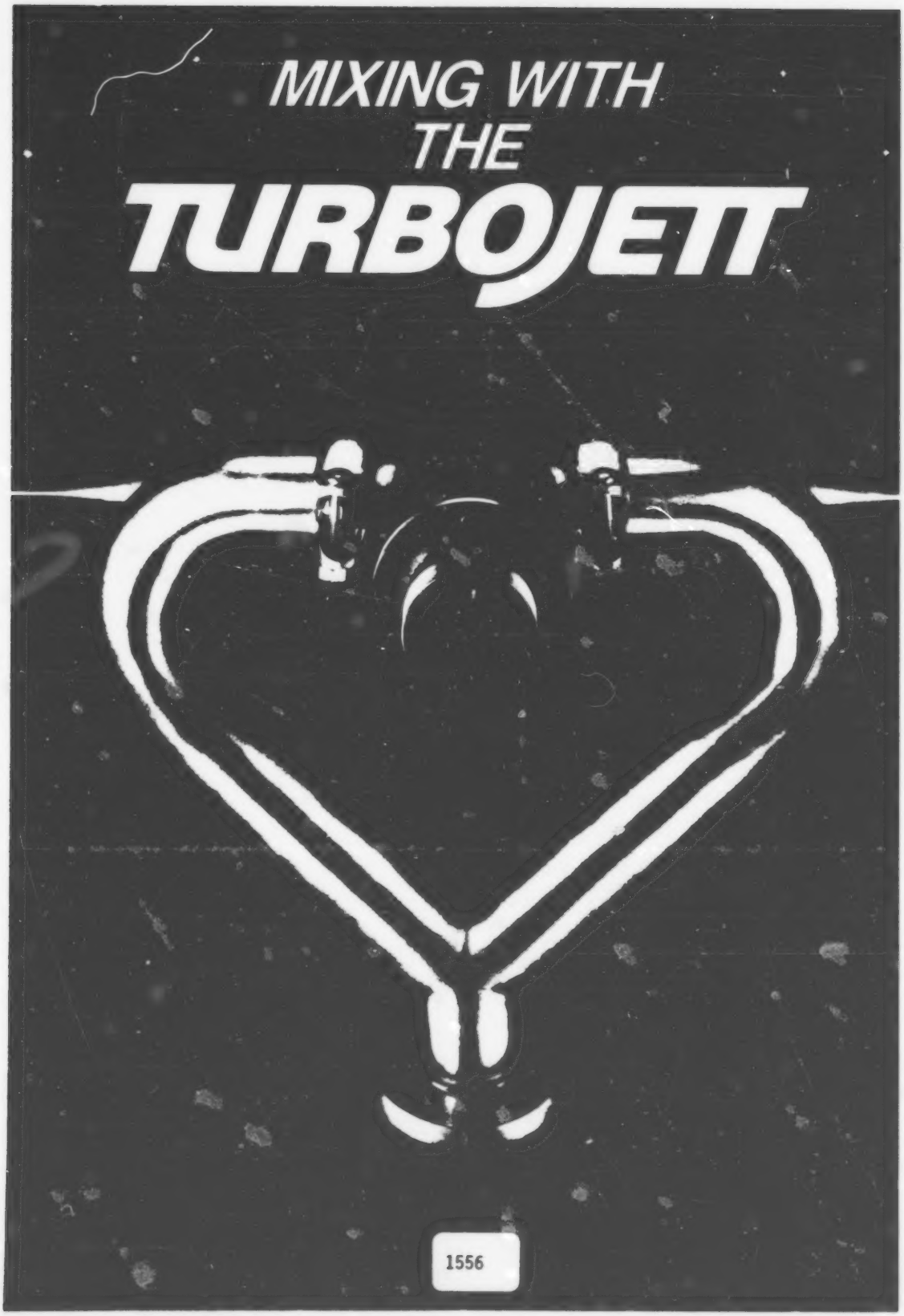
The 1000 gpm model aspirates 400 cfm air.

Barrett and Haentjens have tested, with satisfactory results, the use of dry lime and even limestone dust for direct application in the Turbojet to remove iron from AMD. They are now working on a dry lime delivery system.

The first commercial scale Turbojet system is being installed at SOHIO COAL CO.'s Guys Run coal preparation plant at Fairmont, West Virginia. It will use NaOH as reagent purchased dry and fed as a 20% solution.

Barrett, Haentjens and Co. are eager to combine the Turbojet and HDS processes and with their hydrorake sludge transport system.

MIXING WITH THE TURBOJETT



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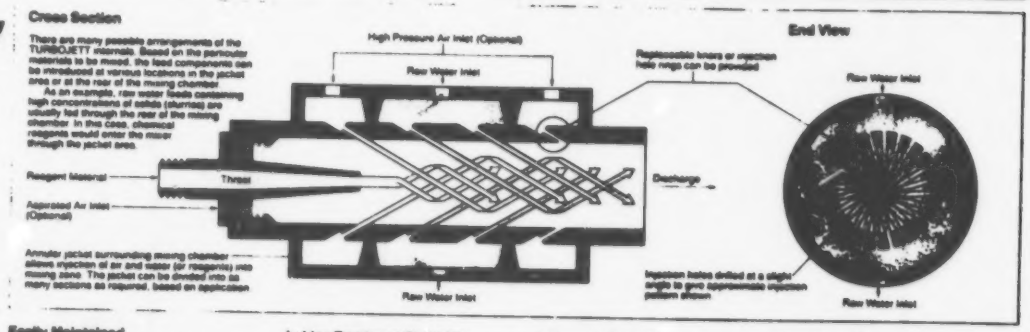
HAZLETON TURBOJETT SYSTEMS*

The TURBOJETT System is a new and unique high intensity turbulent mixer. The TURBOJETT System can be effectively utilized to mix any combination of liquids, solids, and gases. Since the high intensity mixing is done efficiently, the cost of reagents is minimized. The TURBOJETT mixer is easily maintained and has no moving parts. TURBOJETT mixers incorporate all of the elements of a complete treatment process. An entire treatment system can be self-contained and portable.

Cross Section

There are many possible arrangements of the TURBOJETT internals. Based on the particular materials to be mixed, the feed components can be introduced at various locations in the jacket area or at the rear of the mixing chamber.

As an example, raw water feeds containing high concentrations of solids (slurries) are usually fed through the rear of the mixing chamber. In this case, chemical reagents would enter the mixer through the jacket area.



Annular jacket surrounding mixing chamber allows injection of air and water (or reagents) into mixing zone. The jacket can be divided into as many sections as required, based on application

TURBOJETT DESIGN FEATURES

Efficient

Field tests have demonstrated that a TURBOJETT System can meet or exceed the performance of higher cost, stationary mixers and aerators. TURBOJETT mixers effectively utilize chemical reagents when combined with a well controlled and monitored reagent feed system.

Portable

Since the TURBOJETT design requires no mixing or aeration tanks, a complete treatment system can easily be arranged on skids or trailers to be moved from one location to another. Systems can be electrically powered or engine driven.

Adaptable Design

Our engineers will "custom design" a total system to meet YOUR specific needs. Flows larger than 50 GPM can be processed economically. Flows ranging in thousands of GPM can be handled by larger and/or multiple mixers. Materials of construction are available to handle most acidic, alkaline, and/or abrasive mixtures. Designs can easily be up-graded to accommodate increased capacity at minimal cost. Mixer internal porting can be provided as separate, replaceable rings to accommodate changing flow rates or abrasive wear problems. Our engineers can advise you if the TURBOJETT can be retro-fitted to your present operation.

Easily Freeze-Protected

Requiring no reaction vessels, TURBOJETT Systems can be completely drained for freeze protection. Outdoor systems can be designed for intermittent, automatic operation in the coldest of climates.

Easily Maintained

A typical TURBOJETT mixer for 150 GPM is only five inches in diameter and seventeen inches long. It weighs a mere twenty pounds. These mixers are easily inspected, cleaned or replaced. Separate internal rings are available and can be replaced in minutes.

Reduction of Mineral Build-up Maintenance Problems

Many chemical reactions coat the surfaces of piping, mixers and aerators, and often render them completely inoperable. The TURBOJETT is well suited to these situations because of its easily maintained design. Spare nozzle rings or whole mixers can be replaced in minutes. The small size of the mixer lends itself to cleaning in an "acid bath" or similar cleaner.

In Line Treatment Capability

Complete treatment systems can be designed to eliminate open reaction vessels and aerators. Freezing effects of cold weather or the emission of toxic fumes can be avoided because the system is completely contained within a pipeline. Precise control can be achieved because system lag times are short.

Self-Contained Systems

A completely assembled, compact treatment system can be arranged for an engine drive. This flexibility makes the TURBOJETT System ideally suited for treating waters at remote locations. Government regulations for clean streams at remote outfalls can more readily be achieved.

Choice of Materials

TURBOJETT mixers can be provided in a variety of materials to meet your needs for corrosion or abrasion resistance. Our foundries cast over 50 different alloys and have been able to meet the requirements of the chemical, mining, paper, mineral processing and metals industry.

Automatic Control

The TURBOJETT System can be equipped with automatic controls which can continuously monitor the quality of treated water and adjust the reagent feed. Since the lag time between reagent addition and process control measurement is short, control is accurate.

TESTING

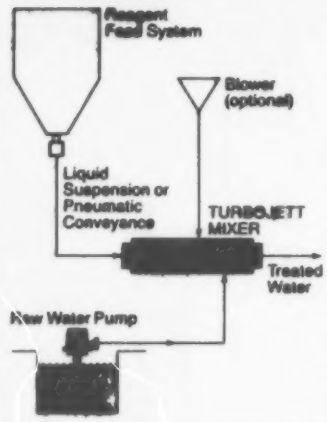
Barrett, Haentjens recognizes that each water treatment problem has its own peculiarities. As such, we offer complete field or pilot testing. While we do not guarantee that our system will successfully treat water in every situation, we offer a complete program for application testing. This allows you to determine how well the TURBOJETT System works in your situation. The approach eliminates any risk, since our design can be tested for each application.

Successful testing has been done under the direction of the U.S. Bureau of Mines in the area of acid mine drainage treatment. Testing in the area has successfully continued with several on-site tests at customer's facilities.

*Patent Pending

Applications Areas	Mixing	Acid Neutralization	Aeration	Chemical Feed/ Conditioning	Waste Treatment	Flotation	Flocculant Feed	Cooling Towers
Coal	●	●	●	●	●	●	●	
Utilities	●	●	●	●	●		●	●
Steel	●	●	●	●	●	●	●	●
Non-Ferrous Metals	●	●	●	●	●	●	●	●
Municipal	●		●	●	●	●	●	
Petro-Chemical	●		●	●	●	●	●	●
Paper	●	●	●	●	●	●	●	
Mining & Minerals	●	●	●	●	●	●	●	
Food Processing	●	●	●	●	●		●	●
Oil Drilling	●	●		●	●		●	

Typical Arrangement



ENGINEERED SYSTEM APPROACH

Barrett,Haentjens offers design, testing and fabrication of a complete TURBOJETT System. Each process is custom designed for your specific needs.

Typical systems include:

TURBOJETT Mixer
Raw Water Feed Pumps
Reagent Storage Tanks
Reagent Feed Equipment
Manual or Automatic Controls
Air Compressor/Blower

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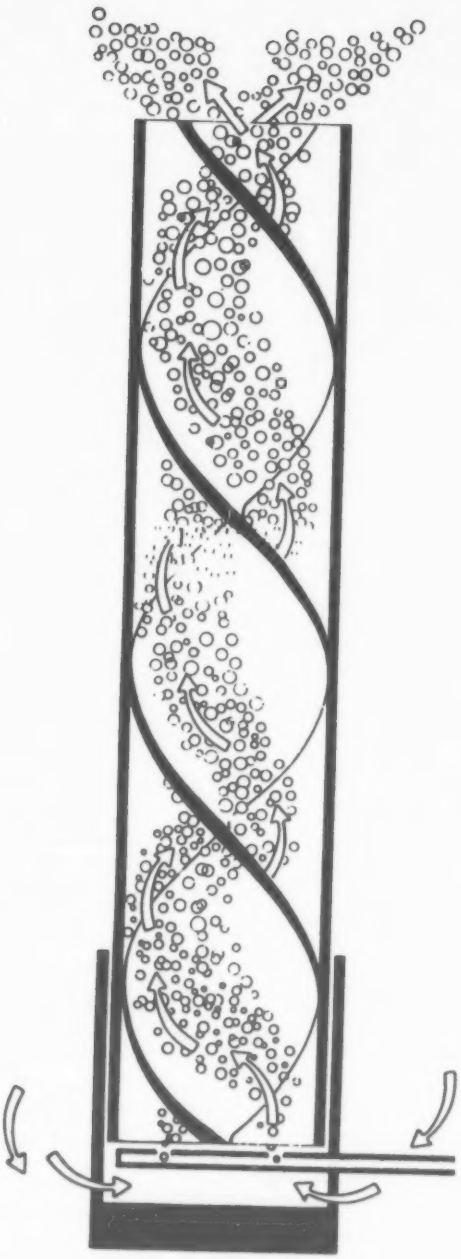

Oxygen transfer efficiency	12.3	%
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Air supply/Helixor-minimum	40.0	m^3/h
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Report of Investigations 8868

BUREAU OF MINES 1984

IN-LINE AERATION AND TREATMENT OF ACID MINE DRAINAGE

By T. E. Ackman[1] and R. L. P. Kleinmann[2]

ABSTRACT

The Bureau of Mines has invented a simple, low-maintenance system to mix and aerate mine water in a pipeline. It consists of a jet pump, which entrains air by Venturi action, and a static mixer, which induces turbulent flow. The system has no moving parts and is designed to use the pressure generated by an existing mine water discharge pump.

The in-line aeration system has been field-tested at a mine site in Greene County, PA, where high ferrous iron (Fe^{2+}) concentrations were causing discharge problems. Discharge concentrations of Fe^{2+} were reduced from 10 to 20 mg/L to 0.2 to 0.9 mg/L by installation of the aeration system. At high influent Fe^{2+} concentrations (47 to 240 mg/L), the system also proved effective, despite low pH conditions (4.6 to 5.6).

Neutralization and aeration were combined into a single step by injecting sodium hydroxide (NaOH) into the port of the jet pump. This resulted in oxidation of the Fe^{2+} within a few seconds, indicating that combining neutralization and aeration optimizes reaction rates.

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[2]Supervisory geologist.
Pittsburgh Research Center, Bureau of Mines, Pittsburgh, PA.

INTRODUCTION

Acid mine drainage (AMD) results from the exposure and subsequent oxidation of sulfide minerals (primarily pyrite) associated with coal and adjacent strata. The acidic reaction products are dissolved by infiltrating rainwater, eventually emerging in acid seeps or springs. Many factors influence the quantity and quality of water handled by a mining operation, but it is not unusual for a single mine to treat 1 million gal of acid water a day. Costs of treatment range up to $500,000 per year, with the entire industry probably spending over $1 million per day.

Conventional AMD treatment consists of four steps: (1) neutralization, (2) aeration, (3) settling and disposal of sludge, and (4) effluent discharge. A flow diagram for a conventional AMD treatment plant is shown in figure 1. Capital costs for such a facility range between $500,000 and $2 million (1).[3] Most treatment plants use lime for neutralization, but NaOH and limestone (2-3) may also be used.

Aeration requirements vary, based upon iron concentrations and flow volume. Iron dissolved in the acidic water is often in the reduced Fe^{2+} state. Before discharge, that iron must be oxidized to Fe^{3+} so that it will hydrolyze and

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

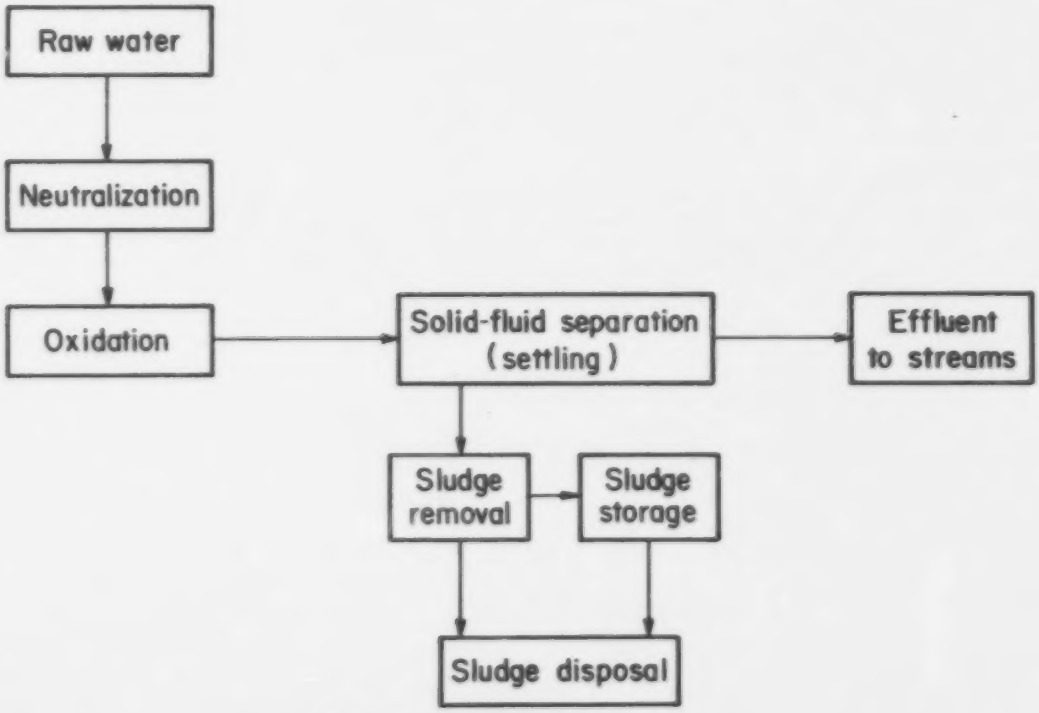

FIGURE 1. - Standard AMD treatment process.

precipitate as $Fe(OH)_3$, commonly known as yellowboy. The rate of Fe^{2+} oxidation is a function of dissolved oxygen (D.O.) and pH:

$$\frac{-d\ [Fe^{+2},\ mol/L]}{dt} = k\ \frac{[Fe^{+2},\ mol/L] \times (D.O.,\ mg/L)}{[H^{+},\ mol/L]^2}, \tag{1}$$

where pH > 3.5, and $k = (1.25 \times 10^{-14})\ h^{-1}\ mg^{-1}\ mol^{-2}\ L^{+3}$, or

$$\frac{-d\ [Fe^{+2},\ mol/L]}{dt} = k\ [Fe^{+2},\ mol/L] \times (D.O.,\ mg/L), \tag{2}$$

where pH < 3.5, and $k = (1.57 \times 10^{-35})\ h^{-1}\ mg^{-1}\ L^{1}$.

Ferrous iron (Fe^{+2}) and H^{+} are given in mols per liter, whereas D.O. is given in milligrams per liter, and "k" is the rate constant obtained from the literature (4-6) and expressed in the appropriate units. Equations 1 and 2 can be integrated to yield relations for the amount of time ($t_{1/2}$) necessary for an initial Fe^{2+} concentration to decrease by 50 pct as a result of oxidation to Fe^{3+}, assuming constant pH and D.O., as follows:

$$t_{1/2} = \frac{(\ln 2) \times [H^{+},\ mol/L]^2}{k\ (D.O.,\ mg/L)}, \tag{3}$$

where pH > 3.5, and $k = (1.25 \times 10^{-14})\ h^{-1}\ mg^{-1}\ mol^{-2}\ L^{+3}$, or

$$t_{1/2} = \frac{(\ln 2)}{k\ (D.O.,\ mg/L)}, \tag{4}$$

where pH < 3.5, and $k = (1.57 \times 1^{-35})\ h^{-1}\ mg^{-1}\ L^{+1}$.

It is obvious from equations 1 and 3 that pH plays an extremely important role above a pH of 3.5 in reducing iron levels. As can be seen from equations 1 through 4, D.O. is also important. Even if aerated, mine water contains only about 8 to 10 mg/L D.O., which is consumed at the rate of 1 mg/L for every 7 mg/L Fe^{+2} oxidized.

To replenish the D.O., settling ponds or lagoons are constructed wide and shallow to maximize diffusion of oxygen into the water and thereby increase D.O. transfer from the atmosphere. However, oxygen diffusion is relatively slow (7), so that at many sites supplementary aeration sources are necessary. For example, diffusion can be increased by increasing turbulence. This is typically accomplished by incorporating a series of open-channel drops in the flow path of the water, which increases the D.O. concentration. Mechanical aerators can also be used to continuously introduce bubbles of air into the water. This continuous replenishment of D.O. is effective in maintaining a rapid reaction rate, but it also has disadvantages: A separate aeration tank or basin is required; there are high initial capital costs; and there are operating costs associated with power consumption and maintenance, especially where gypsum precipitation is a problem.

This report describes a Bureau-designed treatment system, currently in full-scale operation, which has proven to have economic and environmental advantages over conventional treatment. The In-Line Aeration and Treatment System, or more simply, the In-Line System (ILS), functions in existing AMD pipelines using the energy of existing mine water discharge pumps. It offers reduced maintenance, operating, and capital costs, as well as improved reaction time.

ACKNOWLEDGMENTS

The authors thank Kitt Energy Corp. and especially R. Kantzlieter, senior environmental engineer, and T. Simonetti, environmental engineer, for their cooperation and assistance. The authors also gratefully acknowledge the cooperation of Walter Sarsfield, mine inspector, Pennsylvania Department of Environmental Resources. Important technical assistance and interpretation of data were provided by engineering technicians R. Lipscomb and A. Woods and mining engineering technician J. Odoski, of the Bureau of Mines. Finally, a special thanks to Mark Place of John P. Place, Inc., who played a principal role in the conception and design of the ILS.

FIELD TEST

UNIT DESCRIPTION

The ILS consists of two off-the-shelf components: a jet pump (8) and a static mixer (fig. 2). Both components can be described as aeration and mixing devices. Jet pumps are simply nozzles that entrain air by Venturi action (fig. 3). The jet pump used was made of polyvinyl chloride (PVC). Water enters under pressure generated by the existing mine water discharge pump and is converted by the jet pump into a high-velocity stream. This stream then passes through a suction chamber, which is open to the atmosphere. If the system is being used for neutralization as well as aeration, the suction chamber also serves as the injection point for the neutralizing material (e.g., lime, NaOH or potassium hydroxide (KOH), or finely ground limestone). Alternatively, the neutralizing material can be mechanically injected into the line by a metering pump anywhere before the ILS. After passing through the jet pump, the flow enters the static mixer (fig. 4). The static mixer consists of 1-ft sections of pipe made of copolymer polypropylene resins, laminated together end to end with fiberglass. Inside each section is a 1-ft helix that forces the water to follow a spiral path. Helixes are used routinely in sewage and industrial waste water treatment plants as vertical airlift aeration and mixing units, but that design was modified somewhat for this horizontal application. Each helical unit was rotationally offset 90° from its neighbor, thereby interrupting the corkscrew every foot and enhancing the mixing action. Eight 1-ft sections were used, which provided the

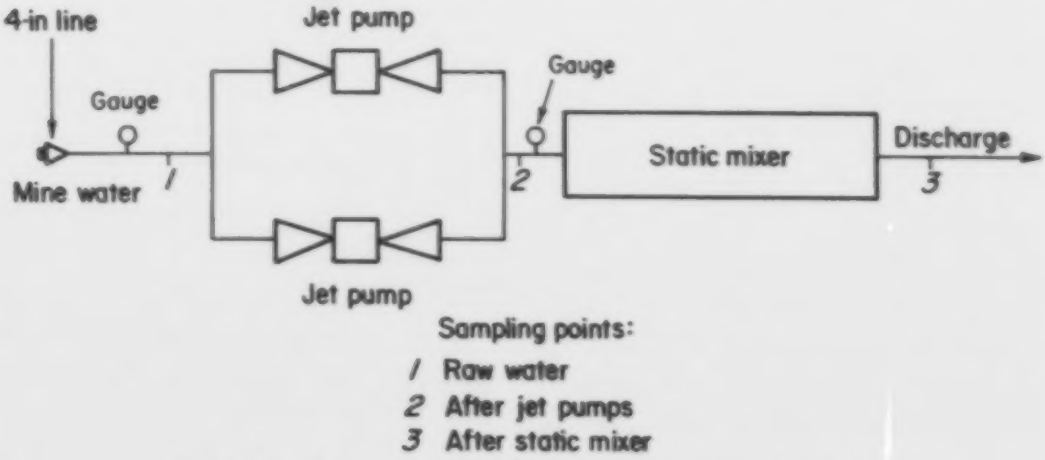

FIGURE 2. - Schematic of in-line aeration and treatment system (ILS).

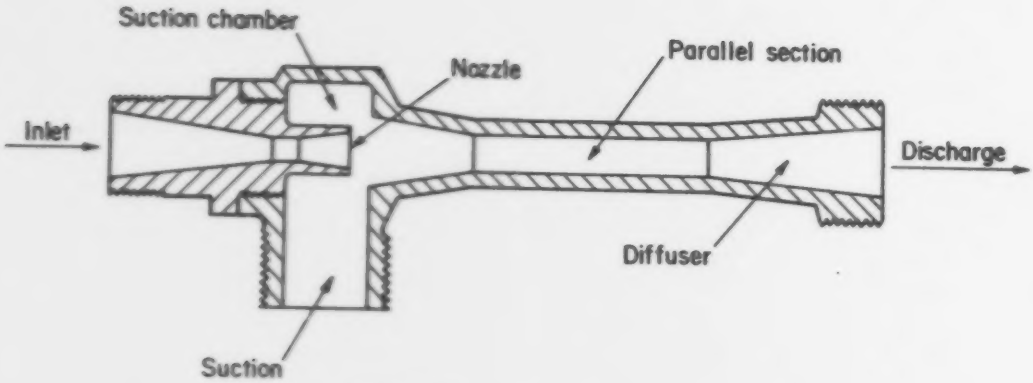

FIGURE 3. - Jet pump diagram.

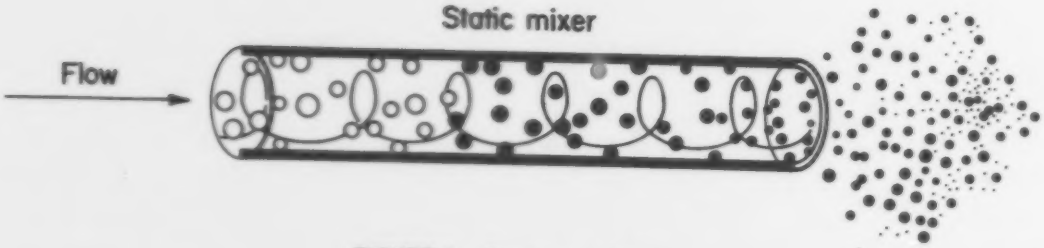

FIGURE 4. - Static mixer diagram.

contact time of a normal 32-ft pipe because of the induced spiral flow.

AERATION FIELD TEST

The ILS was tested and is currently in operation at a remote site in Greene County, PA. Historically, the mine water discharge from this site required no treatment. However, early in 1982, water quality began to deteriorate. In April 1982, the mine operator asked the Bureau of Mines for technical assistance because iron concentrations at the discharge end of the mine water settling ponds were exceeding legal discharge limits. Bureau investigators analyzed the water entering the settling ponds from the underground mine and found that Fe^{2+} levels were erratic but often exceeded 100 mg/L. D.O. was measured at 7.2 to 8.0 mg/L from the discharge pipe at the surface. Given the estimated detention time of the two settling ponds (about 4 days) and the influent pH (6.2-6.6), equation 1 was used to determine that sufficient oxygen was not available for complete Fe^{2+} oxidation and that additional aeration was needed to increase the rate of reaction and allow time for the $Fe(OH)_3$ to settle. As an alternative to mechanical aeration, the ILS was installed at the end of the discharge pipe from the underground mine on May 14, 1982 (fig. 5). It would actually have been preferable to splice the ILS in further up the pipeline to provide additional contact time. However, the operation of the jet pump has limitations in terms of back pressure from the discharge side of the line.

Monitoring of the discharge from the pond began on the fourth day after installation of the ILS. Ferrous iron

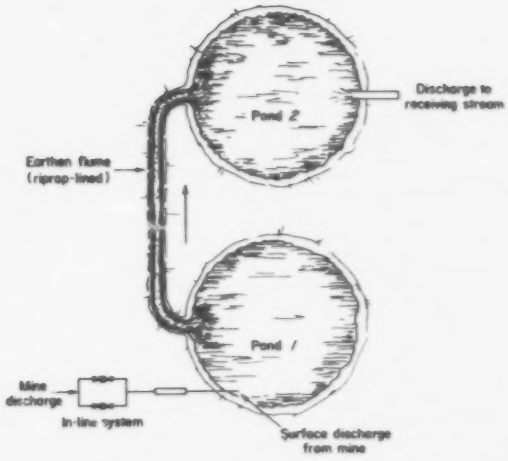

FIGURE 5. - Schematic of test site.

concentrations dropped from 10 to 20 mg/L before installation of the ILS to 0.2 mg/L on May 20. Subsequent Fe^{2+} concentrations ranged from 0.2 to 0.9 mg/L. Total iron concentrations fell from over 20 mg/L to less than 2 mg/L.

However, raw water quality continued to worsen during the summer of 1982 because of reduced pumping at an adjoining mine. Total iron concentrations in the effluent ranged from 2.1 to 20.8 mg/L because of higher influent Fe^{2+} concentrations (up to 240 mg/L) and declining pH (as low as 4.5).

Faced with the necessity of neutralization and yet reluctant to construct a conventional AMD treatment plant, the mining company decided to inject NaOH into the mine waterline. This would allow them to quickly meet acidity and pH standards in the effluent and would also provide water of sufficiently high pH for efficient Fe^{2+} oxidation in the ILS.

Injection of the NaOH (KOH during winter) into the mine waterline proved to be more difficult than the mining company first envisioned. Variations in water quality and flow and problems with the feed pump resulted in inconsistent and inefficient neutralization. Although this caused problems for the mine operator, it allowed rates of iron oxidation to be evaluated over a wide range of pH, with and without the ILS. When the ILS was not being used, the pipe discharge was arranged to provide turbulent conditions for initial aeration as the water entered the pond. Data for this setup is presented in table 1. Water was collected at the pipe discharge and also 1 day later as it flowed from the first to the second pond. This 1-day detention time for the first pond is an approximation and was affected by the amount of sludge accumulated in the pond. Using the discharge of the pond allowed evaluation of data despite the fluctuating water quality. It is important to note that the values in table 1 do not represent site discharge concentrations.

TABLE 1. - Effect of pH on Fe^{2+} concentrations, in milligrams per liter, with turbulent flow aeration but without the ILS

pH[1]	After neutralization	After 1st pond (1 day later)
5.6.....	473	305.0
6.4.....	199	.8
6.5.....	332	71.0
6.5.....	208	.6
6.6.....	351	86.0
7.5.....	208	1.6
8.7.....	320	.1
9.5.....	12.5	.7

[1]The pH was measured before the water flowed into the first pond.

Table 1 demonstrates satisfactory Fe^{2+} oxidation at a pH of 7.5 and above but inconsistent Fe^{2+} oxidation at pH 6.6 and below. The extent of iron removal that is occurring indicates that D.O. is being replenished in the pond by diffusion from the atmosphere. Assuming a fully aerated system and an initial Fe^{2+} concentration of 100 mg/L, one can calculate the minimum time it should take to reduce iron concentrations to an average legal discharge value below 3.0 mg/L at any pH (table 2).

With the approximate 24-h detention time of the first pond, it would be

expected that most of the Fe^{2+} would be removed at pH 6.5 but that the amount oxidized would drop off rapidly below pH 6.5. With less D.O. present, as is the case in the pond, oxidation kinetics should be proportionally slower. The two occasions where Fe^{2+} oxidation remained efficient at pH 6.4-6.5 imply better aeration on these days, perhaps owing to weather conditions.

TABLE 2. - Time required to oxidize 97 pct of 100 mg/L Fe^{2+} at various constant pH's and constant oxygen saturation

pH	Time, h	pH	Time, h
4.5....	3.5×10^4	7.....	3.5×10^{-1}
5.....	3.5×10^3	7.5....	3.5×10^{-2}
5.5....	3.5×10^2	8.....	3.5×10^{-3}
6.....	3.5×10^1	8.5....	3.5×10^{-4}
6.5....	3.5		

Table 3 presents Fe^{2+} concentrations in the mine water when the ILS was used. Unfortunately, pH was lower during the time interval when the ILS was connected than earlier, but this only serves to emphasize that Fe^{2+} oxidation is occurring much faster than would be predicted.

TABLE 3. - Effect of ILS on Fe^{2+} concentrations, in milligrams per liter

pH	After neutralization	After ILS	After 1st pond (1 day later)
4.6..	185	188	4.1
5.3..	240	210	6.0
5.4..	55	52	5.5
5.5..	87	75	5.5
5.6..	141	141	11.0
5.6..	47	44	2.8

For example, at pH 5.5 and an initial Fe^{2+} concentration of 87 mg/L, a detention time of over 10 days should be required to reduce Fe^{2+} concentrations to 5.5 mg/L. Similarly, at pH 4.6 and an initial Fe^{2+} concentration of 185 mg/L, the detention requirements to reduce Fe^{2+} to 4.1 mg/L should exceed 400 days. Yet the Fe^{2+} is being oxidized, despite the low pH.

The mine water flows through the ILS in about 4 s and remains in an effervescent state for perhaps another minute before the bubbles disperse. From equation 3, it can be calculated that approximately half of an initial Fe^{2+} concentration would be oxidized in this short interval at pH 7.5 but only about 5 pct at pH 7.0. Below pH 7.0, the ILS unit is simply raising the D.O. level about 1 mg/L above what might be achieved with a turbulent discharge, which should account for the oxidation of only 5 to 10 mg/L of additional Fe^{2+}. Clearly the ILS is performing much better than would be expected.

The observed oxidation rates suggest that the ILS is either directly catalyzing the rate of iron oxidation in the pond or somehow creating a catalyst. Since turbulent discharge into the pond should mimic the direct effect of the ILS well, it seems that a catalyst is being created by the ILS. Tamura (9) demonstrates that amorphous ferric hydroxide catalyzes the oxidation of Fe^{2+}, at a rate that increases in proportion to available oxygen, surface area, and adsorption of Fe^{2+} on the $FeOH_3$, but decreases with pH. The crystalline phase associated with ferric hydroxide, lepidocrocite (γ-FeOOH), which consists of very small and very thin rectangular plates (5), has also been shown to catalyze Fe^{2+} oxidation (4-5), though again the effect diminishes with decreasing pH. It seems likely that the ILS must be increasing the rate of catalysis by $FeOH_3$ or γ-FeOOH by increasing the rate of particle formation, by altering the particle surface area, or by increasing the availability of oxygen.

IN-LINE NEUTRALIZATION AND AERATION

Because of the problems that the mine company was experiencing with injecting the NaOH into the pipeline, the Bureau suggested that the jet pumps of the ILS could also serve as an injection port. A pilot-scale test was conducted using a 55-gal drum of NaOH and a siphon hose, adjusting the feed rate by valve adjustment so that pH at the ILS discharge

averaged about 7. Four sets of water samples were collected at three points in the ILS: before the jet pumps, after the jet pumps, and after the static mixer. The average values from the test are listed in table 4.

TABLE 4. - Effect of simultaneous in-line neutralization and aeration on water quality during flow through the ILS--pilot-scale tests

Parameter[1]	Before treat-ment	After jet pumps	After static mixer
pH[2].....	4.5	6.7	6.9
Acidity or alkalinity[3]...mg/L..	-810	+45	+70
Ferrous iron...mg/L..	190	4.8	2.4
Total iron.....mg/L..	260	95	40

[1]All values are averages.
[2]Geometric averages (1).
[3]- indicates acidity; + indicates alkalinity.

Once again the Fe^{2+} iron is being oxidized much faster than would be predicted. Based on the average values shown in table 4 for pH and Fe^{2+}, very little Fe^{2+} should be oxidized during the 4 s of contact time in the ILS. Alternatively, one can look at the extent of Fe^{2+} oxidation and calculate that an apparent average pH of at least 8.5 must exist throughout the ILS, despite the measured pH. This apparent contradiction between anticipated and measured values is probably a result of the simultaneous aeration and neutralization. As the NaOH is injected, the instantaneous pH is extremely high (over 10) for a fraction of a second. For that instant, reaction rates are extremely fast, with a reaction halftime measured in microseconds and limited only by D.O., which is being continuously replenished by the jet pump.

If this hypothesis is correct, combining neutralization and aeration should consistently result in high Fe^{2+} oxidation rates. The point of injection for the NaOH was moved to the jet pump port, and samples were collected on randomly selected days over a 2-month period. The oxidation of Fe^{2+} was even more rapid than was observed earlier in the pilot-scale test (table 5). Iron levels in the discharge from the second pond consistently met regulatory requirements for site discharges. In many cases, virtually all of the iron was oxidized after passage through the ILS; on some days, the jet pump alone was sufficient to reduce Fe^{2+} to below detectable limits. This efficiency is attributed to the higher pH's in the system, which in turn reflects the fact that injection of NaOH no longer poses the problem that it did earlier.

TABLE 5. - Effect of simultaneous in-line neutralization and aeration on water quality during flow through the ILS--full-scale operation, Fe^{2+} iron concentration in milligrams per liter

pH after static mixer	Before treat-ment	After jet pumps	After static mixer	After 1st pond
7.2.....	236	89.8	18.0	1.0
7.3.....	148	33.7	ND	ND
7.7.....	193	77.5	ND	1.0
8.4.....	414	ND	ND	ND
8.5.....	180	44.9	15.7	1.0
8.7.....	274	137.0	80.9	2.2
8.7.....	380	ND	ND	ND
9.5.....	1,527	ND	ND	ND
10.0.....	420	390.0	ND	1.0
10.3.....	137	ND	ND	ND

ND Not detected.

COST ANALYSIS

The total capital cost of the ILS was less than $3,000. Operating costs, based on an estimated 10 pct additional power consumption by the mine discharge pump, is about $800 per year. By way of comparison, a mechanical aerator sized for this site would cost $10,000 to $20,000, with an estimated operating cost of about $2,200 per year.

Since the ILS lacks moving parts, maintenance is much simpler for this system than for a mechanical aerator. Icing, a problem sometimes associated with spray

from the mechanical aerator, should not pose a problem with the ILS; and gypsum scale, if it develops, can be dislodged simply by striking the ILS unit.

If the ILS is incorporated in a new AMD plant, space can be conserved by designing ponds that are deeper than normal, since diffusion of oxygen into the pond is no longer essential. This will allow detention requirements to be based solely on settling requirements. Increased pond depths can also reduce pond cleaning frequency, or alternatively, extend the life of a pond used for sludge disposal.

CONCLUSION

The ILS is a simple and inexpensive approach to aeration of mine water. It significantly increased oxidation rates above theoretical limits through the mixing and aeration action of the jet pump and static mixer. At a pH of 5.5, oxidation rates were 10 times faster than anticipated; at pH 4.6, oxidation rates were over 400 times faster than anticipated.

The rate of Fe^{+2} oxidation was further accelerated by incorporating neutralization into the ILS. When NaOH was injected into the injection port of the jet pump, the simultaneous aeration and neutralization maximized the Fe^{+2} oxidation reaction rates, so that almost all of the Fe^{2+} was oxidized as the water flowed through the ILS. The extremely high rate of Fe^{+2} oxidation observed can probably be attributed to the extremely high instantaneous pH in a portion of the flow, which reduced the reaction halftime ($t_{1/2}$) in that portion to microseconds.

The ILS is much more economical than conventional mixing and aeration devices. The total capital cost of the system, at this particular site, was less than $3,000--about one fifth of the price of a conventional aerator. Operating and maintenance costs for the ILS are also much lower than for the conventional mechanical aerator.

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NaOH PRECIPITATION AND THE WANNAMAKER CONTINUOUS CONCENTRATOR

The following account by HOLM and SIMPSON (1981) describes a test of an innovative neutralization-filtration device for AMD treatment.

More information can be obtained directly from the research supervisor:

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The Wannamaker Continuous Concentrator was invented by:

W. W. (BILL) WANNAMAKER
Post Office Box 1121
Camden, SC 29020
(800) 845-2202

A partner in the development of the Continuous Concentrator is:

COLORADO MINERAL AND CHEMICAL CO. LTD.
2885 Mount Herman Road
Monument, CO 80132
(303) 481-3710
George M. Morris

The intention of Mr. Wannamaker and Mr. Morris is not to manufacture and market the Continuous Concentrator as an item of equipment but rather to offer their services, including their knowledge of the design, testing, and operation of the technology, to solve difficult solid-liquid separation and other process problems. They indicate that the equipment can be designed also to operate up to nearly 1000°F also under high pressure, and that it is most effective for removal of particle sizes of 1-10 microns for crystalline solids removal from water.

REMOVAL OF TRACE ELEMENTS AND ACIDITY FROM THE ARGO MINE TUNNEL DRAINAGE

BY

J. DAVID HOLM

DONALD H. SIMPSON

April 1981

Historic Features of Drainage From the Argo Tunnel[1]

The Argo Gold Mill, for years a part of the State Historical Society of Colorado Inventory of Historical Sites, has been nominated to the National Register for inclusion on the National Register for Historic Places.

The mines of Clear Creek and Gilpin were famous but so were many of the problems in mining these areas. Water was seeping into the workings at such a rate that pumps were working 24 hours a day. Ventilation was a serious problem. Finally, transportation of men and the ore they mucked along shafts approaching 1,000 feet in vertical lift was getting far too expensive.

The idea of tunneling into a mountain to reach ore on a slightly inclined plane was not new when it was first applied to mining in the Rockies. During the late 1870's, many miners and speculators started tunneling operations. The Argo Tunnel was one of the few that succeeded.

Incorporating the Argo, Drainage, Transportation and Tunnel Company in 1893, Sammuel Newhouse started a project to intersect the productive ore bodies between Idaho Springs and Central City and provide economic transportation for bringing ore to the surface, drainage for the mine workings and ventilation to the miners.

No one took Newhouse's tunnel very seriously until around 1895 when the Argo started serving as a drainage system for several mines. By February 1896, the tunnel had been driven one mile into the mountain toward Central City. In 1898 the Argo Tunnel had reached a length of 7,000 feet, had intersected 200 mines and over 1,140 veins.

By 1904 the tunnel had been driven 12,000 feet and was serving many mines, including a number of operations that Newhouse had personally acquired. The mines were producing gold, silver, lead, copper and iron sulfides (in demand as a flux by the smelters for a period of time).

During these years, practically all of the mines in the western portion of Gilpin County were having serious drainage problems except for those connected into the Argo. Unfortunately, however, the Argo never successfully negotiated payment for this service from many of the major mines and the stockholders in the Argo lost this revenue.

The Gem, Sun and Moon, Saratoga, Poco, Ophir, Old Town, California, Gunnell, Prize, Gregory-Buell, King Bee, Kansas-Burroughs, Waluga and Bi-Metallic were some of the major mines serviced from 1905 to 1943. Production of precious metals from these mines is estimated to total more than $100 million at old values. Much of this production was a direct result of the Argo.

The Argo Gold Mill became a part of the operation in 1913, three years after the tunnel to Central City was completed at a final length of 21,968 feet.

As is true of the history of most mining operations, the Argo Tunnel and Mill have had a sporadic history of operations, with years of activity followed by years of idleness. This pattern was stopped permanently on January 19, 1943, when blasting on a lateral to the Kansas shaft broke loose a great volume of water which immediately flooded the Argo Tunnel. Four men were killed and the tunnel was closed, as was the flow of ore to the Argo Gold Mill.

Several less serious "blow outs" of toxic mine water occurred during the past 25 years. These voluminous releases of polluted water are believed to be caused by roof collapses in the tunnel which prevent water from draining normally. Instead, water backs up behind these "dams" and tremendous hydrostatic pressures can develop. On May 21, 1980, a near catastrophic release of toxic water occurred which resulted in the temporary shutdown of 5 downstream municipal and industrial water intakes. Clear Creek was severely impacted throughout the entire downstream reach 35 miles to the confluence with the South Platte River.

Characteristics of Drainage from the Argo Tunnel

The Argo Tunnel (formerly the Newhouse Tunnel) is 21,968 feet or 4.16 miles long and intersects about 26 ore veins. The principal geologic formations in the vicinity of the tunnel are Precambrian schist, gneiss and granite. Fractures in these rock types results in their porosity. Construction of the tunnel was undertaken to intersect the largest veins in the Idaho Springs - Central City area at greater depth than the deepest shaft workings. The tunnel decreased mining costs, provided cheap transportation of the ore to the mill and railroad at Idaho Springs, and provided a means for draining the workings. Drainage was a major consideration leading to the construction of the tunnel. Lakes who noted in 1900 that "The arrival of the tunnel at or rather beneath the mines will be an enormous help to (the miners) especially in getting rid of the water with which they are at present overburdened."[2] The drainage currently that "One mine (in the Central City area) for years raised on an average 40 tons (36 t) of water for every ton of ore and rock." The drainage currently enters Clear Creek several hundred feet from the tunnel entrance.

Previous Water Quality Studies

Moran and Wentz (1974) studied the Argo Tunnel drainage in 1973. Two samples were collected - one on January 24th and one on June 28th. The field-measured pH was a 2.8 on January 24th and 2.6 on June 28th, a relatively insignificant difference. Calcium and magnesium concentrations also were very similar on the two dates; however, most dissolved (9.45-micron-membrane-filtered) and total concentrations of cadmium, cobalt, copper, iron, lead, manganese, nickle, silver, and zinc showed a net increase of 1.4 to 2.7 times between January and June. Dissolved cobalt and dissolved lead increased 4.4 and 6.7 times, respectively. Except for cobalt and lead in January, iron in June, and silver at both times, all trace elements were almost completely dissolved (88 percent or greater).[3]

The Argo Tunnel was next studied by Bovles, Cain, Alley, and Klusman (1974) from May 17 through September 28, 1973. They noted no change in flow (1.2 ft^3/s or 0.034 m^3/s) from the tunnel during the period July 3rd to August 16th, and stated that the flow averaged 1.2 ft^3s (0.034 m^3/s) during the period June 25th to August 31st.[4]

Concentrations of dissolved cadmium, copper, iron, manganese, zinc, and sulfate in the drainage on May 17th were higher than during the rest of the study period. Variations in concentrations fo these parameters from June 29th through September 28th were relatively insignificant. The pH varied only from 2.6 to 2.8 for the entire period of May 17th through September 28th. The analytical methods and quality-control procedures used have been endorsed by the U.S. Geological Survey.

Wildeman, Cain, and Ramiriz (1974) published analyses for three samples from the Argo Tunnel for the period October 30, 1973, through February 8, 1974, and found no dramatic changes in major or trace-element concentrations. They used the same analytical methods and quality-control procedures as Boyles, Cain, Alley, and Klusman (1974). Although Wildeman, Cain, and Ramiriz (1974) did not filter their water samples, it has been shwon previously that most trace elements in the drainage are primarily in the dissolved state (p.24).

The definitive study of the quality of water draining from the Argo Mine portal was done in a 1977 study conducted by Dennis Wentz of the U.S.G.S., entitled Mine Drainage Study for the Metropolitan Denver and South Platte River and Tributaries Report (1977). Samples collected over a one year period between 1976 and 1977 were analyzed for a complete suite of chemical parameters. The Argo mine drainage was found to flow at a fairly constant rate of .3 cfs and to contain extremely high concentrations of dissolved salts and toxic heavy metals. Of particular concern in the raw mine drainage are As, Cd, Cu, Fe, Mn, Pb and Zn. Each of these parameters exceed proposed water quality standards for Clear Creek (the receiving stream by at least an order of magnitude). The chemical results of that study are summarized below in Table 1.[5]

The Colorado Mined Land Reclamation Division, Inactive Mine Program conducted a mine drainage impact evaluation project from May 21, 1980 to November 18, 1980. The Argo Mine drainage was sampled on 5 occasions during that period. The first samples obtained on May 21, 1980 were taken almost immediately after a voluminous blow out of mine water was released from the tunnel. Large flows in the range of 4 cfs drained from the tunnel for a period of weeks after the blow out. By June 11, the flows had ebbed to 1.5 cfs and in November a flow of .6 cfs was registered. There is excellent agreement between the chemical sampling results provided by Wentz (1977) and those provided by McLaughlin Industrial Waste Engineers for the Inactive Mine Program. Table 2 presents the later sampling results.

TABLE 1: U.S.G.S. Mine Drainage Study (1977)[1]

Summary of Physical and Chemical Data for the Argo Mine Drainage

Parameter	Concentration Range mg/l	Mean mg/l Concentration	Proposed Water Quality Standard mg/l
Total Dissolved Solids	2710.-3140	2925	No. Std.
pH[2]	2.9-3.1		5.5-9.0
Calcium	320.-550.	435	No. Std.
Magnesium	110.-120	116	No. Std.
Sodium	18.-23.	20.5	No. Std.
Sulfate[2]	1900.-2000.	1951.	250.0
Arsenic[2]	100-150	127.	.05
Cadmium[2]	.140-.170	.152	.002
Chromium	.010-.030	.019	.050
Copper[2]	5.0-6.6	5.92	.06
Iron[2]	160.-200	186.5	1.55 (tot)
Lead[2]	.10-.20	.14	.009
Mangenese[2]	80.0-110.0	93.6	1.1 (tot)
Mercury[2]	.0001-.0002	.00013	.0005
Silver[2]	.010-.060	.028	.0001
Zinc[2]	42.0-49.0	46.3	.55

TABLE 2: Inactive Mine Reclamation Program

Mine Drainage Impact Evaluation[3]

(McLaughlin Industrial Waste Engineers)

Parameter	Concentration Range mg/l	Mean mg/l Concentration	Proposed Water Quality Standard mg/l
Conductivity	2870.-3800. mmlos	x	No. Std.
Cadmium[2]	.23-.29	.215	.002
Copper[2]	6.6-13.0	8.72	.06
Iron[2]	11.0-340.0	181.4	1.55
Lead[2]	.04-.48	.186	.009
Mangenese[2]	47.-120	87.8	1.1
Nickel[2]	.37-.41	.39	.05
Zinc[2]	21.0-63.0	44.0	.55

1. Sampling period Mar. 11, 1976 to Mar. 18, 1977. 14 samples collected & analyzed for each papameter.
2. Exceeds proposed water quality standard.
3. Sampling period May 21 - Nov. 18, 1980. 5 samples collected & analyzed.

Acid Mine Drainage

The production of acid mine drainage occurs when iron sulfides (Pyrite and Marcasite) are oxidized in the presence of water. The interaction of water, air and sulfides produces ferric hydroxide, sulfate and acidity. This oxidation process would not manifest itself if the pyrite were left in its naturally reducing environment. During mining operations, pyrites may be exposed to air and underground workings or above ground in open pits, overburden piles, and tailings piles. Regardless of the location, acid is formed if the pyrite comes in contact with oxygen and water.

Acid is formed in a series of inter-related reactions:

1. Pyrite, (chemical name ferrous sulfide), when exposed to water and air oxidizes to form ferrous (Fe^{+2}) sulfate and sulfuric acid.

2. The ferrous sulfate can then be oxidized by either more air exposure or by bacterial activity to form ferric (Fe^{+3}) sulfate.

3. The ferric sulfate can then contribute further to acid formation in two ways. First it can serve as an oxidizing agent, oxidizing additional sulfides. The sulfur released by this reaction serves as an energy source for a species of acid producing bacteria (thiobacillus thiooxidans). Secondly, the ferric sulfate can be hydrolyzed to form ferric hydroxide and additional sulfuric acid.

Separately or in combination, chemical or bacterial oxidation of pyrites produces acid water. Four equivalents of acid are produced during theis cycle, two during oxidation of sulfide and the remaining two with the resulting hydrolysis of ferric iron.

Increased acidity in turn lowers water pH and can place large concentrations of metal ions in solution. This is especially true for drainage from metal mining districts such as those found in the Rocky Mountains of Colorado. Generally, metal mine drainage has low pH and high metal concentrations. The mobility of these metal ions under natural conditions appears to follow the sequence below:

Most mobile Mn Zn Cu Cd Fe Ni Pb Least Mobile

These metals can be toxic to aquatic life even in small concentrations. In addition, these metals can make water unsuitable for domestic or industrial uses. In Colorado, most of the problems associated with acid mine drainage are found in the mountains where underground mines have been established. Ground water flows through mine workings and picks up acidity as well as dissolved metals. Spoil piles and tailings pollute surface drainage as well.

Acid Mine Drainage Control Methods

Various methods exist for controlling acid mine drainage. They are generally divided into at-source abatement and drainage treatment. At-source abatement refers to techniques used to reduce water contact with sulfide material or to keep acid mine drainage away from streams. Drainage treatment consists of chemical and/or physical means of improving drainage water quality after it has been impacted. Different techniques can be used for surface or groundwater conditions.

A. At-Source Abatement

These techniques are usually preferred for control of acid mine drainage. At-source abatement generally consists of physical structures that require little or no maintenance. In cases where spoils or tailings affect water quality, the following control methods are presented generally in order of increasing cost.

Soil Cover and/or Revegetation

Vegetative cover stabilizes waste piles, reduces erosion and slows surface runoff. However, some plant species increase infiltration and thus may increase acid mine drainage production. Use of soil to cover tailings reduces infiltraiton and provides stabilization. Soil also allows for easier establishment of vegetation. The drawbacks to using soil and vegetation cover involve acquiring the needed soil and seed, transporting this material to an alpine site and having success to the site.

Rerouting Drainage & Water Handling

Diversion of water around tailing piles is another method used to reduce acid mine drainage. This approach is less expensive and perhaps more effective than soil cover and revegetation. One problem is the maintenance of proper channel slope and hydraulic regime. In addition, rainfall can still percolate though spoil material.

Channel Lining

The placement of impermeable material, such as clay, along a channel bottom is another way to reduce water flow into tailings. This method can also be used in conjunction with rerouting.

Spoil Treatment

The placement of impermeable material on top of spoil or the addition of chemicals to spoil for reduction of infiltration through the spoils. Chemical treatment is also used. The long term effectiveness of these types of treatments isquestionable. They are also expensive, especially when dealing with remote sites.

Mine Sealing (Flooding)

Closure and sealing of inactive mines is one way to eliminate acid mine drainage. Flooding of underground mines reduces the oxidation of sulfides and does not allow free drainage. However, the potential exists for the development of large hydrostatic heads. These large heads could rupture the mine seals or force water to be discharged through fracture systems and thus negate the objective. These drawbacks preclude the use of this control technique especially for metal mines in mountainous areas.

Air Sealing

Air sealing is a control measure used to limit the amount of oxygen available to underground workings. Reduction of oxygen leads to a reduction in acid mine drainage produced. This technique would not work well in tunnels that drain extensive workings where air could enter through numerous ventilation shafts.

Time Discharge

This technique can be used with either mine seals or settling ponds. The objective is to store acid mine drainage until high stream flows when it can be assimilated with fewer impacts. The drawbacks to this approach include, design of large enough impoundments, potential for water rights conflict and limited benefits to the stream.

Residence Time Reduction

The less time water is in contact with sulfidic material, the fewer metal ions can be dissolved. Rapid drainage of underground workings by removal of obstructions and lining of channels may reduce metal concentrations in mine drainage. This technique has not, to date, been adequately tested but may yield significant results.

B. Treatment of Acid Mine Drainag

Treatment of acid mine drainage refers to chemical and physical procedures used to improve mine drainage quality. In general, these measures require continual maintenance to be effective. Thus, these measures are implemented only in extreme cases where such water quality improvements are justified.

Alkali Neutralization Followed by Settling or Filtration[6]

Alkali neutralization is the most widely used chemical treatment of acid mine drainage. The addition of alkali material increases pH and causes the precipitation of many metal cations as insoluable hydroxides or carbonates. Several alkali materials are available for use, these include Quick lime, Hydrated lime, limestone, Dolomite, Magnesite, Caustic Soda, Soda Ash and Ammonium Hydroxide. These materials are composed of sodium or calcium, hydroxides or carbonates. All of these agents form a "sludge" when used in the neutralization process. Disposal of this sludge is a major problem.

Several shortcomings are apparent with the use of hydrated lime (calcium hydroxide) and Quick lime (calcium oxide). These compounds can increase hardness and cause gypsum ($Ca\ So_4\ .2\ OH$) to form scaling. In addition, overtreating can occur causing high pH values in the treated water.

The use of Limestone, Dolomite or Magnesite also has serious drawbacks. In the presence of Iron, Iron hydroxide precipitates onto the reaction surfaces of the rock fragments and coates them. Some form of "reactor" is needed to remove the iron coatings and keep the reaction surfaces fresh. When iron is present the pH is limited to about 6.5 due to the formation of carbonic acid. The reaction rate for limestone etc. is dependent upon rock fragment size.

Reverse Osmosis[7]

The process of reverse osmosis involves inducing movement of water from a high solute concentration to a low solute concentration through a membrane filter by the application of pressure. A highly concentrated brine is formed on one side of the filter and clean water on the other side.

Generally, suspended solids must be removed from the water prior to treatment so they will not foul the membrane. High sulfate concentrations in the water to be processed can cause formation of calcium sulfate which can also foul membrances. The pH of the water produced is low and must be treated to reach discharge standards. Disposal of the accumulated brine is another problem. However, this method has been effective for removal of trace metals.

One proposed method for treating brine water is by the use of alkali neutralization. However, the problem of sludge disposal is still present.

Ion Exchange[8]

Ion exchange involves the chemical substitution of a more desirable ion for the less desirable pollutants. A home water softener is an ion exchange unit that exchanges sodium (salt) ions for calcium and magnesium (hardness) ions. Ion exchange is the interchange of ions between a solid medium (resin) and and aqueous solution. Two columns are usually set up, one to remove anions, the other for cations. Mineral contrations in the water produced. Several varieties of ion exchange units have been developed. They differ primarily in the resins used and ions removed. Generally, these units do not remove enough of each ion to meet discharge standards.

Note: Neither reverse osmosis or ion exchange is particularly well suited to the extreme concentrations of severely polluted AMD. Although they will work on the worst water, the practicality of such applications is low.

Electrodialysis

Electrodialysis is similar in principle to reverse osmosis except that electric potential is the driving force instead of pressure. Two membrances bound each cell, one filters anions, the other cations. Ferric iron has been found to foul membranes and must be removed prior to treatment.

Underground Injection of Trace Elements

This method for reducing acid drainage involves injection of an alkali slurry into underground mines. The alkali slurry would be used to neutralize mine drainage before it reached the surface. In addition, a precipitate would form which over time would seal off the mine and stop drainage.

One obvious drawback would be the possibility of failure in the precipitated seal could cause flooding of nearby areas. This is especially true for metal mines in mountainous areas where large heads could develop behind the seal. Another drawback would be the depletion of alkali material over time. The amount of neutralization obtained through this procedure is difficult to determine.

Treatment Costs[9]

Reliable cost figures are difficult to obtain from the literature. Most costs quoted are paper-study costs developed from feasibility studies. A range of reported costs will be presented in Table 3 for the purposes of discussion. It must be emphasized that actual costs depend on a very large number of variables such as plant size, type of equipment, degree of sophistication, water quality, costs of reagents, waste disposal, costs of labor, etc. In reality, these figures mean very little to the specific situation.

TABLE 3: Estimated Range of Costs for Treatment

Method	Estimated Cost Range, dollars/1000 gal.
Lime neutralization	0.20 to 1.30
Limestone neutralization	0.15 to 1.00
Soda ash neutralization	0.40 to 3.00
Sodium hydroxide neutralization	0.50 to 3.50
Reverse osmosis treatment	1.00 to 5.00
Ion exchange treatment	1.00 to 7.00

Neutralization, Precipitate Concentration, and Filtration of Argo Mine Drainage

Neutralization of acid mine drainage is a proven and cost effective method for removing trace elements from solution. However, many of the flocs (precipitates) that form during neutralization reactions are quite light in weight and tend to remain suspended rather than settling out. It is always more difficult in treatment situations to remove the precipitates from suspension than it is to increase the pH, oxidize the trace elements and precipitate them in the first place.

Oftentimes, settling basins or clarifiers are used to separate the flocs from the liquid-solid suspensions created during the neutralization process. It is a problem to make this separation before the slurry reaches the outlet of the settling pond or clarifier. Short circuiting is almost always a problem with settling ponds. Instead of using the entire volume of the basin for settling, only a narrow path from the inlet to the outlet is used. Sometimes baffles are installed in the pond to enhance its suspended solid removal efficiency. In many cases coagulants (chemicals to improve settling) are used to remove suspended solids.

Unfortunately, there is not sufficient land area between the portal of the Argo Mine and Clear Creek, the receiving stream, to allow construction of a settling pond. Filtration systems are also used to remove precipitated solids from solutions. However, most filtration systems remove solids from slurries, which means all of the solids must be removed to obtain a clear liquid. Also, filtration equipment such as the labor intensive plate and frame filter press or the continuous rotary vacuum filter remove solids with a relatively low moisture content. Such filtration systems do achieve their purpose but with high costs and considerable inflexibility.

It is more desirable to remove clear liquid from the suspended solids in the slurry on a continuous basis resulting in variable levels of moisture content in the sludge. In this way the amount of clear water recovered becomes inversely proportioned to the moisture content permitted to remain in the sludge. For this type of filtration, a concentration device is necessary which pumps neutralized slurry through a filter system capable of retaining micron sized particles in the slurry while producing high clarity filtrate. This type of concentration is done most efficiently by passing the slurry through the filter system a number of times and extracting water on a continuous basis. This requires a lower pressure drop for filtration than the common types of equipment which rely on a single pass of the slurry through the filter system with a high pressure drop. Of course multipass filtration of slurries can concentrate the sludge only to the point that the thixotropic nature of the material allows it to be pumped. Where a high percentage of water recovery is desired it is best to concentrate in several stages using separate concentrator modules.

A precipitate concentration and filtration device was tested at the Argo Mine Tunnel. The system used was a Wannamaker Continuous Concentrator furnished by Colorado Minerals & Chemicals Ltd. with a capacity of 57,600 gpd product flow.

This particular continuous concentrator apparatus is a relatively simple device designed to fractionally remove solids from liquid-solid suspensions or slurrys. The continuous concentrator is essentially portable and employs a modular design so that a wide range of flows can be treated. The system uses relatively little floor space and was installed inside a building near the portal of the Argo Mine Tunnel.

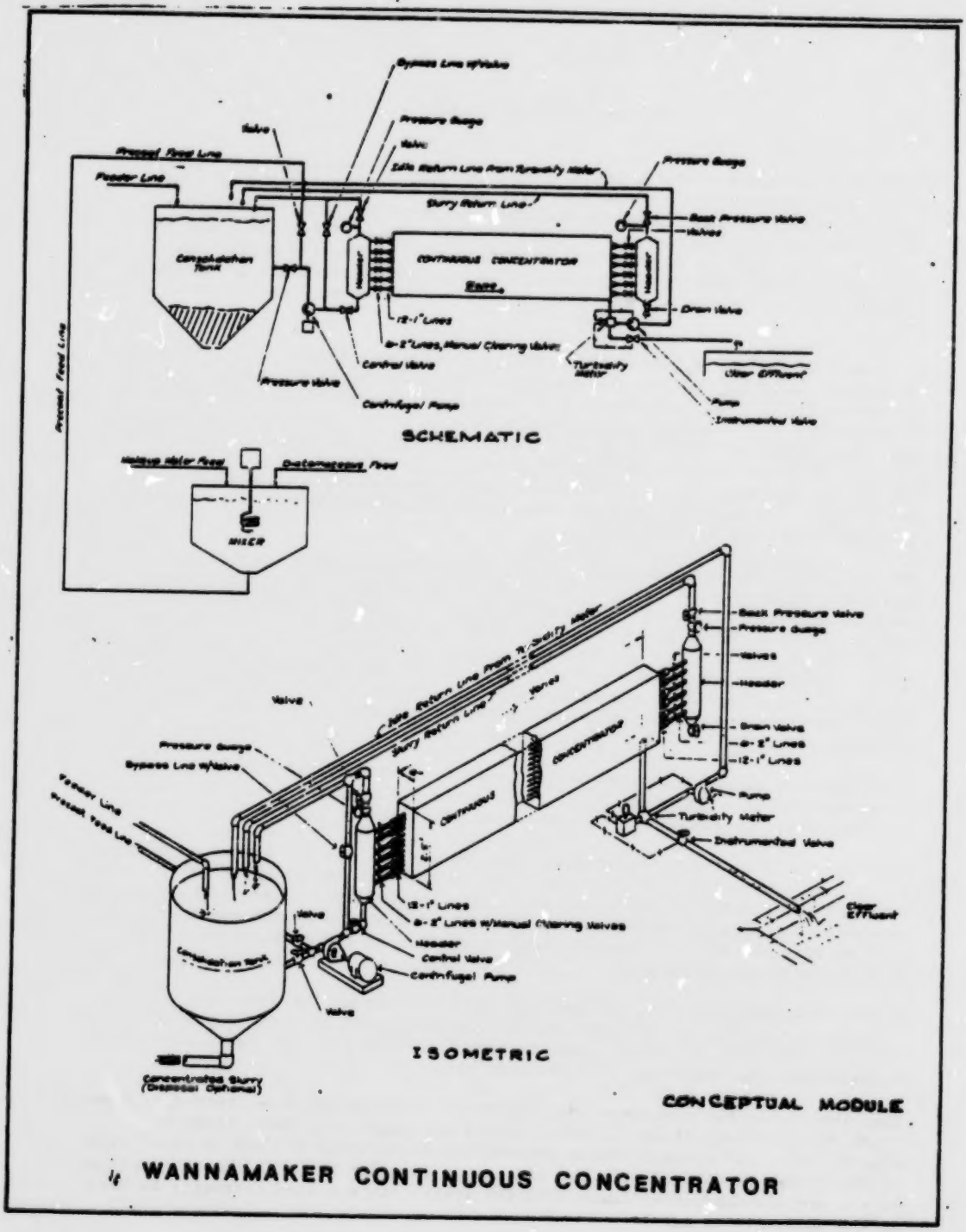
The device was used simply to remove minerals from mine water using a precipitation and filtration process. A schematic of the continuous concentrator apparatus is presented in Figure 1.

Continuous Concentrator System Evaluation

Sampling of the effluent from the continuous concentrator water treatment/minerals recovery system at the Argo Tunnel was performed on October 15, 1980. The test unit was operated as a single stage multipass concentrator with an intermittent feed of raw mine water and a continuous product flow of clear effluent water. The concentrated sludge was discharged from the tank following the experiment. The sludge has not yet been assayed for mineral content.

Samples of processed water or effluent were taken as the system was operated at various pH values. The objective of the sampling program was to determine the optimum pH range which provided maximum precipitation of dissolved metals in the Argo Mine drainage and produced an effluent of acceptable quality. Approximately 450 gallons of raw water draining from the Argo Mine Tunnel was pumped into the concentration consolidation tank and sampled for pH and baseline metal concentrations. Industrial Grade Caustic Soda (NaOH) was then added to the tank in measured increments until the pH of the mine water was raised to 11.5. The mine water and sodium hydroxide were thoroughly mixed using the centrifugal pump and a return line to the consolidation tank. After complete mixing this water was then pumped into the continuous concentrator and the system was operated for 5 minutes and allowed to reach equilibrium. An effluent sample was obtained and analyzed for pH and metal concentrations.

The system was operated continuously and effluent samples were obtained at pH 11.5, 10.5, 9.8, 8.3, 7.2, 6.6, 6.0 and 5.6. The pH was lowered gradually by simply adding raw mine water to the consolidation tank (which had originally been spiked with NaOH). At each desired pH level the system was allowed to equilibrate prior to extracting effluent samples. The pH of all effluent samples was measured immediately with a pH meter. All samples were acidified with HNO_3 and analyzed on an atomic absorption spectrophotometer by the Industrial Laboratories Company. The following parameters were analyzed: Total dissolved solids, sulfate, sodium, arsenic, cadmium, chromium^{+3}, chromium^{+6}, copper, iron, manganese, lead and zinc. The results of the examination of the effect of increasing pH on removal of trace elements from the Argo Mine drainage using the continuous concentrator system are presented below.



WANNAMAKER CONTINUOUS CONCENTRATOR

Effluent Sampling Results

Samples of effluent from the continuous concentrator apparatus were analyzed over nearly the entire pH range. Concentrations of dissolved solids (TDS) specific salts such as sodium and sulfate, and numerous trace metals were determined for each sample. The sample results yield information about the optimum pH value where maximum metal precipitation occurs and accordingly, the best effluent quality is achieved. The results obtained are presented in tabular form in Table 4. The same results are presented graphically in Figure 2.

Although the metals analyzed theoretically precipitate over a large range of pH values, sampling results show that most metals reach their lowest effluent concentration in the range between pH 7 and pH 9. Co-precipitation and other interactions must occur in acid mine drainage in order to produce the results observed. Lead and copper seem to precipitate out of solution in the low end of this range and zinc and cadmium drop out at the high end near pH 9. When the system is operating in the optimal range from the standpoint of removing metal from solution, lead, cadmium, manganese and sulfate remain elevated above proposed water quality standards.

The excessive lead and manganese levels do not present major water quality concerns, since the numeric standards for these parameters are directed at protecting water supplies. The Argo drainage, of course, is not a water supply. Rather, Clear Creek which receives the drainage from the Argo mine is the water supply. The continuous concentrator operating at pH 7.2 reduces lead loading to Clear Creek from .140 mg/l in the raw untreated drainage to .02 mg/l. Lead levels of .02 mg/l are not considered toxic to aquatic life. The first water supply intake below the Argo discharge is some 15 miles downstream just above the town of Golden, Colorado.

The Manganese standard is also set to protect water supplies from undesirable staining effects. Manganese is not considered toxic at the levels discharged by the continuous concentrator system operating between pH 7 and 9.

Cadmium levels in the effluent drop from .29 mg/l in the raw untreated drainage to .004 mg/l when the system is operating at pH 9.2. The proposed water quality standard for cadmium to protect aquatic life is .002 mg/l. The slightly elevated concentration of cadmium that would be discharged by the system might create a weak chemical barrier for certain aquatic species in the mixing zone of the Argo drainage and Clear Creek.

Sulfate does not appear to be affected significantly by the operation of the continuous concentrator system. Sulfate is of concern in water supplies for livestock and people. Clear Creek is used for these proposes currently notwithstanding the discharge from the Argo Mine.

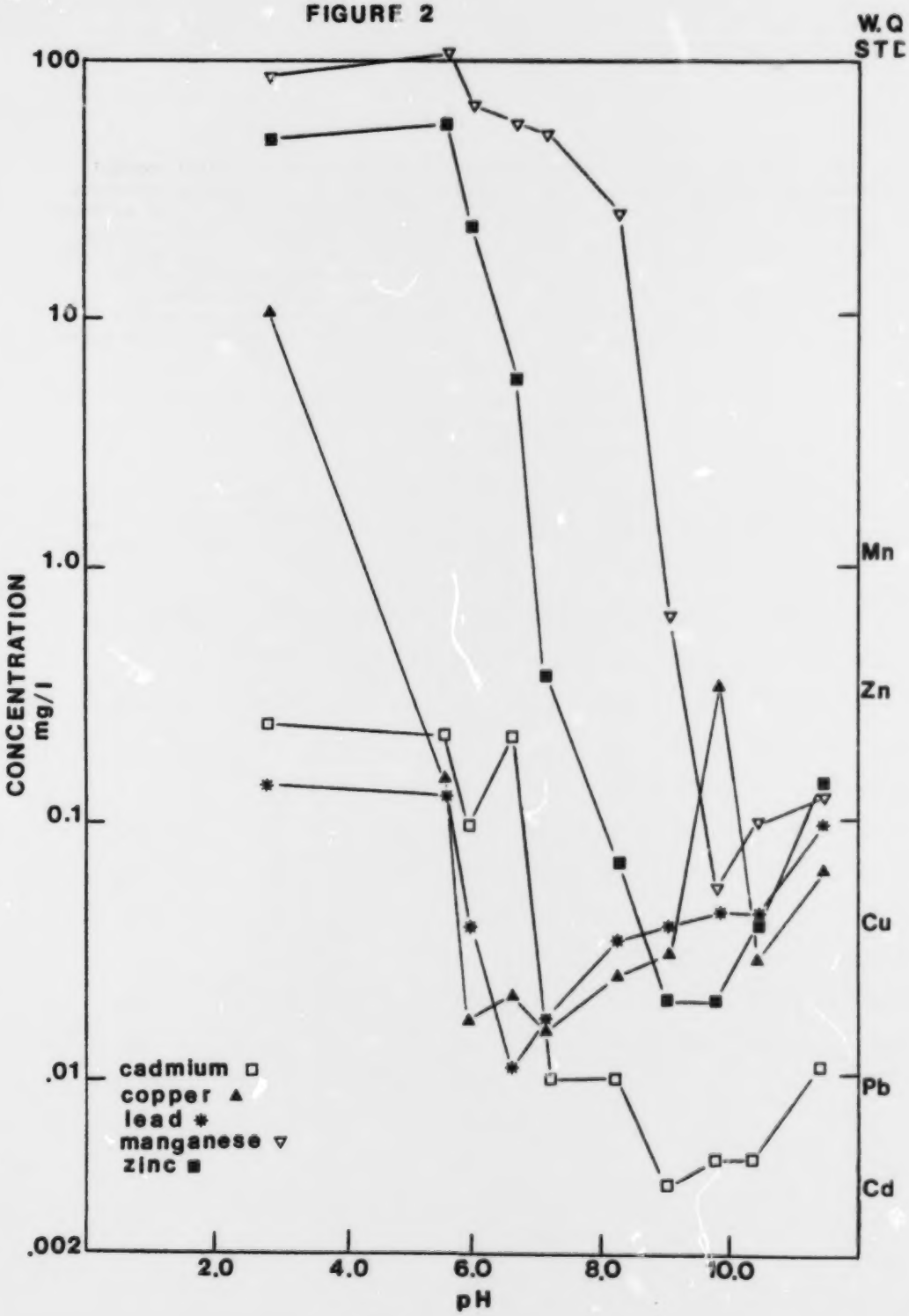
When the continuous concentrator is operated at pH levels lower than 8.3, some trace metal concentrations increase beyond the point considered toxic for aquatic life. Of course, sodium concentrations continue to drop as water within the system is diluted with raw mine water in order to lower the pH. Sodium levels are elevated in effluent from the system since sodium hydroxide is used as the neutralizing agent.

The results of the sampling program indicate that the range providing optimal treatment of the Argo Mine drainage using the continuous concentrator apparatus falls between pH 8.3 and pH 9. Below pH 8.3 metal concentrations in the effluent rise above fish toxic levels. Above pH 9, excessive alkalinity produces toxic effects on aquatic species. While the concentration of sodium in effluent within this optimal pH range is slightly excessive, the tremendous dilution effect afforded by Clear Creek which is the receiving stream, would eliminate any potential impacts to agricultural users. There are no standards for sodium in Clear Creek under the recently proposed standards for the South Plattee Basin.

TABLE 4: Chemical Quality of Effluent when Operating the Continuous Concentrator System with Variable pH.

Parameter mg/l	pH 3.4	6.6	7.2	8.3	9.2	9.8	10.5	11.5	Proposed Water Quality Std. mg/l
Total dis. solids	3560.	3660.	3630.	3610.	3610	3480	3620	5230	No Standard
Sulfate	2100.	1600.	1800	2100.	1600	1500	2300	1800	250
Sodium	170.	250	270	330.	440	540	800	1540	No Standard
Arsenic	.75	.08	.01	.01	.01	.01	.02	.29	.05
Cadmium	.29	.73	.01	.01	.004	.005	.005	.005	.002
Chromium	.03	.10	.01	.01	.01	.01	.01	.01	.050
Copper	14.	36.	.015	.025	.030	.034	.029	.030	.060
Iron	50.	1000.	.01	.01	.01	.01	.02	.06	1.55
Manganese	108.	190.	51.	25.	.65	.005	.10	.10	1.1
Lead	.13	.16	.017	.035	.039	.045	.043	.042	.009
Zinc	63.	160.	.37	.07	.02	.02	.04	.05	.55

FIGURE 2


W.Q
STD
100
10
1.0
0.1
.01
.002
CONCENTRATION
mg/l
Mn
Zn
Cu
Pb
Cd
cadmium □
copper ▲
lead ✱
manganese ▽
zinc ■
2.0
4.0
6.0
8.0
10.0
pH

Conclusions

1. The treatment process of neutralization, precipitate concentration and filtration is effective for reducing trace element levels from the Argo Mine drainage. When the pH of the mine water in the system is raised using NaOH, the concentrations of metal in the effluent are observed to drop radically. The dissolved metals react with the NaOH to form insoluble metal hydroxide compounds which immediately precipitate out of solution. When the slurry of mine water and metal precipitates is pumped into the continuous concentrator, the suspended solids are retained within the system and returned to the consolidation tank. Meanwhile, clear effluent is discharged from the concentrator system.

2. The optimum pH range for operating the continuous concentration system is from 8.3-9.0. The system, operating in this pH range produces a clear colorless effluent from the Argo Mine drainage which meets all applicable water quality standards except those for cadmium, lead, sulfate and perhaps manganese. Cadmium concentrations in the effluent only slightly exceed the cold water aquatic life standards set for Clear Creek for the reach below the Argo Tunnel. Lead concentrations in the effluent would be acceptable for cold water aquatic species but exceed drinking water standards. The first intake for a potable supply is some 15 miles below the Argo Tunnel. The extremely high sulfate concentrations in the Argo drainage are largely unaffected by the treatment system.

3. The treatment process evaluated in this study produces a sludge product composed of metal oxide and metal hydroxide compounds. Whether these metal compounds are individually separable and recoverable was not analyzed in the study. If the oxidized metals are indeed separable and recoverable, markets do exist for the products derived from the sludge produced in the sodium hydroxide neutralization reaction.

4. The operational and maintenance costs as well as equipment costs for the neutralization, precipitate concentration and filtration process evaluated in this study probably fall in the mid range of estimated costs for common acid mine drainage treatment systems (see Table 3). However, if the sludge product is marketable, treatment costs may be reduced or eliminated.

Recommendations

1. Test the neutralization and continuous concentration system on a number of other acid mine drainages in Colorado to assess its effectiveness in removing trace elements from waters having various chemical qualities.

2. Test the neutralization and continuous concentration system handling small, medium and large in-flow volumes.

3. Analyze the sludge products from the neutralization and continuous concentration system. Determine the separability and recoverability of oxidized metals in the sludge. Evaluate potential markets for sludge products.

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APPENDIX A

Toxicity of Trace Elements

The toxicity of trace metals in humans is a complex subject that is dependent upon many factors. In a multi-ion solution, as found in nature, the individual metal ions react, which can cause changes in toxicities compared to a single ion solution. One ion may block the toxicity of another ion. This is known as an antagonistic effect. Two ions can also work together increasing the toxicity of either one alone. This is known as a symergistic effect.

Toxic effects are also a function of the valance state of the element. One particular valence state may be more toxic than another. Also an element may or may not demonstrate antagonistic or synergistic effects or even toxicity based upon its valence state.

Toxicity is also dependent upon an elements interaction with the human body. Some elements (metals) are accumulated in the body and are never released. Thus small concentrations introduced over a long period of time may be harmful. Other elements pass through the human body and never build up. Certain elements, such as Mercury, accumulate not only in humans but in other animals as well. Consumption of these other animals leads to concentration of these elements further up the food chain.

The following is a list of the recognized toxic trace metals found in surface water. The descriptions for each metal includes available information on average intake as well as lethal doses. U.S. Public Health Service (USPHS) levels for drinking water are also presented.

Arsenic

In the trivalent state arsenic can be extremely toxic to humans. It accumulates in body tissue over time, thus small doses can be harmful. Average human intake is approximately 0.9 mg/day. USPHS and Colorado Drinking Water Standards call for .05 mg/l maximum concentrations.

Arsenic may occur in water as a result of mineral dissolution, industrial discharges, or the application of insecticides. Severe poisoning can arise from the ingestion of as little as 100 mg arsenic; chronic effects can appear from its accumulation in the body at low intake levels. Carcinogenic properties have also been imputed to arsenic.

Cadmium

Cadmium has been shown to be toxic to man when ingested or inhaled. Exposure by the former route causes symptoms resembling food poisoning. Biologically, cadmium is a nonessential, nonbeneficial element recognized to be of high toxic potential.

Cadmium is accumulated in the liver and kidneys. A safe intake is considered to be in the range of 55-77 mg/day. USPHS and Colorado drinking water standards recommend levels of .01 mg/l and .002 mg/l to protect aquatic life. Cadmium may function in or may be an etiological factor for various pathological processes including testicular tumors, renal dysfunction, hypertension, arteriosclerosis, growth inhibition, chronic diseases of old age, and cancer.

Chromium

Hexavalent chromium is the more toxic species. However, chromium III is also considered toxic in large quantities. Above the 5 mg/l level chromium begins to concentrate in body tissues. USPHS drinking water standards call for chromium levels of less than .05 mg/l.

Copper

Copper is an essential trace element for the propagation of plants and performs vital functions in several enzymes and a major role in the synthesis of chlorophyll. A shortage of copper in soil may lead to chlorosis which is characterized by the yellowing of plant leaves.

The toxicity of copper to aquatic life is dependent on the alkalinity or hardness of the water because the copper ion is complexed by the anions present in the water, thereby affecting its toxicity. At lower alkalinity or hardness values, copper may be more toxic to aquatic life. Relatively high concentrations may be tolerated by adult fish for short periods of time, but the critical effect of copper appears to be its higher toxicity to the very young or juvenile fish.

Generally not a problem in natural waters, copper may cause a problem in regards to taste or aquatic life in industrial areas or where it is used as an alglicide or for slime control.

Iron

Iron is the fourth most abundant, by weight, of the elements that make up the earth's crust. Common in many rocks it is an important component of many soils, especially the clay soils where usually it is a major constituent. Iron in water may be present in varying quantities dependent upon the geology of the area and other chemical components of the waterway.

Iron is an essential trace element required by both plants and animals. Iron is an essential trace element required by both plants and animals. Iron is an objectional constituent in water supplies for either domestic or industrial use. The iron criterion in water is to prevent objectionable tastes or laundry staining (0.3 mg/l) constitutes only a small fraction of the iron normally consumed and is of aesthetic rather than toxicological significance. In an iron polluted Colorado stream, neither trout nor other fish was found until the waters were diluted or the iron had precipitated to effect a concentration of less than 1.0 mg/l even though other water quality constituents measured were suitable for the presence of trout. Some groundwaters and acid surface drainage may contain considerably more iron than this.

Lead

Lead is a very toxic element that accumulates in human tissues. Very small concentrations over a long time period can be detrimental. An average dose of lead is approximately 240-320 mg/day. Six hundred mg/day may be harmful to the human body. The World Health Organization recommends not more than .05 mg/kg body weight weekly. The toxicity of lead in water, like that of other heavy metals, is affected by pH, hardness, organic materials and the presence of other metals. Lead enters the aquatic environment through mine drainage, precipitation, lead dust fallout, erosion and leaching of soil, municipal and industrial waste discharges, and the runoff of fallout deposits from streets and other surfaces. In drinking water lead should be kept to a minimum; USPHS and Colorado water standards are set at .050 mg/1.

As far as is known, lead has no beneficial or desirable nutritional effects. Lead is a toxic metal that tends to accumulate in the bones of man and other animals. Although seldom seen in the adult population, irreversible damage to the brain is a frequent result of lead intoxication in children.

Manganese

Although rarely present in excess of 1 mg/1, manganese imparts objectionable and tenacious stains to laundry and plumbing fixtures. The low manganese limits imposed on an acceptable water stem from these, rather than toxicological, consideratons. Special means of removal are often necessary, such as chemical precipitation, pH adjustment, aeration, superchlorination, and the use of special ion-exchange materials. Manganese occurs in domestic wastewater, industrial effluents, and receiving streams, but is generally unimportant except as it may enter a potable supply intake.

Selenim

Selenium has a toxic effect on man and animals comparable with that of arsenic, giving rise to similar symptoms. Selenium also has been suspected of causing dental caries in man and of being a carcinogenic agent. Selenium poisoning is usually related to ingestion of food rather than water. It is widely used in industry and is naturally abundant in some soils.

The selenium concentration of most drinking waters is less than 10 ug/1. Concentrations exceeding 500 ug/1 are rare and limited to seepage from seleniferous soils. The sudden appearance of selenium in a water supply might indicate industrial pollution.

Sodium

Sodium ranks sixth among the elements in order of abundance; therefore, it is present in most natural waters. The levels may vary from negligible to appreciable. Relatively high concentrations may be found in brines and hard waters softened by the sodim exchange process. The ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability has been harmed by a high sodium ratio. The alkali hazard involved in the use of a water for irrigation is determiend by the absolute and relative concentrations of the cations. If the proportion of sodium is high, the alkali hazard is high; and, conversely, if calcium and magnesium predominate, the hazard is low.

"Hard water makes soft land and soft water makes hard land." Alkali solids are formed by accumulation of exchangeable sodium and are often characterized by poor tilth and low permeability.

Zinc

Zinc is an essential and beneficial element in body growth. However, concentrations of zinc in water above 5 mg/l can cause a bitter astringent taste and a milky irridescence in alkaline waters. Zinc enters the waterway from mine related drainage, sewage discharges, and by the deterioration of galvanized iron. Zinc may also result from industrial waste pollution.

Zinc is considered toxic to aquatic species at far lower levels than for humans. In low hardness water levels as low as .100 mg/l are toxic to trout. Zinc and copper have a synergistic toxic effect upon cold water aquatic species (i.e. when combined in solution each is toxic at lower levels).

PASSIVE MINE DRAINAGE TREATMENT

Promoting Natural Removal Mechanisms for Acidity and Trace Metals from Mine Drainage

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Michael B. Bishop, Kaman Tempo

ABSTRACT

The most severe mining-related impacts upon water quality in Colorado arise from inactive and abandoned metal mines. This is partly because a mechanism for regulation and control of drainage from inactive mines has not been developed, and no cost efficient techniques for treating inactive mine discharges are available. There is, in most cases, no responsible entity to charge with the task of controlling discharges from such mines. In Colorado, Twenty five watersheds and 450 stream miles have been rendered barren of aquatic life and unfit for other beneficial uses as a result of toxic drainage from inactive mines. There is a great need in this state and throughout the nation for easy-to-construct, at-source treatment systems which effectively reduce acidity and metals concentrations and which do not require significant external electrical or chemical inputs for operation and maintenance. The term "passive mine drainage treatment" is used to describe the entire range of mine drainage abatement techniques which when combined or applied singly address this need. Passive treatment techniques can rely on natural geochemical mechanisms such as neutralization, oxidation, dilution, adsorbtion, and preciptiation, as well as techniques which involve physical intercession into the process of formation of acid mine drainage. This investigation focuses on the description of naturally occurring geochemical processes which have been effective in reducing metal concentrations and acidity at several sites in Colorado and the application of these same mechanisms in a passive treatment design for the Marshall #5 coal mine drainage problem area.

INTRODUCTION

Mine Drainage in Colorado

The most profound and widespread mine-related impacts to streams in Colorado are attributable to inactive and abandoned metal mines. More than 10,000 inactive metal mines exist in the state. These range in size from small prospecting holes to large-scale operations which have literally perforated entire mountainsides. Of course, not all inactive metal mines are significant contributors of stream pollutants.

Twenty-five watersheds and approximately 450 miles of stream are drastically impacted by metal mine drainage in Colorado (Wentz, 1974, Holm, et al 1982). The major sources of pollutant loading (i.e. mine dumps, discharges from adits, mill tailings etc.) within several of these drainages have been identified (Woodling 1976,1977; Davis et.al.1977; Holm, et. al.1979, Holm et.al.,1982; Kepler 1980; Carley, et. al.1981).

Because western coal deposits have low sulfur content, acid mine drainage is not usually a problem at abandoned coal mines. There are perhaps a half dozen examples of metal-laden acidic discharges from coal mines in this state.

Most of the metal mining in Colorado has occurred within a region commonly known as the Colorado Mineral Belt. Most metal mines within this region are located at high altitudes which, in terms of water pollution control and land reclamation, present some unique problems.

Drainage from inactive mines presents the most difficult point source category for which to develop control strategies. Many of the problem areas are located in rugged mountainous terrain which have limited access, especially in winter months. Access problems limit the choice of pollution abatement solutions to those which require little or no routine inspection or maintenance. Each inactive mine drainage problem is unique because of such features as the location of the mine, characteristics of the mineral body, the mining techniques used, and the hydrology of the area. Control techniques for mine drainage are highly dependent on these variables. Actual treatment options for a site cannot be determined until these characteristics are well defined.

The Colorado Department of Health, Water Quality Control Division currently lacks the resources and in many cases the authority to control water pollution from abandoned or inactive mines. The ownership of surface and mineral rights are often held by different parties. It is not uncommon that the present owners were not the operators during active mining but acquired the rights subsequent to mine shutdown. Since the original mining generally was done in a legal manner the liability of past operators and owners is in question. It would be difficult to assign responsibility to present landowners in most cases because of the high costs of reclamation work and small resultant land improvement benefits (Holm,1978).

Passive Mine Drainage Treatment

Given the difficulties of controlling pollution from inactive and abandoned mines in Colorado, there is a great need for mine drainage abatement and control measures which 1) effectively reduce pollution at the source; 2) require minimal heavy construction equipment for installation; 3) do not require significant electrical or chemical inputs to be effective, and 4) require infrequent inspection and maintenance activities. The term "passive mine drainage treatment" is used to describe the various techniques which may be used to reduce pollution from streams given these constraints.

Passive treatment refers in part to the reliance upon natural

geochemical processes for acid neutralization and metals removal. Poor access conditions dictate that only light construction work be required for initial system installation. Given the remoteness of most mines, operation of the treatment system cannot depend upon external power sources and frequent maintenance requirements. The present concept of passive mine drainage treatment utilizes the geochemical mechanisms of neutralization, oxidation, dilution, adsoprtion (cation exchange), co-precipitation, and precipition in order to reduce metals concentrations and acidity in mine drainage. Passive mine drainage treatments must be designed on a site-by-site basis to better incorporate local conditions which can enhance the natural geochemical processes required for treatment and to compensate for unique problems related to access, elevation, surface hydrology, type of mining and specific pollutants. Passive treatment approaches do not eliminate the need for detailed hydrologic evaluations and careful system design work. Rather, such treatment approaches require more rigorous evaluations and "front-end" planning and design. The success of passive mine drainage treatment approaches depend on the application of natural geochemical processes and the reduplication or simulation of naturally occuring metal and acidity removal systems. The goal of passive treatment systems is to reduce pollution to the maximum extent possible. Nearly complete removal of toxicants is possible with active treatment systems (Holm et.al.,1981).

The concept of passive drainage treament is mainly derived from observations of several natural systems in Colorado, where polluted mine drainage flows, in one case, into a small network of beaver ponds (Shuster Mine), and, in another case, into an artificial bog/pond (Delaware Mine). In both examples a significant reduction in heavy metal concentrations and acidity is realized within a very short drainage segment. These observations have been duplicated in bench scale experiments and field trials (Lapako et.al.,1981). Field scale investigations of the feasibility of using a passive mine drainage treatment system at the Marshall #5 coal mine are currently underway.

GEOCHEMICAL PROCESSES AFFECTING ACID MINE DRAINAGE

pH

The solubility of most elements and the stability of their compounds is extremely sensitive to the pH of the aqueous environment. The pH at which these elements precipitate as hydroxides is known as the pH of hydrolysis.

pH explains one mechanism by which trace elements are dissolved and transported in mine drainage or accumulate in stream sediments.
Mine water whose pH is below 4.5 commonly involves oxidation of some form of sulfur, usually sulfides. During the oxidation of sulfide minerals, pH decreases and high acidity values are generated. In this environment many metals are mobile. Mobility is decreased as the pH becomes higher (more alkaline).As acid mine water is diluted with waters of high pH, or as the acid waters react with rocks over which they are passing, the pH of these waters will tend to increase, and trace metals will precipitate out as their pH of hydrolysis is reached. The pH of mine drainage can increase in highly oxidizing conditions as well.

Eh - Oxidation/Reduction Potential

A measure of the oxidizing and reducing tendency of a solution is known by the synonymous terms Eh, redox potential, oxidation potential, and oxidation-reduction potential. The redox potential determines in large part whether many elements remain in solution or precipitate. When iron and magnanese are in a reduced state, that is as Fe^{+2} and Mn^{+2}, they are mobile in most natural enviornments. However, as soon as they are oxidized to the +3 and +4 states, respectively, their mobilities are greatly reduced and they are likely to form precipitates of iron and manganese oxides. In other words, the valence state determines in large part whether these elements remain in solution or precipitate. This is an example of the importance of oxidation-reduction processes.

In addition to abundant oxygen, free drainage is required for oxidation to be a significant process. Redox potential in many ways is analogous to pH. It measures the ability of an environment to supply electrons to an oxidizing agent, or to take up electrons from a reducing agent, just as the pH of an environment measures its ability to supply protons (hydrogen ions) to a base or to take up protons from an acid. The oxidation potential (Eh) is actually a measure of the voltage involved in the addition or removal of electrons during the change of the valence state of various elements (e.g., Fe, Mn, Cu). The energy required to change valence states is modified by pH. Therefore, both Eh and pH determine the concentration of an ion that will remain in solution, and a change in either may be sufficient to cause precipitation. The factors which govern the mobility or deposition of most heavy metal compounds can be summarized as: (1) oxidizing conditions promote precipitation whereas reducing conditions promote solution and, (2) acidic solutions generally promote solution whereas alkaline solutions promote precipitation.

Adsorption by Iron and Manganese Oxides

The hydrous iron and manganese oxides are of particular importance in mine drainage for two reasons. First, during their precipitation, they may incorporate, by coprecipitation, other elements which would normally be unaffected by changes in pH and Eh. Second, once formed, they have the tendency to adsorb (scavenge) elements with which they come in contact. (For this discussion, the term adsorption includes sorption, and is defined as the adhesion of ions or molecules to the surfaces of solid bodies with which they are in contact). The net result of both processes is that many metals, such as zinc and copper, which are normally very mobile, at least in slightly acidic solutions tend to become concentrated in the iron and manganese precipitates (Levinson,1980)

Adsorption (or desorption) of heavy metals such as Mn, Fe, Co, Ni, Cu and Zn occurs in response to the following factors: (1) instream concentration of Fe and Mn; (2) aqueous concentration of other heavy metals; (3) pH; and (4) amount and strength of organic chelates and inorganic complex ions present in the solution, (Levinson 1980).

Adsorption By Organic Matter

Organic (humus) layers in bogs or in soil can accumulate great concentrations of certain metals. In fact, the exchange capacity of humus can be as high as 500 meq/100g compared with clays which rarely exceed 150 meq/100g. Organic matter in swamps and bogs often shows high metal value. However, all metals are not adsorbed equally by organic matter. pH, Eh, and the nature of decaying material are probably important factors which influence adsorption.

The degree of enrichment of elements in the humus layers of bogs depends very largely on the type of aquatic vegetation, since plants vary greatly in their capacity to accumulate various elements. In many natural cases up to 90% of the bog mass is sphagnum, or peat composed of sphagnum remains. Sphagnum establishes itself in a thick, floating mat of sod across the bog. For metal adsorbancy, sphagnum is the next best thing to a sponge. Also peat adsorbs elements about as well as sphagnum (Krouskoff 1967).

The Shuster Mine Drain: A Natural Bog/Pond Treatment System

The Shuster Mine drains polluted mine water into Oak Creek, a tributary of the Yampa River. This mine opening is very near the town of Oak Creek. The town of Oak Creek is located along Oak Creek, approximately 20 miles southwest of Steamboat Springs, Colorado and 180 miles northwest of Denver.

Mining activity in the Oak Creek study area has been connected primarily with the extraction of coal. The coal in the area is bituminous and is associated with the Mesaverde group, which is composed of sandstone and shale of Cretaceous age. Copper has been reported in the district, but the nature of its occurrence is not known (Vanderwilt, 1947).

The Shuster mine drainage contains large concentrations of iron [8 mg/l], manganese [1.7 mg/l], cadmium [15 ug/l], lead [200 ug/l], zinc [40 ug/l]. However, these elevated levels of metals are not observed in Oak Creek even though the Shuster mine drains voluminous quantities of water (.1-9.0 cfs) relative to the flow of Oak Creek (Carley et.al.,1981).

Oak Creek, below the Shuster Mine drainge only exceeded water quality standards for zinc in the spring of 1980, and then it appeared to be caused by a background source. Zinc concentration gradually increased going downstream, independent from the Shuster mine drainage. Cadmium exceeded the water quality standards for Oak Creek in the spring and the fall, but in both cases exceeded the standards for these parameters above the Shuster mine, as well as below. Cadmium levels were only slightly influenced, if at all, by the mine drainage. Lead exceeded the water quality standards for Oak Creek in the spring above and below the Shuster Mine, but with no apparent effect from the mine drainage itself. The pH values for the Shuster drainage range from 5.9 to 7.7. Iron and Manganese were only slightly elevated in Oak Creek below the mine drain (Carley et.al.,1981).

The impact of the Shuster mine on Oak Creek is relatively minor, even though the mine drainage is somewhat spectacular to look at, showing graphic evidence of red staining. A natural phenomenon is occurring at this site which is somewhat remarkable. Mine water is cascaded down the face of the exposed sandstone outcrop below the adit resulting in oxygenation to the point of saturation. Beavers in the area have constructed several ponds and a rather elaborate system of canals and diversions below the Shuster adit. The net result is that the heavily oxidized Shuster drainage filters through the bog-like beaver dams and the effluent is gradually blended with stream water, until finally it joins the main stem. According to local Oak Creek residents, fishing in Oak Creek is about as good above Shuster as below.

Delaware Mine: An Artificial Bog/Pond Treatment Experiment

One of the first experiments in Colorado with metal mine draingage treatment using an artificial pond and bog was done for the Delaware (Blue Magazine) mine in the Peru Creek Drainage (Holm, et. al., 1979). Peru Creek is located just west of the continental divide and drains the west flank of 14,000 feet Greys and Torrey's peaks in Summit county. The Peru Creek area has been mined extensively for silver and other base metals in the last 110 years, with much of the mining having been initiated around 1870 and slowing considerably with the Silver Panic of 1892. For this reason, the sources of acid mine drainage and heavy metals loading are numerous and widespread.

The metal deposits that caused the big rush are predominantly complex ore, a mixture of copper, lead, zinc, and silver sulfide and native gold. One of the significant point sources of acidity and heavy metal loading to Peru Creek is the Delaware mine.

The mine is located on the east side of Cinnamon Gulch, which drains into Peru Creek. The portal is blocked, but effluent flows out through the rubble. There is a yellowish-orange (Fe) precipitate coating the drainage channels. On august 3rd, 1978, the effluent from the Delaware mine was re-routed into a small, heavily sodded pond that had been built before this time. The effluent was previously flowing across a large area of mine waste. Later samples were taken above and below this pond, to analyze the effectiveness of the structure in improving water quality.

Test results (Table 1) from the pond/bog experiment indicated that greater than 75% reduction in total metals loading concentration was achieved just by settling out the suspended solid and through adsorption of disolved metals onto the bog and soil materials in the pond.

Table 1

Delaware Mine Metal Loading (g/day)
above and below pond (Holm et. al., 1979)

	Flow (cfs)	pH	Cd	Cu	Pb	Zn	Fe	Mn
Mine drainage above pond	.33	3.9	1.2	9.0	2.0	343.	525.	277.
Mine drainage below pond	.31	4.5	0.3	2.0	0.1	72.	6.	49.
% reduction in metals loading (g/day)	---	---	75%	78%	95%	80%	99%	83%

Marshall #5 Coal Mine: Passive Treatment by Design

The Marshall #5 coal mine is located one half mile south of the town of Marshall and 4 miles south of Boulder, Colorado. This mine is one of the few inactive coal mines in Colorado which discharges a significant amount of metaliferrous acidic mine water. The water drains out across a portion of the Boulder City Open Space Lands.

This site has good potential for applying passive treatment principles patterned after the natural treatment systems described earlier. For water quality treatment the system is separated into two stages. The firxst stage of the treatment process involves oxidation and precipitation. Oxidation of the mine effluent is enhanced by creating very turbulent flows. Turbulance is induced by placing groins (rock gabions) in the channel. Fe and Mn are readily preciptated in oxidizing conditions. Other metals, are coprecipitated with the oxides of Fe and Mn. The pH of the drainage also tends to increase in heavily oxidizing conditions. Increasing pH allows further precipitation and coprecipitation.

This first stage of the process is further designed to encourage precipitation as the drainage passes through short sections of limestone cobbles which are placed in trenches periodically between the turbulance groins.

The second stage of the process involves small rock check dams, composed of durable limestone which are designed to temporarily detain the mine drainage and allow it to filter through heavy organic peat and living bog plant materials. The initial design concern was to select a suitable structure that would hold a deposit of peat materials and yet allow percolation of mine effluent through the peat materials.

The U.S. Forest Service has developed design criteria for low cost rock check dams that have provided a successful means of controlling gulleys in arid/semiarid regions of the west (Heed, 1966). The rock check dams are ideally suited to the construction of an artificial peat bog because of their ease of construction, durability, readily

available materials (loose rock) and the ability of the structure to feely pass water. The rock check dams not only serve as the structure to hold the peat moss but also tend to further aerate the acid waters.

In the case of the Marshall #5 treatment system, the key design elements to be considered are aimed at providing a stable, highly permeable rock structure that contains sufficient storage for a simulated peat and moss bog. For a loose rock structure of this type it is important to key the dam into the stream bed and stream banks. This measure prevents flow from eroding around the structure. Heede (1966) tested several dam configurations and found that loose rock dams should not exceed 6 feet in height. Therefore, the peat storage volume available behind the dam is dictated by the cross section of the stream. Since no upland watershed affects the flow of the mine drainage the appropriate spacing between dams is only influenced by the upstream extent of the peat moss in relation to the toe of the next upstream structure. Two structures have been designed for the Marshall #5 drainage. It is also considered important to provide rock aprons and similar bank protection below each structure to prevent undercutting, as well as, a properly designed spillway over each of the rock check dams.

The check dams function as retention devices to store plant materials and peat which are capable of adsorbing heavy metal contaminents. This simulated bog is composed of cured peat wood chips and hydrophilic acidophilic aquatic vegetation (Table 2). The shoreline of the loose rock impoundments is heavily revegetated with plant materials capable of metal uptake and which can tolerate acidic conditions . In time hopefully the organic litter from this vegetation will recharge the adsorptive capacity of the bog system.

Table 2

Bog Community Species to be Included in Simulated Bog at Marshall #5 Coal Mine (Hutnik et.al.,1973; Vallantine, 1971; Weber, 1976)

Aquatic Species	Terrestrial Species with High Water Tolerance	
Spnagnum Moss	Grasses:	Red-top
Water Hyacinth		Tall Wheatgrass
Pondweed		Western Wheatgrass
Horned Pondweed		Basin Wildrye
Frogbit		Tall Fescue
		Weeping Lovegrass
		Birdsfoot trefoil
Riparian Species	Forbes:	Strawberry Clover
Broad-Leaved Cat-tail		White Sweetclover
Field Horsetail		
	Trees:	European Black Alder
		Gray Birch
		Black Locust

Two other important features have been added to the design of the rock check dams to better faciliate metal adsorption (cation exchange) with the impounded peat materials. These design elements serve to facilitate flow of water through the peat materials and through the rock structures. A rock sub-drain is placed under the peat moss and a light gravel cover is placed over the peat moss. These features allow drainage through the lower portion of the peat moss and serve to hold the peat in place.

The loose rock check dam is designed to enhance metal adsorbtion and cation exchange. The result is a low cost, low maintainence artificial peat bog which filters the mine effluent.

Conclusion

The serious problem of acid mine drainage affecting water resources in Colorado is exacerbated by the fact that water is in such short supply. An arid state like Colorado, cannot afford to allow entire watersheds to remain incapable of sustaining beneficial uses because of the toxicity and aesthetic problems attributable to acid mine drainage. On the other hand, active mechanical treatment systems for hundreds of significant point sources of toxic mine effluent cannot be constructed, because of the huge amount of capitol this would require and the fact that this approach is not always appropriate for particular mine drainage problem areas.

Passive mine drainage treatment techniques are being developed which utilize and enhance natural geochemical processes for acid neutralization and metals removal. Such techniques rarely provide for total removal of toxicants from mine drainage. However, by accellerating the processes of oxidation, precipitation and adsorbtion, passive treatment techniques can provide significant reductions in pollution and decrease the overall length of impacted stream segments. The efficacy of passive treatment techniques is demonstrated from observations of natural systems and bench scale experiments(Lapako et.al.,1981). These observations and expermental results have been incorperated into the design of a passive mine drainage treatment system for the Marshall #5 coal mine.

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Theoretical Assessment and Design Considerations for Passive Mine Drainage Treatment Systems

by

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ABSTRACT

The most severe mining-related impacts upon water quality in Colorado arise from inactive and abandoned metal mines. This is partly because a mechanism for regulation and control of drainage from inactives mines has not been developed, and no cost efficient techniques for treating inactive mine discharges are available. There is, in most cases, no responsible entity to charge with the task of controlling discharges from such mines. In Colorado, 25 watersheds and 450 stream-miles have been rendered barren of aquatic life and unfit for other beneficial uses as a result of toxic drainage from inactive mines. There is a great need in this state and throughout the nation for easy-to-construct, at-source treatment systems which effectively reduce acidity and metals concentrations and which do not require significant external electrical or chemical inputs for operation and maintenance. The term "passive mine drainage treatment" is used to describe the entire range of mine drainage abatement techniques which when combined or applied singly address this need. Passive treatment techniques can rely on natural geochemical mechanisms such as neutralization, oxidation, dilution, adsorbtion, and precipitation, as well as techniques which involve physical intercession into the process of formation of acid mine drainage. This investigation focuses on the description of naturally occurring geochemical processes which have been effective in reducing metal concentrations and acidity at several sites in Colorado and the application of these same mechanisms in a passive treatment design for the Marshall #5 coal mine drainage problem area.

I. Introduction

Mine drainage, particularly from inactive metal mines presents the most difficult point source of pollution to control and abate in the State of Colorado. Many mine drainage problem areas are located in rugged mountainous terrain which have limited access, especially in winter months. Access problems limit the choice of pollution abatement solutions to those which require little or no routine inspection or maintenance. Each inactive mine drainage problem is unique because of such features as the location of the mine, characteristics of the mineral body, the mining techniques used, the topography, and the hydrology of the area.

Given the difficulties of controlling pollution from inactive and abandoned mines in Colorado, there is a great need for mine drainage abatement and control measures which 1) effectively reduce pollution at the source; 2) require minimal heavy construction equipment for installation; 3) do not require significant electrical or chemical inputs to be effective, and 4) require infrequent inspection and maintenance activities. The term "passive mine drainage treatment" is used to describe the various techniques which may be used to reduce pollution from mine discharge given these constraints. The primary objectives of passive treatment systems for acid mine drainage are to increase the effluent pH and to obtain the maximum possible reduction in concentrations of dissolved heavy metals. Natural geochemical processes such as pH modulation and neutralization, aeration , dilution, cation exchange and adsorption, sorption and co-precipitation are relied upon to achieve these objectives at the effluent source (1).

Basic components of a passive treatment system include an ion exchange medium, limestone barriers or energy dissipators and cascades or waterfalls. An organic ion exchange medium (such as a peat bog) can be used to extract metals from the drainage, limestone is used to neutralize acidity, and waterfalls or gabions provide aeration and carbon dioxide exsolution, increasing the dissolved oxygen in the effluent and helping to raise pH.

Passive mine drainage treatment systems are designed on a site-by-site basis to be well adapted to local environmental conditions. Site specific treatments are required to compensate for unique problems related to access, elevation, surface hydrology, specific pollutants, type of mining and legal restrictions such as water rights and land use controls. While passive treatment approaches minimize the need for ongoing maintenance, they do not eliminate the need for detailed hydrologic evaluations and careful system design work. Such treatment approaches require rigorous site evaluations and "front-end" planning and design. The success of passive mine drainage treatment approaches depend on the application of techniques which emulate and enhance naturally occurring metal and acidity removal processes. The efficiency of passive treatment systems is determined in general by three major factors: the chemical processes involved in the formation of acid mine drainage, the natural geochemical processes applied in the components of a passive treatment system, and engineering and legal constraints.

II. Chemical Processes in Acid Mine Drainage

Formation of Acid Mine Drainage

The formation of acid mine drainage and the chemistry of the resultant solution following its discharge from the mine is extremely complex. However, careful consideration of the chemical processes is indispensable prior to designing passive acid mine drainage treatment systems. A review of the literature reveals that the majority of acid mine drainage investigations have been directed primarily toward the behavior of iron. This is due to the belief that acid mine drainage is the result of the oxidation of iron sulfides (represented in general by pyrite) in the presence of water and atmospheric oxygen. Iron is released into solution and sulfuric acid is produced in a self-propagating cycle of chemical reactions. Study of the behavior of the solution as a complete entity, including other metals commonly present in acid mine drainage has been neglected.

Stoichiometrically, the reactions are summarized by Stumm and Morgan (2) as:

(1) Initiator Reaction: $FeS_2\ (s) + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{\ 2-} + 2H^+$

(2) Propogation Cycle: $Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O$

(3) " " $FeS_2\ (s) + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{\ 2-} + 16H^+$

(4) Hydrolysis Reaction: $Fe^{3+} + 3H_2O = Fe(OH)_3\ (s) + H^+$

In the first reaction, sulfur is oxidized to sulfate whereby H+ is generated and Fe^{+2} is released into solution (3). This oxidation process may be accomplished either directly by atmospheric oxygen or by the simple dissociation of pyrite in solution, followed by oxidation by aqueous oxygen (2,4). Ferrous ions are then oxidized to produce ferric ions in the first step of the propagation cycle (reaction #2). In the initial stage of the propagation cycle, the natural alkalinity of the water is sufficient to prevent ferric iron from remaining in solution, and insoluble ferric oxides are produced and precipitated forming the characteristic yellow sediment known as "yellow-boy". The formation of ferric oxides, however, is accompanied by a release of hydrogen ions, which causes the pH to decrease. When the pH has dropped enough to allow ferric iron to remain in solution, the second step of the propagation cycle begins (reaction #3). Ferric iron, a powerful oxidizing agent, assumes the primary role in the oxidation of pyrite (5). Ferric iron is reduced to ferrous iron to produce more sulfate and acidity, and then is reoxidized to ferric iron (reaction #2), and so on. For each mole of pyrite oxidized, four moles of acid are produced in the overall cycle. The ferric oxides, which precipitated during the earlier stage of the cycle (reaction #2), when the pH was above the solubility range of ferric iron, may serve as a reservoir of additional ferric ions once the pH is lowered. This allows continuation of the cycle with continued exposure of the ferric ions to solid pyrite even in the absence of atmospheric oxygen. Once this cycle is established, atmospheric oxygen no longer plays a significant part in the oxidation process (2).

The powerful oxidizing action of ferric ions may also be responsible for the release of other metals such as Cd, Cu, Pb, Zn and Mn from their sulfide forms (6,2). Ferric ion, produced in the oxidation of the pyrite that is invariably present in any sulfide ore deposit, assumes the role of oxygen thereby releasing the divalent metal ion and elemental sulfur (7).

Kinetics

The rate-determining step in the series of reactions that produce acid mine drainage is the oxidation of ferrous ion (reaction #2). Singer and Stumm (2) showed that in an abiotic system the oxidation of Fe^{+2} by oxygen was a function of pH. At pH values greater than 4.5, the rate of the reaction is pH-dependent. At pH values less than 3.5, the rate of the reaction becomes independent of pH, and the rate of the reaction is slowed considerably. Singer and Stumm (2) reported a half-time of about 1,000 days at a pH of 1. This is extremely slow in comparison to the rate of oxidation of pyrite by Fe^{+3} (reaction #3). In highly acidic pH conditions the half-time of this reaction is 20 to 1,000 minutes according to Garrels and Thompson (5).

The hydrolysis of ferric ion to produce insoluble ferric hydroxide (reaction #4) is also a much faster reaction. Experimental results reported by Stumm and Morgan (2) indicated that this reaction was also pH-independent in the low pH range, and that the presence of anions (such as sulfate) tended to increase the rate of hydrolysis.

Microorganisms

In addition to the effect of pH on the reaction process, microorganisms play a significant role in the formation of acid mine drainage. As previously discussed, the oxidation of Fe^{+2} occurs extremely slowly in the acid pH range typical of acid mine waters. Were it not for the obvious presence of a catalytic agent, the formation process would essentially cease once the pH had dropped below 5.

The acidophilic iron-oxidizing bacterium Thiobacillus ferrooxidans is generally believed to be responsible for the catalytic. T. ferroxxidans derives its metabolic energy from the oxidation of Fe^{+2}, a process that, in turn, creates the acid environment in which it thrives (pH from less than 1 to pH 4.5).

The significance of T. ferrooxidans in the formation of acid mine drainage is that it allows the continuation of the propagation cycle by rapidly providing a steady source of Fe^{+3}, the primary oxidant of pyrite. In addition, the extreme acid environment it creates allows Fe^{+3} to remain in solution thereby facilitating the weathering process.

III. Passive Treatment Mechanisms

pH Modulation

Metals can be removed from solution by increasing the pH to beyond the solubility range, the point at which the ions will precipitate as insoluble compounds (figure 1). The composition of these compounds will depend on the nature of the ions present. In general, metal ion solubility increases by several orders of magnitude with each unit decrease in pH under ideal conditions of complete dissociation of the oxide or hydroxide (8). Studies of iron solubility reported from investigations of acid mine drainage treatment systems have shown that ferrous iron will remain in solution up to pH values greater than 9.0, while ferric iron will precipitate as ferric hydroxide at pH values less than 5.0 (9,10).

pH also plays a role in the oxidation of ferrous iron. At low pH values (less than 3.5), the oxidation process is pH-independent, and is extremely slow (6). As the pH increases above 4.5, the reaction becomes pH-dependent and the rate increases (6,4). At pH values greater than 8.0, the rate of the reaction increases a hundredfold for each unit increase in pH (9,11). However, according to Gordon and Bonner (12) organic and inorganic ligands can affect the oxidation rate of iron in natural waters. Therefore the rate should be determined on a case-by-case basis.

FIGURE 1

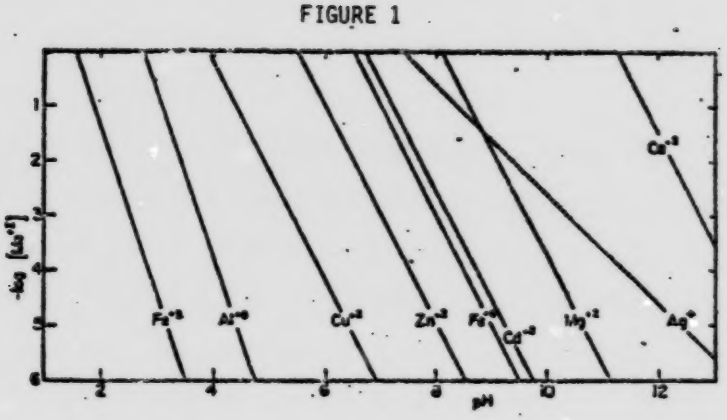


Figure 1 Solubility of oxides and hydroxides. Free metal ion concentration in equilibrium with solid oxides or hydroxides. The occurrence of hydroxo metal complexes must be considered for evaluation of complete solubility (Stumm and Morgan 1970)

Manganese oxidation rates are also pH-dependent, and increase as the pH increases (13,14). Manganese will remain in solution for longer distances in the effluent than will iron due to the greater solubility of the divalent Mn cation, which is the predominant form of the ion at low pH values (15). In aerated waters, pH values of 10 or higher may be necessary to precipitate the oxide (10). The actual rate of oxidation in natural environments has been observed to be higher than that predicted, and it is believed that the process is also influenced by microorganisms (12).

Aeration: Aeration is one method of pH modulation available in a passive treatment system. As mineral acidity (H+) is neutralized, carbonic acid is produced from the evolved carbon dioxide. This tends to buffer the pH and low pH values may be maintained. Under tranquil flow conditions, a maximum pH of 6 to 6.5 is predicted, which is the point at which calcium carbonate reaches a saturation equilibrium (10,20). The buffering effect and approach toward solubility limits tends to slow the neutralization process in the pH range of 4 to 8 (20). The pH may be increased, however, by adding turbulence to the water. Aerating the water allows the carbon dioxide to be liberated (exsoluted) to the atmosphere thereby reducing the concentration of carbonic acid (16). Gordon et al. (15) reported a pH value of 8.4 as being associated with carbon dioxide stripping.

The result of pH increase as a function of carbon dioxide removal is presented in figures 2,3,4, and 5.

FIGURE 2

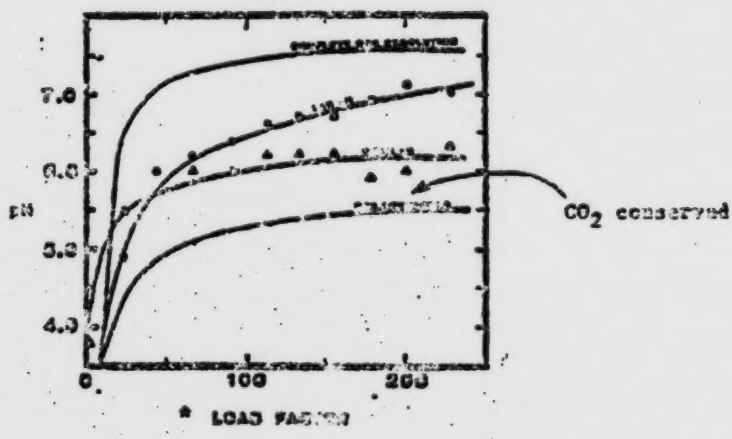


Figure 2 Observed pH - Load Factor Relationships. The upper and lower curves are computed values for the limiting CO_2 cases, i.e.

1. All of the CO_2 generated is driven off.
2. None of the CO_2 generated by the dissolution of limestone is lost.

The observed values fall between these two extreme cases. (Duncan 1982)

FIGURE 4

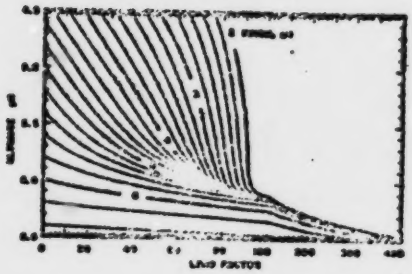


Figure 4 Process design curves for tranquil flow through barrier after exsolution of carbon dioxide downstream of barrier

FIGURE 3

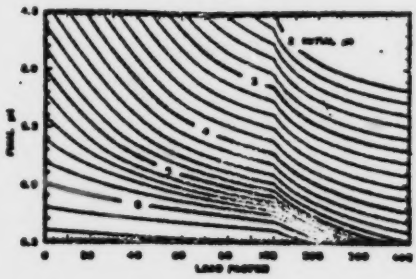


Figure 3 Process design curves for tranquil flow through barrier and before exsolution of carbon dioxide

FIGURE 5

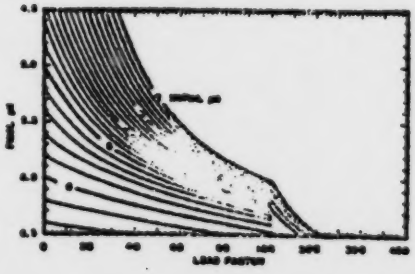


Figure 5 Process design curves for violently turbulent flow through the barrier such that carbon dioxide is released instantaeously (Pearson and McDonnell 1975b)

Limestone Neutralization: Limestone is frequently used in conventional mine drainage treatment systems for pH modulation, to enhance iron oxidation and to neutralize acidity. In the neutralization reaction, sulfuric acid combines with dissolved calcium carbonate to produce calcium sulfate, water, and carbon dioxide:

$$(5)\ H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2$$

Ferric ions, produced during the oxidation of ferrous iron, react with calcium carbonate to form insoluble hydroxides (reaction #6):

$$(6)\ Fe_2\ (SO_4)_3 + 3CaCO_3 + 3H_2O = 2Fe(OH)_3 + 3CaSO_4 + 3CO_2$$

The neutralization of acidity by limestone is controlled by the following reactions according to Pearson et al. (17,18,19).

$$(7)\ CaCO_3\ ^{(s)} + H^+ = Ca^{++} + HCO_3\ ^-$$

$$(8)\ HCO_3\ ^- + H^+ = H_2CO_3$$

$$(9)\ H_2CO_3 = H_2O + CO_2(g)$$

Because equations 7 and 9 are heterogeneous, they are the slowest of the three reactions and are therefore rate-limiting. According to Duncan (19), the effects of temperature, ionic strength, and intensity of turbulence can be neglected and the rates of equations 7 and 9 are dependent only on the concentration of mineral acidity (H+) and the concentration of dissolved carbon dioxide.

Additional factors that must be considered in limestone neutralization treatment are particle size and limestone composition. As particle size increases, the quantity of limestone required also increases. In general, the smaller the particle, the greater the surface area per unit volume. Increased surface area enhances the reactivity (21). Increases in the magnesium content of the limestone will also increase the quantity of limestone required. Neutralization efficiency increases as the Ca/Mg ratio increases, thus calcite is more suitable than dolomite or magnesite (10). Limestones composed primarily of pure calcium carbonate have been shown to be the most efficient neutralizing agents (11). Equally efficient are low calcium limestones containing calcite and a large surface area.

Limestone coating or armoring may occur even at low concentrations of metal ions. Armoring will result primarily from the deposition of aluminum oxides and clays. This effect may reduce the reactivity of the limestone to 20 percent of that of clean limestone, but will not completely deactivate the neutralization process (Kleinmann, 1983, 1984; Duncan, 1982).

Temperature does not have a great influence upon the neutralization reactions. While reaction rates and the behavior of dissolved ions are influenced by changes in temperature and pressure, the effects of moderate departures (a few atmospheres, or plus or minus 10 to 15 deg C.) from standard conditions (1 atmosphere, 25 deg C.) are not significant (Hem, 1970; Duncan, 1982).

Cation Exchange

The primary mechanism for the removal of dissolved metals in a passive treatment system is through cation exchange. Both sphagnum moss and peat have high cation exchange capacities. Certain zeolites may be used for this purpose, as well. However zeolites are more costly, not as readily available, and require more frequent maintenance than peat and sphagnum.

Sphagnum: Cation exchange in sphagnum is believed to take place within the submicroscopic channels in the cellulose of cell walls. The cell walls become impregnated with pectic and phenolic compounds, and a zeolite-like structure results. Sphagnum recurvum and sphagnum fibriatum have been shown to be extremely effective in removing Fe^{+2} from acid mine drainage water. In studies by Kleinmann, ferrous iron concentrations were reduced by 88% on the average and total iron removal averaged 50 to 60 percent(24,39). Nearly all of the iron removal was accomplished within the first 12 linear feet (approximate volume, 12 cu ft) of the sphagnum mat. The sphagnum was

ineffective in removing sulfate, Mn, Ca, Mg, and Al, however. Concentrations of these ions remained virtually unchanged after passage through the moss. Concentration of other ions such as Zn, Pb, Cu, and Cd were not mentioned. Acidity and pH were not significantly altered by the sphagnum. The cation exchange capacity of the moss was periodically monitored and found to remain high throughout both studies (24,39).

Although in Kleinman's study, the sphagnum was under stress at times due to inundation and the lack of an organic substrate, it remained viable(24). This may account for the consistency of the high cation exchange capacity values. New exchange sites are undoubtedly produced as the moss grows. Viability should be improved when the moss is grown under natural conditions, which should in turn improve the maintenance of high cation exchange capacities. The relationship between the rate of saturation and growth rate is still unknown, however. The effects of iron hydroxide clogging are also unknown. The following conclusions have been drawn from several investigations of the cation exchange properties by sphagnum by Bell, Clyma , and Kleinmann (22,23,24):

1. Trivalent and divalent ions are more readily adsorbed than monovalent ions in solutions containing Fe, Mg, and Ca in concentrations similar to those of natural waters.

2. Cation exchange sites persist either through metabolic regeneration or through creation of new sites in the hydrogen form.

3. Anion exchange abilities of sphagnum are negligible compared to cation exchange abilities.

4. Cation exchange capacity decreases with increasing pH and/or increasing cation concentration.

Peat: Peat is an organic material that results from the partial decay of plant material. When vegetative matter falls into water or onto soils that are continually saturated with water and where atmospheric oxygen is largely excluded, bacterial decomposition is greatly inhibited and the partially decayed matter accumulates.

The cation exchange properties of peat are attributed to the humic acids found in peat. Humic acids are derived from the partial decay of plant tissues. The precise mechanism of humus formation and the chemical definition of humic acid are not known (25). The structure of humic acid molecules is not well understood either. Humic acids have a high, widely-varying molecular weight. Krauskopf (26) and Forstner (27) defined various types of humic acids according to the molecular mass. Humins have the highest molecular weight, followed by humic acids and fulvic acids, which are the lightest of the three groups and are the most soluble form of humic substance. Fulvic acids appear to have a higher exchange capacity than humic acids (28). Forstner attributes this to the large number of functional groups present in the low-molecular mass of fulvic acid and to the greater solubility of the acid.

The total cation exchange capacity of peat has been reported by a number of investigators. Given and Dickenson (28) summarized a number of these investigations, and reported a range of 20 to 200 meq/100 gm dry peat. Fuchsman (29) reported hydrogen exchange capacities per 100 gm of humic acid at pH values of 4.5, 6.4 and 8.1. They were 170.0, 286.3 and 400.0 meq/100 gm, respectively. Forstner et al. (27) reported similar values. These examples of total cation exchange capacities for peat gave no indication of the conditions under which the capacities were determined.

Forstner (27) and Moore et al. (30) stated that the bonding ability of humic acids was 3 to 4 times greater for divalent metal ions than for trivalent ions. Jonasson, as reported by Forstner(27), gave the following order of bonding strength for various divalent metal ions on humic or fulvic acid:

$$UO2 > Hg > Cu > Pb > Zn > Ni > Co$$

The cation exchange ability for peat appears to correlate with the pH of the environment, generally decreasing with increasing pH, as in the case of sphagnum. Peat is known to possess high water retention capabilities and moss peat may hold as much as 15 to 30 times its own weight in water (31). Once the peat is dried, however, much of the water retention capability is lost, and the peat becomes essentially impermeable to water.

The use of raw peat as a cation exchanger in acid mine drainage waters may pose some problems. As previously stated, raw and dried peat is virtually impervious to water. Establishing flow through the peat may be difficult. If the peat remains impermeable, water will simply flow over the top of the bog thereby reducing contact area and time and lowering the exchange rate. Fulvic acid is readily leached from raw peat over a broad pH range. The acid is extremely soluble and complexes easily with metal ions. As a result, metals may remain in the effluent for longer distances. Humic acid, which begins to dissolve at pH 6, may also be leached. Therefore, although peat may possess good exchange capacities, its physical characteristics may limit its usefulness in a passive treatment system.

Sulfuric acid treated peat may offer several advantages over the use of natural undried, untreated peat. The sulfuric acid treatment involves heating dried peat in the presence of concentrated sulfuric acid (4.0 ml to 1.2 grams dried peat) at 150°C for 2 hours. Acid treatment greatly improves the flow-through characteristics and thus will allow greater contact between the water and the exchange sites. Fulvic acid leaching does not begin until pH levels are raised to above 7 or 8 if the peat is acid treated. Treating peat in this manner tends to equilibrate the cation exchange capacities of peats from different locations as well. Flow rate, pH, and the presence of competing ions are the primary factors that determine the effectiveness of heavy metal ion removal by sulfuric acid treated peat. These factors can in part be compensated for by providing a sufficient excess of exchange sites. Ansted (40) found that by increasing the ratio of meq of exchanger to meq of metal ions from 6.25 to 20.8, the simultaneous recovery of a mixture of metal ions was essentially 100%.

Sulfuric acid treated peat also offers an advantage over the use of sphagnum moss in that sulfuric acid treated peat has been shown to be highly effective in the removal of Mn, whereas sphagnum appears incapable of reducing Mn concentrations. Sulfuric acid treated peat has also been shown to be highly effective in the removal of Zn^{+2}, Pb^{+2}, Cd^{+2}, and Cu^{+2}, whereas the removal of these ions by sphagnum has not yet been observed.

The two primary disadvantages to using sulfuric acid treated peat in a passive treatment system are the difficulties associated with the acid treatment process in the field, and the fact that sulfuric acid treated peat is not self-regenerating. Large scale production of sulfuric acid treated peat has not yet been attempted and the logistics of such production will have to be assessed. Once the peat becomes saturated with metal ions, it will have to be replaced and either regenerated or discarded. Both of these factors will increase the level of maintenance of the treatment system.

Sorption and Coprecipitation

Sorption of heavy metals such as Co, Ni, Cu, and Zn by hydrous Fe and Mn oxides may be a principle controlling factor in the distribution of these metals in solution (32). Sorption (and desorption) of these metals is dependent upon a number of factors, but is primarily controlled by pH. pH values must first be high enough to allow the formation of Fe and Mn oxides. In the low pH range of acid mine drainage, manganese oxides may never be

present. Ferric hydroxide may be present, but it is incapable of sorbing positively charged metal ions at pH values below 5.2. In addition to pH controls, if sufficient metals extraction is provided by the ion exchange medium in the treatment system, neither of these oxides may be present in sufficient quantities to provide significant sorption effects. Thus, the effects of sorption and coprecipitation may not be significant mechanisms for passive mine drainage treatment.

Complexing

The phenonemen of metal ion complexing is often cited as the reason for the presence of metals in solution at Eh/pH values outside the range of stability of the soluble form of the ion. Complexing is also believed to inhibit the oxidation rates of soluble Fe^{+2} and Mn^{+2}, thereby inhibiting the rate of precipitation of the less soluble oxides, and decreasing ion exchange and adsorptive capabilities (2,27). Gordon (15) and Gordon and Bonner (12) cited the inhibitory effects of tannic acid, glutamine, and humic ligands on the oxidation of Fe^{+2} in natural waters. They also referred to the enhancement of Mn solubility in the presence of tannin, carbonic acid, and lignin.

Complexing of metal ions with humic and fulvic acids may reduce cation exchange capabilities. Rashid, as reported by Forstner and Wittman (27), stated that one-third of the total bonding capacity in humic matter may be attributed to cation exchange, while the remaining two-thirds are attributed to chemical sorption and organic complexes. Hem and Durum (33) reported the following sequence of divalent metal ion-fulvic acid complex strengths at pH 5:

$$Cu > Pb > Fe > Ni > Co > Zn$$

Biological Extraction

Metals extraction may be provided by microorganisms and by plants growing in or near the effluent. Bacteria, algae, and fungi will affect dissolved metal ion concentrations either by direct accumulation of the metals within their body structures or by producing sufficient changes in the aqueous environment to facilitate precipitation of the metals from solution.

The iron bacteria Gallionella, for example, is known to accumulate dissolved iron from solution, which in turn is secreted by the organism in long strands of hydrated Fe^{+3} oxides. The bacterial cell lives at one end of the group of strands. The secreted oxides form a spongy, rust-like crust on the effluent substrate. Gallionella may also accumulate manganese in a similar manner (34,15). Sulfate reducing bacteria, Desulfovibrio and Clostridium, indirectly remove metals from solution by generating hydrogen sulfide under anaerobic conditions. In the presence of hydrogen sulfide, metal ions form insoluble sulfides and precipitate (10,35).

Oborn (36,37) and Oborn and Hem (38) have examined the effects of aquatic biota on iron in natural waters, both experimentally and from the literature. Iron is removed from water most vigorously during the active growing season and returned to the water upon death and decay of the organism. Bacteria may deposit iron released in this fashion as iron ores at the water-sediment interface where dissolved oxygen is depleted.

Martin (8) suggests the use of Eichhornia Crassipes (water hyacinth) as a means of treating acid mine drainage. Water hyacinths are effective in the removal of lead, mercury, and other metals, and are capable of concentrating the metals as much as 10,000 times that of the ambient solution concentration. Water hyacinth has been suggested as a possible aquatic species to be used in the bog. Since water hyacinth is a tropical/subtropical plant, it is unlikely to survive the winters at high elevations. Duckweed is often used in combination with water hyacinth, since it is more resistant to freezing temperatures (41). Duckweed, however, forms a thick mat over the water surface that tends to deplete the dissolved oxygen content and Eh of the water. Water hyacinth forms a similar type of mat, but does not reduce the dissolved oxygen or the Eh (38). Toxicity of the effluent on the plants and the effects of bioaccumulation and biomagnification on plant consumers must also be considered.

Kleinmann (39) suggested that anoxic conditions in the bog may be desirable. The production of hydrogen sulfide gas would utilize the excess hydrogen ions produced in the cation exchange reactions in the bog and metal ions, precipitated as insoluble sulfides, would be more permanently immobilized than in the plant tissues of the bog. The effectiveness of other acidophilic plant species native to the Southern Rocky Mountain region is unknown.

Dilution

Dilution provides the principal treatment for most streams impacted by mine drainage which have not been treated by other interventions. The dilution effect of tributary streams may be attributed to the natural bicarbonate buffering systems of the incoming waters. The buffering effect may be destroyed, however, if the acidity of the receiving stream is too high or if calcareous materials are not readily available in the tributary streams. Dilution may be important in neutralizing acidity unaffected by the limestone, but its importance will depend on the performance of the limestone beds.

IV. Passive Treatment System Design

The process of designing a passive treatment system is dictated by both chemical and physical constraints. Theoretical assessments of the primary chemical processes involved in passive treatment of acid mine drainage are vital to the design process because they determine the type and quantities of materials (peat, limestone, etc.) necessary to achieve desirable treatment goals, they determine the most efficient arrangement of the system components, and they facilitate predictions of expected results. The results of the theoretical assessments then must be adapted to the physical and engineering constraints of the site. The treatment system must be designed to function for long periods of time through extremes in weather conditions, flow conditions and variations in water quality at the site with minimal

maintenance required while continuing to provide adequate treatment. In most cases, installation of passive treatment systems cannot involve major alterations of the existing landscape in the vicinity of the mine discharge. The process of designing a system that will achieve optimum results therefore requires addressing that which is theoretically possible within the physical constraints of a particular site.

General Site Evaluation

A general evaluation of the watershed affected by the mine drainage is required to delineate the physical, engineering and legal constraints of the site, and to define the nature and extent of the problem. Information which is especially important includes detailed descriptions of the local topography and mine configuration, the method of mining, and the local geology. Water rights information, local land use policies and current landownership patterns must be known. Soil types in the area must be defined in order to determine runoff volumes. Vegetation types must be determined to facilitate reclamation of the site following installation of the treatment system. Local climatological data, historical water quality data and flow data must also be provided. Much of the information necessary for site evaluation is available from the literature and other accessible information sources (e.g. large scale topographic maps, mine maps, soils, and vegetation surveys, etc.) prior to any site visitation.

Hydrologic Investigations

Detailed hydrologic information is vital in the design of a passive treatment system. Any structure incorporated into the design should be capable of passing a 100 year storm event. Therefore, the watershed contributing to the flow of the mine discharge must be carefully evaluated from the standpoint of peak flow runoff.

Next, the flow regime of the mine discharge and any springs and minor tributaries which contribute to it's flow must be evaluated. Historic records of flow measurements can be extremely helpful. Seasonal variations in the mine discharge and hydrologic responses to such activities as irrigation practices, nearby mining activities, water storage facilities etc., should be assessed.

Fairly detailed stream channel measurements of the mine drainage are necessary. Both longitudinal and cross sectional profiles must be prepared from actual surveys. Such information is essential for the evaluation of alternate locations for the components of the treatment system.

A baseline water quality monitoring program which is integrated with the flow measuring system must be established as early as possible in the design process. A minimum of a year's worth of pollution loading data (pollutant concentration x flow) should be available for the mine discharge prior to the design and construction of a passive treatment system. The number of water

quality samples taken, the number of sampling sites and the range of parameters analyzed must be determined on a case by case basis. Factors to be considered in this determination include the flow regime of the mine drainage, the geochemical properties of the ore body or coal seam which was mined, and the soils in the watershed area. Additional water quality considerations include the range of beneficial uses in effect for the mine drainage and it's receiving streams and any applicable water treatment and discharge regulations.

Selection of Treatment Materials and Components

The selection of treatment materials should be based on theoretical considerations and the results of previous treatment projects. At the present time limestone appears to be the most suitable material for neutralizing acidity in a passive treatment system. Selection of the limestone should be based on Ca/Mg ratios since these ratios will in large part determine the quantity of stone that will be required. The selection of a cation exchange medium is less definitive at this time. Sphagnum moss and peat, either raw or acid-treated offer the best possibilities for metals extraction, although the advantages and disadvantages of each must be carefully weighed prior to the final selection. Aeration can be provided by riprap, groins and gabions, cascades and waterfalls. The selection of treatment materials and the design of the individual components are made following the site evaluation and hydrology investigation.

Determination of Structure Locations

Siting of treatment structures is accomplished with the aide of the channel profile and cross section surveys conducted during the hydrologic investigation. Generally, cation exchange systems for metal removal will be located upstream of neutralization and aeration structures. This will help to minimize coating and clogging problems on the neutralization medium. Also, acidity is released in the cation exchange process.

The placement of any structure in the channel where the channel does not follow the natural gradient may call for channelization or realignment of the stream course at those particular points to avoid "short-circuiting" around the structures after installation.

Construction and Reclamation Plan

The elements of a passive treatment system construction plan include equipment and material specifications, excavation diagrams, structure installation instructions, and site reclamation procedures. The plans must be detailed enough so that contractors unfamiliar with passive treatment pricipals can construct the system and rehabilitate the disturbed area with minimal supervision.

System Evaluation and Monitoring Plan

Given the relative novelty of passive treatment techniques and the lack of data concerning their performance and efficiency, every installation should be evaluated and monitored. The monitoring plan should address water quality and treatment efficiency in terms of acidity and metals removal, as well as performance of individual components. Data derived from these evaluations will aid in the development of design criteria for future passive treatment systems.

V. Design Example: Marshall No. 5 Passive Mine Drainage Treatment System

The Marshall No. 5 coal mine is located one-half mile south of the town of Marshall and 4 miles south of Boulder, Colorado. It is one of the few inactive coal mines in Colorado which discharges a significant amount of metaliferrous, acidic water. While the water emanating from the mine is not particularly toxic, the drainage offers an excellent demonstration site for a passive mine drainage treatment system.

General Site Evaluation

Mine Configuration: This mine was operated by the Marshall Coal Company intermittently from 1863 to 1939. This company operated a complex of seven mines in the area of the No. 5 Mine. The mine was a drift room and pillar type operation encompassing about 2 acres of underground workings..

Geology and Mining: The Marshall Project area is located in the Denver Coal Region and the Boulder-Weld coal field. Geologically, the project area is underlain by the Larimie formation(s) which dep 4 degrees to the east-southeast. The coal seams in the area lie within a sequence of sedimentary rocks consisting of interbedded shales, claystones, sandy shales, coal beds, and then beds of sandstones. The coal seam mined at the Marshall No. 5 Mine was ranked subituminous and was 8.0 - 9.0 feet thick. There is no further coal analysis information available.

Baseline Soils and Vegetation: Three types of soils are present at the study site: Te (terrace escarpments - hydrologic soil group B), Ro (rock outcrop - hydrologic soil group D), and HaD (Hargraeve fine sandy loam - hydrologic soil group B) (43,44). It was assumed for this study that 90% of the study site (watershed area) is covered by soil types Te and HaD, with the remaining 10% covered by soil type Ro. Soils are shallow and in many areas are merely a thin layer of cobbles over sandstone or shale.

Vegetation at the site is composed primarily of mixed grasses and herbaceous materials. Brush, shrubs, and some ponderosa pine are present in areas and pockets where soil moisture is retained. Several small areas are present where surface disturbances from mining have weakened or destroyed the mature native plant communities. These areas have been invaded by pioneer and transition plant species.

Local Climatology: Average annual precipitation in the project area is 18.5 inches. Regionally the area is characterized by a high plains, continental climate regime. Prevailing winds are from the west. The average growing season is approximately 148 days.

Land Use: In the past, the primary land use was for grazing and mining. At present, the major land uses are grazing, recreation, and residential.

Landownership: The area surrounding the Marshall No. 5 coal mine is Boulder city open space. Consent for reclamation work has been obtained from the Boulder Open Space Board.

Hydrologic Investigations

Surface and Ground Water Regime: The perennial flow from the Marshall No. 5 Mine is the sole expression of ground water on the site. The mine discharges 17 to 70 gallons of water per minute. Repetitive flow measurements of the mine discharge has shown very consistent results. Surface water from the project area is drained by Marshall Creek which flows into South Boulder Creek. Both of these streams are perennial drainages. The drainage basin or watershed in the immediate vicinity of the Marshall No. 5 coal mine adit encompasses approximately 14 acres.

Water Quality: Observed iron concentrations range from 3,500 - 7,200 mg/l and manganese levels average 1,400 mg/l. Zinc concentrations average 98 mg/l and lead levels remain constant at 17 mg/l. pH values range from 4.2 - 4.5. The drainage contains little alkalinity (8 mg/l), but sulfate concentrations are elevated to 340 mg/l. Repetitive water quality sampling of the drainage has shown very consistent results.

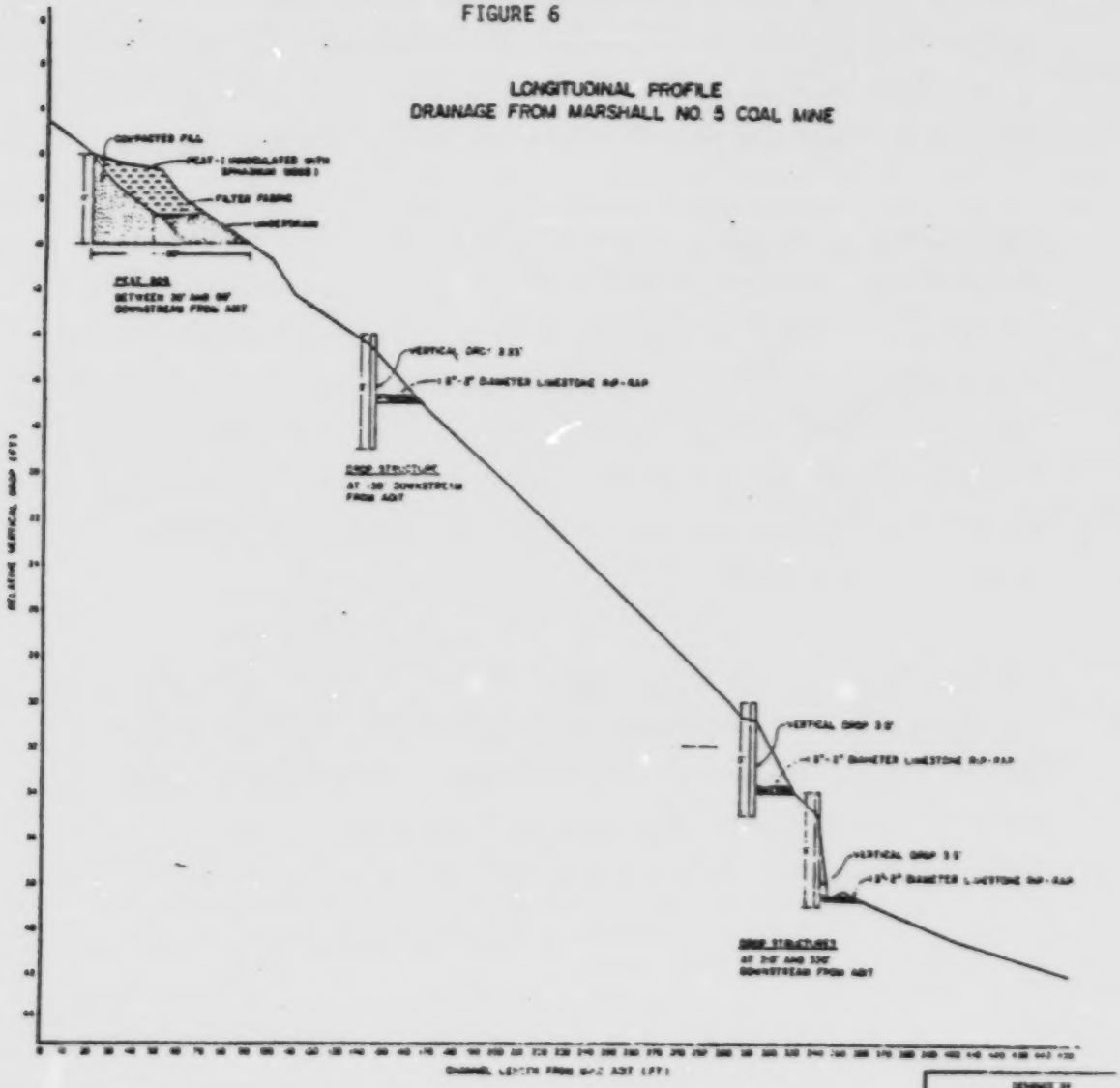
Peak Runoff from 100-year, 24-hour Storm: The peak flow or the study watershed was found to be 3.89 cubic feet per second (cfs) using the methodology developed by the Soil Conservation Service of the U.S. Department of Agriculture (42,43,44). Structures to be installed in or near the drainage channel must therefore be designed to safely pass and/or withstand 3.89 cfs.

Stream Channel Measurements: A total of 10 cross-sections were measured at 50 foot intervals beginning at the mine adit and continuing downstream for 450 feet. The longitudinal stream profile (Figure 6) was surveyed over the same distance. Large trees and thick underbrush prohibited further surveying downstream from that point. It was felt, however, that the major inflection points in the stream had been determined within this distance, and that all of the passive treatment structures would be placed along this upper reach of stream.

Baseline Water Quality Monitoring Program: The U.S. Geological Survey has sampled and analyzed the water draining from the Marshall No. 5 coal mine over the past 7 years. This data is available through the STORET automated water quality information system. In addition the Colorado Inactive Mine Reclamation Program has sampled this mine drainage over a 3 year period.

FIGURE 6

LONGITUDINAL PROFILE
DRAINAGE FROM MARSHALL NO. 5 COAL MINE



Kaman Tempo

There is a suprising degree of consistency in the concentrations of water quality parameters sampled in these investigations.

Water Quality Regulations: The requirement for a point source discharge permit was waived by the Water Quality Control Division of the Colorado Department of Health due to the novelty of the project. The "404" Dredge and Fill Permit was also waived due to the minute quantities of flow from the mine.

Water Rights: There is a legal water right for the water issuing from the Marshall No. 5 Mine. The presence of the right necessitated a written consent from the owner for right of entry to construct the Marshall No. 5 passive treatment system. The owner of the water rights maintains the right to inspect monitoring devices (weirs) above and below the system to insure that the treatment system does not decrease the quantity of water.

Selection of Treatment Materials and Components

The Marshall No. 5 treatment system is composed of three components. The first is a small rock check dam composed of durable limestone or river rock behind which is placed a heavy layer of natural peat moss. Sphagnum moss will be transplanted onto the surface of the peat "bog". The peat moss will provide heavy metals extraction through cation exchange. The second component of the system is a series of small drop structures placed in the channel to provide aeration. Limestone cobbles compose the third component. These cobbles will be placed below the drop structures to armour the stream channel and to provide a source of alkalinity for the neutralization of mineral acidity.

The proposed configuration and selection of materials for the Marshall #5 treatment system is in accord with the information derived from the literature with the exception of the use of natural, untreated peat for cation exchange. One of the outcomes of the field demonstration will be an evaluation of the permeability characteristics of natural peat in this application. If permeability problems are encountered which cannot be overcome with minor modifications to the bog, the natural peat will be replaced with acid treated peat. At this time the determination of the quantities of materials necessary for optimum treatment efficiency is largely dictated by spatial constraints and materials availability.

Determination of Structure Locations:

Based on the stream channel profile (and resultant gradient) and the cross-sections, it appears that the most suitable locations for the check dam peat bogs are within the first 150 feet downstream from the mine adit or downstream of the "falls" (which are approximately 330 to 340 feet downstream of the adit). In these areas the stream course appears to be following the natural gradient, whereas from 150 feet to 300 feet downstream from the adit, the stream seems to follow an old mine road or path instead of the topographic lows (natural gradient).

At a distance of approximately 300 feet downstream from the adit, where the "falls" occur (see Figure 6), a vertical structure containing limestone is feasible. This structure allows for the neutralization of acid drainage, while allowing the flow to pass through at a relatively fast rate, thereby prolonging the life of the limestone.

There are several feasible locations for drop structures. The relatively low gradient probably precludes the use of riprap to cause turbulent flows without first increasing the gradient. The natural flows are generally too small and too slow to provide a noticeable increase in aeration by using riprap. However, by using drop structures to increase the gradient in various locations, aeration may be increased. It appears that the most feasible locations for the drop structures are between 50 and 300 feet downstream from the adit.

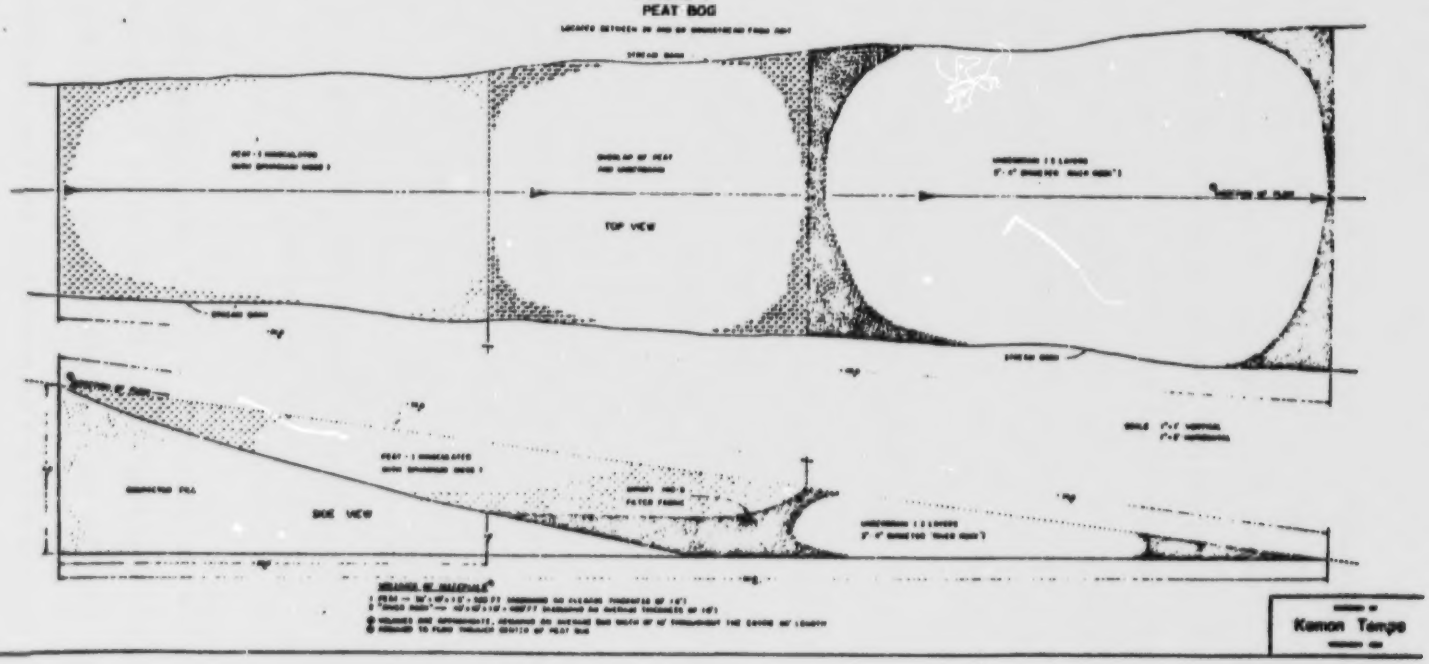
Construction and Reclamation Plan

The following equipment is necessary in order to install the treatment system: tractor/loader/backhow, sheepsfoot compactor or vibratory compactor, dump truck, flat bed truck, water truck, water pump, 4" flexible hole (75'), revegetation equipment.

Materials necessary for the work include: 20 cu yds natural peat moss, 1.5 cu yds pure crushed limestone (size 2" to 3" diameter), 15 cu yds river rock (size: 3" to 4" diameter), 0.5 cu yds pea gravel, 25 sq yds of Marafi 140-S filter fabric, approximately 50 wooden stakes and 60 board feet of 1 x 6" wooden boards. Three steel weirs (A-36 gauge) primed and asphalt coated and measuring 3' x 5', will serve as drop structures.

The excavation for the peat bog is a wedge shaped cut measuring 5' high by 60' in length and 10' in average width. The material to be excavated appears to be saturated. Plan view and cross section views of the peat bog are presented in Figure 7. The bottom of the excavated area shall be compacted by

FIGURE 7
PEAT BOG



making multiple passes (20-30) over the excavated area with a suitable piece of heavy equipment or sheepsfoot or vibratory compactor. The 1" x 6" wooden boards shall be placed on edge using the stakes to direct the underflow in the bog in a meandering fashion. Mine drainage shall be diverted from the weir structure around the area of excavation in a 4" flexible hose prior to construction of the simulated peat bog. This temporary diversion shall remain in-place for the duration of the bog construction work. The river rock and filter fabric shall be placed as shown on the "Peat Bog" diagram (Figure 7).

Three asphalt coated steel drop structures are to be prefabricated and installed by the contractor. The drop structures will be keyed a minimum of 1.5' into each side slope to ensure stability and to prevent flow around the edges of the structures. The area below the drop structures shall be excavated according to the dimensions shown on the attached "Design Criteria for Drop Structure". Each excavation shall be filled with loose limestone in the configuration shown on the attached "Design Criteria for Drop Structure."figure * All earth material excavated during construction of the V-Notch Weir simulated peat bog and drop structures will be stockpiled in a controlled manner which minimizes the area of disturbance. All material in excess of the amounts necessary for backfilling around installed structures will be removed from the site as specified in the site clean up provision which follows below. However, if the excess material is found to be suitable as a plant growth medium, the material can be spread on the surface of the disturbed areas as topsoil in accordance with the Disturbed Area Regrading specifications which follow below.

All excess excavated and stockpiled material, excess gravel, river rock, limestone, peat, boards, wooden stakes and any other garbage and debris remaining on-site as a result of construction activities should be promptly removed from the site and disposed of at the nearest city or county approved land fill. This material may be salvaged by the contractor. All areas disturbed during construction are to be regraded to a smooth land form which provides proper drainage through the area and which blends in with adjacent undisturbed area topography. Following regrading, all disturbed areas including access ways are to be ripped or chiseled to a depth of 4"-6" (rip cuts on maximum 12" centers) in order to alleviate compaction and provide a suitable seedbed.

All ripped or chiseled areas shall be fertilized and revegetated using species which are well adapted to the site. All areas broadcast seeded shall be tilled with a disk harrow or other suitable device in order to cover the seed prior to mulching. This operation is not required on areas drill seeded. Straw mulch (pest or weed-free to the extent possible, not moldy or rotten) will be surface blown or otherwise evenly spread onto all seeded areas.

System Evaluation and Monitoring Plan

The performance of the Marshall No. 5 passive mine drainage treatment system will be evaluated carefully. Because of the inclusion of weirs in the design of the drop structures it will be possible to accurately measure the impact of the system upon the volume of mine water passing through it. Also, accurate flow measurements are essential to assess treatment efficiency in terms of acidity and heavy metals removal. Water samples will be collected from

stilling basins behind the three weirs, and at a point further downstream. In addition, peat and limestone samples will be analyzed to determine cation exchange rates and to evaluate limestone coating. The monitoring program will be conducted over a 12 month period with sampling frequency decreasing as the variance in parameter concentrations is determined.

Many other system performance characteristics will be evaluated including; natural peat permeability, sphagnum (S. recurvum V. brevifolium) transplanatability onto natural peat saturated with acid mine drainage, and the efficacy of acid treated peat in this application.

VI. Treatment System Cost

The cost of the Marshall No. 5 passive mine drainage treatment system is considered in three phases: feasibility and design, construction, and system evaluation.

Treatment Feasibility and Design Costs	
General Site Evaluation	$1,500.00
Hydrologic Evaluation	$1,290.00
System Design	$2,290.00
total	$5,030.00

Treatment System Construction Costs	
Materials	$ 750.00
Equipment Rental	$2,800.00
Labor	$2,300.00
total	$5,850.00

System Evaluation	
Water Sampling and Analysis	$3,600.00
Peat and Limestone Analysis	$ 600.00
total	$4,200.00

VII. Conclusions and Recommendations

Acid mine discharges from inactive mines are perpetual point sources of pollution which can wreak havoc upon receiving streams. Access to inactive mine drainage problem areas is often severely limited. Therefore, pollution control measures which do not require constant electrical or chemical inputs and frequent operation and maintenance activities are most desirable. "Passive" mine drainage treatment approaches are designed to control pollution from mine effluent using techniques which emulate and enhance naturally occurring metal and acidity removal processes. Natural geochemical processes such as pH modulation and neutralization, aeration , dilution, cation exchange and adsorption, sorption and co-precipitation are relied upon to achieve these objectives, at the effluent source.

Basic components of a passive treatment system include an ion exchange medium, a neutralization medium, and an aeration device. An organic ion exchange medium, such as a peat bog with sphagnum moss, seems to offer the best potential for metals extraction in a passive treatment system. Limestone, high in $CaCO_3$, appears to be the most suitable material for neutralizing acidity. Limestone is used for flow barriers or riprap in cascades and for energy dissipation and channel armoring, below waterfalls. Waterfalls, cascades or gabions provide aeration and carbon dioxide exsolution, increasing the dissolved oxygen in the effluent and helping to raise pH.

The process of designing a passive treatment system is dictated by both chemical and physical constraints. Assessments of the primary chemical

processes involved in a given acid mine drainage determine the type and quantities of materials (peat, limestone, etc.) necessary to achieve desirable treatment goals. They also determine the most efficient arrangement of the system components. Generally, cation exchange systems for metal removal will be located upstream of neutralization and aeration structures because acidity is released in the cation exchange process. This configuration also helps to minimize coating and clogging problems on the neutralization medium. The selection of treatment materials and the design of individual components for passive treatment systems are made following detailed site evaluations and hydrologic investigations. The Marshall # 5 Passive Mine Drainage Treatment System Design is presented as an example of this design process.

Every passive treatment installation should be evaluated and monitored. The monitoring plan should address water quality and treatment efficiency in terms of acidity and metals removal, as well as performance of individual components. Data derived from these evaluations will aid in the development of passive treatment design criteria for future systems.

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Doc. No. 1258

PASSIVE SYSTEMS FOR AMD TREATMENT

Several passive systems have been observed in nature as described by HOLM, BISHOP, and TEMPO (?) whose paper is inserted here.

HOLM and GUERTIN (1984) describe the design of a passive system for AMD abatement employing a cascaded flow of AMD over limestone rocks in such a way as to provide a high degree of attrition and aeration. This was followed at the abandoned Marshall Mine near Boulder, Colorado, by a settling area and polishing by aquatic plants in an ecologically engineered bog. Their paper is inserted below.

PASSIVE SYSTEM #1: MARSHALL NO. 5 COAL MINE, BOULDER, COLORADO

The idea of maintaining and funding a water treatment facility in perpetuity to treat AMD is not at all attractive. The cummulative cost to a company, and even to the national economy, of treating acid mine drainage from the same site over a period of say 200-400 years would be high. If a mine or waste impoundment cannot be restored to achieve a satisfactory walk-away situation, the next best thing is to employ a passive water treatment system which, hopefully, will work for years without attention. More information on the later results of the field tested passive AMD treatment facility are most encouraging, and further details can be requested from J. David Holm whose address is given above.

PASSIVE SYSTEM #2

The U.S. Bureau of Mines at the Bruceton Research Station just south of Pittsburgh has experimented with a passive AMD treatment system using plants, particularly sphagnum moss. Their work has developed to the point of building a pilot scale mobile perspex portable bog which was transported from site to site on an experimental and demonstration basis. Further field evaluations and tests are in progress with interesting results and observations.

A sphagnum moss bog was shown to be capable of oxidizing ferrous to ferric ions which then are partly precipitated and removed in the bog. It was anticipated that a final polishing of effluent would be achieved by limestone neutralization also in a passive system since earlier work by the USBM and others indicated that limestone more effectively removes ferric than ferrous ions.

Phase I of a test demonstration program with the Portabog system was completed for the USBM and reported on in May, 1983, by PEER CONSULTANTS and BREHM LABORATORY (1983). The results were not as encouraging as had been hoped because

of difficulties in stabilizing the portable bog. In actual bog conditions alongside coal mine spoil banks, AMD flowing in with very high ferrous ion levels and low pH were found within 10 feet of the inflow point to have been almost completely oxidized to ferric and that pH increased from around 2 to 4. Ferric hydroxide also tended to be coagulated and flocculated by the plants and, on settling to the anaerobic zone of the bog some way below the surface, there was evidence of conversion from ferric hydroxide to ferrous sulfide by reaction with H_2S generated in situ by anaerobic microbiological activity which gets its energy from decaying plant biomass below the surface and sulfates in the water.

Further work on this system will undoubtably be carried out in due course. Meanwhile, additional information might be available from:

U.S. BUREAU OF MINES
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Dr. Robert L. Kleinmann
Patricia M. Erickson

PEER CONSULTANTS, INC.
1160 Rockville Pike #202
Rockville, MD 20852

BREHM LABORATORY
Wright State University
Dayton, OH 45435

PASSIVE SYSTEM #3 - AMAX LEAD COMPANY, BUICK MILL

The following accounts were extracted from tests that are 10 years old and may well be out of date. Two major effluent streams produced from the mine and mill at AMAX's Buick Mill, which recovers zinc and lead concentrates, are 1,000 gpm (5,680 m^3/d) underground mine water pumped directly to the primary tailings pond and mill tailings wastewater released at 15,000 m^3/d to the same tailings pond.

In the 425 acre-feet (523,000 m^3) tailings pond, heavy particulates settle out, and decanted water discharges at a rate of 3785 m^3/d through a spillway to a stilling pond and then to a series of shallow meanders. In these meanders, algae are encouraged to grow providing a trap for fine particles and heavy metals. Finally, a 100 acre-foot (123,350 m^3) sedimentation pond followed by a baffled outlet prevented the algae from discharging into the receiving stream, Strother Creek. The system had a calculated retention time of 60 days. The effectiveness of the system has been documented by JENNETT and HARDIE (1974), and an investigation into its effectiveness in removing trace organics was made by JENNETT amd WIXSON (1977). The system was developed in conjunction with a research team from the University of Missouri - Rolla. It appears that some constituent in flotation mill tailings encourages the growth of algae, and there has

been some speculation that it may be residual flotation reagents or their degradation products.

The combined mine-mill effluent of the Buick Mine constitutes the major volume of the stream waters of the receiving stream. Due to the location of the tailings lagoons some two miles from the mill with about a 100-foot drop in elevation, it was difficult if not impossible to recycle millwater or to separate the mine water.

The meander modification of this treatment plant was developed when laboratory and field data indicated that algae effectively removed heavy metals and trace nutrients.

Algae detach themselves periodically during their life cycle so it was necessary to construct a final polishing lagoon at the end of the polishing system. This small lagoon provides further retention time for the effluent in order to settle accumulated and dislodged algae and aquatic plants and their accompanying heavy metal solids. A detailed study was completed by ERNST (1976).

Figure 30A indicates the levels of lead found in the algae below Strother Creek operations before the meander system, and 30B shows the levels after the meander was developed. The average character of the water quality in the effluent is shown in Table 23. The heavy metals ratio as defined by the state of Missouri is an estimate of the efficiency of the overall system in treating this effluent. The heavy metals ratio is a ratio of the existing level of a particular heavy metal to that allowed by the state of Missouri. Figure 31 shows the decrease in heavy metals ratio as the waste passed through the meander treatment process. Figure 30C shows how the algae in the meanders effectively removes metals prior to effluent release. In addition, Figure 31 shows the average lead and zinc concentrations in the water of the meanders indicating their effective removal.

More up-to-date information on the performance of the passive effluent treatment system at the Buick Mine and Mill can be requested from:

MICHAEL KEARNE
Director, Safety, Health &
Environmental Services
AMAX Lead Company of Missouri
Route KK
Boss, MO 65440
(314) 626-4211

It was concluded by JENNETT and WIXSON (1977) that levels of trace organics were reduced by the biological passive treatment system employed. The water treatment system at the Buick Mine-Mill-Smelter removed 87% of the trace organics in the raw effluent before treatment. By far the largest amount of trace organics were introduced in the mill where flotation reagents are used as opposed to the mine water.

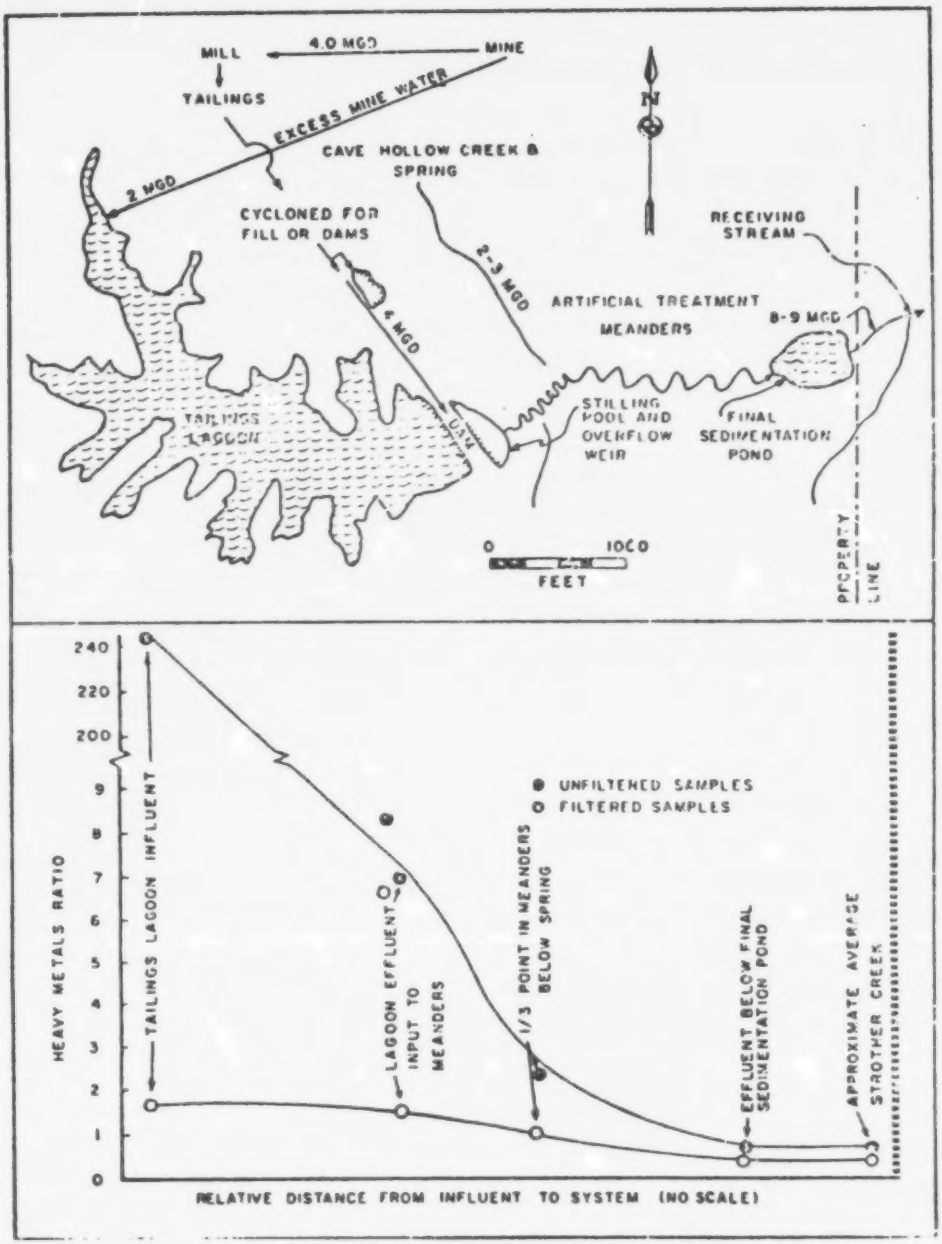


Figure 31. Schematic and Distribution of Metals Within the AMAX Meander Treatment System

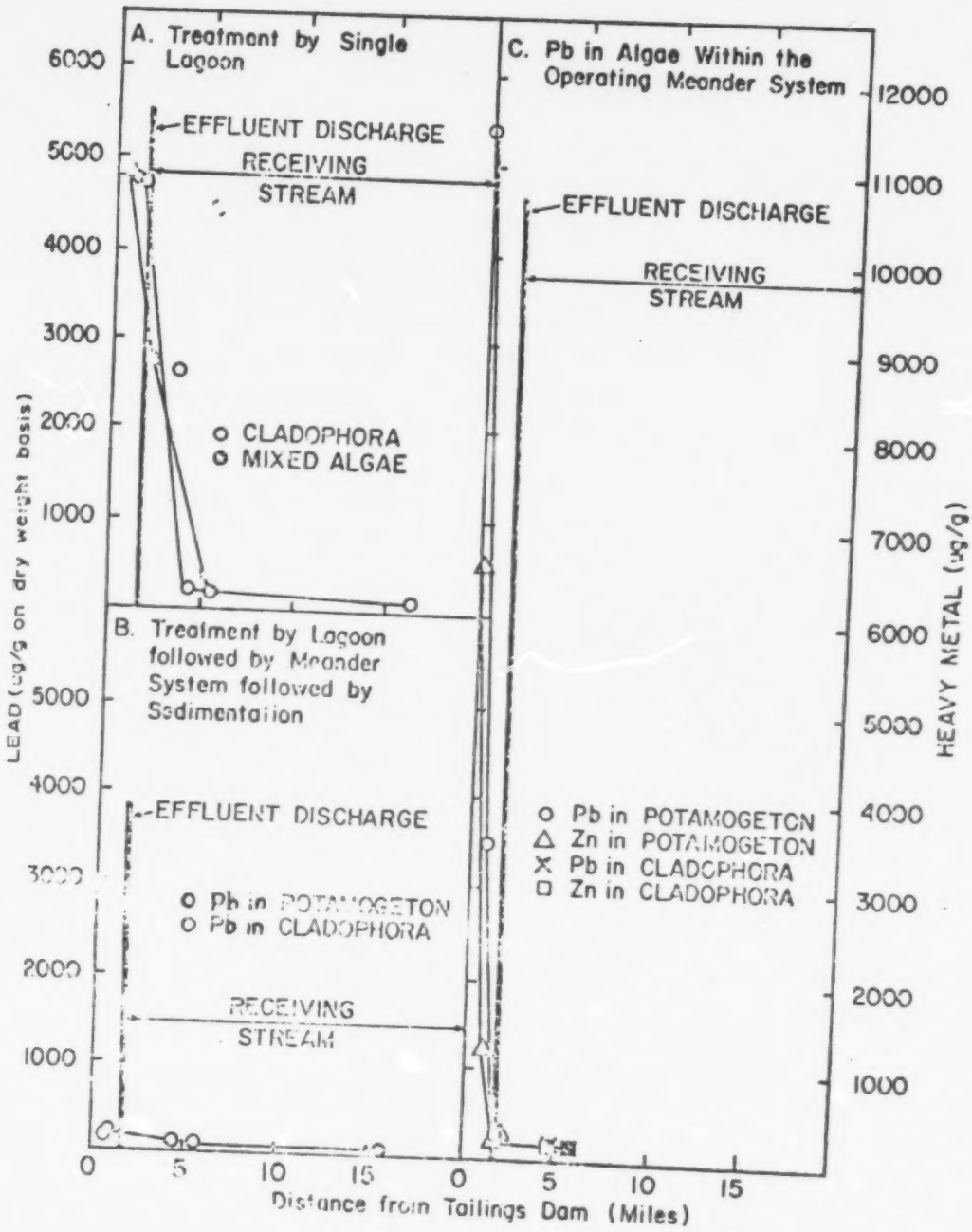


Figure 30. Algal Lead Content - Before, After and Within the Algal Meander Treatment System

SOURCE: WIXSON, ED. (1977)

Average Water Quality Characteristics at the Meander Effluent Stream (From Ernst (110))

Parameter	Average	Maximum	Minimum	No. of analyses
Temperature °C	26.8	30.0	25.0	8
pH units	8.6*	8.9	7.4	7
Turbidity units	5.1	13	1.5	9
Dissolved oxygen mg/l O_2	12	18.3	8.8	9
COD mg/l O_2	12.4	35	2.2	9
Total kj-nitrogen mg/l N	1.0	1.4	0.7	8
Nitrate nitrogen mg/l N	1.17	5.21	<0.01	6
Nitrite nitrogen mg/l N	0.009	0.017	<0.005	4
Total phosphorus mg/l P	0.19	0.34	<0.01	6
Total hardness mg/l $CaCO_3$	275	295	255	9
Calcium hardness mg/l $CaCO_3$	158	188	134	8
Total alkalinity mg/l $CaCO_3$	147	174	133	9
Total dissolved solids mg/l	432	504	338	9
Total suspended solids mg/l	31	96	0	9
Calcium mg/l	60	75	44	8
Lead total mg/l	0.038	0.10	<0.025	9
dissolved mg/l	0.025	0.025	<0.025	9
Zinc total mg/l	0.031	0.10	0.01	9
dissolved mg/l	0.034	0.08	0.01	9
Copper total mg/l	<0.01	0.01	<0.01	4
dissolved mg/l	0.01	0.015	<0.01	4
Manganese total mg/l	0.201	0.60	0.035	9
dissolved mg/l	0.02	0.07	<0.01	9
Cadmium total mg/l	<0.01	<0.01	<0.01	2
dissolved mg/l	<0.01	<0.01	<0.01	2

*Median

SOURCE: WIXSON, ED. (1977)

JENNETT and WIXSON (1979) pointed out that although effective, biological treatment through the use of meanders for metals and organics removal, the long-term benefits to the environment would be naught unless a technology is developed on a timely basis to close the ponds out at the end of the operation in a way that fixes the metals. They felt that this aspect required research and development.

Additional information on passive biological polishing ponds and their design and performance at AMAX's Buick Mine in the New Lead Belt can be obatined from:

UNIVERSITY OF MISSOURI - ROLLA
Center for International Programs and Studies
Rolla, Missouri 65401
(304) 341-4208
Bobby G. Wixson
Director and Professor of Environmental
Health

PASSIVE SYSTEM #4, NEW LEAD BELT, MISSOURI

(Former Arrangement - Now Changed)

Traditional practice in the mining industry has previously dictated that the mine and mill effluents be combined and treated in a single lagoon or tailings pond. This method was used over ten years ago in the New Lead Belt Region but did not work properly. Nuisance algal growth developed below mine-mill tailings pond effluent discharges in virtually every case where this was the sole method of treatment.

Faced with the problem of excessive algal blooms and their associated high levels of heavy metals and evidence that receiving stream water quality was declining as measured by the benthic diversity indices, the mining companies responded with changes in their waste treatment systems. It had been shown by WIXSON (Ed.) (1977) that the single tailings pond treatment systems commonly used by the industry to treat both mine and mill wastes simultaneously were insufficient to protect the streams of the Ozarks. Most mines treated their wastes by combining both mine and mill effluents for retention in very large deep ponds formed by building tailings stems across nearby valleys. Often considered a simple method of treatment, tailings ponds are deceptively complex because they are often required to perform a number of functions simultaneously.

Many treatment functions should take place in the tailings lagoon, including:

a. Removal of tailings solids by sedimentation.
b. Acid neutralization.
c. Formation of heavy metal precipitates.
d. Sedimentation of metal precipitates.

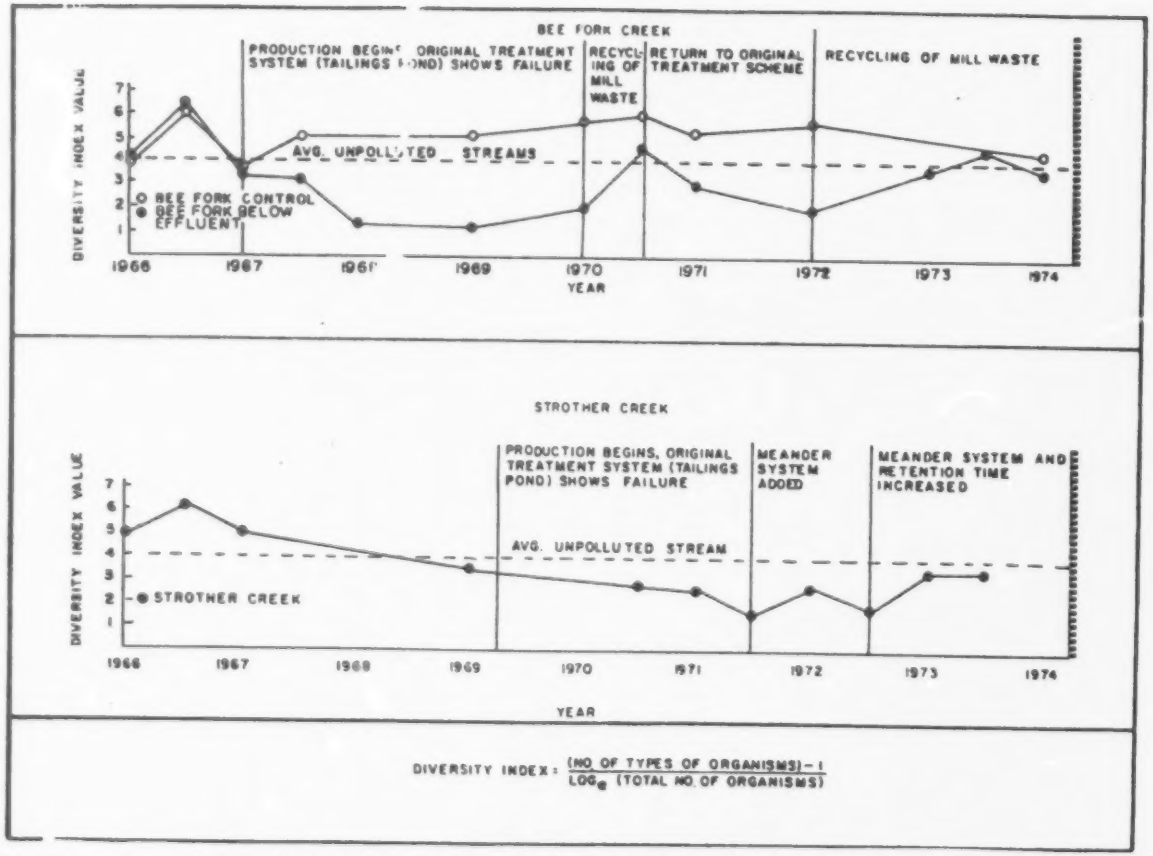


Figure 27. Diversity Index Values for Benthic Animals in Strother and Bee Fork Creeks, (Adapted from Ryck and Whitley).

e. Perpetual retuention of settled tailings and precipitates.
f. Stabilitzation of oxidizable constituents.
g. Balancing action for influent quality and quantity fluctuations.
h. Storm water storage and flow balancing.

The most critical of these functions are sedimentation of heavy metals and tailings, effluent stabilization, and ultimately, solids disposal.

In a design of a tailings pond, standard settling tests are of little value. Pond geometries are varied and cannot be reflected in standard settling tests. A detention time of 30 days is recommended by the Canadian Bureau of Mines with a minimum required detention time of 5 days. Some authors have suggested that the pond area should be 10 to 25 acres/1,000 tons (4-10 ha/1100 metric tons) of solids. In a study of tailings ponds of the New Lead Belt, it was found that those ponds, of at least 20 acres (8 ha) surface area and 5 to 15 feet (1.5 to 4.6 m) depth, were sufficient to remove the zinc content of mine and mill effluents. It was the settling velocity of these zinc particles which governed the pond size. Tailings ponds of smaller surface areas were efficient in removing lead and copper since these are generally denser minerals.

At St. Joe Minerals' Fletcher Mine and Mill, tailings decant water is recycled, and mine water was treated in a series of lagoons.

Recycling

In 1968, the Fletcher operations of the St. Joseph's Mineral Corporation in the New Lead Belt produced an effluent which was discharged into Bee Fork Stream with treatment by only a single tailings lagoon. Above the mine discharge, Bee Fork Stream was a typical clean Ozark Stream. There were usually seasonal blooms of algae, especially in the vicinity of springs. Below the confluence of the stream and mining effluent, a persistant mat-like biological community developed in the stream which, once established and without heavy storm activity to scour the stream bed, often reached problem levels. These dense algal mats trapped the fine silt material and heavy metals which then choked out benthic life.

In order to eliminate these problems, the St. Joe Minerals Corporation initiated a waste treatment system schematically shown below. It essentially treated the mine water in a series of five sedimentation ponds and recycled the mill water for reuse. Extra makeup water required at the mill came from the mine water and was included in the recycle loop. According to JENNETT and WIXSON (1977), heavy metals measured in the receiving stream declined precipitously since the multiple pond system was installed.

More recently, the minewater has been separately collected in a single 22-acre pond where suspended sediments are settled, and oil and grease trapped before discharge to the creek.

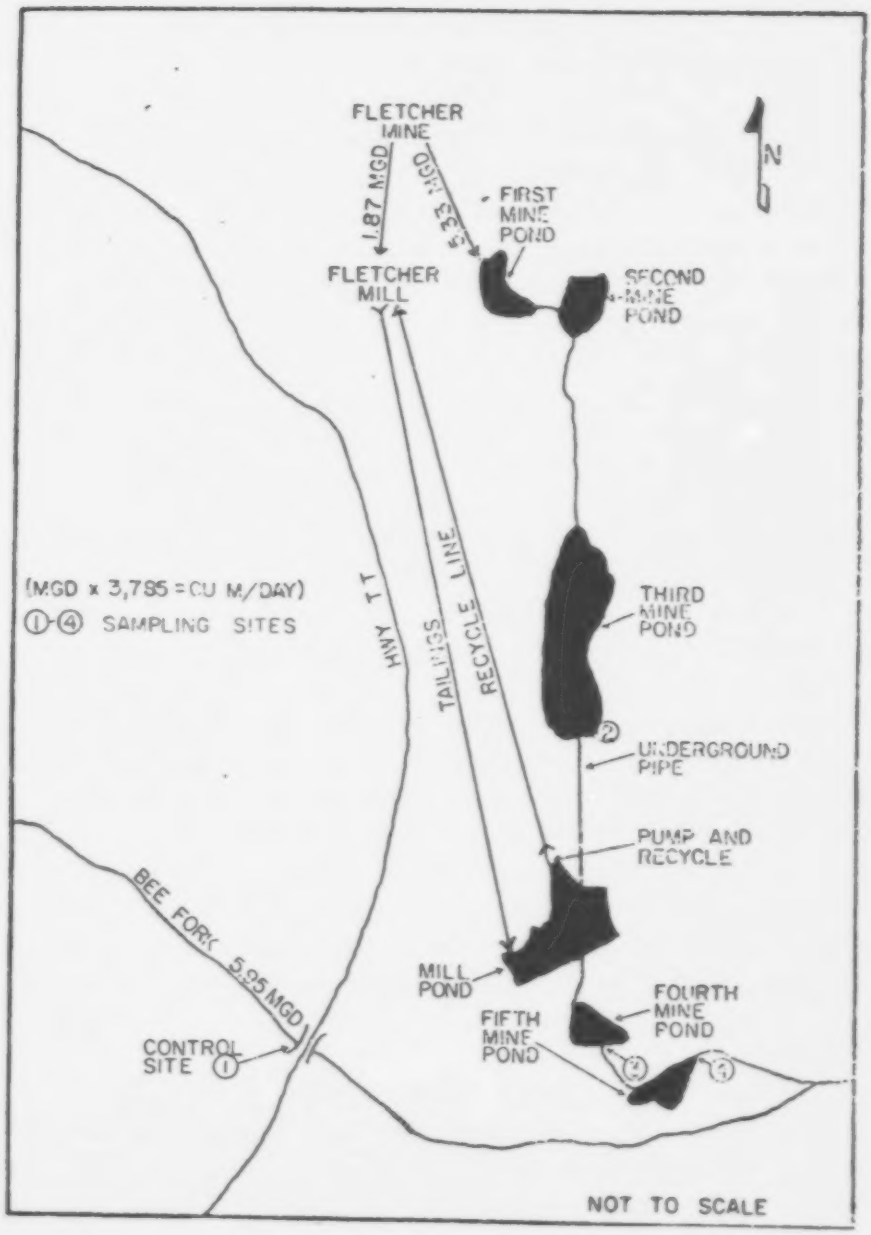


Figure 28. Fletcher Treatment System (Adapted from Gale, et al. (50))

Note: The System has now been completely changed and the above is shown as an interesting example only, rather than to describe the Operation.

In summary, the system as it exists today consists of a zero discharge mill and tailings system and a settled minewater discharge authorized by an NPDES permit.

More information can be obtained, if needed, from:

JOHN CARTER
St. Joe Minerals Corp.
Post Office Box A
Monaca, PA 15061
(412) 774-1020

In 1976, the Missouri Dept. of Conservations reported that the quality of the stream as measured by the Benthic Diversity Indices had returned to premining levels indicating that the system has been effective in controlling pollution.

PASSIVE SYSTEM #5: ST. JOE MINERALS, EDWARDS TAILINGS EFFLUENT, EDWARDS, NEW YORK

At ST. JOE MINERALS' Edwards Mill tailings decant system, tailings treated by lime addition are discharged into a large tailings pond separated by the tailings dam from a large swampy marsh into which the tailings dam decant solution discharges. Samples taken at a culvert about 2,000 feet downstream across this marshy bog indicate clearly that heavy metals values are polished in the marsh. In this case, the bog is natural. It is shallow with a wide variety of aquatic plants which seem to grow in a relatively evenly distributed fashion throughout the marsh providing good contact between water and plants. The data as observed by ST. JOE staff in 1974 are presented in the attached excerpt from a company internal report.

Further information is provided in the next chapter or can be requested from :

ST. JOE MINERALS COMPANY
Mining Division
Balmat, NY 13609
(315) 287-2500
J. G. (Mike) Reilly

PASSIVE SYSTEM #6: ST. JOE MINERALS PIERREPONT MINE

At ST. JOE MINERALS' new Pierrepont lead-zinc mine in upstate New York, minewater is discharged at 400 U.S. gpm (2,200 m^3/d) via a series of ponds which incorporate lime neutralization, settling, and polishing.

In all, 11 acres of ponds have been installed comprising:

Pond #1	2 Acres	Metal Precipitation and Settling:	Milky Appearance
Pond #2	3 Acres	Settling:	
Pond #3	6 Acres	Polishing:	0-6' Deep Bog
Total	11 Acres		

Regulatory Limits (New York State)

New York State has proposed new ultra-low metal water quality standards which, at the time of the RANDOL visit, still had not been approved but seemed well on their way to being so.

New York is an agreement state. Their RCRA and Clean Water Act regulations are administered by:

DEPT. OF ENVIRONMENTAL
CONSERVATION
Albany, NY

About 200 contaminants are included in the new proposed water quality limits, mostly chlorinated organics and the like which would not be expected in flotation mill tailings effluent, but the water quality limits for metals, as proposed, are potentially a serious problem for base metal mines.

Two general regulatory levels have been proposed for different classes of water in 6NYCRR Parts 701 and 702: For classes of water designated AA, A, A-S, B, C, and for D (fish passages). Metals levels for discharge to a trout stream designated Class C_T (i.e., suitable for fishing and swimming and for trout protection) into which the Pierrepont minewater is ultimately discharged, would meet the following standards:

EXAMPLES OF (NOVEMBER 84) FINAL NY STATE
PROPOSED WATER QUALITY STANDARDS mg/l (ppb)
CLASS C WATERS

Cu Max. = Exp (0.905 [ln Hardness ppm] - 1.785)
Fe Max. = 300 mg/l
Pb Max. = Exp (1.34 [ln Hardness ppm] - 5.245)
Zn Max. = 30 mg/l
Cd Max. = Exp (1.16 [ln Hardness ppm] - 6.14)

What these boil down to are the following maximum allowable limits at various hardnesses:

Hardness (ppm)	50	100	200
Cu Max. (ug/l)	5.8	11	20
Pb Max. (ug/l)	1	2.5	6.4
Zn Max. (ug/l)	30	30	30
Fe Max. (ug/l)	300	300	300

Meeting the proposed new regulatory limits will be very hard and, in some cases, virtually impossible to meet from a technical standpoint, let alone the cost factor.

A further existing regulation in New York specifies that for discharge to C_T class waters, i.e., a trout stream, allowable temperature increases are regulated. The warmer the water, the lower the amount by which the temperature can be raised. For example, if the stream water temperature is between 50-70°F, then the temperature can be raised no more than 2°F.

Biological Polishing

Pond #3 installed at Pierrepont is six acres in size and varies in depth from 1- 6 feet Pond depth can vary 2 feet with the season. An artificial meander has been established in the design of the pond.

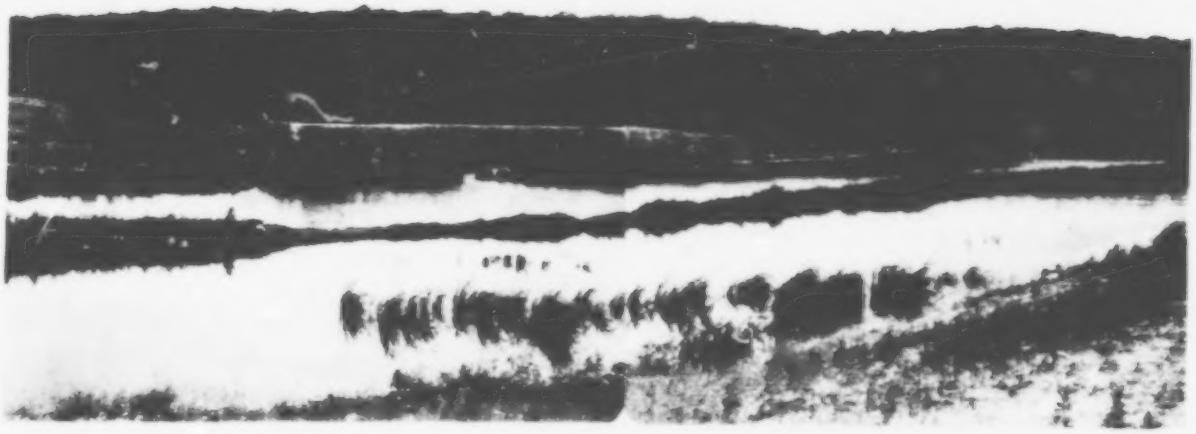
The intention was to allow volunteer aquatic plants to grow in the pond which would act as a polishing media.

Performance

At the time o' the RANDOL visit, the composition of the mine effluent had still not reached a steady state, it being a new mine. A considerable amount of sulfide minerals were observed in the wasterock from which the roadways and pond walls had been constructed, and these may ultimately, on oxidizing, yield considerable amounts of AMD contaminants to the water. At the present inlet to the No. 1 pond, zinc values were 0.2 ppm soluble andd 0.3 ppm total zinc indicating that lime addition and biological polishing will be needed especially if the new New York effluent regulations are confirmed which would require Zn below 0.1 ppm water quality standard.

A problem for which no answer has yet been found lies in meeting the temperature limit during the hot summer months, although it would be expected that trout would be smart enough to move far enough up or downstream to make themselves comfortable during the hot days.

The #1 pond inlet was at 54°F.
The #1 pond discharge was at 70°F.
The #3 pond discharge was at 78°F.



Clearly, the ponding used to remove contaminants is causing the water to warm up to well beyond the regulatory limit for discharge to the stream. Being a small stream, it was considered likely that the warm effluent would have a major impact on the stream temperature which was already marginal as a trout habitat.

At the time of the visit in May, 1984, the aquatic plants had not yet become established in the pond to any marked extent. It was not known to what extent the shade and transpiration effects of the plants would cool the pond water in future, or how ST. JOE MINERALS would overcome this problem.

More up to date information could be requested from:

ST. JOE MINERALS COMPANY
Mining Division
Balmat, NY 13609
(315) 287-2500
J. G. (Mike) Reilly

Edwards Tailings Effluent:
Effect of Passage Through a Portion of Cedar Lake "Swamp."

1. General

This test was undertaken in order to indicate the effect, if any, on the heavy metal content of the tailings effluent after having passed through a swampy area.

2. Location Features

After discharge from the Edwards Mill tailings pond, the water passes through a low-lying area (locally known as Cedar Lake Swamp). The so-called swamp is vegetated by trees, brush, clumps of grass, mosses, ferns, etc. Water passing through the area is caused to spread out because of minor ground relief due to tree roots, decaying logs, and frost pressure-ridges. Water appears to cover about half of the area and is several inches deep.

3. Sampling

The downstream sampling point selected was the culvert under the Trout Lake Road, about 1500 feet from the tailings pond overflow (see Map).

Daily grab samples were taken for five days, upstream (Tails) and downstream (Culvert), and each day's samples were analized for both "Total" and "Dissolved" heavy metals.

4. Results of Testing

4.1. Table 1. shows the five day averaged upstream and downstream values ("Total") as well as the 1973 averages for the Tails.

4.2. Table 2. shows the correlation between the "Total" and the "Dissolved" values, indicating that the metals were not filterable. (Filter media used was Gelman Type A with a DOP test rating of 0.3", 99.7%.)

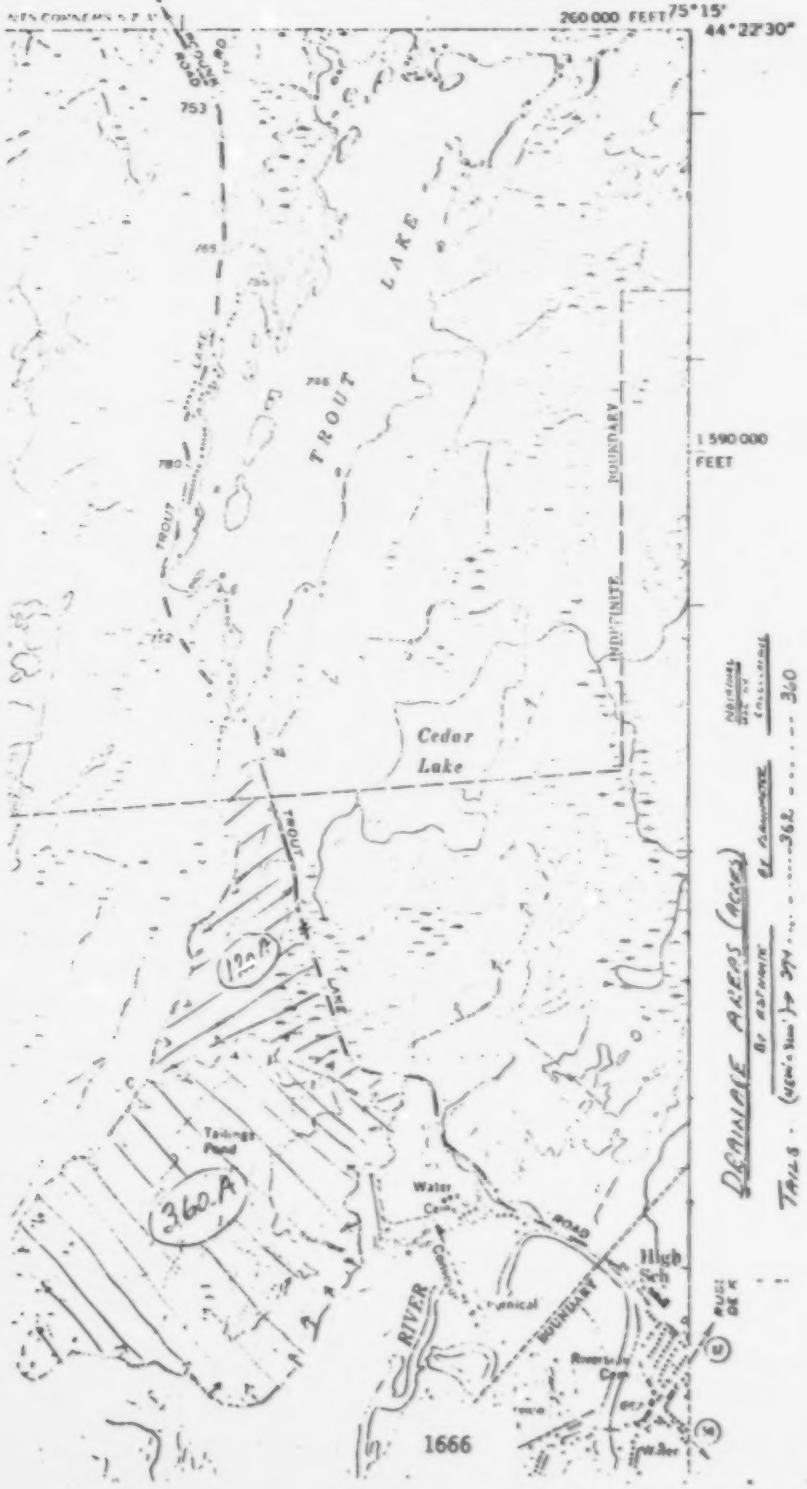
J.G. Reilly
5/17/74

EDWARDS QUADRANGLE
NEW YORK–ST. LAWRENCE CO.
7.5 MINUTE SERIES (TOPOGRAPHIC)
SE/4 GOUVERNEUR 15' QUADRANGLE

RUSSELL 1:62 500

FROM 1956 USGS
SCALE: 1" = 2000'

N

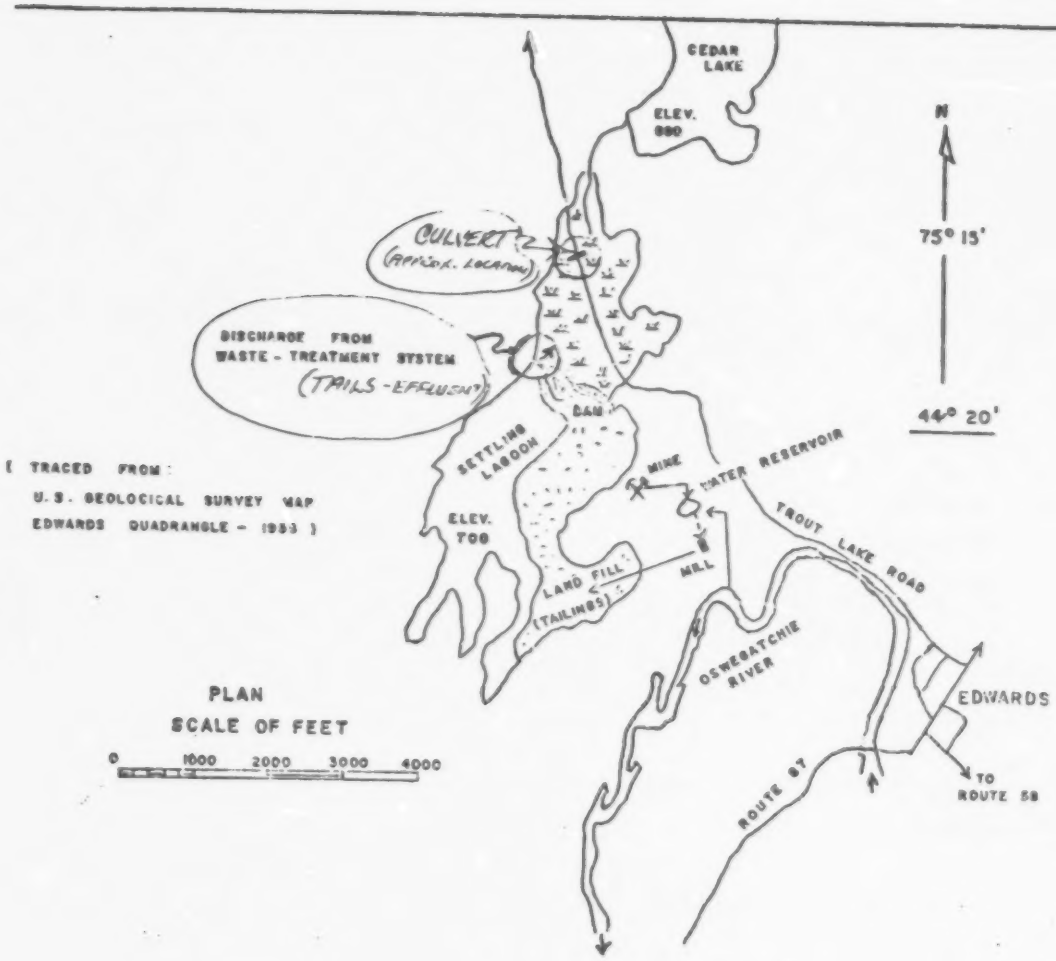


DRAINAGE AREAS (ACRES)

	BY ASTHMIRE	BY RAMSPOTT	DIFFERENCE
TAILS. (NEW'S DAM) TO 394	362	360	
CEDAR LAKE BASIN (EXCLUDING TROUT) TO 610	499	500	
CEDAR LAKE BASIN (INCLUDING TROUT)	861	860	
(CEDAR LAKE (INCLUDED) (INCLUDES ABOVE)	476	(70)	

JBL
5/10/79

1666



Location of Outfall & Discharge
to Cedar Lake Inlet Creek
at Edwards

St. Lawrence County, N.Y.

Application by St. Joe Minerals Corp.

sheet 1 of 1 June 28, 1971

EDWARDS TAILINGS EFFLUENT

- 5-day test - samples taken May 3, 4, 6, 7, and 8, 1974.
- Assays-run for each day and averaged.
- "Tails" sample - overflow from tailings lagoon (E-001).
- "Culvert" sample - swamp drainage at Trout Lake road, 1,500 feet downstream from tails dam.

- In ppm (Total Assays) -

	5-DAY TEST AVERAGE			YEAR 1973 AVERAGE
	Tails	Culvert	Culvert % Change From Tails	Tails
Suspended Solids	4.4	2.7	-39%	9.0
An	0.23	0.09	-61%	0.20
Pb	0.040	0.028	-30%	0.038
Cu	0.025	0.007	-72%	0.016
Fe	0.14	0.05	-64%	0.25
Mn	0.91	0.008	-91%	0.151
TDS	-	-	-	1,064
pH	-	-	-	7.2
Hardness	-	-	-	480*

* Hardness: Average of Only Two Samples (1974).

TDS REMOVAL FROM TREATED AMD

In parts of the world there is concern about TDS in acid mine drainage, even after treatment. For example, conventional lime neutralization and the HDS process precipitates metals, but can result in a saturated gypsum effluent solution (somewhere around 2,000 mg $CaSO_4$ depending on temperature). NaOH precipitation of metals is more expensive in most cases because the cost of this reagent is higher than lime--by several hundred percent in some cases. Even so, the use of NaOH results in an equivalent increase in the sodium levels in effluents which, in some parts of the world (South Africa, for example), are also regulated.

HOLM and SIMPSON (1981), in their discussion on the removal of trace elements and acidity from the Argo Tunnel drainage near Denver, Colorado, indicate a "proposed water standard" which includes a maximum level of $SO_4^{=}$ at 250 mg/l. It is not known what the

basis for proposing this relatively low level of $SO_4^=$ is, but it is certainly clear that this would not be met by any conventional lime or sodium hydroxide precipitation process in treating most AMD streams.

The industrial and residential area known as Pretoria, Witwatersrand, Vereeniging, Sasolburg (PWVS) is served by the Vaal Dam through the Rand Water Board as the main regional water authority. The quality of this water supply is impacted by several industries of which the mining industry on the Witwatersrand is the most conspicuous. Due to the macro-recycle of water draining from the area into the Vaal Dam, TDS is building up to an extent that its impact has an annual cost to the economy in terms of enhanced corrosion, detergent use, etc. of several hundred million dollars. The likelihood of new regulatory limits on TDS in point source discharges has been indicated.

In order to reduce the TDS of acid mine drainage and/or treated acid mine drainage requires the use of desalination processes such as reverse osmosis, evaporation, ion exchange, electrodialysis, etc. Desalination processes were discussed in some detail in separate chapters of this report including some detail of a pilot scale demonstration of the new seeded slurry reverse osmosis process.

It is appropriate to mention three processes of interest where TDS levels must be reduced from AMD:

- The Alumina-Lime-Soda Process
- Seeded Slurry Reverse Osmosis
- Low Pressure Ultrafiltration with Charged Membranes

ALUMINA-LIME-SODA PROCESS

The alumina-lime-soda process has been shown to be able to reduce $SO_4^=$ concentrations to 250 ppm without difficulty through a two-stage process in which raw water is treated with sodium aluminate and lime to pH 12.0-12.1. Effluent from stage 1 is pH adjusted by adding CO_2 to pH 7.

The principles, performance, and economics of the alumina-lime-soda process are described by NEBGEN, et al. (1976) below.

Based on reactions for the process shown by the above authors, RANDOL fails to comprehend how the addition of sodium aluminate, lime, and CO_2 avoids buildup of sodium ions in the product solution as they claimed: "Since the sulfate anion is removed in the reaction, there is no net addition of sodium to the finished water as there is in conventional lime-soda ash softening."

More information and possibly updated economics analysis of the Alumina-Lime-Soda process may be possibly requested from:

MIDWEST RESEARCH INSTITUTE
Kansas City, MO
(816) 753-7600
J. W. Nebgen
D. F. Weatherman
M. Valentine
E. P. Shea

COMMONWEALTH OF PENNSYLVANIA
Dept. of Natural Resources
Post Office Box 1467
Harrisburg, PA 17120
(717) 787-7668
Robert Buhrman

Variations of the alumina-lime-soda process are described in two Russian papers.

PREDERII, et al. (1979) described a two-stage wastewater purification system developed to remove Cu^{2+} and $SO_4^{=}$ from copper mining wastewaters. In the first stage, the wastewater is stirred at 700 rpm with a $Ca(OH)_2$ suspension at pH 12.35 (the optimum condition). After settling, the clear liquor still contains up to 2,000 mg/l SO_4. In the second stage, the clear liquor was treated with $Al(OH)_5Cl$ and $Ca(OH)_2$ at pH 11.9 to precipitate $3CaO.Al_2O_3.3CaSO_4.31H_2O$. The clarified wastewater was then discharged. The neutralization step resulted in a precipitate of $CaSO_4$ containing entrained Cu and Zn. The precipitate, after drying, could be used as a metallurgical flux.

SAL'NIKOVA, et al. (1981) showed how Ca and SO_4 concentrations of tailings leachate were reduced from 800 and 2,140 mg/l to 180 and 300 mg/l respectively by precipitation with aluminous cement to give insoluble, non-toxic ettringite cement. The concentrations in minewater were reduced from 310 and 3,570 mg/l to 100 and 300 mg/l respectively. The smaller amounts of Cu, Fe, Zn, and Mg, which were present, were also reduced.

		Before Treatment	After Treatment
Mill Tailings Effluent	Ca	800	180 mg/l
	SO_4	2,140	300 mg/l
Minewater	Ca	310	100 mg/l
	SO_4	3,570	300 mg/l

Recovery of Potable Water from Acid Mine Drainage by the Alumina-Lime-Soda Process

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Midwest Research Institute, Kansas City, Missouri

In some parts of the country, particularly in Appalachia, water of potable quality is in short supply because of acid drainage from coal mining activities. The acid mine drainage can be converted into potable water by several desalination techniques, the usual ones being ion exchange or reverse osmosis. Such systems require a technology that is different from that used in conventional municipal water works, e.g., lime-soda ash softening. The alumina-lime-soda process, which is discussed in this paper, offers an alternative for recovering potable water from certain acid mine drainages without the need for sophisticated desalination procedures. Alumina-lime-soda is a chemical desalting process in which calcium sulfate derived from lime-neutralized acid mine drainage can be precipitated as calcium sulfoaluminate, thus yielding a product water in which sulfate concentrations are reduced to less than 250 mg/liter.

The key to the alumina-lime-soda process lies in the use of sodium aluminate as a treatment chemical. Sodium aluminate has long been known as an effective flocculating agent for turbid waters. In the case of the alumina-lime-soda process, however, the aluminate ion is a species onto which both calcium and sulfate ions can attach themselves and precipitate. In general, one mole of aluminate ion will remove about one mole of calcium sulfate. Since the sulfate anion is removed in the reaction, there is no net addition of sodium to the finished water as there is in conventional lime-soda ash softening.

For the particular case of acid mine drainage, alumina-lime-soda offers some other advantages, since the mine drainage usually contains dissolved iron and aluminum. The *in situ* aluminum can be converted to aluminate ion by adding excess lime to the mine drainage during neutralization. Aluminate ion so produced tends to remove calcium sulfate in a manner similar to that of sodium aluminate. Iron also tends to remove calcium sulfate as calcium sulfoferrite, though not as effectively as aluminum. Because the process operates on the alkaline side (*p*H of 12.0) and in the presence of air, all iron (II) is oxidized rapidly to iron (III) where it is readily removed from the system.

General details of the alumina-lime-soda process are discussed below, followed by application of the process to the acid mine drainage situation.

DESCRIPTION OF THE PROCESS

The principles of the alumina-lime-soda treatment are outlined in Fig. 1. The process operates in two stages. Stage 1 involves the treatment of raw water with sodium aluminate and lime. Effluent from the first stage is alkaline because of excess lime needed to maintain *p*H conditions. Thus, carbon dioxide at stage 2 is added to reduce *p*H and remove excess lime as calcium carbonate.

The chemistry of stage 1 involves the precipitation of a calcium sulfoaluminate at a *p*H of 12.0 to 12.1. The composition of the calcium sulfoaluminate is $2CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot XH_2O$. Each mole of alumina added as sodium aluminate will precipitate 5 moles of calcium, 2 moles of which are as calcium sulfate and 3 moles as lime. This composition seems to be roughly a 50-50 mixture of two well-characterized calcium sulfoaluminates, $3CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot 31H_2O$ and $CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot 12H_2O$. Thus the purpose of sodium aluminate is the removal of both calcium cations and sulfate anions.

The lime removes magnesium and bicarbonate alkalinity. Magnesium is precipitated as the hydroxide, and bicarbonate precipitates as calcium carbonate. The process is capable of removing both carbonate and noncarbonate hardness in the raw water.

The lime also serves to maintain the *p*H of the stage 1 reaction at 12.0 to 12.1. This *p*H is necessary to produce the calcium sulfoaluminate having the composition $2CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot XH_2O$. If the stage 1 *p*H is above or below the 12.0 to 12.1 range, smaller amounts of calcium sulfate are removed. This role of the lime appears to be associated with the equilibrium between aluminate ion (AlO_2^-) and aluminic acid ($HAlO_2$). The sulfoaluminate is precipitated by aluminate ion. Hence sufficient hydroxide (from the lime) must be present to shift the equilibrium towards

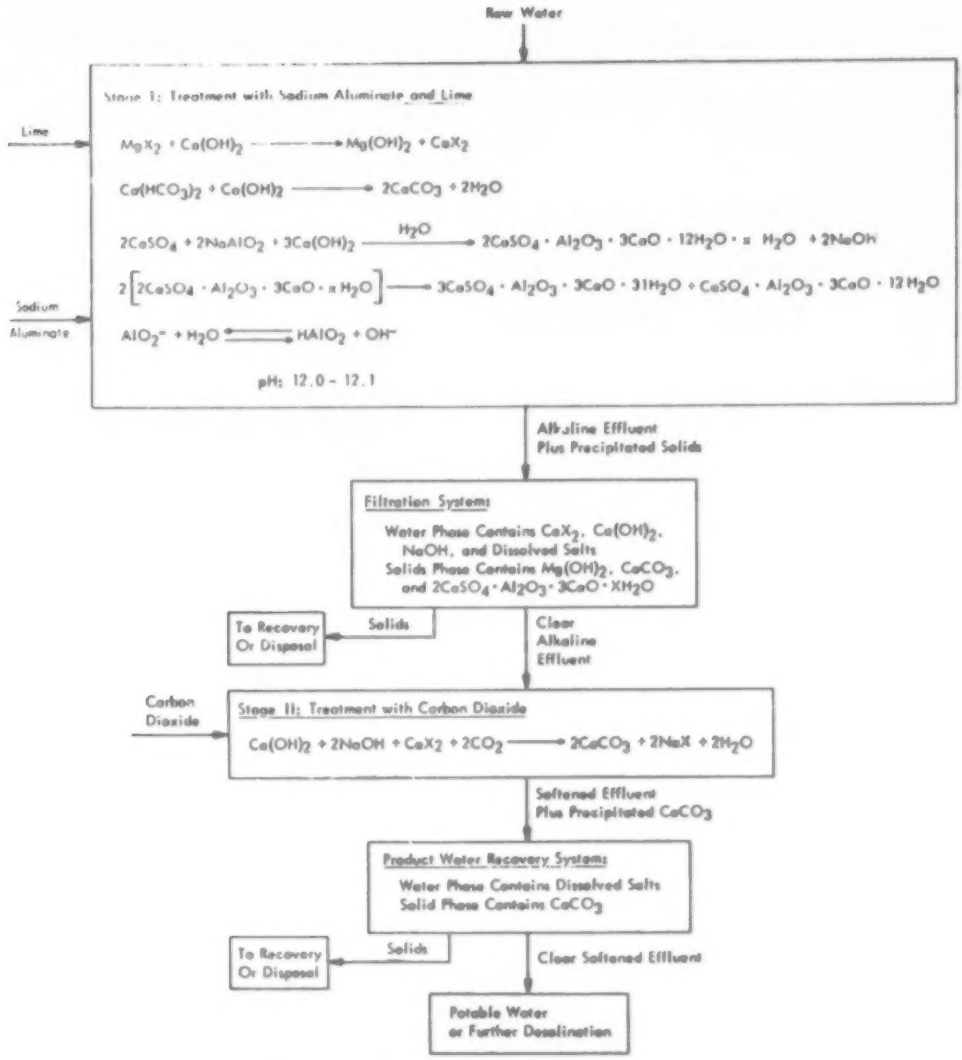

Fig. 1. Basic Scheme of the Alumina-Lime-Soda Process.

aluminate ion. We have found experimentally that the equilibrium conditions in the *p*H 12.0 to 12.1 is optimum for the process. The residence time needed for stage 1 is approximately 90 min.

Following stage 1 reactions, treated effluent is separated from the precipitated solids by filtration. The solids are microcrystalline and are readily dewatered using vacuum filtration or gravity filtration on sand. Dewatered solids can be safely disposed of in landfills since they contain no noxious materials. About 98% of the treated water is recovered in the stage 1 effluent.

The stage 1 effluent is alkaline, containing about 600 mg/liter causticity as $CaCO_3$. The causticity is removed together with residual hardness by carbon dioxide neutralization in stage 2 of the process. The

Effluent from stage 1 thus contains 100 mg/liter of sulfate along with 600 mg/liter of causticity as excess lime. In order to bring down the *p*H and remove the lime, carbon dioxide is added in the second stage. This chemistry is straightforward, and no difficulties were encountered in the field studies. The important consideration in stage 2 is to keep the carbonation to a minimum in order to prevent resolubilization of calcium carbonate as calcium bicarbonate. Thus, the stage 1 effluent should be carbonated to a *p*H of 10.3, the point of minimum solubility of calcium carbonate. At this point, the *p*H 10.3 aqueous phase is separated from the calcium carbonate solids, and a little more CO_2 can be added to drop the *p*H to near 7.0.

Because the sulfate level in stage 1 effluent is 100 mg/liter, raw acid mine drainage can be used to neutralize a part of the stage 1 effluent rather than carbon dioxide. The amount of raw acid added at this point can be determined by the level of sulfate desired in the final product water. This partial neutralization can result in significant savings for CO_2 costs in stage 2.

CHEMICAL COSTS OF THE ALUMINA-LIME-SODA

Chemical costs of the alumina-lime-soda process hinge upon the cost and availability of sodium aluminate. The July 1975 price of dry sodium aluminate is $245.00/metric ton ($270.00/ton). Thus the current sodium aluminate price is $0.176/kg ($0.135/lb.) on a bulk basis. Liquid sodium aluminate costs $0.194/kg ($0.088/lb.) on an 18,000-kg (40,000-lb.) basis. When converted to a dry basis, the cost equivalent today of sodium aluminate is about $0.44/kg ($0.20/lb.), rendering liquid sodium aluminate noncompetitive with the solid in full-scale plant operations. Thus, liquid sodium aluminate was not considered in cost estimations.

If a number of alumina-lime-soda plants using mine drainage with sulfate concentrations in the 1,100- to 1,200-mg/liter range totaling 19 million liters (5 million gal.)/day were built, one would need approximately 5,500 to 7,300 metric tons (6,000 to 8,000 tons)/year of dry sodium aluminate. If the

Table 2.
Proctor No. 1, Hollywood, Pennsylvania, Raw and Treated by Alumina-Lime-Soda: 25% Treated in Stage 1

	*Before Treatment**	*After Treatment*
*p*H	3.8	7.0 to 8.0
Acidity, mg/liter as $CaCO_3$	180.	0.
Sulfate, mg/liter as SO_4	300.	250.
Chloride, mg/liter as Cl	Unknown	Unknown
Bicarbonate, mg/liter as $CaCO_3$	0.	35.
Calcium, mg/liter as Ca	6.	58.
Magnesium, mg/liter as Mg	15.	14.
Sodium, mg/liter as Na	8.	20.
Iron, mg/liter as Fe	30.	nil
Aluminum, mg/liter as Al	20.	nil
Manganese, mg/liter as Mn	Unknown	nil

	Commercial Dry Sodium Aluminate		*Calcined Sodium Aluminate*	
	Quantity	*Cost*	*Quantity*	*Cost*
Chemical Requirements (kg/cu m):	*Kg*	*$/cu m*	*Kg*	*$/cu m*
Carbon Dioxide	0.02	0.003	0.02	0.003
Sodium Aluminate	0.04	0.012	0.04	0.006
Hydrated Lime, 93% $Ca(OH)_2$	0.24	0.011	0.24	0.011
Total Chemical Costs ($/1,000 cu m)		0.026		0.020
Chemical Requirements (lb./1,000 gal.):	*Lb.*	*$/1,000 gal.*	*Lb.*	*$/1,000 gal.*
Carbon Dioxide	0.20	0.010	0.20	0.010
Sodium Aluminate	0.37	0.050	0.30	0.024
Hydrated Lime, 93% $Ca(OH)_2$	2.03	0.041	2.02	0.040
Total Chemical Costs ($/1,000 gal.)		0.101		0.074

*Raw AMD data from present study.

alumina-lime-soda process were applied to areas having other kinds of problems, e.g., high calcium sulfate waters in the western states, the demand for sodium aluminate would increase further. This quantity represents about a 50% increase in the demand for the chemical. In addition, high grade sodium aluminate would not be required. Thus, it is likely that the price would drop substantially by the time the process is developed to full scale.

An alternative approach to sodium aluminate would be its manufacture by calcining bauxite and soda ash, rather than by its crystallization from sodium aluminate solution. Process principles are almost identical with those associated with Portland cement manufacture, except that the temperature of the rotary kiln is in the 900 to 1,100°C (1,650 to 2,000°F) range rather than in the 1,300 to 1,500°C (2,350 to 2,700°F) range. Approximate composition range of sodium aluminate produced from calcining bauxite-soda ash mixtures will be: Na_2O, 37 to 40%; Al_2O_3, 52 to 54%; and SiO_2, 5 to 7%.

Sodium aluminate produced by the calcination of bauxite and soda ash would be less pure than that presently produced commercially. Bauxite contains siliceous impurities that result in the formation of sodium silicate as well as sodium aluminate. However, the soda fraction of the sodium silicate is useful in the alumina-lime-soda process, so its presence is not detrimental. The silica will be precipitated in the sludge and not appear in the product water. The important constituent in the product is the sodium aluminate, since the alumina fraction is all important for sulfate removal.

The calcining of sodium carbonate and bauxite is a straight line process closely resembling the manufacturing process for cement. The same general types of equipment used in cement manufacturing are needed for calcining soda ash and bauxite to yield sodium aluminate, carbon dioxide, and water. The general types of equipment are: crushing, grinding, rotary kiln, and conveying and handling.

The selling price of sodium aluminate (85% purity) is estimated to be \$0.176/kg (\$0.08/lb.). This price compares to aluminate produced as a specialty product (72% purity) of \$0.298/kg (\$0.135/lb.).

Tables 2 and 3 are estimated chemical costs for treating the two raw mine drainages studied to sulfate levels of 250 mg/liter. The costs are based on two kinds

Table 3.
Proctor No. 2, Hollywood, Pennsylvania, Raw and Treated by Alumina-Lime-Soda: 80% Treated in Stage I

	*Before Treatment**	*After Treatment*
pH	2.8	7.0 to 8.0
Acidity, mg/liter as $CaCO_3$	700.	0.
Sulfate, mg/liter as SO_4	750.	250.
Chloride, mg/liter as Cl	Unknown	Unknown
Bicarbonate, mg/liter as $CaCO_3$	0.	35.
Calcium, mg/liter as Ca	8.	20.
Magnesium, mg/liter as Mg	25.	10.
Sodium, mg/liter as Na	2.	145.
Iron, mg/liter as Fe	100.	nil
Aluminum, mg/liter as Al	40.	nil
Manganese, mg/liter as Mn	Unknown	nil

	Commercial Dry Sodium Aluminate		*Calcined Sodium Aluminate*	
	Quantity	*Cost*	*Quantity*	*Cost*
Chemical Requirements (kg/cu m):	*Kg*	*\$/cu m*	*Kg*	*\$/cu m*
Carbon Dioxide	0.18	0.02	0.18	0.02
Sodium Aluminate	0.51	0.15	0.41	0.07
Hydrated Lime, 93% $Ca(OH)_2$	1.58	0.07	1.56	0.07
Total Chemical Costs (\$/cu m)		0.24		0.16
Chemical Requirements (lb./1,000 gal.):	*Lb.*	*\$/1,000 gal.*	*Lb.*	*\$/1,000 gal.*
Carbon Dioxide	1.48	0.07	1.48	0.07
Sodium Aluminate	4.26	0.58	3.46	0.28
Hydrated Lime, 93% $Ca(OH)_2$	13.17	0.26	13.03	0.26
Total Chemical Costs (\$/1,000 gal.)		0.91		0.61

of sodium aluminate—"dry" sodium aluminate that is available commercially, and "calcined" sodium aluminate that is manufactured by heating a soda ash-bauxite mixture to 1,000°C (1,832°F). Dry sodium aluminate contains water of crystallization and hence contains less active alumina than does calcined. As can be seen from the tables, the use of the calcined sodium aluminate is preferred because of its lower cost.

The chemical costs have been calculated using the following bases:

Chemical	*Cost ($/kg)*	*Cost ($/lb.)*
Dry sodium aluminate	0.298	0.135
Calcined sodium aluminate	0.176	0.080
Hydrated lime, 93%	0.044	0.020
Carbon dioxide	0.110	0.050

Using the calcined sodium aluminate, the chemical costs for a mine drainage of low acidity (Proctor No. 1) are about $0.074 per 1,000 gal., and those for a somewhat stronger mine drainage (Proctor No. 2) are $0.61 per 1,000 gal. It is unlikely that the Proctor No. 1 drainage would be treated by alumina-lime-soda, since only 25% of the volume needs to be treated to drop the sulfate level in product water from 300 to 250 mg/liter. In this case, conventional neutralization would bring this water very nearly to potable standards.

On the other hand, 80% of the Proctor No. 2 drainage is treated to bring sulfate levels from 750 to 250 mg/liter at a cost of $0.61/1,000 gal. product water. When operating costs are added to the chemical costs, it is estimated that total water recovery costs will range from $1.04/1,000 gal. in a 0.5 MGD plant to $0.79/1,000 gal. in a 5.0 MGD plant. Thus, the alumina-lime-soda water recovery costs are competitive with other processes for recovering potable water from acid mine drainage.

ACKNOWLEDGMENTS

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SEEDED SLURRY REVERSE OSMOSIS/EVAPORATION

Seeded slurry reverse osmosis is discussed in greater detail in the chapter on reverse osmosis desalination and in a trip report on East Rand Proprietory Mines Ltd. in Appendix I.

Although demonstrated only at 5 m^3/d, the results are sufficiently encouraging to allow speculation that if a desalination process is to find an application, this one is the most likely to be useful.

A flow diagram of the 5 m^3/d test unit and also for a 10,000 m^3/d plant are shown below.

Seeded slurry R.O. employs tubular R.O. modules through which a seed slurry of precipitated solids is recirculated with the feed solution. In this manner, a feed solution approaching gypsum saturation can be fed to the unit and a desalinated product recovery achieved up to 95% or more without the concentrate fouling the membrane despite total salt levels in the concentrate reaching many times saturation level. This is because as the concentrate exceeds saturation point, salts precipitate out on the slurry solids rather than on the membrane.

The R.O. modules installed in the test plant were operated at 4,000 kPa or 600 psi.

By employing the seeded slurry recycle concept, applicability and water quality conditions have been shown to be dramatically extended allowing for a greatly improved operating range.

The seeded slurry R.O. and evaporation process was described by REAMS GOODLOE (1984) at the RANDOL Workshop on Water Management and Water Treatment Technology which is inserted in the chapter on Desalination.

OPERATING LIMITS FOR R.O. MODULES

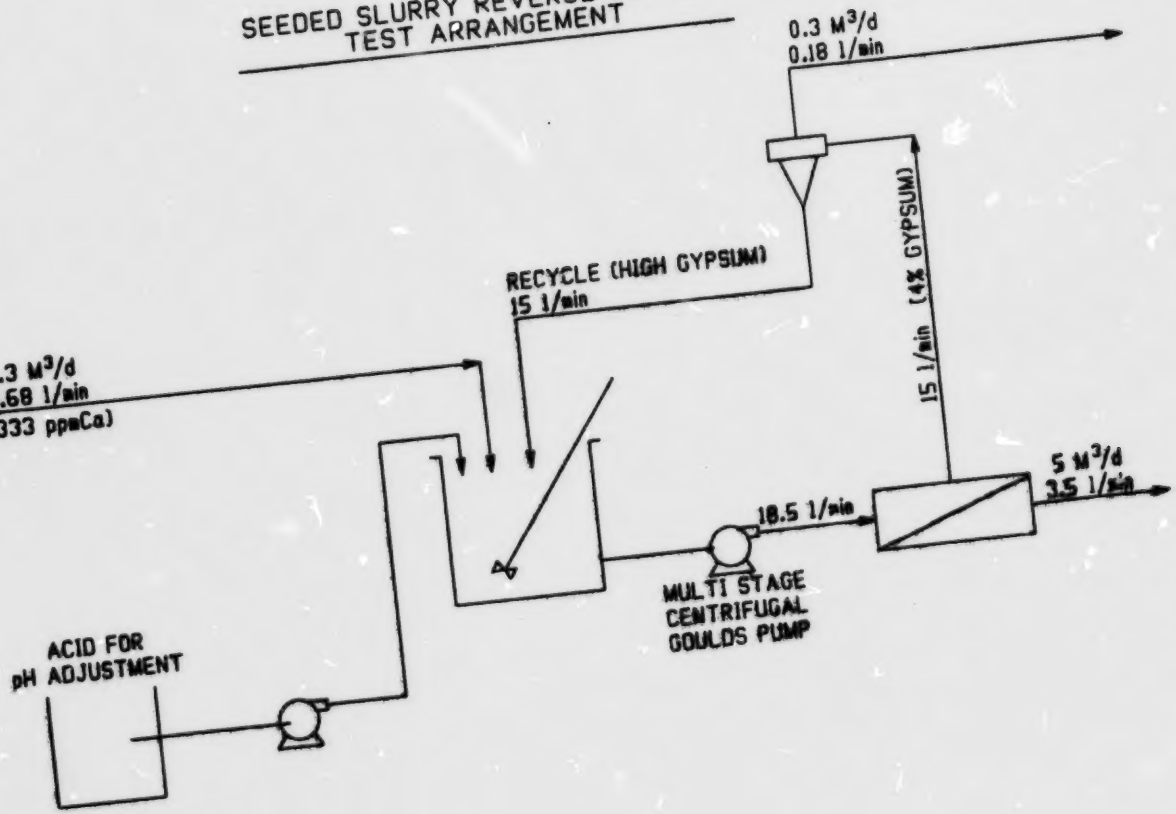
Composition of Concentrate	Conventional R. O.	Seeded Slurry	
		Feed	Conc.
Mn	0.1 ppm max	8.4	69 ppm
Fe	0.1 ppm max	6.4	100 ppm
Al	low	280	
Heavy Metals	very low for metals that precipitate e.g. Co, Ni, Sr, Ba		
Sr	very low	40	
Ni	very low	8.0	
Co	very low	2.0	
Silica	160 ppm in reject	No limit	
$CaSO_4$ in reject	1.5-2 times solubility (around 3000 ppm)	No limit	

An interesting set of data was obtained for one application of SRO. It is believed that the data reflects acid mine drainage water treatment by SRO in a situation analagous to ERPM.

SEEDED SLURRY R. O. TEST DATA REFLECTING 93% RECOVERY FROM ACID MINE DRAINAGE CONTAINING GYPSUM

Sample labelled	Raw Mine Water	Recirculation Sump	Permeate
pH Value	4.00	4.50	5.00
Conductivity uS/cm at 25°C	2600	12,000	550
Suspended Solids Dried at 105°C	50	45,000	LT 1
Volatile Suspended Solids Ignited at 450°C	6		
Total Alkalinity ($CaCO_3$) to pH 4.5	Nil	Nil	2.0
pH 3.7	17.0	40 filtered	13.0
Total Hardness ($CaCO_3$)	1300.0	5500	70
Calcium (Ca)	350	450	10.0
Magnesium (Mg)	120	1000	10.0
Sodium (Na)	130	1500	60
Potassium (K)	15	60	4
Total Strontium (Sr)	3	40	0.1

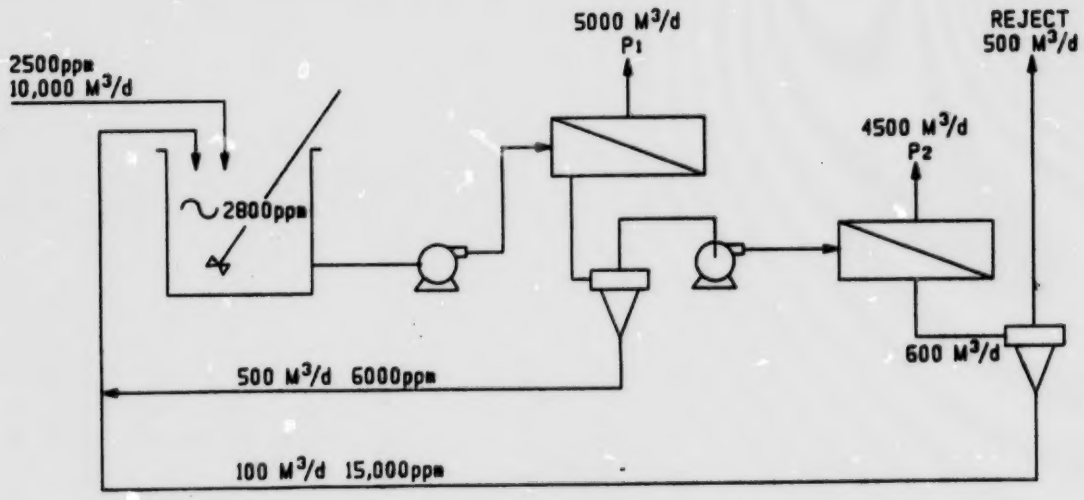
SEEDED SLURRY REVERSE OSMOSIS
TEST ARRANGEMENT



SEEDED SLURRY R. O. TEST DATA REFLECTING 93% RECOVERY FROM ACID MINE DRAINAGE CONTAINING GYPSUM (Continued)

Sample labelled	Raw Mine Water	Recirculation Sump	Permeate
pStrontium in filtered (0.8 u) sample (Sr)		10	
Total Barium (Ba)	0.04	0.50	LT 0.02
Barium in filtered (0.9 u) sample (Ba)		LT 0.02	
Free Ammonia (N) (as received)	8.0	40	3.0
Nitrite Nitrogen (N)	0.10	0.08	0.10
Nitrate Nitrogen (N)	8.0	15.0	6.0
Chloride (Cl)	90	400	50
Fluoride (F)	1.0	8.0	LT 0.1
Sulphate (SO_4)	1600	8000	100
Total Phosphate (P)	0.2	0.8	0.1
ortho Phosphate (P)	LT 0.02	LT 0.02	LT 0.02
Reactive Silica (SiO_2)	40	90	10.0
Total Aluminium (Al)	25	300	0.5
Aluminium in filtered sample (Al)			
0.8 u	25	50	0.5
0.45 u	25	50	0.5
Total Iron (Fe)	6	100	0.06
Iron in filtered sample (Fe)			
0.8 u	0.25	0.7	LT 0.02
0.45 u	0.25	0.6	LT 0.02
Total Manganese (Mn)	8.0	70	0.50
Manganese in filtered sample (Mn)			
0.8 u	8.0	70	0.50
0.45 u	8.0	70	0.50
Total Zinc (Zn)	2.0	18.0	0.10
Zinc in filtered sample (Zn)			
0.8 u	2.0	14.0	0.10
0.45 u	2.0	14.0	0.10
Total Lead (Pb)	0.1	1.2	LT 0.02
Lead in filtered sample (Pb)			
0.8 u	0.1	0.5	LT 0.02
0.45 u	0.1	0.5	LT 0.02
Total Copper (Cu)	0.3	3.04	LT 0.01

CONCEPTUAL SEEDED SLURRY
REVERSE OSMOSIS ARRANGEMENT



SEEDED SLURRY R. O. TEST DATA REFLECTING 93% RECOVERY FROM ACID MINE DRAINAGE CONTAINING GYPSUM (Continued)

Sample labelled	Raw Mine Water	Recirculation Sump	Permeate
Copper in filtered sample (Cu)			
	0.8 u	0.3	0.8 LT 0.01
	0.45 u	0.3	0.3 LT 0.01
Total Cobalt (Co)		2.0	17.0 0.10
Cobalt in filtered sample (Co)			
	0.8 u	2.0	15 0.10
	0.45 u	2.0	15 0.10
Total Chromium (Cr)	0.08	0.90	LT 0.02
Chromium in filtered sample (Cr)			
0.8 u	0.05	0.09	LT 0.02
0.45 u	0.04	0.07	LT 0.02
Total Nickel (Ni)	8.0	70	0.30
Nickel in filtered sample (Ni)			
0.8 u	8.0	50	0.30
0.45 u	8.0	50	0.30
Total Cadmium (Cd)	0.02	0.12	LT 0.005
Cadmium in filtered sample (Cd)			
0.8 u	0.02	0.06	LT 0.005
0.45 u	0.02	0.06	LT 0.005
Absorbance at 275 nm	0.05	0.246	0.011

Chemical results in mg/l
LT = Less than
Samples filtered through 0.45 microns unless otherwise specified.

ANALYSIS OF SUMP DEPOSIT MATERIAL

A sample of the sump deposit slurry was filtered on a 0.45 u filter and the sediment dried at 105°C prior to analysis.

Loss on ignition - % loss on drying to 180°C	5.00
180 - 450°C	2.00
450 - 600°C	3.00
600 - 1000°C	2.00

Acid insoluble (siliceous material)	5.00%

Analysis of dried materials in mg/kg

Copper (Cu)	30
Iron (Fe)	2300
Manganese (Mn)	20
Cobalt (Co)	30
Chromium Cr)	30
Cadmium (Cd)	2
Nickel (Ni)	200
Lead (Pb)	30
Zinc (Zn)	30
Aluminium (Al)	6200
Barium (Ba)	200
Strontium (Sr)	750
Calcium (Ca)	250,000
Magnesium (Mg)	500
Sulphate (SO_4)	550,000

The 5 R. O. modules installed in series at the ERPM seeded slurry desalination test plant were supplied by a South African firm:

BINTECH (PTY) LTD.
P. O. Box 344
Paarl, Cape
South Africa
(02211) 23031
D. B. Smit
Johan Barnard
Peter Swart
Commercial Manager

Operation of the Malbak R.O. modules costs (including capital recovery) are estimated between R0.50-R1.00/m^3 (U.S. \$0.25-\$0.50/m^3).

More information can be obtained on the results of other seeded Reverse Osmosis tests that have been performed from the patent holders of the concept.

RESOURCES CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 824-2400
Telex: 350166 RCC SEA
Russell Vandenberg
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RESOURCES CONSERVATION COMPANY
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Pat di Benedetto

DISCUSSION SRO

1. Seeded slurry R. O. as demonstrated by RCC represents a major breakthrough in desalination technology in that membrane fouling is avoided even when recovery is increased to a point where the concentration levels of gypsum in the reject rise to many times saturation which would result in fouling in the conventional application of R. O.

2. Slurry seed is kept in the dihydrate gypsum form for recycling. This is controlled by temperature.

3. A second major advantage of seeded slurry R. O. is that the compact concentrate slurry has a high solids content, i.e., it is compact and less costly to dispose of safely. One way would be to take the SRO reject and recover more water by evaporation resulting in a dry solid waste for disposal. Another would be to mix the reject with a pozzolin to make a pozzolinic waste for landfill disposal. Typical pozzolins would be cement, or power plant flyash.

4. In the recycle flow the concentration of calcium reaches about 440 ppm which is not much more than the level of 330 ppm Ca in the feed solution. This is because calcium is removed from solution by the seed crystals.

5. Silica and alumina levels are also effectively controlled by the seed slurry. A typical slurry seed contains 5% SiO_2.

6. Because the seed slurry contains solids, it would be expected that there could be abrasion damage to the membrane surfaces. This does not, however, appear to occur.

7. Abrasion of pump impellers etc. could be expected but has not been apparent. In the ERPM test unit, however, some abrasion of the choke valve at the end of the pressure system is believed to have occurred. In a full scale system a different pressure maintaining system would be used. e.g., an orifice plate. It is not known to what extent abrasion will be a problem here.

8. It is expected and hoped that the ERPM tests will proceed using larger scale plants and that their data and experience will be released to industry for general use.

Others involved in the desalination test program joint effort include:

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Telex: 30464 SA
Dr. M. E. Henzen
Chairman
Piet E. Odendaal
Senior Advisor

LOW PRESSURE ULTRAFILTRATION WITH CHARGED MEMBRANES

BHATTACHARYYA, DIBAKAR; GRIEVES, ROBERT B.; SHELTON, SHEILA (1979) reported on tests of low-pressure ultrafiltration with negatively charged, noncellulosic membranes which were shown to be a feasible process to remove dissolved metals (and sulfate) and suspended solids from acid mine drainage. The process achieves "good" water flux without membrane fouling and adequate ultrafiltrate quality at a high recovery. The authors compared the ultrafiltration results with reported results for lime precipitation, settling, and reverse osmosis treatment field studies in terms of treated water quality, reusability, concentrate (sludge) production rates, water recovery, and membrane flux behavior. Unlike the lime precipitation and settling process, the low pressure ultrafiltration product water is not saturated with gypsum.

Possibly, more information on this process and on any more recent developments may be obtainable from:

DIBAKAR BHATTACHARYYA
Dept. of Chemical Engineering
University of Kentucky
Lexington, KY 40506
(606) 257-9000

It is believed that the U.S. EPA is currently concentrating a considerable effort into the evaluation of many new emerging membranes for low pressure reverse osmosis and ultrafiltration. An EPA contact that is involved in this work is:

TOM POWERS
U.S. EPA
26 West St. Claire Street
Cincinnati, OH 45268
(513) 684-7506

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FOR

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.).....	Milligrams per liter.....	17.12
Milligrams per liter.....	Grains per gallon (U.S.).....	0.05841
Milligrams per liter.....	Tons per acre-foot.....	.001360
Tons per acre.....	Metric tons per hectare.....	2.217
Grams.....	Ounces (avoirdupois).....	.03527
Ounces (avoirdupois).....	Grams.....	28.35
Gallons (Imperial).....	Gallons (U.S.).....	1.2009
Acre-feet.....	Gallons.....	325,851
Acre-feet.....	Cubic feet.....	43,560
Cubic feet.....	Cubic meters.....	.028317
Cubic feet.....	Gallons.....	7.481
Cubic meters.....	U.S. Gallons.....	264.2
Cubic meters.....	Imp. Gallons.....	220.0
1,000 m^3/d.....	I gpm.....	152.8
1,000 m^3/d.....	U.S. gpm.....	183.6
U.S. gallon.....	Cubic meter.....	0.3785

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  - Bacteria 1857
- Removal of Selected Inorganic Pollutants from Uranium Mine Waste Water by Biological Methods, BRIERLEY, et al. (1980) 1861
- Control of Heavy Metals in Lead Industry Effluents by Algae and Other Aquatic Vegetation, Gale, N. L., and Wixson, R. G. (1979) 1873

References 1884

STANDARD TREATMENTS

Standard treatment practice for effluents might include the following. This classification is subject to debate and is made on a tentative basis:

Process	Removal of
1) Lime Precipitation and Settling	: Fe, Mn, Cu, Pb, Zn, Cd, Ni
2) Precipitation as Ferroarsenate	: As
3) Aging and Oxidation	: Thiosalts and Thiosulfate
4) Ion Exchange	: Uranium, Molybdenum
5) Coprecipitation with $BaSO_4$	: Radium
6) Alkaline Chlorination	: Cyanide, Ammonia
7) Natural Degradation	: Cyanidation Effluents

The "standard" treatment practices often work well but can be subject to climatic constraints and other limitations. In several cases, their performance is inadequate to remove contaminants to the levels required to render effluents "non-toxic" and to meet some proposed and even existing regulatory requirements. Even the way the "standard" techniques are applied varies significantly from company to company and even within a mining company and from site to site. The previous chapter on acid mine drainage

treatment discussed some observations made in visits to effluent treatment plants. This chapter includes items reported in the literature and identifies some of the new and innovative technologies that are in the experimental and development stages. Often, available information was scanty, and the reader is again cautioned to regard comments and observations as a guide requiring confirmatory testing in all cases for any specific application.

SIX CARDINAL RULES

Sponsors are urged never to lose sight of the six cardinal rules for process selection and design which will be appropriate for most mining and milling environments:

1) Look at the needs of a problem using a circumspectual systems approach. Whatever is treated may have a side effect, either beneficial or detrimental, present or future. The need to treat an effluent may perhaps be alleviated altogether by recycling.

2) Prevention is better than cure. Appropriate design at the outset can greatly reduce the volume of effluent to be treated and, in some cases, avoid the need for perpetual treatment and maintenance after the operation closes down.

3) Use available abatement assets - e.g., natural attenuation qualities of soil or subterrain; residence time in the tailings dam or reclaim solution pond; or a biological polishing pond.

4) Avoid sensitive, sophisticated high technologies wherever possible. Keep the process simple, flexible, and "operator proof."

5) Reliability is essential where effluents are treated before discharge to sensitive environments, particularly streams and lakes supporting fisheries. One failure event can do as much damage as not having the installation at all. Provision is needed in such cases for continuous on-line monitoring and a means of impounding and returning effluents that do not meet the discharge criteria.

6) Design for maximum flow and load, not the average requirement.

OTHER TREATMENT AND POLISHING PROCESSES

Numerous other processes have been employed for the treatment or polishing of acid mine drainage and other effluents or have potential future applications. Several of these are discussed in later chapters where removal of individual metals are discussed. Some of these technologies are still in the developmental stages for AMD treatment yet may have

some potential for special cases. Some of these are definitely in the category of frontier technologies and are included in this discussion only as a means of documenting the people and factors involved.

- Recovery of Values by Selective Precipitation
- Recovery of Values Using IX
- Desalination of AMD Using CIX
- Sulfide Precipitation of Metals
- Metal Removal by Insoluble Starch Xanthates/Cellulose Xanthates
- Chelation for Metal Removal
- Liquid-Filled Membranes
- Biological Oxidation of Ferrous to Ferric
- Biological Sulphate Removal
- Biological Metal Removal Process
- Agricultural Waste Products for Metal Removal and pH Adjustment

RECOVERY OF VALUES USING SELECTIVE PRECIPITATION

Several AMD effluents contain a range of metals which in the past have been considered for potential resource recovery. This possibility was closer to reality, perhaps, just after the OPEC oil crisis when metal prices all rose to new highs, cobalt in particular.

The effluents from several South African gold and uranium mines contained copper, nickel, cobalt, and manganese values.

Several years ago a chemistry approach using selective precipitation was devised to separate and recover at least cobalt and manganese, the latter in a suitable form to be a raw material for electrolytic manganese production. This was described in a paper, and more information could be requested from Max Harris, one of the authors, or Dr. Philip Lloyd who drew RANDOL's attention to the potential.

Years ago Max Harris, in conjunction with a subsidiary of GENCOR LTD. (then GENERAL MINING AND FINANCE CORP.), operated a manganese recovery plant treating gold-uranium mill effluents. Since then, he has found it more economic to use manganese ore, however, and the old manganese production near Krugersdorp, Transvaal, has shut down.

At current base metal and cobalt prices, the incentive to try and recover metals from such effluents has greatly diminished.

MR. MAX HARRIS
Executive Vice Chairman
Delta Management (Pty) Ltd.
Post Office Box 323
Nelspruit 1200
South Africa
(01311) 25171
Telex: 4-20798 SA

DR. PHILIP LLOYD
Managing Director
EMS Minerals Pty Ltd.
Post Office Box 585
Bedfordview - Johannesburg
South Africa
(011) 53-9030

JANKE, DENNIS, and DIEBOLD, FRANK E. (1983) tested selective precipitation of Al, Ca, Cu, Fe, Mg, Mn, Ni, Si, and Zn from acid minewater from mining of porphyry copper ore. Lab scale experiments were made with and without the addition of an oxidizing agent and $S^{=}$. The potential recovery by selective precipitation was estimated to be 85% plus for sulfide precipitation selectively of copper and zinc as sulfides and hydroxides of Fe, Al, Mn, and Mg. The titraton endpoint is optionally determined by measurement of the specific electrical conductance and ionic strength.

The authors are located at Butte, Montana, 59701, where they are employed by the MONTANA APPLIED RESEARCH GROUP.

RECOVERY OF VALUES USING IX

Several ion exchange applications are used to treat mine and mill effluents to render these suitable for discharge and/or to recover metal values. There appear to be additional opportunities in this direction, and the literature is full of reported applications, often on bench scale; it is difficult to sort out which are of practical value.

Examples of existing operations that come to mind are:

1) U_3O_8 recovery, QUIVIRA MINING COMPANY, Grants, New Mexico.

2) U_3O_8 recovery, COTTER CORP., Schwarzwalder Mine, Golden, Colorado.

3) U_3O_8 recovery, DENISON MINES, Elliott Lake, Ontario.

4) Copper recovery, El Teniente, Chile.

5) Molybdenum recovery, Climax Molybdenum Division of CLIMAX, Colorado.

In each of the above cases except the last, a valuable resource is recovered. In the case of Climax Molybdenum, economics did not justify the recovery of molybdenum values from the eluate.

QUIVIRA MINING CO., AMBROSIA LAKE, NEW MEXICO

Seepage and minewater pumped from underground stopes of the QUIVIRA MINING COMPANY's Ambrosia Lake operations near Grants, New Mexico, contain 10-12 ppm U_3O_8. Uranium is removed from this water by ion exchange, and radium is precipitated using $BaCl_2$ prior to discharge.

Macro recycling of water and seepage from the tailings dam into the underground workings of mines located close by have resulted in a steady buildup of competing ions with the result that the metallurgical efficiency of the simple two-stage continuous ion exchange system has deteriorated over the last several years. For these solutions, a more sophisticated multiple-stage continuous ion exchange system such as the NIMCIX system developed in South Africa would be required to bring the tailing level of uranium down. More details of the QUIVIRA MINING COMPANY CIX system are included in the trip report in Appendix I or may be requested from:

QUIVIRA MINING COMPANY
Post Office Box 218
Grants, New Mexico
(505) 287-8851
Jonathan Ma, Metallurgical Manager

The best way to remove uranium from minewater is to use the water in the mill and to recover the uranium in the process. In this case, the volume of water that must be pumped from the mines is far in excess of that needed by the mills. Also, NPDES permits can be granted to discharge treated minewater which is not permitted for mill tailings decant solution which has to be evaporated rather than discharged in net evaporation sites such as in New Mexico where "zero discharge" is mandated.

U_3O_8 RECOVERY, COTTER CORPORATION, GOLDEN, COLORADO

At the COTTER CORPORATION's Schwarzwalder Mine, Golden, Colorado, uranium is recovered from a 520 U.S. gpm flow of minewater which arrives at the treatment plant at pH 7.5-7.8. Uranium is removed from this minewater containing 3-3.5 ppm U_3O_8 to an effluent level of 10-20 ppb using an innovative Himsley-designed downflow continuous ion exchange system.

This uranium recovery system is described in greater detail in a trip report titled COTTER CORPORATION in Appendix I, by PALMER and HIMSLEY (1984) and HIMSLEY

and BENNETT (1984). Uranium is eluted from the resin to yield a very small volume of eluate containing 10-15 g U_3O_8/l which is shipped to the COTTER CORPORATION's mill at Canon City, Colorado, where it is inserted into the uranium recovery process. The remarkable aspect of this operation is that a fixed bed ion exchange process can achieve such phenomenal results.

The ideal solution to minewater containing uranium is to use it in the mill as process water but in this case, the mill is remote from the mine, and the water must be discharged as an effluent.

URANIUM RECOVERY, DENISON MINES LTD., ELLIOTT LAKE

Minewater from underground workings at Elliott Lake is acidic due to oxidation of sulfides, and it contains some uranium. This minewater must be treated before it can be discharged. DENISON MINES LTD. has resolved to make it worthwhile to treat this minewater by using it to leach as much uranium as possible from the stopes before pumping it to the surface. Not much is known about how DENISON applies this form of in situ leaching except that acidic water is sprayed over certain stopes and then collected for pumping to the surface where the uranium solution is blended into the mill solution which allows uranium to be recovered before the water is discharged with the tailings.

More information might be available from:

DENISON MINES LTD.
Post Office Box B - 2600
Elliott Lake, Ontario
Canada P5A 2K2
(705) 848-9111
J. L. Chakravatti

COPPER RECOVERY, EL TENIENTE MINE WATER, PERU

In 1984, a new solvent extraction plant was started up to recover copper from minewater at the El Teniente Mine.

	Aqueous Flow Rate	Copper Production
Minimum	250 m^3/h	Less than 1,000 Tons/Year
Nominal	612 m^3/h	4,060 Tons/Year
Maximum	900 m^3/h	4,611 Tons/Year

At nominal flow rates and below, the plant operates in a conventional counter-current, two-extraction, two-strip mode. For higher flowrates, the plant can operate with the

aqueous feed in parallel through extraction. The flow is seasonal and coincides with the spring snow melt. High copper tenors of 2 g Cu/l and more often coincide with high flows at the beginning of the runoff.

More information can be obtained from the company that designed and installed the copper recovery plant:

DMC ENGINEERS AND CONSTRUCTORS
Division of Davy McKee Corp.
Post Office Box 55000
San Ramon, CA 94583
(415) 838-1166
Telex: 337635
Dr. M. A. Cocquerel,
Vice President, Technology

COPPER RECOVERY, CENTROMIN, PERU

CENTROMIN has installed an SX-electrowinring plant to recover copper from a 4,000 gpm (26,000 m^3/d) acid mine drainage stream at pH 1.3 at Cerro de Pasco.

More information might be available from:

CENTROMIN PERU
Carabaya 891
Casilla 2412
Lima 1, Peru
Oscar Delgardo

MOLYBDENUM RECOVERY, CLIMAX, COLORADO

At Climax, Colorado, AMAX, INC. has installed a water treatment plant to remove contaminants including molybdenum from decant solution from the Climax Molybdenum tailings pond system prior to discharge to the creek system that flows into the Denver water supply.

Installation of a plug flow Chemseps continuous ion exchange unit is capable of reducing molybdenum from 2.0-20.0 mg/l to around 1.0 ppm or less in effluent as described by GOTT and LAFERTY (1977).

The system used weak-base amine type anion exchange resins for two reasons: 1) the molybdenum adsorption capacities were greater; and 2) the resin's high affinity for the hydroxyl ion allows for effective elution with smaller alkaline requirements. The resin was regenerated using sulfuric acid, not only because of its lower cost, but also to avoid contamination of the effluent water with chloride ions.

When the CIX plant was first operated, there were several mechanical problems which resulted from the attempt to operate at a too ambitious specific flow rate recommended by the designers. This led to internal screen failures.

Meanwhile, AMAX has found alternative ways to remove molybdenum from their tailings effluent, and subsequently a way has been found to meet their effluent discharge regulations without the need for molybdenum removal using the CIX system.

Even when the CIX plant was operated, it was found to be non-economical to recover the molybdenum values.

ION EXCHANGE PROCESSES - EXAMPLES

KENNEDY, et al. (1984) reported on the development of an ion exchange process for recovery of cobalt and nickel from primary lead smelter residues. One of the authors, A. A. Worcester, is employed by ST. JOE MINERALS.

CHOPRA (1984) provided an update of the Chem-Seps continuous ion exchange system for pollution control, and SLATER, et al. (1978) showed the results of a continuous CIX unit to treat a synthetic minewater containing 56 ppm Cu, 3.5 ppm Ni, 0.3 ppm Co, 1 ppm Fe, and 20 ppm Ca at pH 4 using a bed of strong acid resin Amberlite 200D in the sodium form which was eluted using saturated NaCl.

MORAWE (1984) showed how ion exchange can be used to remove fluorides from aqueous solutions which could possibly be useful for treatment of high fluoride mine waters as occur in some parts of the world.

Several consultants and authors have pointed out how soils and bedrock can attenuate the migration of metal species by natural processes including the ion exchange properties of the underlying materials which is a form of ion exchange of a sort.

CRONCE, et al. (1980) discussed the effect of lime and unlimed soils on the acid coal mine drainage and concluded that some soils, after liming, remain relatively unchanged even after considerable quantities of water have been applied. Where acid mine drainage was irrigated, growth of ryegrass and tall fescue was not adversely affected although it was significantly increased by liming and by increased levels of acid water irrigation.

WILMOTH, et al. (1979) compared the effectiveness of lime neutralization, reverse osmosis, and ion exchange for their effectiveness in removing ppm levels of ten trace elements from acid mine drainage under typical field conditions. The metals tested were As, B, Cd, Cr, Cu, Hg, Ni,P, Se, and Zn. Treatment by lime neutralization was very effective in removing As, Cd, Cu, Ni, and Zn and relatively ineffective in rejecting B.

The two-bed (strong acid-weak base) ion exchange system was very affective in removing all the trace elements except P and B. None of the treatment methods was effective in removing P.

McGARVEY and UNGAR (1980) describe some selective ion exchange resins for metal recovery which could be useful in selective resource recovery from some AMD streams, although the IX systems and economics would have to be taken into consideration.

DESALINATION OF AMD USING CIX

One of the problems associated with the use of ion exchange in desalination or contaminant removal from effluents is that in order to regenerate the system, more chemicals must be added to the system. This ultimately leads to the need to dispose of still more salts in the final concentrate than were in the water to start with.

HENDRY (1982) described a continuous counter current ion exchange CCIX process which was developed at the University of Cape Town for desalination of mineralized effluents and brackish water. The process utilizes macroporous resins in a strong cation/weak anion sequence. Removal of organic matter by the anion resin results in color and odor removal and about 70% reduction of the COD of humus tank effluent.

No pretreatment is required, and resin has been in use over the equivalent of more than two years of continuous operation without significant fouling or loss of capacity. The author claims that any required degree of desalination is attainable. The basic four-column system (cation load and regeneration pair and anion load and regeneration pair) of counter current fluidized bed multi-stage contactors attain greater than 80% water recovery using up to 1.0 N sulfuric acid and 0.2 N lime slurry as regenerants. Low solubility of $CaSO_4$ in the cation waste liquid and column operating problems if high lime concentrations are used set limits on water recovery. The calcium content of the feed water affects water recovery.

New techniques using a five-column system permits by-product recovery and/or reuse of spent regenerants and result in over 90% water recovery. Capital cost estimates for a 10,000 m^3/d plant are R5 million (US$2.5 million), and operating costs are R0.30-R0.40/m^3 for removal of 500 ppm TDS. More recent work involves contacting the resin with a lime slurry to generate a gypsum slurry which could be elutriated from the regeneration column and evaluation of carbon adsorption polishing of the ion exchange product to produce potable water.

This process has not come to the forefront in South Africa for the treatment of acid mine drainage. One problem is the complexity of operating a five-column CIX system. The

CCIX process may yet be improved further to become a contender for the emerging desalination market in South Africa.

More information can be obtained from:

B. A. HENDRY
Department of Chemical Engineering
University of Cape Town
Private Bag
Rondebosch 7700
South Africa

SIROTHERM

A second continuous ion exchange process for desalting brackish underground and surface waters is the Australian Sirotherm process described by BALTO (1975) and BALTO, et al. (1982). In the first paper it was reported that problems of synthesizing polymers with adequate thermally regenerable capacity and rates of salt uptake were overcome. Pilot plant trials were claimed to have confirmed a technically feasible and economically viable process.

The major CSIRO contribution to ion exchange technology has been the invention of resin systems which can be regenerated by washing them with hot water. Sirotherm resins are polymers of the weak electrolyte type which must always be employed as a mixture of polymers containing basic and acid groups. The sites for adsorption of ions are formed from the uncharged groups by transfer of protons from the acidic to the basic species:

$$R'CO_2H + R''NR_2 + Na^+ + Cl^- \underset{\text{Hot}}{\overset{\text{Cold}}{\rightleftharpoons}} R'CO_2^-Na^+ + R''NR_2H^+Cl^-$$

The overall equilibrium is temperature sensitive with the uncharged forms of the resins being favored at higher temperatures. The driving force behind the equilibrium is the large increase in the ionization of water that occurs on heating--about 30 fold from 25° to 85°C. The additional protons and hydroxyl ions suppress the ionization of the weak electrolyte resins.

A major effort has been made to develop the Sirotherm process into a useful desalination tool. A magnetic microbead resin product was developed and is marketed by ICI AUSTRALIA LTD., which exhibit very interesting hydraulic properties which could possibly be applied to ion exchange systems beyond Sirotherm. CSIRO has developed continuous multi-stage adsorption and regeneration contactors.

The Sirotherm system has been demonstrated on a commercial scale for primary desalination of boiler feed at an ICI soda ash plant at Osborne near Adelaide, Australia. A 1,000 m^3/d demonstration continuous plant has been installed to remove NaCl from softened municipal wellwater at Leaderville, East Perth.

CONCLUSIONS ON SIROTHERM FOR AMD DESALINATION

1) Most AMD dissolved salts consist of sulfate, metal ions, Fe, Cu, Pb, Zn, and after treatment with lime, metal salt concentrations decrease, but Ca values increase.

   Consequently, the Sirotherm process, which is designed for NaCl removal, is not applicable to most AMD desalination needs.

2) Recovery of water product by Sirotherm is around 85% which leaves a large volume (15% of feed volume) to be disposed of as a concentrate.

More information on the Sirotherm process resins and applicability would be available from:

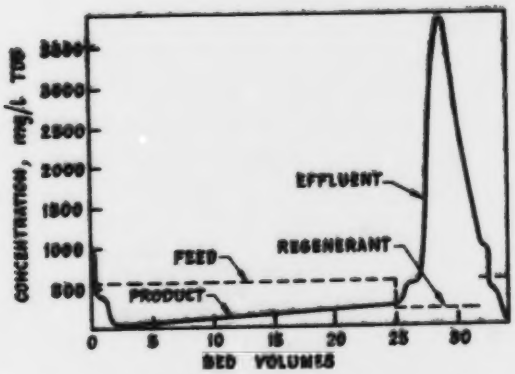


Figure 6. Concentration profile for treatment of a water simulating the Osborne application.

ICI AUSTRALIA LTD.
ICI House
1 Nicholson Street
Melbourne 3001
Australia
(03) 665-7111
Murray Anderson

ICI AUSTRALIAN OPERATIONS PVT LTD.
Central Research Laboratories
Newson Street
Ascotvale, Victoria
Australia 3032
(03) 377-2288
Bernie Reichert,
Polymer-Materials Research

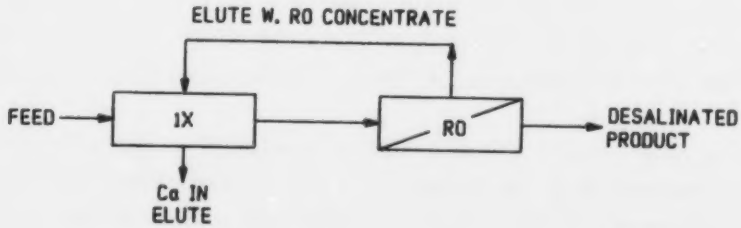
CSIRO
Division of Chemical & Wood Technology
Bayview Avenue
Private Bag 10
Clayton, Victoria
Australia 3168
(03) 542-2244
Telex: AA 35675
Brian A. Bolto

AMDEL
The Australian Mineral Developement
Laboratories
182 Wittenoon Street
East Perth, WA 6000
(06) 325-7311
Telex: AA 94893
Neville Blesing, Manager

UNIVERSITY OF CALIFORNIA - SALINE WATER CONVERSION

The University of California has conducted intensive research on nearly every aspect of water desalination for nearly 30 years. The group working on ion exchange is located at the University of California at Berkeley under Gerhard Klein as manager, Theodore Vermeulen and Clayton Radke as faculty participants, and Jelena Sinkovic as staff. The Sorption Processes Group investigates purification and separation problems insoluble by conventional methods of water treatment.

This group favors ion exchange over other types of feedwater pretreatment for desalination based on the group's past and current work on alkalinity reduction and scale prevention showing that ion exchange gives more secure process control at a lower overall cost. Such studies have enabled the state's agricultural wastewater desalting demonstration plant to utilize reverse osmosis on high-sulfate waters without risk of fouling. The feedwater being freed from calcium, the reject brine is low enough in calcium to regenerate the ion-exchanger without any purchase of chemicals.



Although no specific IX processes have been mentioned specifically for AMD treatment, the University of California pool of fundamental ion exchange experience may be of some help in evaluating IX problems.

UNIVERSITY OF CALIFORNIA
Sorption Process Group
Berkeley, California
Professor Theodore Vermeulen
Professor Clayton Radke
Jelena Sinkovic

SULFIDE PRECIPITATION

Sulfide precipitation offers several advantages over lime precipitation. To date, sulfide precipitation is not routinely used for the removal of metals from AMD although it is used in many metal plating operations, and it is also used for purification of electrolyte in the manufacture of electrolytic manganese as described in the trip report on Delta Manganese in Appendix I.

One aspect that requires careful consideration is the disposal of sulfide sludges. Preliminary studies have indicated that metal ion leachability is lower for metal sulfide sludges than for hydroxide sludges. However, the long-term impacts of weathering and bacterial or air oxidation have not yet been evaluated. Necessary precautions for environmentally safe disposal of sulfide sludge have not been established.

It would appear that sulfide precipitation may offer a more powerful polishing step in conjunction with lime precipitation and HDS or even limestone treatment of AMD, but this has yet to be demonstrated on a large scale application, although LARSEN and ROSS (1976) demonstrated a two-stage sulfide polishing process acid mine drainage treatment in Colorado with apparent success.

There also appears to be a useful biological polishing potential in which the anaerobic deeper levels of bogs or marshes yield adequate H_2S or FeS through bacterial reduction of sulfate ions or plant-derived organic sulfur to polish solutions without the need to add sulfide. This, in fact, seems to be one of nature's cleansing mechanisms.

To date, the only location where a sulfide precipitation application was encountered in a mining environment was at COMINCO LTD.'s Con Mine at Yellowknife, Northwest Territory. Reference to the COMINCO addition of NaHS and $FeSO_4$ to a gold mill tailings effluent is made in a trip report included in Appendix I. In this case, the sulfide precipitation of metals is effective even in decomposing metal cyanide complexes.

The Sulfex process which uses the addition of freshly prepared FeS rather than direct addition of sodium sulfide or sodium hydrosulfide. The Sulfex patent is assigned to:

THE PERMUTIT COMPANY, INC.
Post Office Box 355
E49 Midland Avenue
Paramus, NJ 07652
(201) 967-6000
Telex: 134-488
Robert V. Nagiel,
Product Manager, Waste Treatment

ROBINSON and SUM (1980) of the Boeing Commercial Airplane Co. prepared a comprehensive analysis of the cost of sulfide precipitation of heavy metals in industrial process waters for the EPA. They describe a side-by-side comparison of three sulfide methods and two hydroxide methods of wastewater treatment conducted on actual wastewaters on a continuous flow bench scale model treatment plant. Their tests were not able to include the PERMUTIT Sulfex process because of legal difficulties.

Performance, capital, and operating cost parameters for each of these processes as shown by ROBINSON and SUM (1980) are indicated in their conclusions inserted below. More information may possibly be available from:

BOEING COMMERCIAL AIRPLANE CO.
Manufacturing Research and Development
Seattle, WA 98124
(206) 655-2606
Alan K. Robinson
Joyce C. Sum

INDUSTRIAL POLLUTION CONTROL DIVISION
Industrial Environmental Research Laboratory
Cincinnati, OH 45268
Hugh B. Durham

Additional information on sulfide precipitation is included in the following references:

BHATTACHARYYA, D., JUMAWAN, A.B., and GRIEVES, R.B. (1979) Separation of Toxic Heavy Metals by Sulfide Precipitation Separation. Science and Technology 14(5), pp441-452. Sulfide precipitation of a synthetic solution containing As, Se, Cd, Zn, Pb, and SO_4 found that at low sulfide dosages, As and Se were removed due to coprecipitation on the other metal hydroxide precipitates at pH 8.5.

SCOTT, M.C. (1979) Sulfide Process Removes Metals, Produces Disposable Sludge. Industrial Wastes, July/August 1979.

YELIGAR, M.B., BAGENSICI, G., and SCHLAUCH, R.M. (1981) Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide. EPA Project Summary EPA-600/S2-81-142, September 1981. This describes a demonstration plant to evaluate performance and costs of the SULFEX process at the Holly Carburetor Company, Paris, Indiana. It was pointed out that where more than one flow is to be treated or where variation in metal content

occurs from time to time, it is essential to insert an equalization tank to dampen fluctuations in wastewater flow and metal concentrations into the reactor-settler unit.

In their tests, the best removals of As and Se were obtained from synthetic solutions at a post-precipitation pH of 5.0 to 5.5 and at a sulfide dosage of 0.3 mM. For waters containing moderate to high concentrations of Fe, the arsenic removal was considerably higher as in the case for actual wastewater from a copper smelter scrubber from which at a sulfide dosage of 5.0 mM and a final operating pH of 8.0-8.5, removals of Cd, Zn, and Cu were greater than 99%, and As and Se removals were 98 and over 92% respectively. Arsenic and selenium removals were primarily due to adsorption on precipitates.

INSOLUBLE STARCH XANTHATES/CELLULOSE XANTHATE

No commercial-scale use of insoluble starch xanthates or cellulose zanthate for removal of metals from mine or mill effluents was identified. Nevertheless, encouraging results in the use of these materials in the treatment of plating wastes makes it worth mentioning this technology for consideration if and when particularly difficult levels of metals must be removed, perhaps to fulfill the needs of a special situation.

Insoluble starch xanthate was developed for application in the removal of metals from dilute solutions by the U.S. Dept. of Agriculture:

U.S. DEPT. OF AGRICULTURE
Northern Regional Research Center
Peoria, IL 61604
(309) 685-4011
R. E. Wing

Insoluble starch xanthate is used, according to WING (1983), in doses of around 0.154 g/l, i.e., 0.30 lb. per ton water (0.154 Kg/m^3).

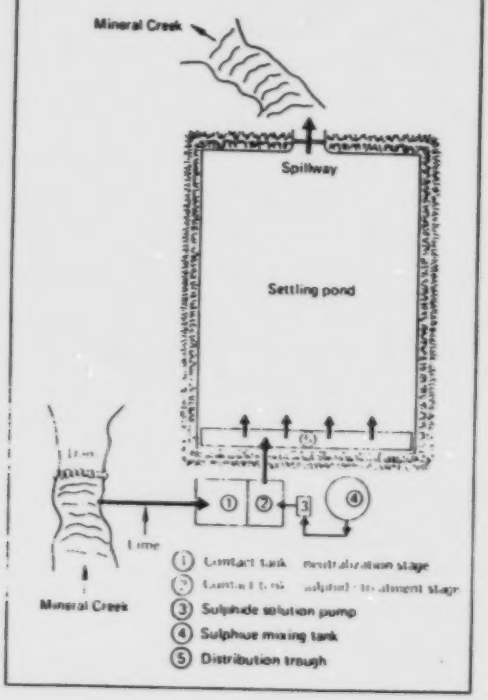
Insoluble starch xanthate is manufactured by:

POLLUTION TECHNOLOGY SYSTEMS
2922 Benton Street
Garland, TX 75042
(214) 272-4010
Dale MacFeeters, President
Michael Coward

The price of insoluble starch xanthate is around $1.80/lb, and it is intended by the makers for use in the polishing of solutions rather than for primary treatment. The same manufacturer makes a dithiocarbamate product X-2000 which is intended for primary treatment. Cost of this product is $8/gallon.

Two-stage process chemically treats mine drainage to remove dissolved metals

Fig. 1—Field treatment system for mine drainage



H. Peter Larsen and Laurence W. Ross, University of Denver

TREATMENT OF MINE DRAINAGE WATERS has fast become a necessity for all mining operations, and regulations governing discharge into local waterways can be expected to become even more stringent. One aspect of mine water treatment—removal of dissolved metals—can be accomplished by a two-stage process developed at the Denver Research Institute (DRI). The first stage of the process treats the waters by lime neutralization to eliminate Fe and Al. A second stage then removes Cu, Zn, Mn, and heavy toxic metals (Hg, Cd, As) by adding sulphide to the waters.

The quantitative effect of both stages of treatment can be predicted by a mathematical description based on the equilibrium relations involved:

$$mM^{+d} + dD^{-m} \rightarrow M_mD_d \downarrow \qquad (1)$$

where M is the metallic cation of charge $(+d)$ and D is the anion of charge $(-m)$.

The removal of dissolved metals by neutralization (stage 1) is predicted quantitatively. Total sulphide addition to achieve removal of specific metals is predicted for stage 2.

Table 1 provides the set of numerical constants used to describe the system mathematically. These values were selected from the literature as yielding the best approximation to measured results. Butler[1] has pointed out that K_{sp} values are often so small that they are outside the realm of realistic measurement. Therefore, a set of values that gives consistent results is all that is needed.

DRI process successful in field studies

Field investigation for the DRI process included erection of a treatment pond beside Mineral Creek in the

Fig. 2—Results of sulphide addition to Idaho drainage sample

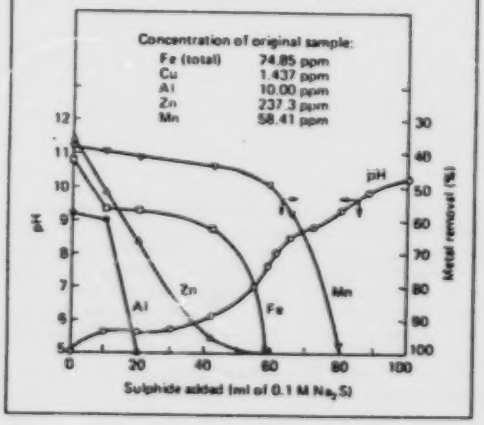


Fig. 3—Results of sulphide addition to Montana drainage sample

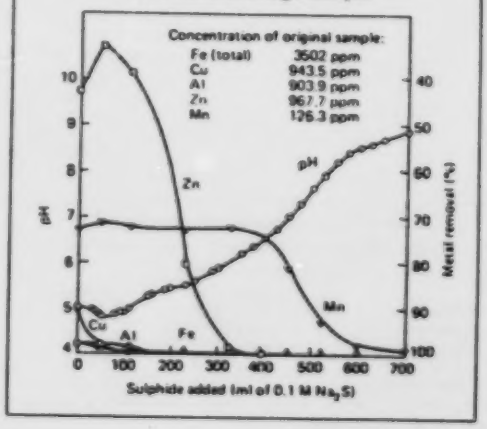


Fig. 4—Measured vs. computed values for neutralization of mine drainage
(Mineral Creek, Colo.)

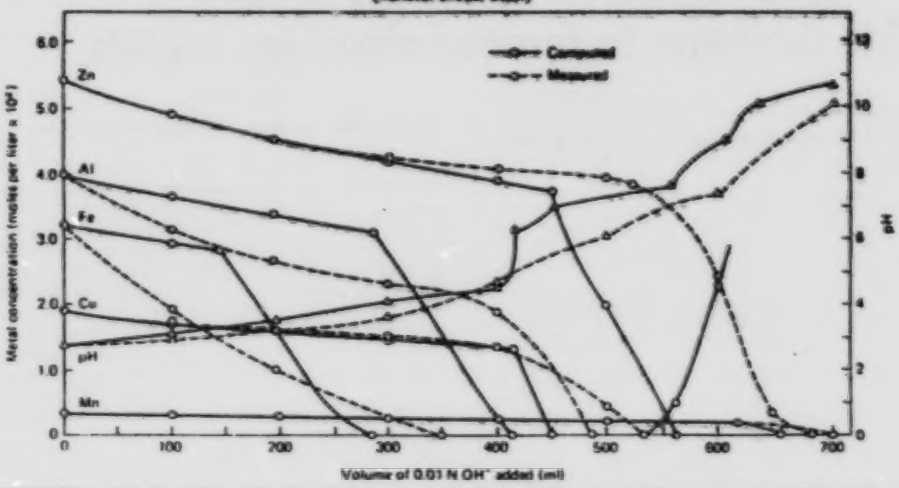


Fig. 5—Theoretical vs. measured results for neutralization of mine drainage
(Mineral Creek, Colo.)

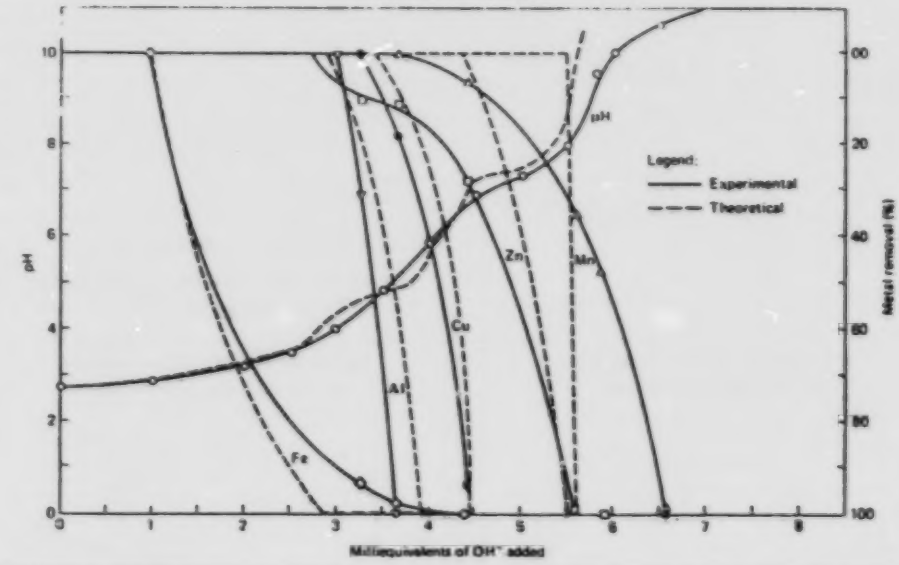


Table 1—Solubility-product constants for hydroxides and sulphides of heavy metals in mine drainage

	Hydroxide	Sulphide
Ferric iron	1.1×10^{-36}	2.0×10^{-88}
Aluminum	1.2×10^{-32}	—
Cupric copper	6.0×10^{-20}	7.7×10^{-36}
Zinc	7.1×10^{-18}	1.6×10^{-24}
Manganese	1.6×10^{-13}	2.5×10^{-13}

Rocky Mountains, west of Denver, Colo. Fig. 1 shows the design of the pond. A single pond can be used to separate the minerals of potential economic value (e.g., Cu and Zn) from Fe and Al, because $Fe(OH)_3$ and $Al(OH)_3$ will not settle when a pond is even slightly agitated by surface breeze. The sulphides, on the other hand, precipitate almost immediately after being introduced into the settling pond.

Control of pH in the two stages of the process was quite simple, requiring only good mixing for 3 to 5 min in the

contact chambers (1 and 2 in Fig. 1). Neutralization of the influent from pH 2.6 to pH 5.0 was achieved in the first stage, and sulphide addition in the second stage brought the pH to 6.5—the ambient regional pH.

Fig. 2 is an experimental plot of the behavior of metals in a drainage water sample from an Idaho mine tunnel after treatment by the DRI process. Mn was completely removed, although previously reported dual processes had removed Mn only partially.[2] The DRI process also succeeded in completely removing the toxic metals As, Cd, and Hg.

Fig. 3 shows the pattern of metal removal from a sample of drainage water taken in Montana. All Cu was apparently removed by neutralization before pH 3 was achieved.

Simulation of two-stage DRI process

Equation 1 is the basis for mathematical simulation. For example, the precipitation of ferric iron occurs as

$$Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$$

and the terms in equation 1 now become: $d = 3$, $m = 1$, $M = Fe^{3+}$, and $D = OH^-$.

The dissociation of water must also be considered:

$$H^+ + OH^- \rightarrow HOH$$

Finally, when the anion is sulphide ion, two additional equilibria must be expressed.

$$H^+ + S^{=} \rightarrow HS^-$$
$$H^+ + HS^- \rightarrow H_2S$$

With the values reported in Table 1, equilibrium for the five metals of interest can be computed as a function of their concentration, the solution pH, and the amount of sulphide added. The two-stage DRI process was simulated by assuming a starting mixture consisting of typical Mineral Creek water, then raising the pH to 5.0, after which a given amount of sulphide was added.

Fig. 4—a set of curves for neutralization alone—illustrates the most difficult case to compute, because the liquid volume is changing. The plot in Fig. 4 suggests the presence of an unreported metal. The lag of pH rise and the delay in Zn precipitation indicate that another cation may be consuming OH^- ion. The unreported metal could be Mo, common in the Rocky Mountains but never reported in state or Federal routine sampling. Alternately, the metal could be As, which has been found in waters of this region in concentrations up to 20 ppm.

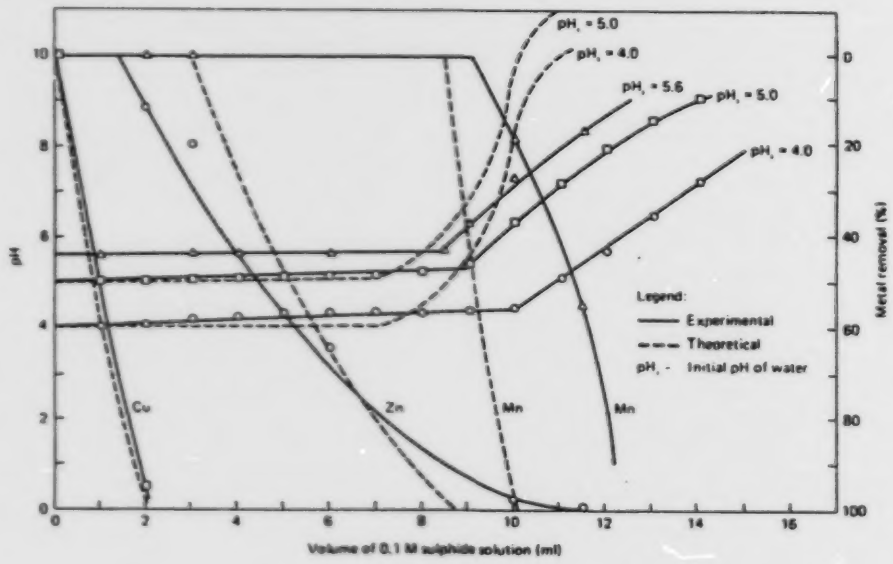
Computation is simpler when the sample of mine drainage water doesn't undergo a volume change. This is the case when solid chemicals, such as lime and sulphide, are added. Fig. 5 shows the results of such a computation for neutralization, and Fig. 6 shows the results of sulphide addition alone. The neutralization plot (Fig. 5) is fairly satisfactory at all points, but the plot for sulphide addition (Fig. 6) appears useful mainly as a predictive tool for Cu and Zn precipitation. □

References

1) Butler, J. M., *Ionic Equilibrium: A Mathematical Approach*, Addison Wesley, New York, 1964.

2) Zawadzki, L. A. and Glenn, R. A., "Sulphide Treatment of Mine Drainage," Bituminous Coal Research Inc., BCR Report L 241, Monroeville, Pa., July 1, 1968.

Fig. 6—Theoretical vs. measured results for sulphide treatment
(Mineral Creek, Colo.)



United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-81-081 Aug. 1981

EPA

Project Summary

Characterization of Boliden's Sulfide-Lime Precipitation System

M. Blythe, K. Schwitzgebel, J. C. Terry, Christina Sund-Hagelberg, and D. Bhattacharyya

The Project Report summarized here provides information on the soluble sulfide precipitation process (Na_2S) used at a copper/lead smelter for treatment of wastewater. The study presents the results of a sampling study which aimed to define the process kinetics of a full scale plant. The generation of H_2S gas, metals removal, and sludge handling are discussed.

Excellent removal of most metals, including arsenic was shown. Process control problems prevented 99%+ removal of all metals, however.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Sulfide precipitation is an effective process for the treatment of industrial wastes containing highly toxic heavy metals. The attractive features of the sulfide precipitation process are: attainment of high degree of metal removals over a broad pH range, effective precipitation of certain metals (such as: As, Cu, Cd, Hg) even at very low pH, low detention time requirement in the reaction tank because of the high reactivity of sulfides, and the feasibility of selective metal recovery. With sulfide precipitation, the high reactivity of sulfides (S^{2-}, HS^-, H_2S) with heavy metal ions and the very low solubilities of the heavy metal sulfides over a broad pH range are features not found with the hydroxide precipitation processes.

Industries engaged in metal finishing or metal production operations use large quantities of contact process water, and the spent process wastewater streams contain moderate to high concentrations of As, Cd, Cu, Zn, Pb, Hg, etc. Various physico-chemical treatment methods to remove heavy metals have been reported in the literature. Hydroxide (lime) precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial wastewaters. However, the minimum solubilities for different metals occur at different pH values and the hydroxide precipitates are amphoteric in nature and thus maximum removal efficiency of mixed metals cannot be achieved at a single precipitation pH. Hydroxide precipitation of arsenic cannot be achieved at any pH value. Arsenic precipitation occurs only at very high pH when lime is used to form calcium arsenate.

Sulfide precipitation (with Na_2S or NaHS) is an effective alternate technology. Sulfide precipitation processes to remove heavy metals have gained considerable importance[1-4]. The overall objective of this investigation is to establish the effectiveness of the sulfide

*Table 3. Residual Metal Concentrations Obtained with Na_2S Precipitation of Actual Wastes**

pH = 8.0
Sulfide dosage = 0.5 X

Waste	Sulfide Dosage	As	Se	Cd	Zn	Cu	Fe
				Concentration, mg/l			
Batch I	5mM (162 mg/l S)	1.0-2.0	0.5-1.0	0.06-0.2	1.0-1.4	0.1-0.2	0.5-0.8
Batch II	14mM (448 mg/l S)	1.0-2.5	1.0-3.0	0.05-0.08	0.8-1.1	0.2-0.5	0.4-0.5
Batch III	18mM (576 mg/l S)	110-160 (9.5)**	1.0	0.02-0.06	0.3-1.3	0.08-0.5	0.2-0.6

* filtered through 0.45 μ filter (after sulfide precipitation)
**at molar Fe/As = 1 (by adding Fe^{3+})

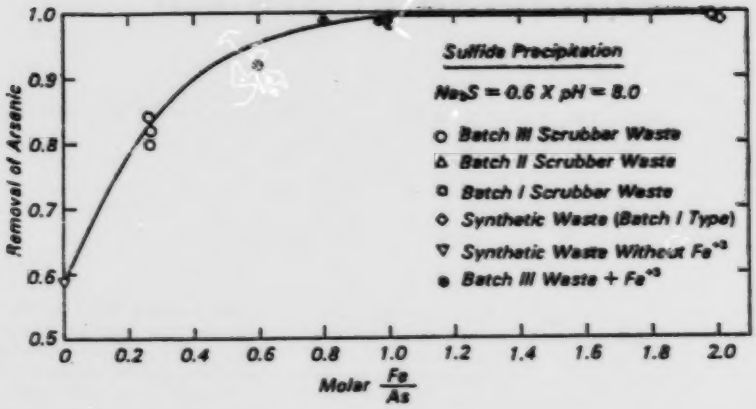


Figure 3. Effect of molar feed ratio of Fe/As on arsenic removal by a combination hydroxide - sulfide precipitation.

reagent by dissolved SO_2 (sulfite) present (Table 4) in the wastewater. The control technique of sulfide dosage by pH rise was found to be insufficient for simultaneous arsenic and zinc removal at optimal efficiency. In order to understand the importance of sulfite-sulfide side reaction at acidic pH values, bench-scale studies were conducted with single metal salts in the presence of sulfite at acidic pH values. Depending on the metals studied, part of the Na_2S was consumed by SO_3^{2-} to form elemental sulfur and thiosulfate. Even with sulfide overdoses at low pH values no H_2S gas loss from the solutions occurred (also observed in full-scale tests) due to SO_3^{2-} - H_2S reactions. At stoichiometric Na_2S dosages (to form AS_2S_3, ZnS, etc.) the sulfite-sulfide reaction played an important role only during precipitation of As and Zn at low pH values. The decrease in separation for As and Zn in the presence of sulfite is shown in Figure 5. For ZnS formation (because of low solubility product) the sharp increase in residual Zn concentration (as shown by cross-hatched area) and consumption of SO_3 (as shown by a decrease in SO_3 concentration) are evident from Figure 5. The effects of sulfide-sulfite reaction were found to be negligible above pH 5.

In summary, the feasibility of a combination of hydroxide-sulfide precipitation (at pH 8-9) process, and a process involving sulfide precipitation (at pH 3-5) followed by lime precipitation, is established to achieve a high degree of separation of heavy metals and arsenic. The combination hydroxide-sulfide process required only 60% of the theoretical Na_2S dosage to provide effective separations of heavy metals and arsenic. Simple sulfide precipitation at pH 3-4 also provided excellent removals for Cu, Cd, Hg, and Pb. For precipitation of arsenic and zinc sulfide at pH < 5, the side reaction between sulfite (if present in wastewater) and sulfide must be considered. Hydrogen sulfide gas formation was never found to be a problem during precipitation because of the high reactivity of sulfides and heavy metals.

This project was supported by a research grant (R804568) from the U.S. Environmental Protection Agency to the University of Kentucky.

References

1. Lantz, J.B., "Evaluation of a Developmental Heavy Metal Waste Treatment System," *Naval Construction Battalion Center Report No. ER-314-40-6* (1979).

Table 4. Analysis of Inlet Wastewaters (Full-Scale Plant)

Parameter	Concentration, mg/l
pH	1.9-2.8
As	130-450
Zn	30-60
Pb	20-40
Cd	3-16
Cu	3-5
Hg	2-4
Fe	5-20
Sulfite (dissolved SO_2)	600-1000
SO_4	1500-2000
Fluoride (F)	90-130

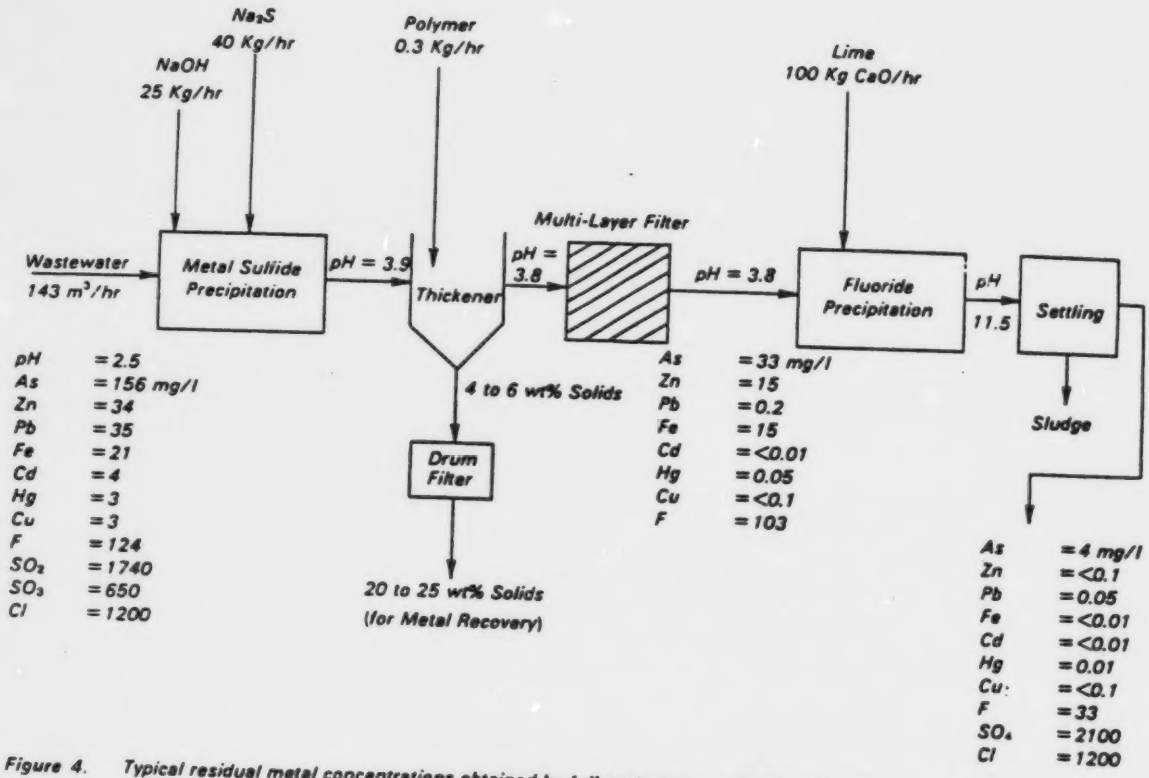


Figure 4. Typical residual metal concentrations obtained by full-scale test run (Boliden Metall).

2. "Control and Treatment Technology for the Metal Finishing Industry: Sulfide Precipitation," EPA Technology Transfer Report No. EPA 625/8-80-003 (April 1980).
3. Bhattacharyya, D., Grieves, R.B., and Jumawan, A.B., "Separation of Toxic Heavy Metals by Sulfide Precipitation," *Sep. Sci. and Technology, 14*, 441 (1979).
4. Bhattacharyya, D., et al., "Sulfide Precipitation of Heavy Metals from Non-Ferrous Metal Production Wastes," *51st Annual Conference—Water Pollution Control Federation*, California (1978).
5. Larson, H.P. and Ross, L.W., "Two-Stage Process Chemically Treats Mine Drainage to Remove Dissolved Metals," *Operating Handbook of Mineral Processing*, 349 (February, 1976).
6. Schlauch, R.M., and Epstein, A.C., "Treatment of Metal Finishing Wastes by Sulfide Precipitation," *EPA 600/2-77-049* (1979).

Table 5. Removal of Metals by Sulfide Precipitation and by Sulfide Precipitation Followed by Lime Precipitation (Full-Scale Process)

Component	% Removal: Sulfide Precipitation*	% Removal: Sulfide + Lime Precipitation**
As	67-87	96-99
Zn	51-75	99
Pb	97-99	97-99
Cd	99	99
Cu	>90	>90
Hg	99	99
Fe	2-26	>99
Fluoride	0	70-78

*Sampling point 7 in Figure 2
**Sampling point 8 in Figure 2

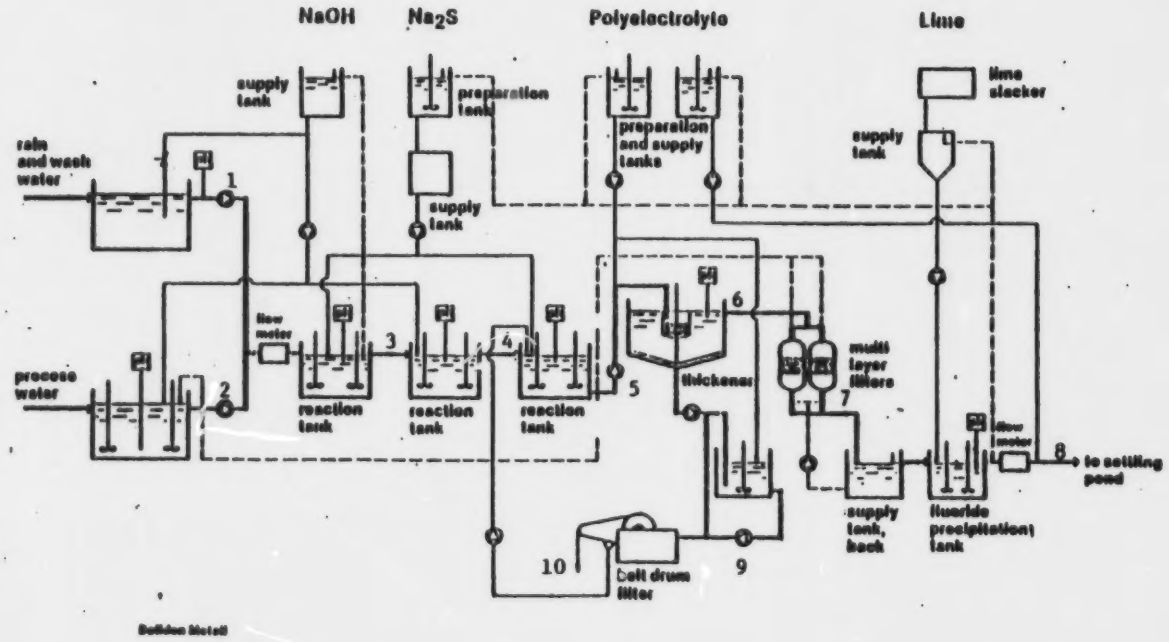


Figure 1. Sulfide precipitation plant.

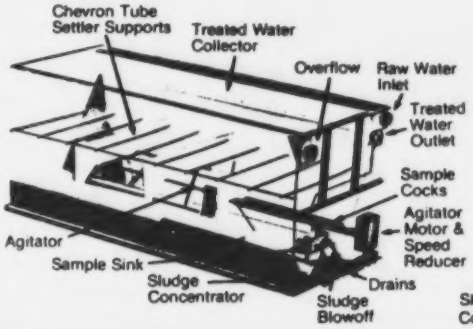
TABLE 2. VOLUMES AND DIMENSIONS OF PROCESS VESSELS

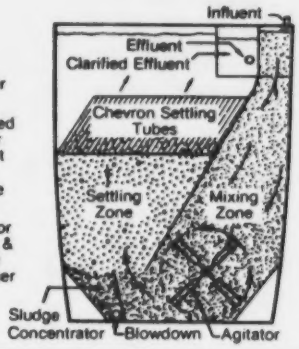
Surge tank rain and wash water		180	m^3
Surge tank process water		140	m^3
Reaction tank 1		55	m^3
Reaction tank 2		36	m^3
Reaction tank 3		50	m^3
Thickener width		15	m
depth		3.5	m
volume		620	m^3
Multilayer filter width		3	m
depth:	anthracite sand	0.43	m
	garnet sand	0.33	m
	bearing material	0.23	m
Calcium fluoride precipitation tank		124	m^3
Sludge tank		45	m^3
Size of drum filter		47	m^2
Size of lime slaker		900	kg/h

M. Blythe, K. Schwitzgebel, J. C. Terry, Christina Sund-Hagelberg, and D. Bhattacharyya are with the Department of Chemical Engineering, University of Kentucky, Lexington, KY 40506.
Alfred Craig, Jr. is the EPA Project Officer (see below).
The complete report, entitled "Characterization of Boliden's Sulfide-Lime Precipitation Plant," (Order No. PB 81-209 272; Cost $9.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Permutit Package Precipitator

The Permutit Precipitator offers a highly efficient means for removing impurities from a liquid by precipitation, adsorption, settling and upflow filtration. This unit has found wide application among municipalities and industries for water and waste water clarification. It is universally accepted for coagulation and clarification and for the removal of suspended matter, color, iron, manganese, silica, and heavy metals, in addition to softening and dealkalization.





Precipitator Applications

Turbidity Removal
The Precipitator's sludge blanket is particularly efficient in removing small particles that are difficult to remove by other filtration processes. The proper mixing of chemicals causes the formation of a large, tough floc throughout the sludge blanket. This assures the maximum adsorptive and straining effect in removing turbidity. Final polishing of the water may then be accomplished with filters.

Color Removal
Color is removed from water by the use of coagulants applied in the most favorable pH range. In addition, certain waters may require clay, chlorine, polyectrolytes, or activated carbon. The Precipitator is particularly applicable for color removal due to the intimate contact between the water and the adsorbents in the mixing and sludge blanket zones.

Alkalinity Reduction
The Precipitator may be operated to reduce calcium bicarbonate alkalinity alone or to reduce both calcium and magnesium alkalinity. Its efficient use of chemicals is most effective for this application.

Silica Removal
One of the methods for the removal of silica from water has been the use of metallic hydroxide sludges as silica adsorbents. In Precipitator installations the efficient use of the adsorbent powers of the sludge has proved to be of great value for silica removal.

Taste and Odor Removal
The Precipitator is widely used for the removal of tastes and odors from water supplies. Activated carbon is fed into raw water, entering the the Precipitator at the same time that coagulant chemicals are introduced. The adsorbent properties of the activated carbon are utilized to the fullest extent during the prolonged and intimate contact with agitated and suspended sludge provided by the Precipitator.

Heavy Metals Removal
The dense sludge blanket of the Precipitator is especially effective when precipitating metals as sulfides or hydroxides. This property offers a critical advantage where permissable discharges of metal residuals are limited to fractions of a part per million.

Precipitator Advantages

Superior Performance
Low turbidity Precipitator effluent is virtually always superior to the effluent of conventional clarifier-softeners.

Excellent Chemical Efficiency
Action of suspended sludge in the mixing zone and upflow through the sludge blanket achieves highly efficient chemical utilization.

Positive Agitation
Large, slow moving agitator blades completely mix water, chemicals and sludge.

Effective Sludge Blanket
Sludge blanket particles are effectively distributed from top to bottom for optimum contact and filtration.

Easy Installation
Precipitator tanks are shipped set up with agitator and reducer assembled and installed.

Adaptable To Tube Settlers
Permutit Chevron shaped tube settlers can easily be installed to increase flow rate up to 40 percent over standard capacity. Tube settlers support grids are built into all Precipitators.

Adapts To Variable Flow Rates
As the rate of flow changes, the height of the sludge blanket adjusts to a level which provides the proper area for the new rate.

Lengthened Filter Runs
The low turbidity effluent of a Precipitator places very little load on downstream filters. This permits longer filter runs than previously possible and lowers treatment costs.

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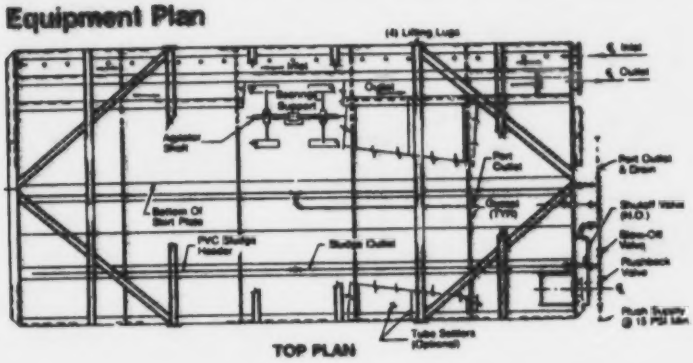
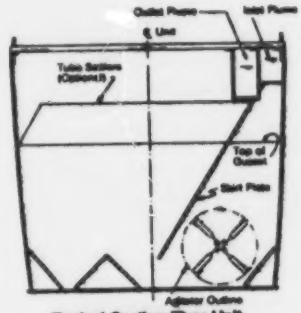
Technical Data

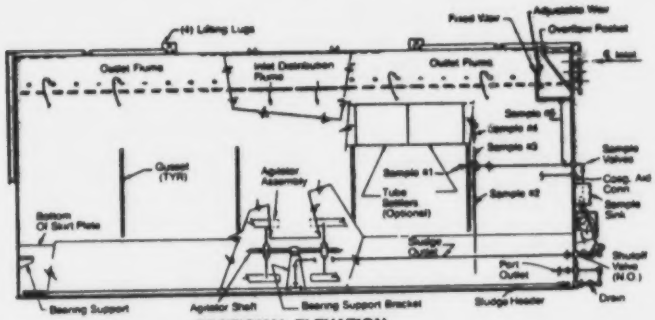
Equipment Plan



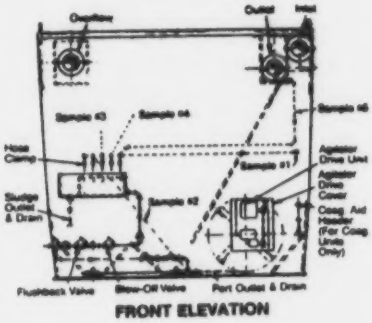
TOP PLAN



Typical Section Thru Unit (Model No. 6)



SECTIONAL ELEVATION



FRONT ELEVATION

Unit shipped set-up with agitator drive, agitator, sludge and port headers, all sample valves and piping and coagulant assembly (if required), shop installed.

Components furnished by Permutit, field installed by others: external sludge blow-off, flushback lines and valves and (optional) tube settlers.

Interior and exterior surfaces of tank to be commercially sandblasted per spec. SSPC-6 and shop primed one coat Inertol #621 or equal.

Performance Characteristics and Dimensions

Model No.	Max. Flow Rate GPM*		Surface Area Sq. Ft.	Tube Settling Area Sq. Ft.	Unit Size W x L x H	Agitator Motor HP	Inlet Outlet Overflow Size (ins.)	Sludge Blowoff & Flushback Valve Size (ins.)	Detention (gals.)**	Weight (lbs.)	
	Without Tube Settlers	With Tube Settlers								Shipping	Operating
1	44	60	35	25	8'x 5'x10'6"	½	3	1	2,600	6,000	27,700
2	88	120	70	50	8'x10'x10'6"	½	4	1½	5,200	9,000	52,500
3	132	180	105	75	8'x15'x10'6"	½	6	1½	7,800	12,000	77,000
4	175	240	140	100	8'x20'x10'6"	½	6	2	10,400	15,000	101,700
5	220	300	175	125	8'x25'x10'6"	¾	8	2	13,000	18,000	126,300
6	250	350	200	150	9'x25'x10'6"	¾	8	2	15,000	19,000	144,000
7	280	400	225	175	10'x25'x10'6"	¾	8	2	16,800	20,000	160,000
8	310	450	250	200	11'x25'x10'6"	¾	8	2	18,600	21,000	176,000
9	340	500	275	225	12'x25'x10'6"	¾	10	2	20,500	22,000	192,800
10	460	680	375	300	12'x34'x10'6"	1	10	2	27,700	30,000	260,800
11	540	800	440	350	12'x40'x10'6"	1	12	2	32,500	35,000	305,800
12	620	920	505	400	12'x46'x10'6"	1½	12	3	37,350	38,000	349,200

*Typical capacities when used for removal of suspended matter, color, taste and odor, and for softening and dealkalization applications. Contact Permutit for flow rates applicable to silica removal, heavy metals reductions, and other special applications, and flow rates higher than listed.

**Detention time 60 minutes.

Package Precipitator/Solids Contact/Clarifier

Suggested Specifications

Scope
The intent of these specifications is to provide complete factory fabricated Precipitator type clarification equipment to treat _____ gpm total flow. The detention time at design capacity shall be one hour (40 minutes minimum with optional tube settlers). The equipment to be installed shall be ____ wide × ____ long × 10'-6" high.

General
Furnish _____ Permutit standard model _____ automatic horizontal Precipitator unit(s).

Tank
The Precipitator outer tank shall be fabricated of ¼" steel plate complete with bottom. The tank shall include inlet and effluent distributing flumes constructed of ¼" steel plate along the entire inside length for proper distribution and collection of the water. The mixing compartment is to be separated from the sludge filter compartment by a ¼" steel water tight sloping baffle. Inlet, outlet, overflow and drain connections shall be provided on the tank.

Internals
A complete paddle type agitator mechanism shall be furnished consisting of shaftings, paddles, water lubricated bearings and guides, designed so as to assure complete agitation of the mixing zone and avoid settling of material on the bottom of the Precipitator. The agitator drive shall consist of ____ HP, T.E. motor with speed reducer, required sheaves and belts for speed adjustment in a 4:1 range.

The unit shall inlude provision for the collecting, concentrating, and blowoff of sludge and back flushing of sludge lines. The sludge concentrator shall run the length of the unit at the bottom of the sludge filter compartment. A perforated PVC sludge blowoff header shall be installed in the concentrator. A PVC port header shall also be provided to move material too heavy to be carried into the sludge concentration zone. Timers, solenoid valves, and diaphragm valves for controlling the automatic desludging of the Precipitator and the automatic back flushing of the concentrator headers shall be provided.

Sampling
Five ½" sample lines and sample points shall be provided. The points of sampling shall be: in the upper portion of the mixing zone, in the sludge concentration zone, in the lower sludge blanket zone, in the upper sludge blanket zone, and in the effluent water zone. The sample lines shall terminate in a sample sink attached to the Precipitator tank.

Finish
The steel tank and internal parts are to be commercially sandblasted, primed with one (1) shop coat of Inertol No. 621, or equal, and shipped set-up with all internal components including agitator, sludge and port piping installed.

Operation
The unit shall provide a highly efficient means for removing impurities from a liquid based on the upflow sludge blanket principle. It shall include an inlet flume, a mixing compartment, and upflow sludge filter compartment, a sludge concentration zone and an effluent flume.

Chemically dosed water introduced into the inlet flume shall be uniformly distributed to the mixing compartment over the entire length of the unit. The agitators in the mixing compartment shall assure intimate contact between water and chemicals, and keep the sludge blanket in proper suspension. The sloping baffle separating the mixing compartment from the sludge filter compartment shall serve not only to keep the mechanical agitators from disturbing the sludge blanket, but also to provide a gradually increasing upflow area to enhance settling. The resulting sludge blanket provides for entrapment and holding of fine particles. Units not providing baffles which separate the mixing and sludge filter zones will not be acceptable.

The maximum area of the upflow Precipitator section (the greatest available clear water disengaging area) shall provide for an upward velocity not exceeding 1.25 gpm per sq. ft. when operating at design capacity. (For optional operation with tube settlers the upward velocity shall not exceed 2.4 gpm per sq. ft. of tube settler area, and tube settlers shall occupy an area not less than 70 percent of the maximum Precipitator section).

Work By Others
Receive, unload, and set equipment on concrete foundation pad. Provide and install all external piping and electrical work. Finish paint.

Options
- Inlet Flow Meter
- Meter Initiated Blow-Off Cycle
- Inlet Control Float Valve
- Tube Settlers
- Chemical Feed Equipment
- Pump Suction Tanks
- High Low Float Switches
- Transfer Pumps
- Chemical Feed Timers
- Manual Starter for Agitator Drive Motor

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SULFIDE PRECIPITATION OF HEAVY METALS

by

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CONCLUSIONS

OVERVIEW

Three sulfide precipitation processes that use soluble sulfides have been demonstrated (in a continuously operated bench-scale plant) as practical waste treatment processes for removing heavy metals from wastewater. The levels to which heavy metals can be reduced, and the costs of treatment compared to conventional lime treatment, are developed in this report.

The lime, sulfide polished and filtered (LSPF) process is the optimum sulfide process. For many wastewaters, treatment by the lime process followed by filtration is almost as effective as the LSPF process and costs far less.

EFFECTIVENESS OF PROCESSES FOR REMOVING HEAVY METALS

Based only on the reduction in concentration of five heavy metals (cadmium, chromium, copper, nickel, and zinc) in the effluents analyzed and without considering cost:

- The lime only, clarified (LO-CL) process is the least effective.
- Processes lime only, clarified and filtered (LO-CLF) and lime with sulfide, clarified (LWS-CL) are equally effective and better than the LO-CL process.
- Processes LSPF and lime with sulfide, clarified and filtered (LWS-CLF) are equally effective and better than any of the other three.

OPERATING AND CAPITAL EQUIPMENT COSTS

Each of the improvements to the basic LO-CL process carries a cost penalty. Tables 1 and 2 show that:

- The addition of a filtration operation (conversion to the LO-CLF process) adds from 0.4 to 0.7 percent to the operating costs and from 0.8 to 1.7 percent to the capital costs.
- The addition of a sulfide polishing operation, which includes filtration (conversion to the LSPF process), adds from 4.8 to 8.6 percent to the operating costs and from 8.6 to 11.6 percent to the capital costs.
- Conversion to a lime-with-sulfide process increases the capital cost by 6.2 to 11.6 percent; for a small plant, the process increases the operating cost by 7.1 to 7.8 percent, and for a medium or large plant, the process increases the operating cost by 26.4 to 39.5 percent.

TABLE 1. COMPARISON OF OPERATING COSTS

Operating cost of: / Plant capacity	Conventional lime plant with no filtration	Lime plant with filtration added (%)	Lime plant with sulfide "polish" operation, including filtration (%)	Lime-with-sulfide plant with no filtration (%)	Lime-with-sulfide plant with filtration added (%)
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
37.85 m^3/day (10,000 gal/day)	\$5.96/m^3 (\$22.6/1,000 gal)	+0.7	+4.8	+7.1	+7.8
757 m^3/day (200,000 gal/day)	\$0.90/m^3 (\$3.39/1,000 gal)	+0.4	+8.0	+26.4	+26.8
1,893 m^3/day (500,000 gal/day)	\$0.55/m^3 (\$2.08/1,000 gal)	+0.5	+8.6	+39.0	+39.5

TABLE 2. COMPARISON OF CAPITAL COSTS

Capital cost of: / Plant capacity	Conventional lime plant with no filtration	Lime plant with filtration added (%)	Lime plant with sulfide "polish" operation, including filtration (%)	Lime-with-sulfide plant with no filtration (%)	Lime-with-sulfide plant with filtration added (%)
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
37.85 m^3/day (10,000 gal/day)	\$233,000	+1.7	+11.6	+9.4	+11.6
757 m^3/day (200,000 gal/day)	\$799,000	+0.8	+11.6	+9.1	+10.0
1,893 m^3/day (500,000 gal/day)	\$1,296,000	+1.1	+8.6	+6.2	+7.2

SLUDGE DISPOSAL COSTS

The costs developed here include estimates for sludge disposal, which are based on the assumption that a sulfide sludge will not carry any significant cost penalty. At this stage, we do not know the additional surcharge, if any, that might be added to the disposal charges for a sulfide sludge.

EFFECTIVENESS OF SPECIFIC PROCESSES FOR REMOVING HEAVY METALS

The same order of preference as that given on page 2, with more details about individual metals, can be seen in Tables 3 and 4, which show the mean levels of the five metals before and after treatment.

The tables show that cadmium, copper, and zinc follow the same hierarchy as we established on page 2; that is, LO-CL is least effective, LO-CLF and LWS-CL are more

effective, and LSPF and LWS-CLF are most effective. The logarithmic mean removal of these three metals is 96.3 percent or greater for the two most effective processes, with a logarithmic mean effluent concentration of less than 50 μg/L.

Nickel removal does not follow the established hierarchy completely; when the logarithmic means are considered, the five processes are roughly equivalent. When the arithmetic means are considered, the hierarchy is the same as that established for cadmium, copper, and zinc. The logarithmic mean nickel removal is 88.4 percent or

TABLE 3. ARITHMETIC MEAN INFLUENT AND EFFLUENT CONCENTRATIONS FOR THE FIVE PROCESSES

Concentrations in μg/L (values in parentheses are percentage reductions from raw feed)

Heavy metal	Raw feed	LO-CL	LO-CLF	LWS-CL	LSPF	LWS-CLF
Cadmium	4,805	144 (97.00)	103 (97.86)	25 (99.48)	13 (99.37)	8 (99.83)
Copper	4,136	963 (76.72)	673 (83.73)	521 (87.40)	96 (97.68)	70 (98.31)
Chromium	26,006	603 (97.68)	58 (99.78)	370 (98.58)	58 (99.78)	86 (99.67)
Nickel	18,617	2,021 (89.14)	1,561 (91.62)	1,506 (91.91)	652 (96.50)	751 (95.97)
Zinc	259,865	8,385 (96.77)	6,629 (97.45)	491 (99.81)	517 (99.80)	422 (99.84)

TABLE 4. LOGARITHMIC MEAN INFLUENT AND EFFLUENT CONCENTRATIONS FOR THE FIVE PROCESSES*

Concentrations in μg/L (values in parentheses are percentage reductions from raw feed)

Heavy metal	Raw feed	LO-CL	LO-CLF	LWS-CL	LSPF	LWS-CLF
Cadmium	135	31 (77.04)	18 (86.67)	8 (94.07)	5 (96.30)	4 (97.04)
Copper	673	109 (83.80)	63 (90.64)	49 (92.72)	21 (96.88)	16 (97.62)
Chromium	1,039	136 (86.91)	24 (97.69)	108 (89.61)	24 (97.69)	32 (96.92)
Nickel	976	156 (84.02)	118 (87.91)	155 (84.12)	93 (90.47)	113 (88.42)
Zinc	23,904	820 (96.57)	210 (99.12)	195 (99.18)	46 (99.81)	31 (99.87)

* Log average of x_1 through $x_n = \log^{-1}\left(\frac{\sum_1^n \log x}{n}\right)$

greater for the two most effective processes, and the logarithmic mean nickel level in the effluents is 113 μg/L or less.

Chromium removal is not significantly improved by the presence of sulfides. That is, the unfiltered effluents (LO-CL and LWS-CL processes) showed logarithmic mean concentrations that were about equal at 136 and 108 μg/L, and the logarithmic means for the filtered effluents (LO-CLF, LSPF, and LWS-CLF) were also about equal at 24, 24, and 32 μg/L, respectively. This grouping clearly indicates that filtration after clarification had exerted a marked effect. Logarithmic mean chromium removal rates are 86.9 percent or greater for the unfiltered effluents and 96.9 percent or greater for the filtered. Logarithmic mean chromium levels of 32 μg/L or less were obtained in the effluents from the filtered processes and 136 μg/L or less in the unfiltered.

These findings agree with the observation that chromium, unlike the other metals considered, precipitates a hydroxide, not a sulfide, in the presence of sulfide ions. Thus, no difference would be anticipated between the removal rates of hydroxides precipitated by lime and hydroxides precipitated by sulfides. The solubility constant of the hydroxide would govern in both cases.

Lead was removed effectively in some tests, such as Runs 5, 8, 14, and 15. In each of these, the removal efficiency is 96.6 percent or greater for all five processes. However, in many other runs, the efficiency of removal is poor, ranging from 0 to 77 percent. In two cases, Runs 1 and 4, a striking improvement was noted in the effluents from filtered processes compared with the effluents from unfiltered processes. In Run 1, the removal efficiency of the filtered process is 91.1 percent or greater, but virtually no removal took place in the unfiltered process. In Run 4, the filtered-process removal efficiency is 82 percent or greater, but the efficiency is only 30 to 64 percent for the unfiltered process. Further work is needed to determine the underlying causes of these variations in the effectiveness of the processes. Based on the present tests, for lead removal, the sulfide processes apparently have no advantage over the lime process.

When the sulfide processes are used, silver removal is not significantly different from conventional lime processing.

Tin is removed efficiently by all processes in Runs 3, 7, and 12, with greater than 95-percent removal efficiency. Runs 4 and 5 are less efficient, with removal ranging from 19 to 86 percent. The sulfide processes are no more efficient than the conventional lime processes.

CONTROL OF SULFIDE CONCENTRATION BY SPECIFIC ION ELECTRODE

The dependability of the sulfide specific ion electrodes that were used to control sulfide levels was excellent during the 6-month period while the bench-scale plant was in operation. Ruggedness, freedom from drift, and ease of electrode maintenance were roughly intermediate when compared to those of a typical combination pH electrode and to those of an oxidation-reduction-potential (ORP) probe.

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WATER & WASTE TREATMENT FOR INDUSTRY & MUNICIPALITY

THE PERMUTIT COMPANY INC P.O. BOX 355, E. 49 MIDLAND AVENUE, PARAMUS, N.J. 07652 PHONE: 201-967-8000, 212-564-7902, TELEX 134-488

August 29, 1984

Hans Von Michaelis
Randol International Ltd.
21578 Mountssield Drive
Golden, CO 80401

Gentlemen:

In response to your inquiry in connection with Permutit's Sulfex™, we are pleased to enclose the following literature for your review and consideration:

EPA Project Summary (Sept. 1981)	-	Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide
Technical Bulletin (5885C)	-	Sulfex™ Heavy Metals Waste Treatment Process Questions and Answers
Industrial Wastes Reprint (July/August 1979)	-	Sulfide Process Removes Metals, Produces Disposable Sludge
EPA Rules for Platers	-	1984 Compliance for Everyone

If you should have any questions or require additional information about Sulfex™, please do not hesitate to contact the undersigned at this office.

We wish to thank you for your interest in our products and look forward to being of further service.

Very truly yours,

Robert V. Nagiel

Robert V. Nagiel
Product Manager, Waste Treatment

/dsm

Enclosures

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-81-142 Sept. 1981

EPA

Project Summary

Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide

M. B. Yeliger, G. Bagenski, and R. M. Schlauch

M. B. Yeliger, G. Bagenski, and R. M. Schlauch are with the Permutit Company, Inc., Monmouth Junction, NJ 08852.
Mary K. Stinson is the EPA Project Officer.

The complete report, entitled "Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide," (Order No. PB 81-233 579; Cost: $9.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161

The demonstration of a now patented sulfide precipitation process ("Sulfex" ™), which removes heavy metals from metal finishing wastewaters, was performed to verify its operational practicability and performance quality. Operational data was also gathered for an economic evaluation of this process.

The study was performed at a carburetor manufacturing plant in Paris, Tennessee. Here, "Udylite" processes are used for chromate conversion coatings on aluminum and zinc carburetor castings before assembly.

A newly installed sulfide precipitation system removes chromium and zinc from the plant's combined metal finishing process wastewater. It also removes suspended material such as precipitated aluminum, iron, and phosphates. Major steps in the system are: equalization and neutralization of untreated wastewater, precipitation of metals and sedimentation of suspended solids, polishing of settler effluent with dual media filtration, and final dewatering of settled sludge.

Results show all metals and suspended solids were removed to levels well below both the City of Paris sewer system limitations and the State of Tennessee guidelines for indirect discharges to sewer systems. A dewatered sludge was produced as a firm, dry cake in a filter press without the use of conditioning agents. No hydrogen sulfide odor was detected from the reaction process treated effluent, or the solid waste produced. Jar tests were demonstrated to be a valuable tool for maintaining good process control and economical operation.

The chemical cost of sulfide precipitation has been found to be directly dependent upon the concentrations of combined zinc and hexavalent chromium present during the sulfide reaction process. Sulfide precipitation was shown to be an economical as well as effective treatment process for this type of wastewater.

This report was submitted in fulfillment of Grant No. S-804848 by Holley Carburetor Division of Colt Industries under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 11, 1978 to August 11, 1978, and work was completed as of August 25, 1978.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In April 1974, a laboratory and pilot-plant study of a new wastewater treatment process, using sulfide precipitation, was sponsored by the Metal Finisher's Foundation under Grant No.

R802924-01 from the Environmental Protection Agency. In July 1978, another study was undertaken to demonstrate effectiveness, operability, and cost of this new process called "Sulfex"™ as a full-scale installation at Holley Carburetor Company in Paris, Tennessee.*

Laboratory and Pilot-Plant Study

This work is described in the report "Treatment of Metal Finishing Wastes by Sulfide Precipitation" EPA-600/2-77-049, February 1977.* The project involved precipitating heavy metals normally present in metal finishing wastewaters by a novel process which employs ferrous sulfide addition as well as by conventional treatment using calcium hydroxide for comparison purposes. A simulated metal finishing wastewater containing common heavy metals and chelating agents was used in this laboratory and pilot-plant study. Sulfide precipitation was demonstrated to be a technically viable process that is superior to conventional hydroxide precipitation for removal of copper, cadmium, nickel, chromium, and zinc from the given influent.

Full-Scale Study

The present study was made during the startup of a 7.9 m^3/hr (35 gpm) wastewater treatment system at a carburetor manufacturing plant. Here, the production of carburetors produces wastewater from chromate conversion coating of zinc and aluminum castings by a "Udylite" process. Combined wastewaters from these metal finishing operations contain heavy metal pollutant concentrations in excess of local and state limits set for direct discharge to the city sewer system. Therefore, a safe, reliable, and economic wastewater treatment process was needed by the manufacturer to meet the imposed discharge requirements.

The metal finishing operations used at the plant involved degreasing, deburring, deoxidizing, acid etching, and chromate bath treatment to give carburetor castings corrosion resistant coatings. In the process, various materials including zinc, hexavalent chromium, aluminum, ortho- and polyphosphates, silicates, organic surfactants and chelants, as well as chelated metals, are released into the plant's wastewater discharge.

Since manufacturing specifications vary, all castings do not undergo treatment by each of these finishing operations. Furthermore, the production schedule is quite variable. As a result, the composition of the wastewater fluctuates periodically on hourly, daily and weekly bases.

This type of metal finishing operation is generally used for providing corrosion resistant coatings on surfaces of a wide variety of metal parts, components and appliances. Consequently, these wastewater characteristics are typical of many industrial manufacturing discharges that have to be treated to meet present and future discharge standards.

The laboratory and pilot-plant study had demonstrated the effectiveness of sulfide precipitation on a synthetically prepared metal finishing wastewater. The full-scale system study at the plant is useful in further proving that the process is practical under actual manufacturing conditions. For example, Table 1 summarizes the overall effectiveness of the process in removal of pollutants. Figure 1 shows the total chemical operating cost, on a per shift basis. Other variables and economics are described individually on per shift and per year basis. Therefore, this study shows how practical, controllable, and economical it is to operate the process under the fluctuating contaminant loadings that are characteristic of many metal finishing wastewaters.

Conclusions

Effectiveness

The effectiveness of the sulfide precipitation process has demonstrated that heavy metals can be removed from metal finishing wastewaters to very low levels. The effluent quality produced by this wastewater treatment process (as monitored by direct flame atomic absorption and diphenyl carbazide colorimetric methods for metal analyses) reveals that the process achieves metal values close to or less than are *routinely* detected by the accepted analytical methods (i.e. Cr and Fe detected at 0.05 mg/l, Cu and Zn detected at 0.01 mg/l).

Economics

The chemical cost of the sulfide precipitation process is directly dependent upon the influent metal loading of various heavy metals. At the carburetor plant, influent zinc and hexavalent chromium are the metal concentrations that dictate the dosage of ferrous sulfide that is required. Here, the chemical cost of sulfide precipitation is competitive with the cost of conventional bisulfite and hydroxide treatment for removal of average concentrations of zinc and hexavalent chromium in the untreated wastewater (i.e. about 34 mg/l Zn and 34 mg/l Cr^{+6}).

When hexavalent chromium is present in combination with other heavy metals, as it is at this plant, there can be a savings in equipment cost with sulfide precipitation since the metals can be removed simultaneously in one step. But, as the concentration of zinc (or other heavy metals increases) the chemical cost of direct treatment by sulfide precipitation becomes increas

Table 1. Average Wastewater Compositions During "Sulfex"™ Study

Metal	Untreated* influent	Treated* effluent	Most stringent state or city limit for Paris, Tenn. STP
	(mg/l)	(mg/l)	(mg/l)
Zn	39.5	<0.07†	0.04
Fe	0.52	0.10	—
Cu	<0.01	<0.01	0.5
Cr	32.3	<0.04	1.0
Cr^{+6}	35.6	<0.01	0.05
TSS	46.5	<1.0	<1600

*Average of 22-day test monitoring period (7/11 to 8/11/78).
†This value is the calculated maximum average for all effluent zinc analysis during this period. As illustrated, elimination of the atypical first sample value (1.5 mg/l Zn) gives an average effluent zinc of less than 0.03 mg/l.

*Schlauch, R.M. and A.C. Epstein. "Treatment of Metal Finishing Wastes by Sulfide Precipitation," EPA-600/2-77-049, Environmental Protection Technology Series, Industrial Environmental Research Laboratory, Cincinnati, Ohio, Feb 1977, pp. 1-74.

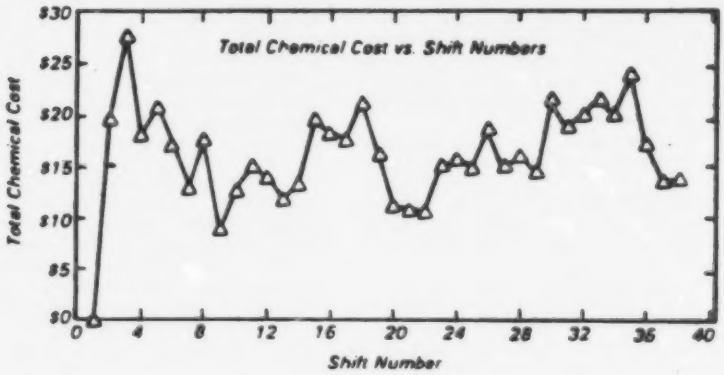

Figure 1. Total chemical cost as a function of time

ingly more than by hydroxide precipitation. At Holley, the chemical cost for sulfide precipitation treatment is justified since conventional treatment cannot effectively meet the city sewer limitations (i.e. 0.1 mg/l zinc maximum).

In all cases, however, the relative economics can be evaluated beforehand by the average heavy metal concentrations present in the wastewater. In some cases, it may be more economical to remove the bulk of the heavy metals by hydroxide precipitation, and apply sulfide precipitation as a polishing step when stringent criteria must be met.

Most of the basic equipment used for the sulfide precipitation process is the same as would be required for a conventional wastewater treatment process. Therefore, major capital costs as well as operating costs are estimated to be commensurate for both of these treatment processes.

Operation

The operation of the wastewater treatment system at the carburetor plant is basically simple. Good control is maintained because the system is designed to handle sudden changes in wastewater flow and composition.

An equalization tank is an essential part of the system for dampening fluctuations in wastewater flow and metal concentrations into the reactor-settler unit. The concentrated waste sump receives spent metal finishing baths and slowly feeds them into the equalization tank. This sump is essential to minimize variations that could complicate the operation and downgrade the effectiveness of the waste treatment process.

Since it is possible that some residual suspended solids carryover can occur periodically from the settler, the dual-media filter is necessary to ensure removal of suspended metals from the effluent before discharge to the city sewer system.

Without further use of coagulants or conditioners, a filter press will provide excellent dewatering of the settler sludge. A dry sludge cake is produced that releases easily from the press and is ready for disposal.

Control

The pH control of the neutralization process is accomplished in the equalization tank. This type of system is satisfactory for maintaining an appropriate pH for effective metal precipitation in the reactor-settler unit. High concentrations of hexavalent chromium in the wastewater can cause moderate pH increases in the reactor-settler effluent. Controlling the pH at 8.0 in the neutralization step is an effective way of compensating for this pH increase.

Periodic visual jar tests performed on the reactor-settler influent are a satisfactory means of monitoring and controlling optimal ferrous sulfide and polyelectrolyte dosages. These visual tests, for determining chemical dosage requirements, eliminate the need for laboratory analysis of influent heavy metals.

Operating Personnel

The need for wastewater treatment system operators must be determined on the basis of each plant. Due to frequent variation in the mode of the metal finishing operations at the demonstration plant, a full-time operator is required on each shift to monitor the wastewater treatment system. However, in installations where manufacturing processes are not as variable on a daily and weekly basis, a full-time operator may not be required on each shift.

Recommendations

The sulfide precipitation process has demonstrated that more complete metal removal can be obtained and acceptable effluent quality achieved, as opposed to conventional hydroxide treatment of metal finishing wastewaters. But the cost of precipitating most heavy metals (except hexavalent chromium) is higher by sulfide methods than by the hydroxide methods on a per unit weight of metal removed basis.

Present day technology reveals that *hydroxide precipitation* removes high percentages of zinc and other metals from metal finishing wastewaters. However, this removal method can still allow unacceptably high residuals of heavy metals in the treated effluent for discharge.

Therefore, in cases of very high metal loadings, a combination of the two methods in series should prove to be an economically attractive way of achieving superior quality effluents. Sulfide precipitation, is thus precipitation, as a polishing step following conventional hydroxide recommended when either heavy metal loadings on new systems are high enough to warrant the additional equipment or a conventional treatment system already exists.

PERMUTIT®
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SULFEX™ Heavy Metals Waste Treatment Process

Sulfex is a proprietary system developed by Permutit for removing heavy metals from process waste streams. Sulfex has particular application for the treatment of metal finishing and plating waste waters and for removing chromates and similar metallic constituents from cooling tower blowdown effluent. A practical and economic waste treatment process, Sulfex sets a new criteria for effective control of heavy metal pollution.

Questions and answers about the Sulfex treatment process . . .

1. Why are the regulatory agencies concerned over the discharge of so called "heavy metals"?

Because heavy metals, which include zinc, copper, cadmium, nickel, chromium, mercury, lead, etc., have been found to have a delayed but very serious impact on the natural food chain going from algae through lower aquatic life to higher animals and humans. The natural concentration of such metals in surface water is exceedingly small, but concentrations are increased along the food chain until toxic levels can destroy certain species. For instance, populations of shell fish have been eliminated in some areas, and there have been cases of brain damage, birth defects and death to human beings attributed to "biomagnification" of some heavy metals.

When heavy metals are discharged into municipal sewage treatment plants, there is some danger of direct toxicity to essential bacteria. Normally, the heavy metals concentrate in the sludge produced. This sludge can be toxic to some plants if applied to land, or toxic to marine life if dumped at sea.

Much more is to be learned about the delayed effects of heavy metal discharge. It is evident, however, that the discharges should be minimized.

2. What industries or operations typically discharge these metals?

The plant waste streams of metal plating and finishing operations, certain textile, dye and pigment operations, mercury cell operations, metal fabricators, smelting and ore handling operations and cooling tower blowdown usually contain one or more of these toxic metals.

3. What do the regulations call for?

Federal regulations require the "best practical technology" to be applied by 1977, and "the best available technology" to be applied by 1983. The discharge permit system, as administered in different geographical locations, may set more specific requirements, and any local regulatory agency can set more stringent demands but not less stringent demands than the federal government.

Discharges going into a municipal treatment system may have different limitations than discharges into surface water.

It is wise to determine the local regulations before action is taken.

4. What has previously been considered the "best practical technology" for treating waste containing heavy metals?

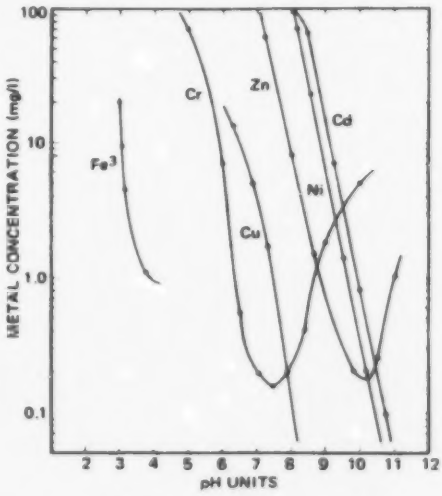
In many cases, mixtures of these heavy metals have been treated by pH adjustment with either lime or caustic soda to cause precipitation of metal hydroxide sludge. This is sometimes called "Lime and Settle" process or the hydroxide process.

Chromium presents a special problem when it is present as a chromate, or in its hexavalent state. It first must be reduced to the trivalent state before it can be precipitated as a hydroxide. The reduction step commonly is carried out at a pH of about 2 with a reducing agent such as sulfur dioxide gas, sodium metabisulfite, or ferrous sulfate. When the reduction is complete, the pH must be raised to allow the chrome hydroxide to form. Therefore, hexavalent chrome wastes are normally isolated from other wastes and treated separately.

5. Are there any problems or inadequacies with the hydroxide process?

Yes, the hydroxide process is often not capable of removing enough of the heavy metal contaminants to achieve specified discharge levels. There are a number of reasons for this.

(a) A metal such as zinc reaches a minimum solubility at a specific pH, and further additons of hydroxide can cause the zinc to become more soluble. Trivalent chrome behaves the same way, but requires a different pH to achieve minimum solubility. When there is a mixture of these metals it is not possible to precipitate them both to low levels. The following graph (published by the EPA) illustrates this relationship.



Precipitation of metal salts versus pH

(3) It has also been found that materials such as oils and grease, soaps or other organics, can interfere with the separation of the hydroxide precipitate from the water effluent.

(4) Particularly important, chelating or complexing agents, which tend to prevent precipitation of the hydroxides, sometimes are present in the waste water.

Another problem is that some metals require a very high pH to precipitate as hydroxide to low levels, the effluent water must then be neutralized before it can meet discharge pH limitations.

6. What are the chelating or complexing agents and how do we know if they are present?

Materials such as "EDTA", gluconates, ammonia complexes, Rochelle salts etc., are often added to plating solutions to keep the heavy metals in solutions. In many cases, when plating operators purchase proprietary solutions from supplers, the chemical compositions are not provided. An analysis may be made for a total organic content or an attempt to indicate whether or not such materials are present. But normally it is necessary to experimentally determine how completely the metals are precipitated.

7. Are the metal sulfides a great deal less soluble than the metal hydroxides?

Yes, as can be seen from the following table:

Approximate Solubilities of Metals
ppm in pure water

Metal	As Hydroxide	As Sulfide	Factor*
Iron	5×10^{1}	1×10^{-4}	5×10^{5}
Zinc	3×10^{2}	1×10^{-6}	3×10^{8}
Cadmium	3×10^{0}	1×10^{-6}	3×10^{6}
Nickel	7×10^{1}	6×10^{-8}	1×10^{7}
Copper	2×10^{-2}	2×10^{-13}	1×10^{11}
Lead	2×10^{0}	6×10^{-9}	3×10^{8}
Mercury	6×10^{-4}	1×10^{-21}	6×10^{17}
Silver	2×10^{1}	4×10^{-12}	5×10^{12}
Chromium	1×10^{-3}	(No Precip)	

$$\text{Factor} = \frac{\text{Solubility as Hydroxide}}{\text{Solubility as Sulfide}}$$

Kep data from 11th edition of Lange's Handbook was used to calculate solubilities.

8. Why has sulfide precipitation of heavy metals not been favored over hydroxide precipitation?

Because, as a practical matter, most waste water streams are subject to variations in both flow rates and metal concentrations and there is no practical way to add the exact amount of soluble sulfide for corresponding to the metal to be precipitated. If too little is added, all the metal will not be precipitated. If too much is added, the excess sulfide will be in the water effluent, and there can be a problem with the evolution of H_2S gas which has an objectionable odor and can be toxic above certain concentrations.

9. How does the Permutit Sulfex Process overcome the problem of supplying a sufficient amount of sulfide without allowing excess sulfide to discharge with the water or into the air?

It turns out to be relatively simple, considering the solubility and chemistry of iron sulfide. Knowing the expected flow rate of the heavy metal to be precipitated, an excess amount of sulfide is provided so that under normal conditions, all of the heavy metal can be converted to a sulfide. Iron is also provided in a quantity so that all of the sulfide added can be precipitated as iron sulfide. To the extent that there is any excess iron in the waste, this is precipitated as iron hydroxide by maintaining the pH results in the [illegible] range. Under these conditions there is no significant discharge of soluble sulfide or iron with the water effluent and no appreciable rate of H_2S.

If there is a temporary increase in the amount of heavy metal running into the treatment system, so that the heavy metal requires more sulfide than the amount being added, sulfide will be withdrawn from excess iron sulfide sludge maintained in the system.

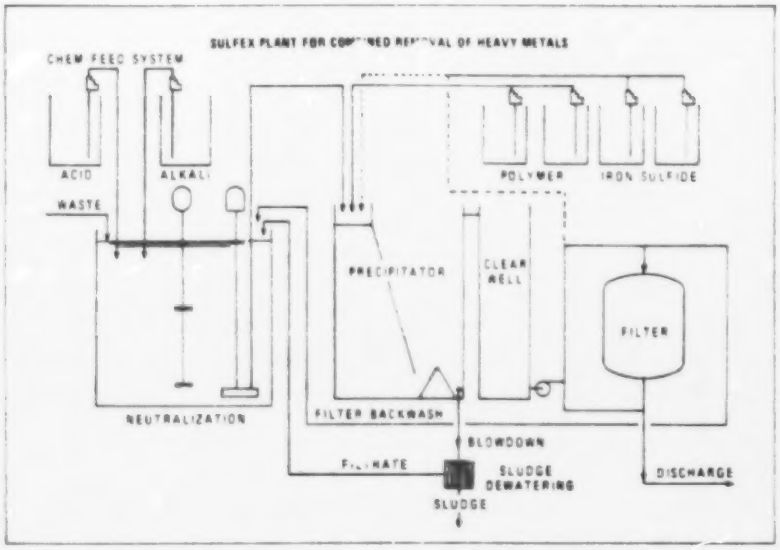
In practice, the sulfide normally is added as a mixture made from sulfide precipitate which in some respects can be compared with a dispensable ion exchange resin for critical soluble heavy metals from the waste water. It is not necessary to match the addition rate of the iron sulfide exactly with the flow rate of heavy metals so long as some excess iron sulfide and iron hydroxide is normally removed with the sludge.

10. How is the capture of the very small or near colloidal precipitates controlled in the Permutit Sulfex Process?

Generally the well demonstrated Permutit Precipitator sludge blanket clarifier is used to continuously remove suspended and near-colloidal particles from the raw water.

For low flow rates, another type of filter may be selected. A polishing filter often is specified to give further assurance that the effluent is sparkling clear and free of waste solids.

The Permutit Company, Inc., has a great deal of practical experience in removing suspended solids and near-colloidal materials from raw water and waste water. This experience forms an important basis for the Permutit Sulfex Process.



11. What levels of heavy metal removal have been achieved using the Permutit Sulfex Process?

Levels under [illegible] ppm have been achieved for all heavy metals and levels down to [illegible] ppm with some. It should be noted that these are normal conditions at work affecting the extent of metal removal including the presence of chelating agents.

12. Are all chelating agents equally troublesome?

No, the low solubilities of the metal sulfides can overwhelm the presence of most commonly used chelating agents. Not all metals respond the same. In some tests, sulfide precipitated copper in the presence of ammonium, gluconate, pyrophosphate, citrate, and Rochelle salts to levels of 0.01 - 0.02 ppm. Under comparable conditions with citrate, the level was 0.16 ppm, and with EDTA it was 1.7 ppm. However, with more effluent contact with iron sulfide solids, the effluent level was maintained under 0.1 ppm, even in the presence of EDTA.

13. How do such numbers compare with levels achievable by the hydroxide process?

Under comparable test conditions above, the copper was 2.3 ppm with citrate and 2.6 ppm with EDTA and 0.1 ppm with pyrophosphate. In general, the levels achieved by sulfide precipitation are lower than the levels achieved by hydroxide precipitation.

The most dramatic difference occurs when hexavalent chrome is in the waste water. In this case the hydroxide process fails completely to remove chrome. The sulfide process typically gave test levels of chrome under 0.05 ppm. Even when EDTA was also present, the chromium was reduced to 0.1 ppm or less.

14. How does the Permutit Sulfex process work so well when the chromium is initially present as a chromate in the hexavalent condition?

The Sulfex reagent, iron sulfide, has the ability to reduce hexavalent chrome by the following reaction:

$$CrO_4^{=} + FeS + 4\,H_2O \rightarrow Fe(OH)_3 + Cr(OH)_3 + S^{0} + 2\,OH^{-}$$

Note that chromium precipitates as the hydroxide rather than the sulfide.

15. Does this mean that the chromate bearing solutions do not have to be isolated and treated separately when the Sulfex process is used?

Yes.

16. What kind of guarantee will Permutit make regarding its Sulfex Process?

Permutit will guarantee the chemistry of the process and the workability of the equipment supplied, based on certain input conditions as agreed upon, but obviously, Permutit cannot be responsible for the day-to-day operation of the equipment or a failure to meet quantitative limits that may be imposed by regulatory agencies. Where there is any question regarding the presence of chelating agents, or other organics that might interfere with the process, laboratory tests and in some cases pilot plant tests are recommended.

17. Is there a charge for laboratory tests or a pilot plant?

Yes. Permutit charges a nominal fee for a laboratory study and a rental fee for pilot plant equipment. Usually, if equipment is subsequently purchased, the charges for a laboratory study or pilot study will be refunded.

18. What is the cost and the availability of the chemicals required?

The iron sulfide slurry used in the Permutit Sulfex Process is normally made from ferrous sulfate, a soluble sulfide, and lime. The quantities needed are relatively small compared to their great availability. Either sodium hydrosulfide or sodium sulfide, and either lime or sodium hydroxide, may be purchased. Costs should be established through local chemical suppliers.

19. How does the cost of operating the Permutit Sulfex Process compare with the cost of operating hydroxide process?

The cost of the chemicals can be significantly less for the Sulfex Process under certain conditions. For instance, when hexavalent chrome must be treated, the simplicity of the one-step operation is much better than the alternative of sequentially using acid, sulfur dioxide, and lime.

The cost of operating the hydroxide process depends both on the total water flow and the metal concentration. In many cases, a great deal of lime is required simply to achieve the high pH, after which acid must be added to reduce the pH to an acceptable level for discharge. Note that where one unit of hydroxide is required to change the pH from 7 to 8, 1,000 units are required to achieve a pH of 11.

In both the hydroxide process and the Permutit Sulfex Process, comparable facilities are needed to add the reactant chemicals and separate the resulting sludge.

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20. What about sludge disposal from the Permutit Sulfex Process?

The sludge produced is a mixture of metal sulfides and hydroxides in a flocculated, dewaterable condition. The metal sulfides are very insoluble, and chemically equivalent to many of the naturally occurring metal ores that comprise part of the land mass. However, it is recommended that the sludges should be disposed of where they will not be washed into surface water or contacted with inorganic acids. A land-fill disposal site is normally preferred. Permutit also supplies sludge dewatering equipment.

21. Can heavy metals be recovered from the sulfide sludge?

In some cases, this probably could be justified. However, the Permutit Company has not been involved in this.

22. If a plant has existing facilities for operating the hydroxide process, can they be converted to handle the Permutit Sulfex Process?

In many cases, yes. There are options of utilizing available equipment for the Sulfex Process, or alternatively to add new facilities for the Sulfex Process to treat the effluent from the hydroxide process. Each case should be considered separately.

23. Are there any patent royalty charges relative to the Permutit Sulfex Process?

Yes, but Permutit is primarily interested in selling the specialized equipment related to the Permutit Company experience. However, a royalty charge has been established which is intended to be relatively small compared to the advantages of the Sulfex Process.

24. What are the royalty charges?

For low flow rates, there is a minimum charge currently set at $365 per year. For higher flow rates, where continuous flow equipment would normally be used, the annual charge is computed from the design flow basis. The cost diminishes from about $0.10/1,000 gal. at 25 gpm to under $0.02/1,000 gal. at high flow rates, as determined by an exponential equation. Consult your product specialist for the exact charge.

25. Please review the benefits of Sulfex Process.

Performance: The metal residuals in the effluent are normally lower than can be obtained by the hydroxide process, due to the lower solubility of the metal sulfides and the better ability to overcome most of the chelating or complexing agents.

Cost: The chemical cost may be significantly less, depending on the quantity and types of metal or metals to be treated. This is because hexavalent chrome can be reduced and removed in one step along with other metals and it does not have to be segregated for reduction pretreatment. Also, because sulfides can be precipitated in the pH range of 8-9, it is not necessary to purchase additional lime to achieve the higher pH's required for hydroxide precipitations and additional acid to lower the pH of the liquid effluent before discharge.

26. Are there any disadvantages to the Sulfex Process?

Care must be taken to prevent acids and the sulfides from combining with the release of H_2S, but it is not difficult to maintain this care and prevent odor emission.

Also, since the process is more effective than hydroxide systems, the total weight of sludge to be disposed of is greater, but where wasteful quantities of heavy metal are not being discharged to the sewer, the total amount of sludge produced is relatively unimportant.

27. What if there are cyanides present in the waste stream?

The Sulfex Process is strictly a heavy metal removal system. Any cyanides must be oxidized in a pretreatment step before they are introduced to the sulfex reaction. The Permutit Company can furnish the cyanide destruct system.

28. If new regulations are put into effect requiring a still lower level of discharge, or a "zero discharge", will the Sulfex Process be obsolete?

No. After the heavy metals have been removed by the Sulfex Process, the effluent can be further treated by ion exchange to remove soluble salts, or, treated by reverse osmosis facilities to produce a water which can be recycled within the operation.

29. What data should be collected to allow a proposal to be made for a Permutit Sulfex Process?

1. Nature of the business that generates the waste water.
2. The hours the plant operates per-day. The days the plant operates per-week.
3. List the various process lines and if possible provide a simple flow sketch of them.
4. List the average flow rates of rinse waters from each process line. Provide best possible estimate of the maximum flow the system must handle.
5. How many dump tanks does plant have? What is the volume of each tank? What is the dump frequency for each tank?
6. Include analyses of all rinse waters and dump tanks showing concentrations of all metals which must be removed. Dump tank analyses should be representative of the composition at time of dump or plant should extrapolate present analytical data to represent composition at time of dump.
7. If oil or soap is present in waste waters, this information should be included with relevant analyses.
8. Are chelating agents present? How much? What kind?
9. Will plant management submit design data to environmental authorities or have this data submitted by an outside consultant?
10. Effluent quality requirements will vary depending on where treated waste is discharged. If discharge is to a city sewer be sure to check with the city authorities. If discharge is directly to a river or stream, check with state authorities. What are the allowable effluent quality standards for the plant's wastes?
11. If treated waste water is to be recycled, what quality water is required? (Specifically the permissible dissolved solids content).
12. All waste treatment systems must be designed to "fail safe". In this respect transfer pumps, sump pumps, chemical feed pumps and mixers can be critical items. Repair or maintenance of this equipment should be considered because the treatment system can not function unless all pumps and mixers are operating. Does user plan to shut plant down for maintenance? Does user want all pumps duplicated or does user prefer to stock spare equipment?

30. Are there any further questions?

We know that we did not answer all your questions. Permutit specialists in the Sulfex process are available to you for technical assistance on the application and design of treatment systems. As mentioned, the analytical, laboratory and pilot plant test facilities of the Permutit R and D Center are also available should they be needed.

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An EPA Demonstration Plant For Heavy Metals Removal By Sulfide Precipitation

Murray C. Scott*

The Holley Carburetor Company, a Division of Colt Industries, Paris, Tennessee was awarded a grant by the EPA to demonstrate the effectiveness of a new approach to removal of heavy metals from waste streams by sulfide precipitation. The process, called Sulfex™, was developed by the Permutit Company. Before the process was demonstrated at Holley Carburetor, preliminary pilot plant work was done by the Permutit Company at their research facilities. The work was done under a grant made to the National Association of Metal Finishers by the EPA.

The surfaces of the carburetor castings are of either zinc or aluminum and are chemically treated according to finishing specifications established by the automotive industry. A "Udylite" automatic rack line dips the castings into various treatment and rinse water tanks according to a pre-arranged program. The water rinses following the treatment tanks are the source of contaminated wastewater which must be treated before discharge into the city of Paris sewer system. Figure No. 1 illustrates the automatic line. Rinse flow is on the order of 35 gpm.

There are three basic cycles of treatment: (1) zinc chromate, (2) deoxidize, (3) aluminum chromate. Composite samples of rinse water were collected during each cycle and analyzed. The analytical results obtained are shown in Table No. 1. For design purposes these concentrations were increased by 20% as a factor of safety.

Two metals, chromium and zinc, had to be removed before discharge of this waste into the city sewer. Total zinc was not to exceed 0.10 mg/l and total chromium was not to exceed 1.0 mg/l. These were the effluent limits prescribed by Holley Carburetor in their bid specifications. Whether conventional "lime and settle" would meet these effluent limitations was questionable, as shown by solubility curves for zinc and chromium hydroxides in Figure No. 2.

The amphoteric properties of metal hydroxides frequently make the results of the "lime and settle" approach questionable. An operating pH ideally suited for good removal of one metal causes another metal to go

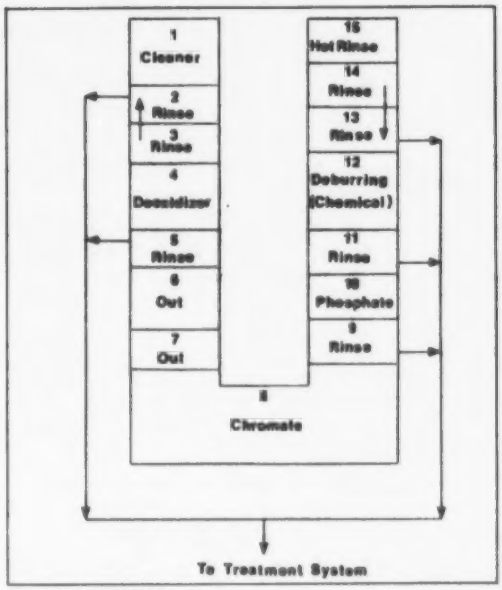

Fig. 1—Automatic line.

TABLE I
PROCESS CYCLES

	Zinc Dichromate	*Deoxidize*	*Aluminum Chromate*
Ca	10 mg/l	8 mg/l	9 mg/l
Mg	4	3	3
Na	50	39	37
K	3	3	3
Fe	1.4	1.7	1.1
Mn	0.02	0.03	0.10
Al	6	13	4
Cr	81	46	57
Zn	71	42	34
Ni	0.05	0.05	0.05
Cu	0.10	0.12	0.07
Pb	0.10	0.10	0.10
Alk	10	12	12
Cl	9	5	6
SO_4	40	18	37
SiO_2	11.3	11.3	10.7
P	65	58	38

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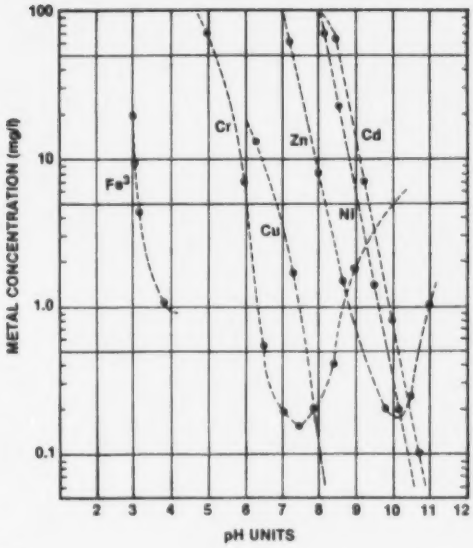

Fig. 2

into solution. The solubility curves shown in Figure No. 2 suggest that the pH best suited for removal of zinc is about 10.0. At this pH (10.0) chromium has a solubility of about 5.0 mg/l, well above the maximum limit specified for this meal. The relationship of the solubilities of chromium and zinc shown in Figure No. 2 are used only to illustrate potential problems that might occur. These solubilities will vary with composition of the waste, but, the amphoteric properties of the precipitated metal hydroxides are forever present. However, if the heavy metals could be precipitated as sulfides, a mixture of metals would not be competing for optimum pH values. Comparison of the solubilities of various metal hydroxides and metal sulfides is shown in Figure No. 3. Not only are the metal sulfides not amphoteric, their solubilities are theoretically orders of magnitude below the metal hydroxides and decrease further with increasing pH.

THE SULFEX™ PROCESS

The Sulfex process uses an insoluble salt as the source of the sulfide ion. Selection of the salt is not random. The solubility of the insoluble salt must be greater than the solubility of the heavy metal sulfide to be precipitated. As indicated in Table No. 2, ferrous sulfide is more soluble than the heavy metal sulfides that would be precipitated from metal finishing waste streams, so the Sulfex process uses ferrous sulfide as the source of sulfide ions.

Solubility products are taken from 11th edition of Lange's Handbook of Chemistry.

The iron sulfide works best when it is a freshly prepared slurry. For practical reasons, pulverized iron

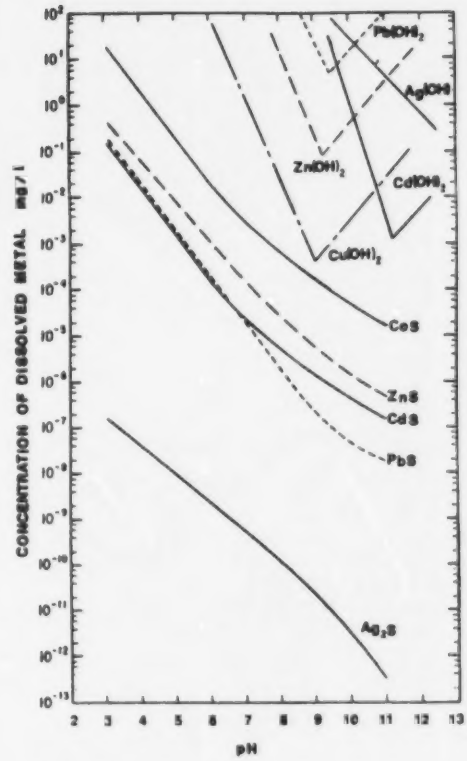

Fig. 3—Solubilities of Metal Hydroxides and Sulfides.

TABLE II
SOLUBILITY PRODUCTS

	Hydroxide	*Sulfide*
Iron	8.0×10^{-16}	6.3×10^{-18}
Zinc	1.2×10^{-17}	1.6×10^{-24}
Cadmium	2.5×10^{-14}	8.0×10^{-27}
Nickel	2.0×10^{-15}	3.2×10^{-19}
Copper	2.2×10^{-20}	6.3×10^{-36}
Lead	8.0×10^{-20}	1.2×10^{-15}
Mercury	3.0×10^{-26}	1.6×10^{-52}
Silver	2.0×10^{-8}	6.3×10^{-50}

sulfide is not used. Since only the surface of the large particle is useful, much of the iron sulfide particle would be wasted. However, freshly precipitated iron sulfide has a great deal of reactive surface. Quantities of iron sulfide required to adequately remove metals from waste streams will vary from 1.2 times stoichiometric to 3.0 times stoichiometric.

Characteristics of the Sulfex[15] process, when properly applied, offer a high degree of flexibility. Because of the low solubility of iron sulfide, the sulfide ion concentration is constantly maintained at about 0.02 ppb. Yet sufficient sulfide is available to accommodate wide variations in influent metal concentrations because the sludge blanket in the clarifier contains a large quantity of active iron sulfide. There is the additional asset of being able to reduce and remove hexavalent chromium in one step. The chemistry of the Sulfex process may be illustrated by two equations:

(1) $Cu(OH)_2 + FeS \rightarrow CuS + Fe(OH)_2$

(2) $Na_2CrO_4 + FeS + 4H_2O \rightarrow$
$Cr(OH)_3 + Fe(OH)_3 + 2NaOH + S$

Because of the low concentration of sulfide ion, soluble sulfide complexes do not form with mercury, tin or silver as shown in the following equations:

$$HgS + S^{=} \rightarrow HgS^{=}_2$$
$$SnS_2 + S^{=} \rightarrow SnS_3^{=}$$
$$Ag + S^{=} \rightarrow AgS^{-}$$

WASTE TREATMENT SYSTEM

The waste treatment system is designed to handle a maximum flow of 35 gpm. The operating day is 16 hours. A schematic of the system is shown in Figure No. 4. The treatment consists of neutralization, precipitation, clarification, filtration and sludge dewatering.

All rinse water comes into a two-compartment basin. The first compartment has a retention time of 105 minutes and the second compartment which normally operates with an average depth of 3 ft. has a detention time of about 80 minutes. The second compartment is operated at a low level so that it may accommodate filter backwash. These two holding compartments help equalize the waste but their primary function is to permit neutralization to a pH of about 8.5. Neutralization is done in two steps by the addition of lime which is controlled in both steps by pH sensing devices. The lime metering pump in the first step operates on-off. In the second step the lime metering pump has electronic stroke

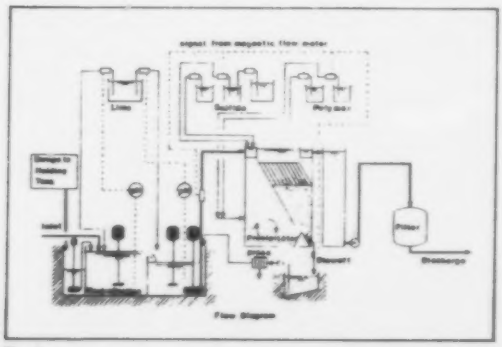

Fig. 4

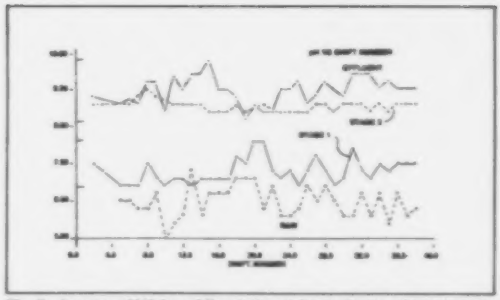

Fig. 5—Average pH Value of Raw Influent, Neutralization Stage I and II, and Precipitator Effluent as a Function of Time.

adjustment which is controlled by degree of deviation from the pH set point. Figure No. 5 shows comparative pH data for the raw waste, 1st stage neutralization, 2nd stage neutralization, and treatment plant effluent. The pH of the precipitator influent was closely controlled, ranging between a high of 9.0 and a low of 8.3; however, after the system was stabilized the pH was usually between 8.3 and 8.7. (The reduction of hexavalent chromium in the clarifier (precipitator) raised the pH and produced effluent pH values generally between 8.4 and 9.6).

Neutralized waste is then pumped to the clarifier where an iron sulfide slurry and a polymer are added. The rate of addition is proportional to influent flow. Jar tests are made twice each shift to determine the iron sulfide and polymer requirement. Timers on the panel board are then adjusted to change the cycle of the chemical feed pumps. The stroke of the pumps may also be changed, if desired, giving further flexibility to control of the chemical feeders.

The clarifier is a sludge blanket type, as illustrated in Figure No. 6. A slowly rotating mixer beneath the curtain baffle promotes floc formation. The floc mixture passes beneath the baffle into a section where the rise rate diminishes as the top of the unit is approached. This produces a blanket with a relatively sharp line of

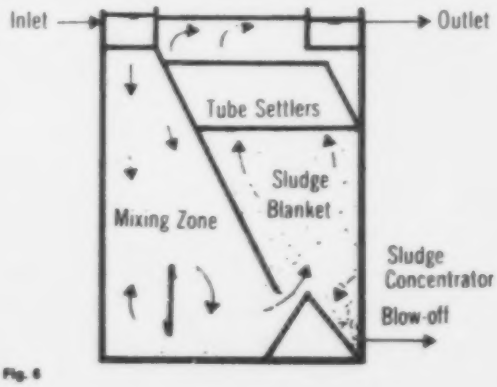

Fig. 6

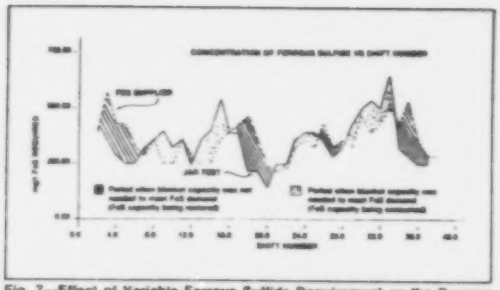

Fig. 7—Effect of Variable Ferrous Sulfide Requirement on the Reverse Ferrous Sulfide Capacity of the Sludge Blanket as a Function of Time.

Note: X's are points where no jar test was made.

demarcation between the top of the blanket and the clear water above the blanket. This blanket of suspended solids, which will range in concentration from 5000 mg/l to 15,000 mg/l, may consist of as much as 50% active iron sulfide. It is this reservoir of iron sulfide which allows the system to accommodate wide variations of influent metal concentrations with no change in the effluent quality.

To illustrate the effect of the iron sulfide reservoir in the sludge blanket, we ran jar tests on grab samples taken from the second neutralization basin to determine the amount of sulfide required. The yellow color of the chromate in the sample was used as an indicator. Source of the iron sulfide for this test was slurry taken from the chemical feed tank. When sufficient iron sulfide slurry has been added to react with all the metals and the hexavalent chromium in the sample, the yellow color disappears. The required iron sulfide dosage indicated by the jar test and the amount of iron sulfide being introduced by the chemical feed system at that time were noted and plotted on the graph shown in Figure No. 7.

Those areas with diagonal lines represent times when the actual feed of iron sulfide exceeded the demand, so active iron sulfide was accumulating in the sludge blanket. The dotted areas represent times when the actual demand from iron sulfide exceeded the feed rate, so active iron sulfide from the sludge blanket was being consumed. Total detention time of iron sulfide in the sludge blanket is about 19 hrs.

The amount of active iron sulfide in the sludge blanket

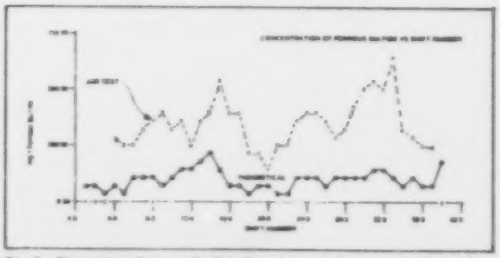

Fig. 8—Theoretical Ferrous Sulfide Requirement Compared with Jar Test Requirement as a function of Time.

Note: X's are points where no jar test was made.

can be controlled by adjusting the rate of feed of the iron sulfide slurry; however, excessive feed rates will increase chemical operating costs. For this reason, we were interested in stoichiometric iron sulfide requirements. The waste was analyzed for metals and then the stoichiometric sulfide requirement was obtained by calculation. A comparison of stoichiometric sulfide requirement and the sulfide requirement indicated by jar testing is shown in Figure No. 8. The jar test sulfide demand varied from 200% to 500% of the theoretical, averaging about 3.5 times stoichiometric. With more operating experience, closer control is expected to reduce the iron sulfide consumption.

The clarifier has a sludge concentrator which is blown off automatically, based on influent flow to the clarifier.

Since the amount of blowoff required is a function of both the hydraulic load and the suspended solids load, the blowoff rate is further controlled by adjusting a timer which determines the length of time the blowoff valve is open. This is estimated by collecting a sample from the unit to determine the height of the sludge blanket in the tube settlers. Two sampling points, one within the tube settlers and one six inches below the tube settlers, permits the operator to determine whether the blanket is too high or too low.

The blowoff is collected in a sump and then pumped through a filter press for dewatering. A polypropylene filter cloth is used. No precoat or body feed is required. Operation is at constant pump drive speed until the pressure builds up to 50 lbs. At this pressure, the resulting cake breaks away cleanly from the cloth. Down time is about 10-15 minutes. Operating time is about 10-14 hours. The unit holds slightly over 5 cu. ft. Dewatered cake is disposed at a local landfill.

The feed to the press contained from 14,000 mg/l to 24,000 mg/l suspended solids. Effluent from the press contained about 3 mg/l suspended solids at the beginning of the run and 22 mg/l at breakthrough (at end of run). Filter cake contained about 25% solids. On a total dry weight basis, the percentages of metals in the filter cake are shown in Table No. 3

The Sulfex process produces more sludge than a conventional "lime and settle" process, because a mole of insoluble ferrous hydroxide is produced for each mole of heavy metal sulfide formed. The excess iron sulfide in the clarifier sludge blanket also adds to sludge volume. This must be taken into consideration and adequate sludge disposal included as part of the overall design of the Sulfex treatment system. For example:

When designing a conventional rinse water waste

TABLE III

Cr	3.3% to 4.5%
Fe	26.9% to 33.0%
Cu	<0.1%
Zn	3.7% to 4.1%
Total Solids	23.4% to 29.3%

treatment system, the waste is usually neutralized before clarification. The addition of iron sulfide to the clarifier converts this treatment system to the Sulfex™ process. This method of applying the Sulfex process results in a substantial increase in sludge production (on the order of 2.8 times) over straight lime treatment. It can only be justified where total metal concentrations are very low, or where there is inadequate space to permit a Sulfex polishing system.

A Sulfex polishing system uses a second clarifier. Iron sulfide and a polymer are added to this clarifier. Chemical requirements are quite low, since only residual metals from the hydroxide process need be treated. In applications of this type, the amount of additional sludge produced by the Sulfex process usually will amount to only 1% to 2% of the total sludge produced by the entire treatment system.

Supernatant from the clarifier is then pumped to a dual media, anthracite-sand, filter which is equipped with an air scour to insure good cleaning during the backwash procedure. Prudence, sound engineering, and requirement of a performance guarantee make filtration mandatory, but excellent quality is possible without filtration, as illustrated in Table No. 4.

TABLE IV

Metal	*Clarifier Effluent mg/l*	*Filtered Effluent mg/l*
Zn	0.1 to 0.5	≤ 0.05
Fe	0.3 to 4.0	≤ 0.50
Cu	≤ 0.01	≤ 0.01
Cr (Total)	0.1 to 1.0	≤ 0.04
Cr^{+6}	≤ 0.05	≤ 0.04
Total Suspended Solids	1.0 to 10	≤ 0.5 - 1.0

Filtered effluent from the treatment system at Holley Carburetor routinely produced metal concentrations lower than detectable by today's accepted analytical methods. Metal concentrations in the influent and effluent are shown in Figures No.'s. 9, 10, 11, 12, 13.

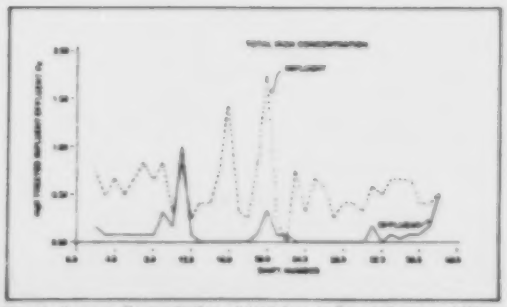

Fig. 9—Average Concentration of Total Iron in Raw Influent and Filter Effluent as a Function of Time.

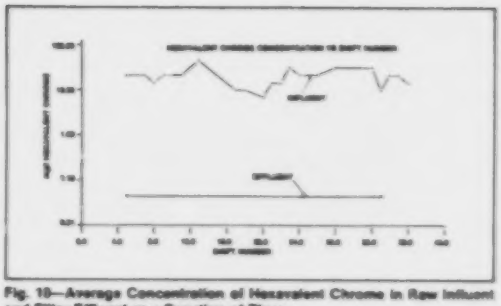

Fig. 10—Average Concentration of Hexavalent Chrome in Raw Influent and Filter Effluent as a Function of Time.

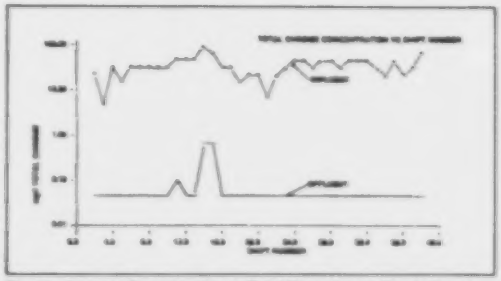

Fig. 11—Average Concentration of Total Chromium in Raw Influent and Filter Effluent as a Function of Time.

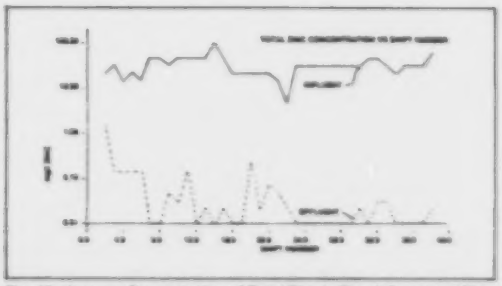

Fig. 12—Average Concentration of Total Zinc in Raw Influent and Filter Effluent as a Function of Time.

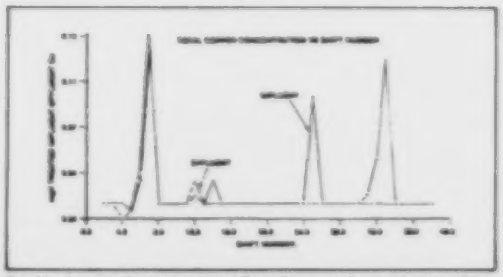

Fig. 13—Average Concentration of Total Copper in Raw Influent and Filter Effluent as a Function of Time.

CHEMICAL OPERATING COSTS

Detailed data was collected over a period of 38 shifts (19 days). This included the startup period when all equipment was checked out and plant personnel were being trained. About 22 shifts (11 days) were required to reach a steady state where operating conditions were considered normal. For this reason only, data collected during the last 16 shifts (8 days) were used for calculating chemical operating costs. During this period, the flow averaged 26 gpm. Metal concentration averaged 34 mg/l Cr^{+6} and 34.7 mg/l Zn. The pH ranged between 5.2 and 6.5

Unit cost for chemicals were as follows:

Ferrous Sulfate	6.75¢/lb
Sodium Sulfhydrate	26.5¢/lb
Lime	4.65¢/lb
Polyelectrolyte	105.0/lb

The total chemical cost per shift is shown in Figure No. 14.

Comparison of the stoichiometric iron sulfide demand for zinc and hexavalent chromium can be used to give a chemical operating cost value to each. The total average chemical cost per shift was $18.50. The kilograms of dry solids produced per shift was 3.24 of which 1.6 kg contains chromium and 1.63 kg contains zinc.

$$\frac{\text{Stoichiometric FeS Requirement for } Cr^{+6}}{\text{Stoichiometric FeS Requirement for } Cr^{+6} + Zn} = Cr^{+6} \text{ fraction}$$

$$\frac{1.67 \text{ kg FeS/kg } Cr^{+6}}{3.01 \text{ kg FeS/kg } Cr^{+6} + Zn} = 0.555, Cr^{+6} \text{ fraction}$$

$$1.0 - 0.5548 = 0.4452, \text{ Zn fraction}$$

$$\frac{0.5548 \times \$18.50}{1.61 \text{ kg}} = \$6.38/\text{kg } Cr^{+6}$$

$$\frac{0.4452 \times \$18.50}{1.63} = \$5.05/\text{kg Zn}$$

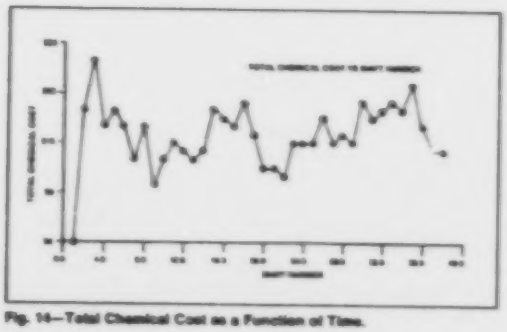

Fig. 14—Total Chemical Cost as a Function of Time.

COMPARATIVE CHEMICAL COSTS FOR CONVENTIONAL TREATMENT

Conventional treatment would consist of the addition of sulfuric acid to reduce the pH to 2.0, the addition of sodium bisulfite to reduce the chromium, followed by lime for neutralization and precipitation of the metal hydroxides. Unit costs for chemicals obtained locally are:

Bisulfite	23¢/lb	($0.5072/kg)
Sulfuric Acid	4.65¢/lb	($0.1025/kg)
Hydrated Lime	4.65¢/lb	($0.1025/kg)
Polyelectrolyte, anionic	225¢/lb	($4.96/kg)

The theoretical requirements to remove one kilogram of hexavalent chromium would be as follows:

(1) Bisulfite - 3 Kg $NaHSO_3$ is required to reduce 1 Kg Cr^{+6}. Since an excess of about 50% over stoichiometric is normally required, the amount of $NaHSO_3$ needed is:

$$3 \text{ Kg } NaHSO_4 \times 1.5 = 4.5 \text{ Kg } NaHSO_3/\text{kg } Cr^{+6}$$

(2) Sulfuric Acid - To acidify the waste water from pH 5.5 to 2.0 - 2.5 requires 516 mg/l 66° Be H_2SO_4, thus:

$$\frac{1 \text{ liter}}{34 \text{ mg } Cr^{+6}} \times \frac{10^6 \text{ mg}}{\text{kg}} = \frac{29{,}411 \text{ liters}}{\text{kg } Cr^{+6}}$$

$$\frac{29{,}411 \text{ liters}}{\text{kg } Cr^{+6}} \times \frac{5.16 \times 10^{-4} \text{ kg}}{1} = 15.18 \text{ kg/kg } Cr^{+6}$$

The stoichiometric requirement of H_2SO_4 for reduction of chromium is 1.42 kg H_2SO_4/Kg Cr^{+6}, therefore, the total acid requirement is:

$$15.18 \text{ kg} + 1.42 \text{ kg} = 16.6 \text{ kg/kg } Cr^{+6}$$

(3) The hydrated lime required to bring the pH back to 8.0 - 9.0 is 750 mg/l as $Ca(OH)_2$. Translating to kg/kg Cr^{+6}:

$$\frac{1 \text{ liter}}{34 \text{ mg } Cr^{+6}} \times \frac{10^6 \text{ mg}}{\text{kg}} = \frac{29{,}411 \text{ liters}}{\text{kg } Cr^{+6}}$$

$$\frac{29{,}411 \text{ liters}}{\text{kg } Cr^{+6}} \times \frac{7.5 \times 10^{-4} \text{ kg}}{1} = 22 \text{ kg/kg } Cr^{+6}$$

(4) Polyelectrolyte - Anionic polyacrylamide polymers are frequently used at dosages of about 1 mg/l, thus:

$$\frac{29{,}411 \text{ liters}}{\text{kg } Cr^{+6}} \times \frac{1.0 \times 10^{-6} \text{ kg}}{1} = 0.03 \text{ kg/kg } Cr^{+6}$$

Summarizing the chemical costs:

Bisulfite	= 4.5 kg × $0.507 = $2.28/kg Cr^{+6}
Sulfuric Acid	= 16.6 kg × $0.103 = $1.71/kg Cr^{+6}
Hydrated Lime	= 22 kg × $0.103 = $2.27/kg Cr^{+6}
Polyelectrolyte	= 0.03 kg × $4.96 = $0.15/kg Cr^{+6}
Total Chemical Cost	= $6.41/kg Cr^{+6}

Comparing the chemical costs for treatment of this waste by conventional methods with chemical costs for treatment by the Sulfex process is difficult, but the following data is a reasonable estimate:

TABLE V

	Conventional	*Primary Sulfex*	*Polishing Sulfex*
For Chromium	$6.41/kg	$6.38/kg	$6.39/kg
For Zinc	0.17/kg	5.05/kg	.17/kg
For Sludge Disposal	1.16	2.32	1.88
Total	$7.74	$13.75	$8.44

With this particular waste, a portion of the sludge comes from precipitation of phosphate. Unfortunately, we did not collect detailed analytical data on phosphate concentrations because removal of phosphate was not required. The original analytical data showed a low phosphate concentration of 38 mg/l as P and a high of 65 mg/l as P. The low concentration was used for estimating the sludge produced by phosphate precipitation and the value was included in the assessment of comparative sludge disposal costs.

Increased chemical usage and increased sludge is the premium paid for primary Sulfex treatment where the FeS is added to the same clarifier that would be used for conventional hydroxide precipitation. The third column in Table No. 4 shows costs for chemicals and sludge disposal for a complete treatment system which includes polishing by the Sulfex process.

COST ANALYSIS

Operating Costs

The yearly operating cost, excluding depreciation and licensing fees, for the treatment system at Holley Carburetor is outlined below. This cost results from charges incurred by operators, utilities and chemicals.

The estimated yearly operating cost, based on plant performance to date, is as follows:

1. Operators Salaries:

$10,800 per operator × 2 operators = $21,600
+ fringe benefits at 40% = 8,640

Total Salaries = $30,240/year

2. Electricity:

$$\frac{203.32\ \text{kwh}}{\text{day}} \times \frac{5\ \text{days}}{\text{wk}} \times \frac{52\ \text{wk}}{\text{yr}} \times \frac{\$0.0191}{\text{kwh}} \quad \$1010/\text{year}$$

3. Water:

$4162\ m^3 \times \$0.053/m^3$ = $220/year

4. Chemical:

$$\frac{\$14.69}{\text{shift}} \times \frac{2\ \text{shifts}}{\text{day}} \times \frac{260\ \text{days}}{\text{yr}} = \$7639/\text{year}$$

5. Sludge Handling and Disposal Cost:

$$\frac{\$15}{\text{day}} \times \frac{260\ \text{days}}{\text{yr}} = \$3900/\text{year}$$

Total Operating Cost is therefore:

Salaries	=	$30,240
+ Electricity	=	1,010
+ Water	=	220
+ Chemicals	=	7,639
+ Sludge Disposal	=	3,900
TOTAL		$43,009/year

Capital costs are itemized as follows:

Equipment	$92,465
Engineering Costs (Consulting, report to state and design for underground tanks)	17,400
Underground Tanks	48,000
Shipping and Installation	21,730
Taxes (on equipment only)	1,089
	$180,684

SUMMARY

Precipitation of heavy metals by sulfide will in most cases permit any plant to economically meet extremely rigid discharge standards but frequent complaints are lodged that disposal of sulfide sludges presents a serious impediment to acceptance of any sulfide process for heavy metals removal. The complaints are not necessarily on solid ground.

In almost all cases the waste streams are neutralized with lime or caustic. This results in the precipitation of metal hydroxides. The next logical step is to remove these precipitated metals by coagulation and settling or any other technique that might be applicable. Sulfide precipitation, if required, should be applied to residual soluble metals which represent a very small portion of the total metals originally present in the waste streams. Is there any reason why this very small sludge portion consisting of metal sulfides cannot be disposed in the same manner as the large portion of metal hydroxides?

The leaching test procedure, described in the Dec. 18, 1978 Federal Register, page 58596, was used to obtain the following comparative data on a sludge produced by the Sulfex process and on a sludge produced by the addition

of lime. A solution containing 20 mg/l of each metal was used for the test. Equal portions of this solution were treated, one by Sulfex™ and the other by lime. The sludge produced by each procedure was then subjected to the leaching test recommended by the EPA. The pH of the Sulfex mixture was 5.7. The pH of the hydroxide mixture was 5.8.

The Sulfex mixture gave no odor of H_2S nor was there any evidence of H_2S detectable by lead acetate paper.

EXTRACT LEVEL mg/l

	EPA Proposed Regulation	*Sulfex*	*Hydroxide*
Arsenic	0.50		
Barium	10.0		
Cadmium	0.10	0.02	1000
Chromium (Total)	0.50	< 0.05	1.5
Lead	0.50	0.20	55
Mercury	0.02		
Selenium	0.10		
Silver	0.50	0.02	0.21
MAY BE CONSIDERED IN FUTURE			
Ni		35	>33
Fe	3	820	< 1
Zn	50	0.36	1475
Cu	10	0.03	259

These data would suggest that disposal of sulfide sludges will present no more of a problem than disposal of hydroxide sludges. Both appear to be material that should be disposed in a secure landfill.

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- The American Electroplaters' Society
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Summary Report

Control and Treatment Technology for the Metal Finishing Industry

Sulfide Precipitation

April 1980

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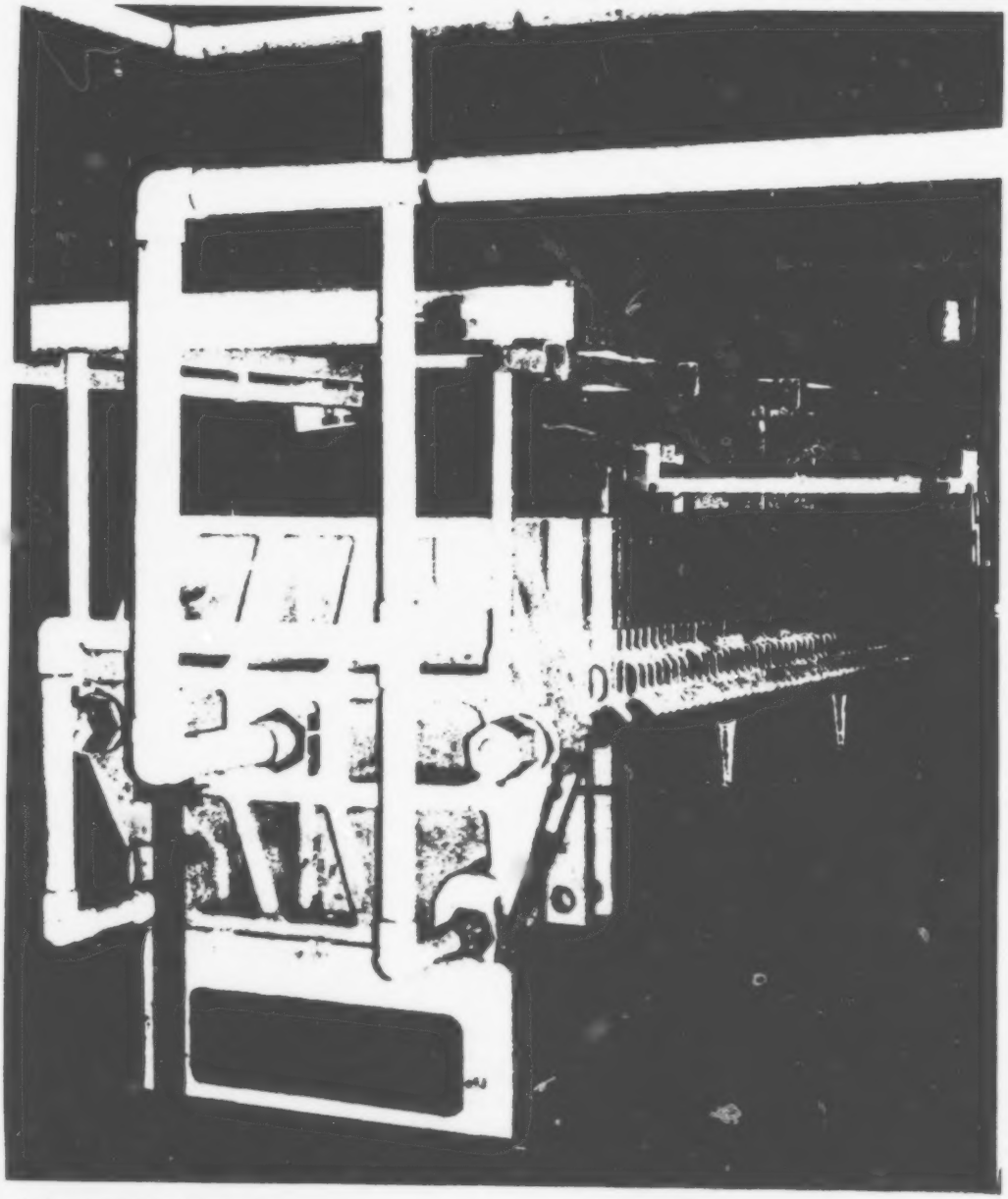
Cincinnati OH 45268



Sludge dewatering filter press

Overview

Today more than 13,000 firms in the United States are engaged either wholly or partially in electroplating or other metal finishing operations. These firms discharge their spent process water to either waterways or publicly owned treatment works (POTW's), and they comprise more individual wastewater discharges than any other industrial category. The pollutants contained in this process water are potentially toxic; therefore, to comply with the Clean Water Act of 1977 (Public Law 95-217), the water must be treated before being discharged to a waterway or a POTW. The regulations require oxidation of cyanide, reduction of hexavalent chromium, removal of heavy metals, and control of pH.

Sulfide precipitation is one among many methods available for removing metals from metal finishing process wastewaters. This summary report series presents information on various technologies that have been demonstrated. Other publications in the series discuss different control alternatives. By providing process descriptions, advantages and disadvantages, and economic characteristics of each system, these reports can facilitate the evaluation of effective means of pollution control by those involved in metal finishing wastewater pollution control.

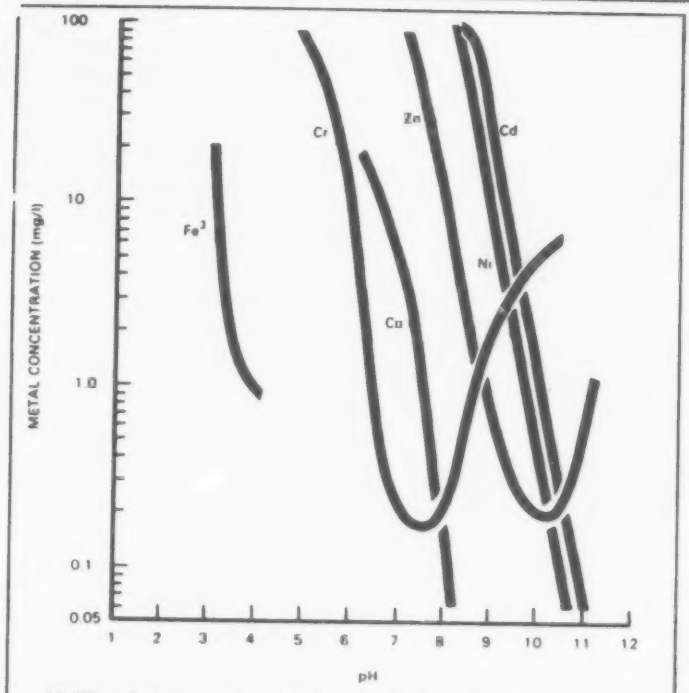
Metals are usually removed by adding an alkali, such as hydrated lime [$Ca(OH)_2$] or caustic soda (NaOH), to adjust the pH of the wastewater to the point where the metals exhibit minimum solubilities. The metals precipitate as metal hydroxides and can be removed from the wastewater by flocculation and clarification. In many cases, the addition of a postfiltration step can reduce further the total metal concentration in the effluent by removing any metal hydroxide carryover.

Some common limitations of the hydroxide process follow:

- The theoretical minimum solubilities for different metals occur at different pH values (Figure 1). For mixtures of metal ions, it must be determined whether a single pH can produce sufficiently low, though not minimum, solubilities for the metal ions present in the wastewaters.
- Because hydroxide precipitates tend to resolubilize if the solution pH is increased or decreased from their minimum solubility points, maximum removal efficiency will not be achieved unless the pH is controlled within a narrow range.
- The presence of complexing ions—such as phosphates, tartrates, EDTA,[1] and ammonia—that are commonly found in cleaner and plating formulations may have an adverse effect on metal removal efficiencies when hydroxide precipitation is used. Figure 2 shows the solubility of nickel ions as a function of pH when precipitated with other metal ions in the presence of certain complexing ions used in a proprietary electroless nickel plating bath.

Despite these limitations, hydroxide precipitation (particularly when followed by flocculation and filtration) produces a high-quality effluent when applied to many waste streams. Often coprecipitation of a mixture of metal ions will result in residual metal solubilities lower than those that could be achieved by precipitating each metal at its optimum pH. In other cases, modification of the hydroxide process has improved its performance in treating waste streams containing complexed heavy metals. This improved performance is usually realized by dissolving another positively charged ion—such as Fe^{+2} or Ca^{+2}—into the wastewater and then precipitating the metals. High-pH lime treatment

[1] Ethylenediaminetetraacetic acid.



SOURCE U.S. Environmental Protection Agency. *Waste Treatment Upgrading Metal-Finishing Facilities To Reduce Pollution.* EPA 625/3-73-002. July 1973

Figure 1.

Metal Solubility as a Function of pH

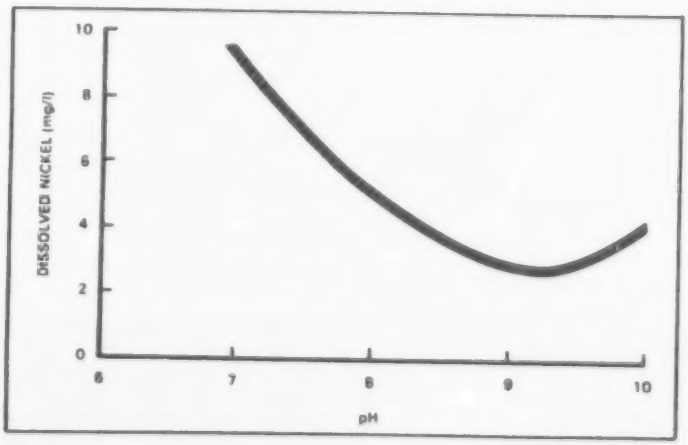


Figure 2.

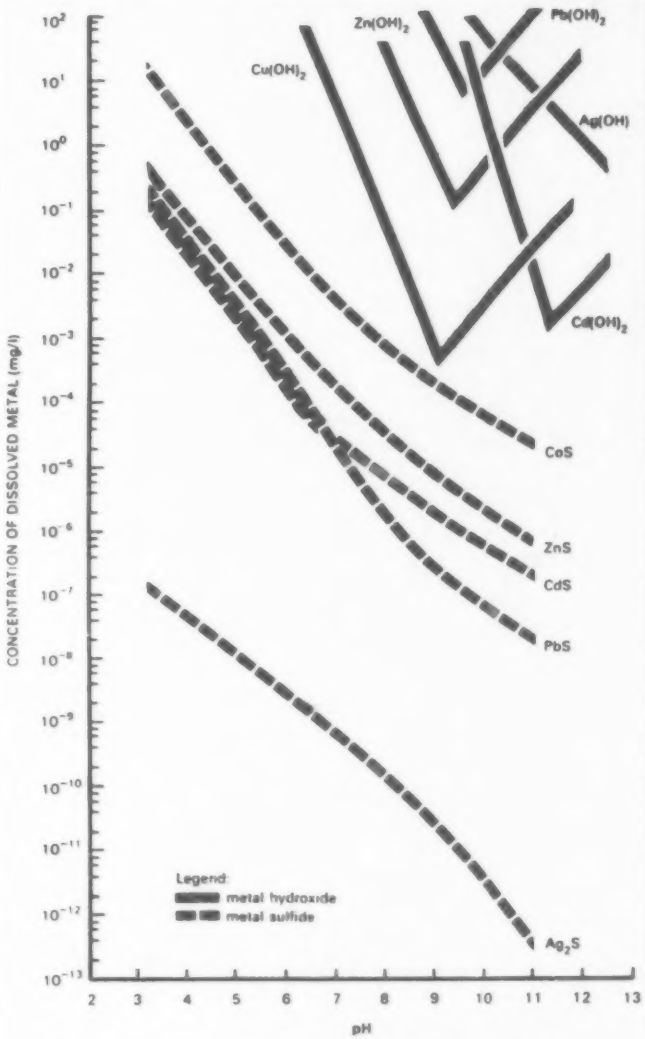
Solubility of Complexed Nickel When Precipitated With Caustic Soda

and ferrous sulfate ($FeSO_4$) precipitation techniques use this principle.

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing various heavy metals from industrial wastewaters. The high reactivity of sulfides (S^{-2}, HS^-) with heavy metal ions and the insolubility of heavy metal sulfides over a broad pH range are attractive features compared with the hydroxide precipitation process (Figure 3). Sulfide precipitation can also achieve low metal solubilities in the presence of certain complexing and chelating agents.

The main difference between the two processes that currently use sulfide precipitation is the means of introducing the sulfide ion into the wastewater. In the soluble sulfide precipitation (SSP) process, the sulfide is added in the form of a water-soluble sulfide reagent such as sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS). A more recently developed process adds a slightly soluble ferrous sulfide (FeS) slurry to the wastewater to supply the sulfide ions needed to precipitate the heavy metals.

In the past, operational difficulties prevented more than minimal application of the SSP process. Recent investigations, however, have eliminated or reduced these problems. Technological advances in the area of selective-ion electrodes have provided a probe that



Note.—Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modern Alkaline Cooling Water Treatment," in *Industrial Water Engineering* (p. 31), Jan.-Feb. 1973.

Figure 3.

Solubilities of Metal Hydroxides and Sulfides as a Function of pH

has proven successful in pilot-scale evaluations for controlling the addition of soluble sulfide reagent to match reagent demand. Eliminating sulfide reagent overdose can prevent the odor problem commonly associated with these systems. In currently operated soluble sulfide systems that do not automatically adjust reagent dosage to match demand, the process tanks must be enclosed and vacuum evacuated to minimize sulfide odor problems in the work area. The formulation of polyelectrolyte conditioners that effectively flocculate the fine metal sulfide particles has eliminated the difficulty in separating the precipitants from the discharge and has resulted in sludges that are easily dewatered.

Recently, a patented sulfide precipitation process called Sulfex™ has proven effective in separating heavy metals from plating waste streams. The process uses a freshly prepared ferrous sulfide slurry (prepared by reacting $FeSO_4$ and NaHS) as the source of the sulfide ions needed to precipitate the metals from the wastewater. The process operates on the principle that FeS will dissociate into ferrous ions and sulfide ions to the degree predicted by its solubility product. As sulfide ions are consumed, additional FeS will dissociate to maintain the equilibrium concentration of sulfide ions. In alkaline solutions, the ferrous ions will precipitate as ferrous hydroxides. Because most heavy metals have sulfides less soluble than ferrous sulfide, they will precipitate as metal sulfides.

An advantage of the insoluble sulfide precipitation (ISP) process is the absence of any detectable hydrogen sulfide (H_2S) odor—a problem historically associated with SSP treatment systems. Another

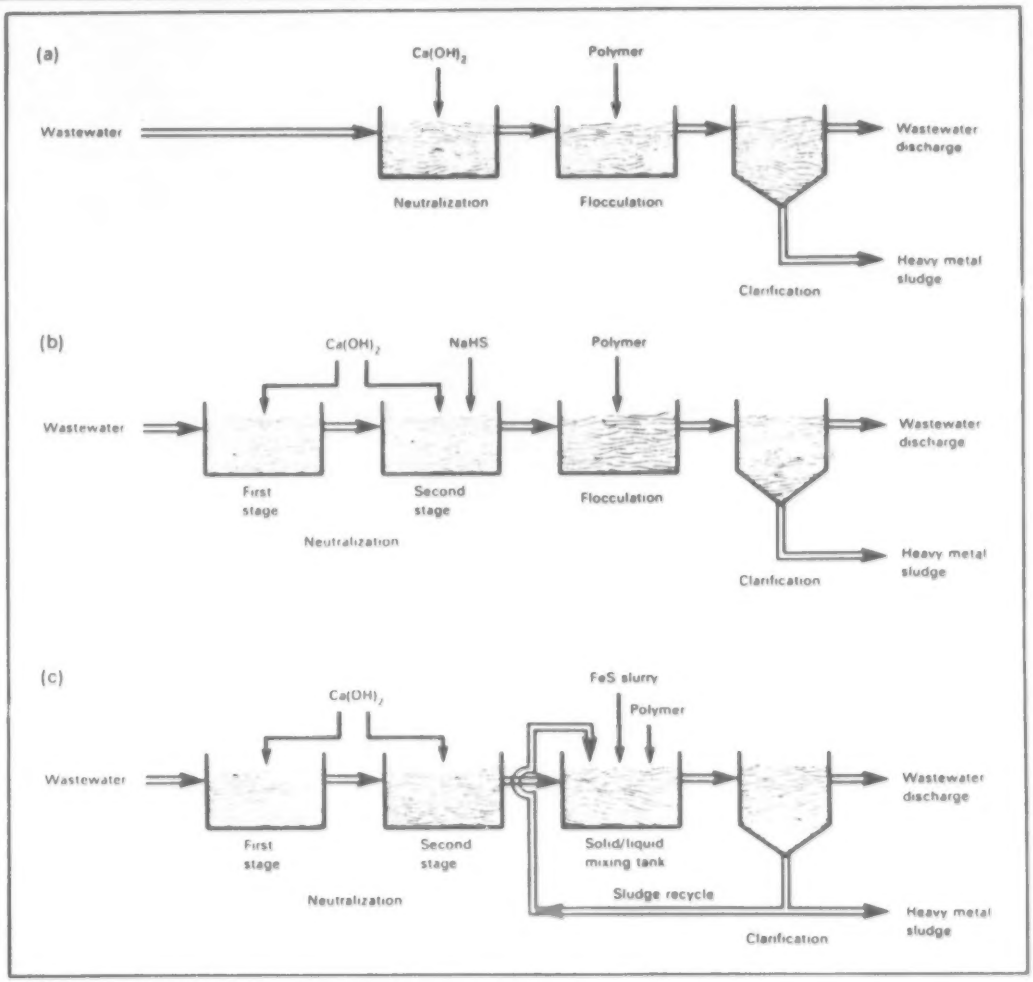


Figure 4.

Wastewater Treatment Processes for Removing Heavy Metals: (a) Hydroxide Precipitation, (b) SSP, and (c) ISP

advantage is that the ISP process will reduce hexavalent chromium to the trivalent state under the same process conditions required for metal precipitation, thus eliminating the need to segregate and pretreat chromium waste streams. Disadvantages of the ISP process include considerably higher than stoichiometric reagent consumption and significantly higher sludge generation factors than either the hydroxide or soluble sulfide treatment processes.

Figure 4 compares typical process flow diagrams of a hydroxide treatment system and both types of sulfide systems. Most of the elements of the sulfide systems are common to the hydroxide precipitation treatment sequence. The sulfide treatment processes also can be used as a polishing system after a conventional hydroxide precipitation/clarification process to

significantly reduce the consumption of sulfide reagent.

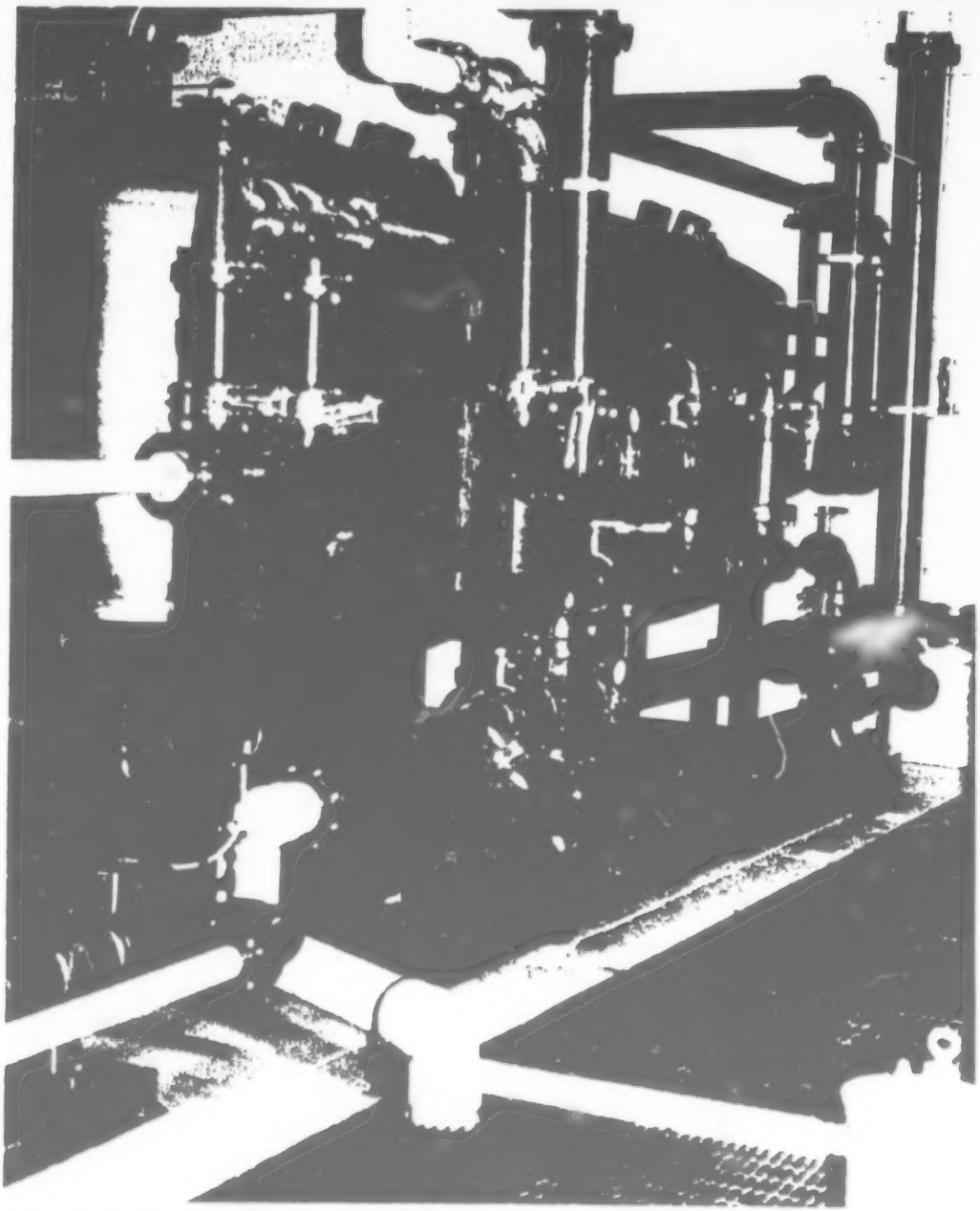
The final selection of a hydroxide or sulfide process should also consider any different constraints for disposal of the resulting sludge. Preliminary studies have indicated that metal ion leachability is lower for metal sulfide sludges than for hydroxide sludges. However, the long-term impacts of weathering and of bacterial and air oxidation of sulfide sludges have not been evaluated.

At this time, the necessary precautions for environmentally safe disposal of sulfide sludge have not been established. This lack of information prevents an evaluation of the impact of generating a sulfide sludge instead of a hydroxide sludge.

This report will evaluate the sulfide precipitation process, assuming that disposal of the residue incurs the same constraints as the hydroxide process.

The importance of design safeguards to avoid the potential hazards associated with sulfide precipitation processes cannot be overemphasized. For example, a sulfide reagent coming into contact with an acidic waste stream can result in the evolution of toxic H_2S fumes in the work area. The potential danger can be minimized by fairly conventional design safeguards, but the safeguards must be well maintained to be effective. Another potential problem for plants discharging to enclosed sewers is the danger associated with residual levels of sulfide in the wastewater. This problem occurs primarily with the SSP processes because the low solubility of FeS in the ISP process controls the residual sulfide concentration at a very low level. Elimination of the H_2S hazard to sewer workers would require either oxidation of the wastewater before discharge or process controls to ensure a low sulfide residual in the discharge.

This summary report is intended to promote an understanding of the use of sulfide precipitation for the removal of heavy metals from industrial waste streams. The report includes a general discussion of sulfide precipitation process theory and an evaluation of both soluble and insoluble sulfide treatment systems in terms of state of development, performance, cost, and operating reliability.



Dual-bed effluent polishing filters

Process Theory

The precipitation of a dissolved metal ion as a metal sulfide (MS) occurs when the metal ion (M^{+2}) contacts a sulfide ion (S^{-2}):

$$M^{+2} + S^{-2} \rightarrow MS \downarrow$$

Most heavy metals encountered in electroplating wastewater will form stable metal sulfides; common exceptions include the trivalent chromic and ferric ions.

The two processes currently employed to precipitate metals as sulfides differ mainly in the method used to introduce the sulfide ions into the wastewater. The SSP process uses a water-soluble sulfide compound; consequently, the concentration of dissolved sulfide depends on the quantity of reagent added. The ISP process mixes the wastewater with a slurry of slightly soluble FeS, which will dissociate to satisfy its solubility product, yielding a dissolved sulfide concentration of approximately 0.02 ppb in the wastewater. Use of FeS as the source of sulfide ions controls the level of dissolved sulfide at a concentration low enough to eliminate any detectable emission of H_2S but still provide an inventory of undissolved sulfide that automatically replaces the sulfide consumed in precipitation reactions.

In the ISP process, the dissolved sulfide ions will precipitate as a metal sulfide any metal with a sulfide solubility less than that of FeS. As shown in Table 1, the only heavy metal with a sulfide more soluble than FeS is manganese. In an alkaline solution, the ferrous ions generated in the dissociation of the FeS will precipitate as hydroxides. Maintaining low levels of ferrous ions in the effluent requires that the pH be controlled between 8.5 and 9.5.

One advantage of the ISP process is the ability of the sulfide and ferrous ions to reduce hexavalent chromium to its trivalent state, which eliminates the need to segregate and treat chromium wastes separately. Under alkaline conditions, the chromium will then precipitate as chromium hydroxide [$Cr(OH)_3$]. The overall reduction reaction is:

$$H_2CrO_4 + FeS + 4H_2O \rightarrow Cr(OH)_3 \downarrow + Fe(OH)_3 \downarrow + S \downarrow + 2H_2O$$

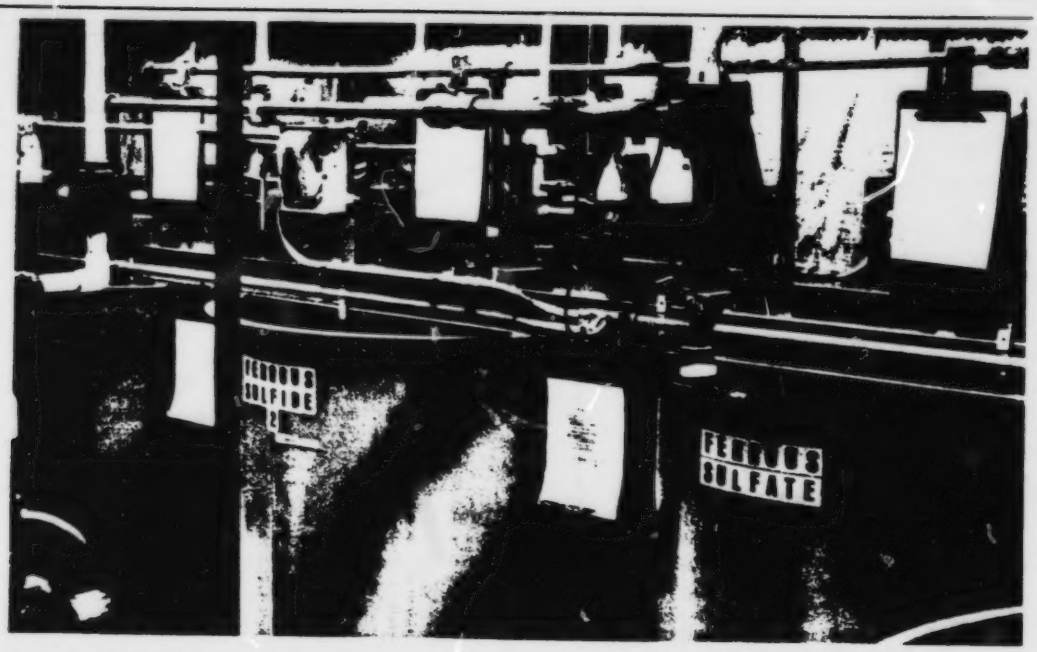
Table 1.

Solubilities of Sulfides

Metal sulfide	K_{sp} (64° to 77° F)*	Sulfide concentration (mol/l)
Manganous sulfide	1.4×10^{-15}	3.7×10^{-8}
Ferrous sulfide	3.7×10^{-19}	6.1×10^{-10}
Zinc sulfide	1.2×10^{-23}	3.5×10^{-12}
Nickel sulfide	1.4×10^{-24}	1.2×10^{-12}
Stannous sulfide	1.0×10^{-25}	3.2×10^{-13}
Cobalt sulfide	3.0×10^{-26}	1.7×10^{-13}
Lead sulfide	3.4×10^{-28}	1.8×10^{-14}
Cadmium sulfide	3.6×10^{-29}	6.0×10^{-15}
Silver sulfide	1.6×10^{-49}	3.4×10^{-17}
Bismuth sulfide	1.0×10^{-97}	4.8×10^{-20}
Copper sulfide	8.5×10^{-45}	9.2×10^{-23}
Mercuric sulfide	2.0×10^{-49}	4.5×10^{-25}

*Solubility product of a metal sulfide. K_{sp} equals the product of the molar concentrations of the metal and sulfide.

SOURCES: Robert C. Weast (ed.), *Handbook of Chemistry and Physics*, 50th ed., West Palm Beach FL, The Chemical Rubber Company (p. B252), 1969. Louis Meites (ed.), *Handbook of Analytical Chemistry*, New York NY, McGraw-Hill (pp. 1-15, 1-19), 1963.



Ferrous sulfide makeup and feed system

In the SSP process, the sulfide ion is capable of reducing hexavalent chromium as follows:

$$2H_2CrO_4 + 3NaHS + 8H_2O \rightarrow 2Cr(OH)_3 \downarrow + 3S \downarrow + 7H_2O + 3NaOH$$

The question of whether a soluble sulfide reagent can reduce and precipitate hexavalent chromium in one step was addressed in a pilot study conducted for the U.S. Navy. The study concluded that the reduction could be accomplished in the presence of ferrous ions (or conceivably some other suitable secondary metal). The ferrous ion acts principally as a catalyst for chromium reduction. Less than stoichiometric dosages[2] of iron are required to effect reduction of most of the chromium. Nearly stoichiometric dosages, however, are required to achieve levels typical of other reduction processes. No operating systems currently employ this one-step process.

[2]Stoichiometric dosage = dosage of reagent required per unit of contaminant based on the chemical formula and relative atomic weights as predicted by the treatment reaction.

SSP Process Chemistry

The addition of a sulfide reagent that has a high solubility in wastewater will yield a relatively high concentration of dissolved sulfide, compared with the ISP process. This high concentration of dissolved sulfide causes a rapid precipitation of the metals dissolved in the water as metal sulfides, which often results in the generation of small particle fines and hydrated colloidal particles. The rapid precipitation reaction tends more toward discrete particle precipitation than toward nucleation precipitation (the precipitation of a particle from solution onto an already existing particle). The resulting poor-settling or -filtering floc is difficult to separate from the wastewater discharges. This problem has been solved by the effective use, separately or combined, of coagulants and flocculants to aid in the formation of large, fast-settling particle flocs.

Another disadvantage of an SSP system is the H_2S odor often associated with it. The odor detection level of hydrogen sulfide—0.1 to 1.0 ppm—is very low compared with the workplace H_2S concentration limit of 10 ppm specified by the Occupational Safety and Health Administration (OSHA) for worker safety.

The rate of H_2S formation in a water solution is a function of pH

(concentration of hydrogen ions) and sulfide ion concentration. The formation of H_2S from dissolved sulfide ions proceeds as follows:

$$S^{+2} + H^+ \rightarrow HS^-$$

$$HS^- + H^+ \rightarrow H_2S$$

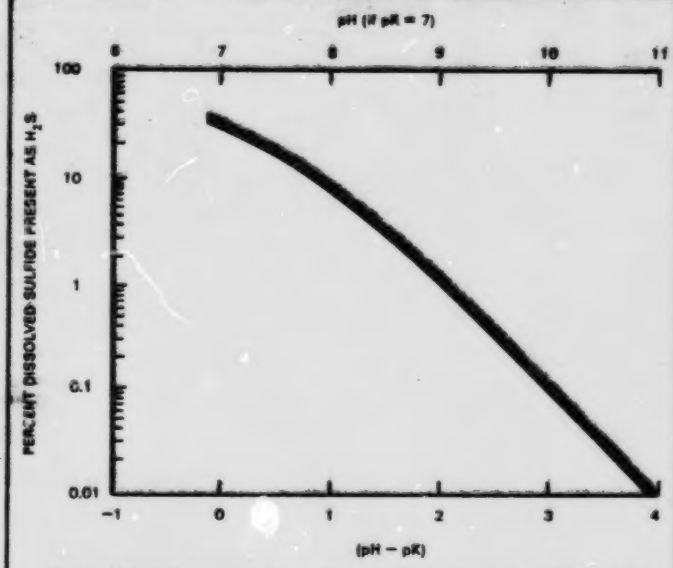
Actually, the strong base S^{-2} is not present in any significant amount except at high pH. For example, at a pH of 11, less than 0.05 percent of the dissolved sulfide is in the S^{-2} form; the remainder is in either the HS^- or H_2S form. Figure 5 is a graph for determining the percentage of the dissolved sulfide in the form of H_2S as a function of the pH of the solution. The relationship shows that at a pH of 9, H_2S accounts for only 1 percent of the free sulfide in solution. The rate of evolution of H_2S from a sulfide solution per unit of water/air interface will depend on the temperature of the solution (which determines the H_2S solubility), the dissolved sulfide concentration, and the pH. In practice, considering typical response lags of instruments and incremental reagent addition, control of the level of dissolved sulfide and pH would require fine tuning and rigorous maintenance to prevent an H_2S odor problem in the work area. In currently operating treatment systems, the H_2S odor problem is eliminated by enclosing and vacuum evacuating the process vessels.

Adding sulfide reagent to wastewater containing precipitated metal hydroxides will result in resolubilization of the metal hydroxides. The dissolving of the metal hydroxides occurs because the dissolved metal ion concentration is now lower than the equilibrium level predicted by the hydroxide solubility. These newly liberated metal ions will be precipitated by any excess sulfide present. The following reactions occur:

$$M^{+2} + S^{-2} \rightarrow MS \downarrow$$

$$M(OH)_2 \rightarrow M^{+2} + 2(OH)^-$$

$$M^{+2} + S^{-2} \rightarrow MS \downarrow$$



Note.—pK (logarithmic practical ionization constant) is used to measure the degree of dissociation of weak acids, in this case H_2S.

Specific electrical conductance of solution at 77° F (μohm/cm)	Value of pK		
	50° F	68° F	104° F
0[a]	7.24	7.10	6.82
100	7.22	7.08	6.80
1,000	7.18	7.04	6.76
50,000[b]	7.09	6.95	6.67

[a]Distilled H_2O.

[b]Seawater.

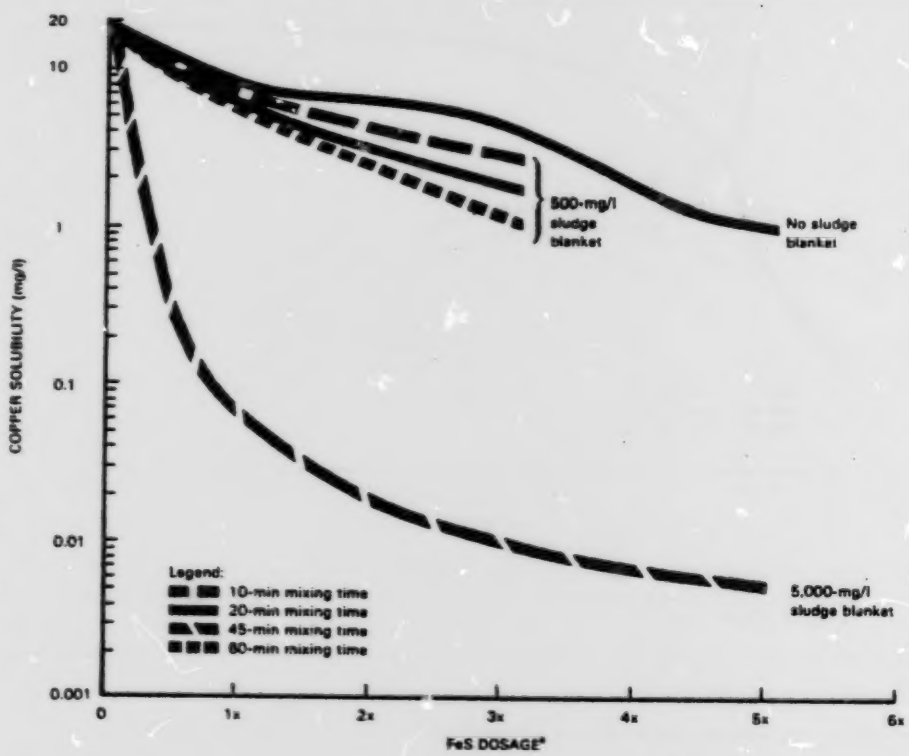
Figure 5.

Percent of Dissolved Sulfide in the H_2S Form

Normally, the precipitated solids are in contact with the wastewater long enough to result in an almost complete conversion of metal hydroxides to metal sulfides. Therefore, the sulfide reagent demand depends on the total metal concentration contained in a wastewater. Consequently, a significant reduction in sulfide reagent consumption could be achieved by separating the precipitated metal hydroxides from the wastewater before adding the sulfide reagent.

ISP Process Chemistry

The Sulfex™ process precipitates dissolved metals as sulfides by mixing the wastewater with an FeS slurry in a solid/liquid contact chamber. The FeS dissolves to



[a]x = stoichiometric equivalent concentration of FeS required to precipitate 20 mg Cu^{+2}/l = 27.7 mg FeS/l.

Note.—Results of jar tests with complexed Cu influent; pH values maintained between 7 and 8 during tests.

SOURCE: U.S. Environmental Protection Agency, *Treatment of Metal Finishing Wastes by Sulfide Precipitation*, EPA 600/2-77-049, Feb. 1977.

Figure 6.

Influence of FeS Dosage, Sludge Blanket Concentration, and Mixing Time on Copper Solubility

maintain the sulfide ion concentration at a level of 0.02 ppb.

The following reactions occur when FeS is introduced into a solution containing dissolved metals and metal hydroxide:

$$FeS \rightarrow Fe^{+2} + S^{-2}$$

$$M^{+2} + S^{-2} \rightarrow MS \downarrow$$

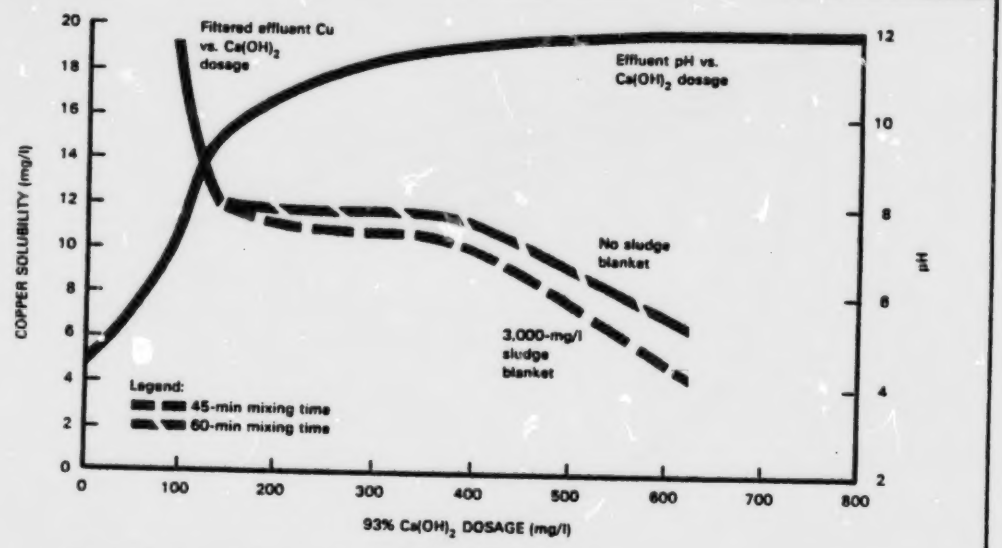
$$M(OH)_2 \rightarrow M^{+2} + 2(OH)^-$$

$$Fe^{+2} + 2(OH)^- \rightarrow Fe(OH)_2 \downarrow$$

The addition of ferrous ions to the wastewater and their precipitation as ferrous hydroxide [$Fe(OH)_2$] results in a considerably larger quantity of solid waste from this process than from a conventional hydroxide precipitation process.

As with SSP, the ISP process achieves an almost complete conversion of previously precipitated metal hydroxides to metal sulfides. The reaction goes to completion because of the long residence time of the solids in the treatment system before discharge.

Figure 6 shows three different factors that affect the ability of FeS



Note.—Results of hydroxide process jar tests with complexed Cu influent.

SOURCE: U.S. Environmental Protection Agency, *Treatment of Metal Finishing Wastes by Sulfide Precipitation*, EPA 600/2-77-049, Feb. 1977.

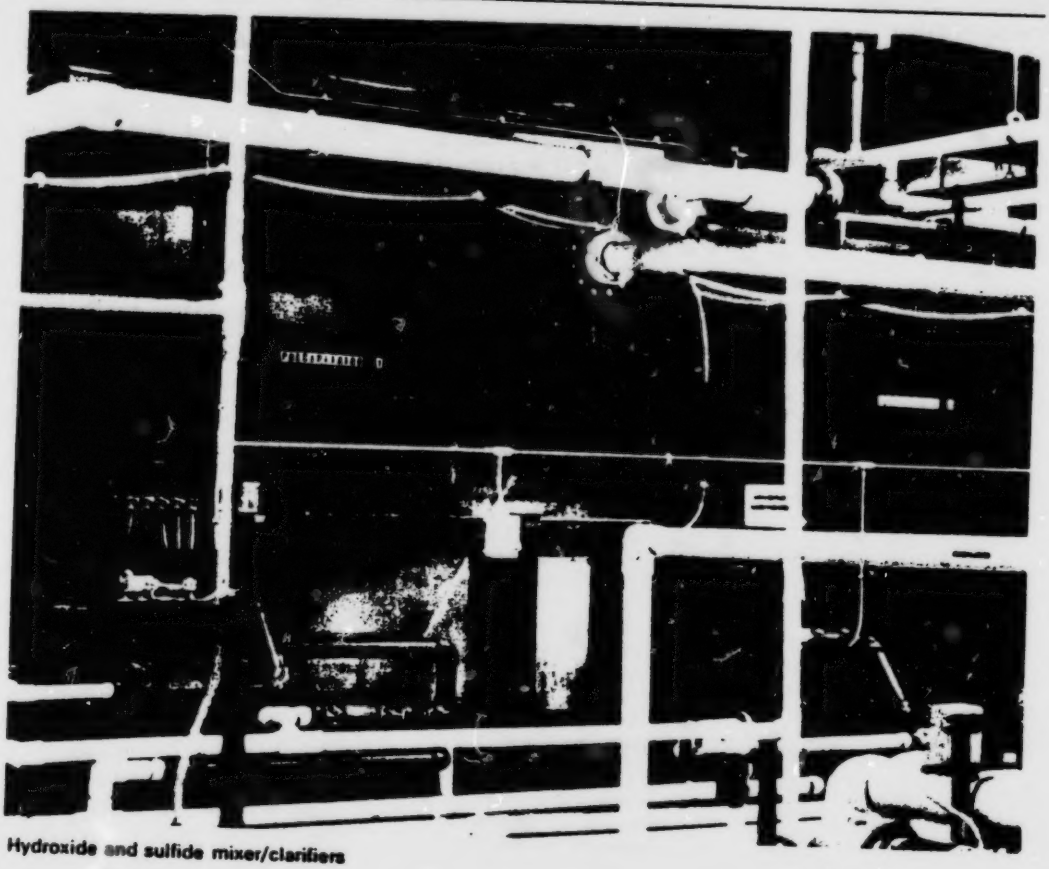
Figure 7.

Influence of $Ca(OH)_2$ Dosage, Sludge Blanket Concentration, and pH on Copper Solubility

to precipitate copper from a solution containing metal complexing compounds. The design criteria that must be addressed are:

- A dense sludge blanket must be maintained in the solid/liquid contact zone.
- Adequate mixing time is required for the precipitation reaction to reach equilibrium.
- From 2 to 4 times the required stoichiometric amount of reagent is needed to realize the low levels of dissolved copper achievable by sulfide precipitation.

To illustrate the relative effectiveness of sulfide precipitation, Figure 7 represents the solubility of copper in the same complexing compound solution as a function of pH. Even at a pH of 12, the level of dissolved copper cannot be reduced below 2 mg/l.



Hydroxide and sulfide mixer/clarifiers

Soluble Sulfide Precipitation

Use of a water-soluble sulfide compound to reduce the solubility of heavy metals in a wastewater discharge is an effective method of improving the performance of a hydroxide precipitation treatment system. This section describes the results of a recent investigation of the use of SSP and presents information on systems currently using the technology.

Pilot Plant Evaluation

Test Description. Currently, there are only a few applications of SSP to treat metal finishing wastewater. To provide a source of the data needed by firms interested in using the treatment process, the U.S. Environmental Protection Agency's (EPA's) Industrial Environmental Research Laboratory funded a pilot study by the Boeing Commercial Aircraft Company to compare and evaluate five treatment systems using variations of SSP and hydroxide precipitation processes to treat metal finishing wastewater. The pilot tests were designed to simulate the three basic process systems shown in Figure 8. The five process variations tested were:

- Lime only, clarified (LO-C)—the conventional process using lime as a neutralizing agent to precipitate the dissolved metals and clarification to separate the suspended solids from the discharge (System A)
- Lime only, clarified, filtered (LO-CF)—the LO-C process with a filtration step downstream of clarification to improve the suspended solids removal (System A)
- Lime with sulfide, clarified (LWS-C)—the LO-C process with controlled addition of a soluble sulfide reagent in the neutralizing chamber (System B)
- Lime with sulfide, clarified, filtered (LWS-CF)—the LWS-C process with a filtration step downstream of clarification to improve the suspended solids removal (System B)
- Lime, sulfide polished, filtered (LSPF)—a polishing sulfide precipitation process featuring lime neutralization and clarification to remove the metal hydroxides followed by addition of a soluble sulfide reagent to reduce the metal solubility and a filtration step to remove the precipitated solids (System C)

These process variations were evaluated with 14 actual raw wastewater feed samples obtained from various industrial firms engaged in electroplating and metal finishing. The pilot plant could operate in any of the five modes and could process 0.034 gal/min (130 ml/min) of wastewater in a continuous treatment sequence. Samples were pretreated as required for chromium reduction and cyanide oxidation. Attempts were not made to reduce hexavalent chromium with sulfide reagent.

In the sulfide process variations, the soluble sulfide reagent addition was controlled automatically by a specific-ion sulfide reference electrode pair to maintain a preselected potential of −550 mV with respect to the reference electrode. The value of −550 mV corresponds to about 0.5 mg/l of free sulfide, which was selected as the control point because at that concentration:

- The curve of electrical potential versus sulfide concentration has its maximum gradient.
- The wastewater solution has no detectable sulfide odor.

The study reported that the dependability of the sulfide specific-ion electrode was excellent during the 6-month test period.

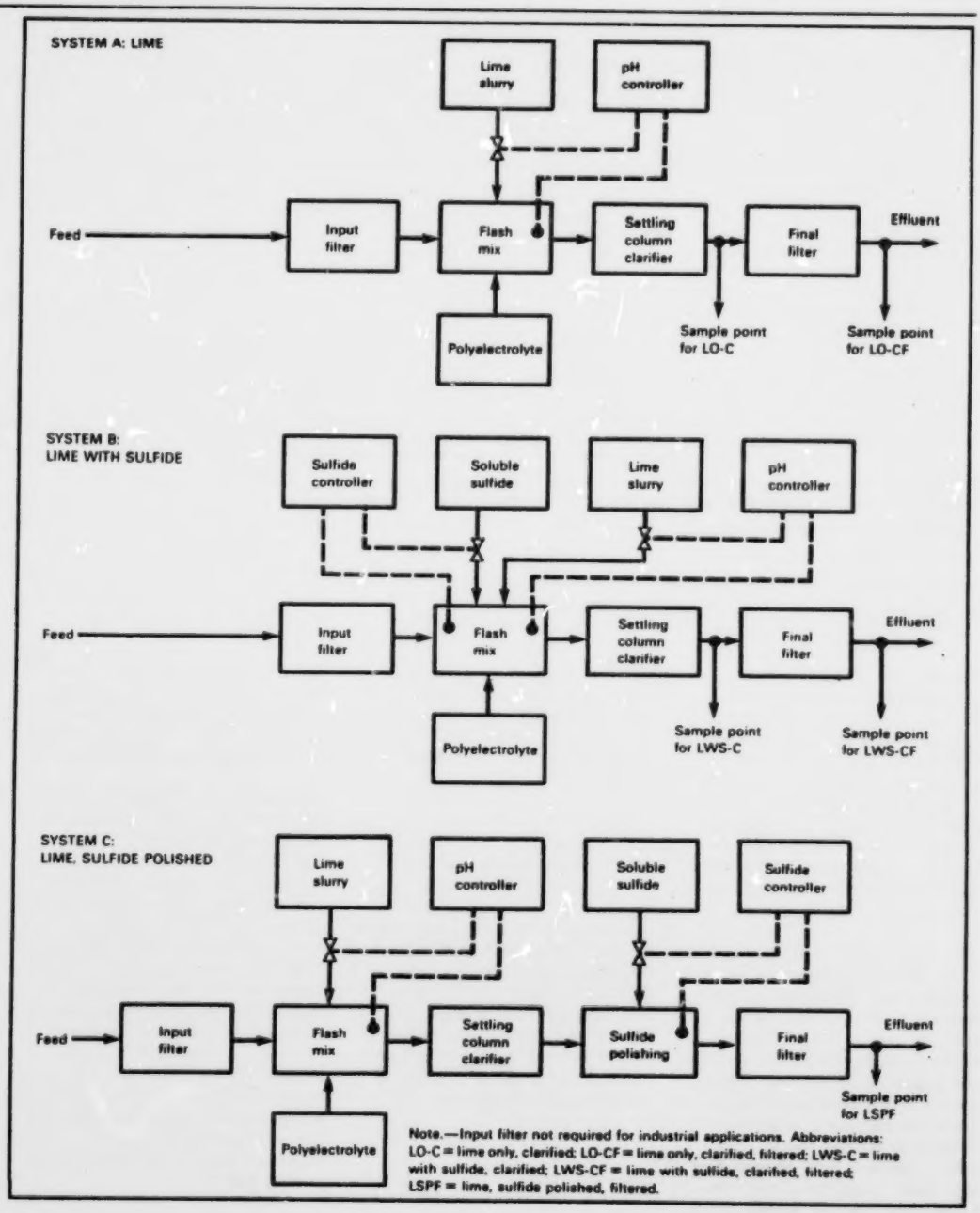


Figure 8.

Metal Precipitation Processes Evaluated in Pilot Study

Table 2.

Wastewater Treatment Process Details of Pilot Tests

Characteristic	Pilot test[a]				
	1	2[b]	3	4	5
Raw feed before treatment:					
pH	1.7	1.2	6.4	2.4	7.1
Conductivity (μmho/cm)	10,600 at 72° F	149,000 at 68° F	12,100 at 77° F	5,600 at 68° F	1,500 at 70° F
Color	Yellow	Colorless	Colorless	Colorless	Pale green
Precipitation pH for LO and LWS processes	8.5	6.2/9.0	9.0	10.0	8.5
Sludge volume (%):[c]					
LO process	18	78/23	(d)	43	5
LWS process	16	78/13	(d)	37	6
Process consumables (mg/l):					
Sulfuric acid for Cr^{+6} reduction	0	0	0	0	339
Sodium sulfite for Cr^{+6} reduction	228	31	0	41	25
Calcium oxide for neutralization	1,500	14,380	911	2,680	145
Sulfide for LWS process	8	381	(d)	400	91
Sulfide for LSPF process	1	5	(d)	141	67

[a]Wastewater by pilot test: 1—high-chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high-zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

[b]Because of the exceptionally large volume of sludge generated by this wastewater, precipitation was accomplished in two stages. First- and second-stage values are separated by a diagonal line; single values apply to the total process.

[c]Sludge volume per solution volume, percent after 1 hour settling.

[d]Data not available.

Note.—LO = lime only; LWS = lime with sulfide; LSPF = lime, sulfide polished, filtered.

SOURCE: *Sulfide Precipitation of Heavy Metals*, EPA Grant 5805413, in preparation.

Test Results. Results of five of the pilot tests are presented in Tables 2 and 3. Table 2 lists the characteristics of the wastewater before treatment, the volume of sludge generated, and the amount of reagents consumed in the treatment. Table 3 compares the amount of metal per liter of raw feed before treatment and wastewater after treatment using the five process variations.

Pilot Test 1 simulated treatment of a wastewater containing a high concentration of chromium and moderate levels of copper and zinc. As can be seen from the effluent quality of the LO-CF process, the hydroxide solubilities of the metals in this wastewater were quite low and use of a sulfide reagent to achieve lower metal solubilities was not required. The significant reduction in the chromium concentration across the filter can be seen by comparing the effluent quality of the LO-C and LO-CF processes. This situation points out how poor solids removal can have significant adverse effects on an otherwise effective metal precipitation treatment system.

Pilot Tests 2 and 3 were performed with wastewaters that were not effectively treated by hydroxide precipitation. In these tests, significantly improved effluent quality was achieved by sulfide precipitation treatment. In Pilot Test 2, the effluent produced by the LO-CF process contained relatively high levels of zinc and copper, 2.3 and 0.8 mg/l, respectively. Treatment with a soluble sulfide compound considerably reduced the effluent concentration of these metals. In Pilot Test 3, soluble sulfide treatment of wastewater with a high zinc concentration was significantly more effective than hydroxide precipitation.

Tests also were conducted on wastewaters containing an assortment of heavy metals at relatively high concentrations. The results of Pilot Tests 4 and 5 (shown in Table 3) indicate that low levels of all metal pollutants could not be achieved by treatment of these particular wastewaters with either hydroxide or sulfide precipitation. In Pilot Test 4, sulfide precipitation removed the cadmium, copper, and zinc to considerably lower levels than the hydroxide precipitation process, but both processes had a high residual nickel concentration in the effluent. A similar situation occurred with nickel in Pilot Test 5.

Table 3.

Chemical Analysis of Raw and Treated Wastewater Used in Pilot Tests.

Contaminant (μg/l)	Raw feed before treatment	Wastewater after treatment[a]				
		LO-C	LO-CF	LWS-C	LWS-CF	LSPF
Pilot Test 1						
Cadmium	45	15	8	11	7	20
Total chromium	163,000	3,660	250	1,660	68	159
Copper	4,700	135	33	82	18	3
Nickel	185	30	38	33	31	18
Zinc	2,800	44	10	26	2	11
Lead	119	119	88	104	59	120
Pilot Test 2						
Cadmium	58	7	12	<5	<5	<5
Total chromium	6,300	4	2	5	7	3
Hexavalent chromium	<5	<1	<1	<1	<1	<1
Copper	1,100	860	848	13	13	132
Nickel	160	30	34	33	23	34
Zinc	650,000	2,800	2,300	104	19	242
Mercury	<1	NA	NA	NA	NA	NA
Silver	16	NA	NA	NA	NA	NA
Pilot Test 3						
Cadmium	34	21	21	1	1	1
Total chromium	3	NA	NA	NA	NA	NA
Copper	20	7	8	2	1	4
Nickel	64	29	29	72	34	31
Zinc	440,000	37,000	29,000	730	600	2,000
Mercury	<10	NA	NA	NA	NA	NA
Lead	45	13	14	9	11	13
Silver	61	4	4	1	3	4
Tin	200	<10	<10	<10	<10	<10
Ammonium	([b])	NA	NA	NA	NA	NA
Pilot Test 4						
Cadmium	58,000	1,130	923	26	<10	<10
Total chromium	5,000	138	103	49	50	37
Copper	2,000	909	943	60	160	929
Nickel	3,000	2,200	2,300	1,800	1,900	2,600
Zinc	290,000	1,200	510	216	38	12
Iron	740,000	2,000	334	563	229	305
Mercury	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Silver	14	14	10	7	7	8
Tin	5,000	129	81	71	71	71
Pilot Test 5						
Cadmium	<40	<1	<1	<1	<1	<1
Total chromium	1,700	109	39	187	17	20
Copper	21,000	1,300	367	2,250	169	11
Nickel	119,000	12,000	9,400	11,000	3,500	5,300
Zinc	13,000	625	10	192	8	5
Iron	NA	2	<2	5	<2	<2
Lead	13	7	5	4	3	3
Silver	6	NA	NA	NA	NA	NA

[a]LO-C = lime only, clarified; LO-CF = lime only, clarified, filtered; LWS-C = lime with sulfide, clarified; LWS-CF = lime with sulfide, clarified, filtered; LSPF = lime, sulfide polished, filtered; NA = not applicable.

[b]Qualitative tests indicated the presence of significant amounts of ammonium.

Note.—Wastewater by pilot test: 1—high-chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high-zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

SOURCE: *Sulfide Precipitation of Heavy Metals*, EPA Grant 5805413, in preparation.

The data on effluent quality from this study suggest the following general conclusions about the treatment of wastewater with either hydroxide or sulfide precipitation for removal of heavy metals:

- In most cases, metal removal can be improved by precipitating metals as sulfides rather than as hydroxides.
- Some wastewaters can be effectively treated to low residual concentrations of all metals present by either hydroxide or sulfide precipitation processes; some wastewaters cannot be effectively treated by either hydroxide or sulfide precipitation.
- Consistent removal of metals to effluent concentrations of less than 1 mg/l requires filtration to remove residual suspended solids. Because fine particles (which include precipitated metals) are only minimally different in density from water, they cannot be effectively separated by clarification and therefore contribute to the effluent metal concentration.

Another significant finding of the study is the quantity of sulfide reagent consumed in precipitating the metals as sulfides. In the LWS processes, the bulk of the test runs consumed between 1.0 and 2.5 times the stoichiometric sulfide reagent demand based on the total mass of metals that form sulfides in the wastewater. This reagent demand factor supports the belief that all metals are precipitated as sulfides and that any metals initially precipitated as hydroxides are converted to metal sulfides.

In the LSPF process, the metals precipitated as hydroxides are separated by clarification before addition of the sulfide reagent. The sulfide reagent demand for most of the LSPF process tests ranged from 2 to 6 times the stoichiometric sulfide reagent demand. The stoichiometric demand in this case can be calculated from the concentration of metals in the LO-C effluent. The study contained no conclusions as to the cause of the significantly higher sulfide reagent demand relative to the stoichiometric requirements.

SSP System Description and Performance

Although only a few plants currently treat their wastewater with SSP, this process has proved effective for precipitation of many of the metals typically encountered in electroplating wastewater. At present, however, no commercial units are demonstrating the treatment of heavy metals at the high concentrations typical of metal finishing industry wastewater. The primary application of SSP has been for waste streams containing low concentrations of metals and complexing agents, which interfere with effective metal removal by hydroxide precipitation.

Figure 9a is a schematic of a continuous SSP system used to treat a heavy metal waste stream discharged from a large mechanical equipment manufacturer. Part of the wastewater results from electroplating and surface finishing operations. The wastewater pH is adjusted to 7.5 in the first-stage neutralizer and is maintained at approximately 8.5 in the second-stage neutralizer. If the pH falls below 7 in the first stage, a low-pH alarm sounds and the pump feeding the second-stage neutralizer is shut off. Consequently, a surge volume is required in the system to store the wastewater until the pH returns to the control set-point. Sodium hydrosulfide is added in the second-stage neutralizer at a rate set to maintain a dosage of 5 to 10 mg of free sulfide per liter of wastewater. Automatic controls are not used to adjust sulfide reagent feed rate to account for changes in demand. The required sulfide reagent addition rate is determined by periodic testing.

The system shown in Figure 9a uses a separate hexavalent chromium reduction system, although the free sulfide can potentially accomplish the reduction. This approach was not evaluated because performing chromium reduction in the second-stage neutralizer would increase sulfide reagent demand to approximately 35 to 50 mg/l of feed (based on consumption equal to twice the stoichiometric reagent demand) and would make sulfide reagent demand considerably more variable. Without an automatic sulfide reagent addition system to match supply with demand, the increased variability in reagent demand would reduce the reliability of the treatment system. The existing chromium reduction unit, which uses sodium bisulfite ($NaHSO_3$) as the reducing agent, reduced the hexavalent chromium to the required level. Therefore, sulfide precipitation was used only to achieve the superior metal removal required by the discharge permit.

The reduction in the metal solubility achieved by adding NaHS to this plant's wastewater is shown in Table 4. The data indicate that the metal solubility decreases as the sulfide reagent dosage increases.

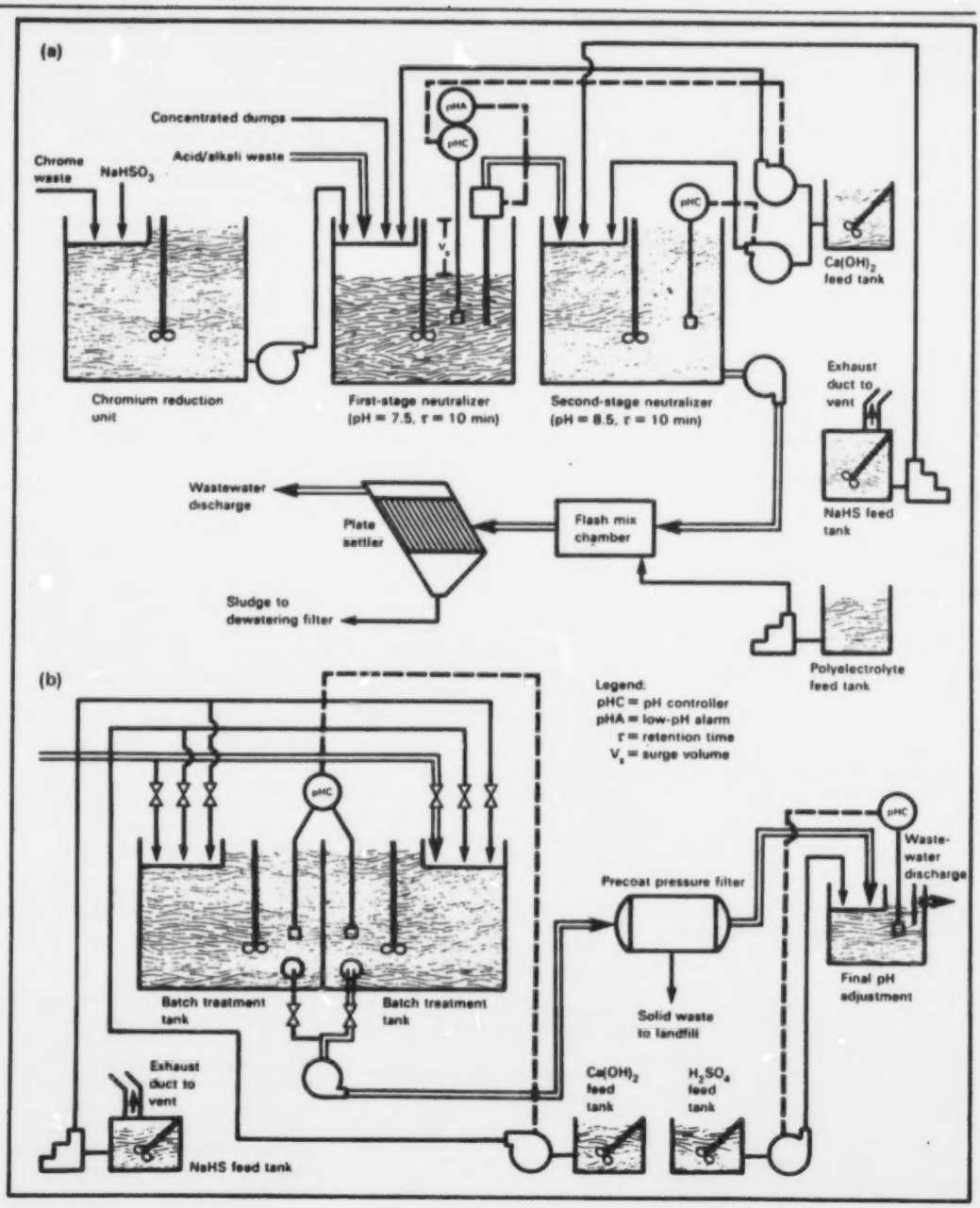


Figure 9.

SSP Treatment Systems: (a) Continuous and (b) Batch

Table 4.

Sulfide Precipitation of Cadmium, Zinc, and Mercury

Metal (mg/l)	Raw waste	Supernatant[a]			
		Hydroxide solubility at pH of 8.5	Sulfide addition (mg/l)		
			1	5	10
Cadmium	2.1	2.0	1.6	0.39	0.08
Zinc	3.0	2.25	1.8	1.5	1.1
Mercury	0.006	0.0027	0.0013	0.001	0.0008

[a]Polyelectrolyte dose = 1 mg/l; settling time of 2 hours.

Note.—Stoichiometric sulfide requirement to precipitate mixture given is 2.1 mg/l of sulfide based on raw waste composition.

Table 4 also shows the solubilities of the metal hydroxides after pH adjustment to 8.5. Effective metal removal is achieved by this treatment system with a sulfide reagent in the sulfide dosage range of 5 to 10 mg/l.

Figure 9b shows a commercially operated batch wastewater treatment system using a soluble sulfide reagent. The system includes two batch treatment tanks, each sized to hold 1 day's wastewater flow. The sequence of treatment follows:

1. The pH of the full, off-stream tank is raised automatically to a value of 11 by the addition of hydrated lime.
2. Depending on the volume of wastewater in the tank, a quantity of NaHS is metered into the tank.
3. The tank is agitated for approximately 30 minutes and a sample is taken, filtered, and analyzed for the metal that is characteristically most difficult to remove.
4. If the metal concentration is low enough, the contents of the tank are pumped through a diatomaceous earth precoat pressure filter and, after final pH polishing (to 8), are discharged. If the reference metal level is not low enough, additional NaHS is added and Steps 3 and 4 are repeated.

Table 5.

Removal of Complexed Copper and Other Metals From Electroplating Wastewater

Metal (mg/l)	Untreated wastewater	Filtrate
Copper	17	0.4
Nickel	0.3	<0.2
Lead	1.85	<0.2
Zinc	0.86	0.4
Tin	4.29	<1.0

Note.—Batch treatment sequence: lime added to pH of 11; NaHS added to equivalent sulfide ion concentration of 20 mg/l (stoichiometric requirement = 10 mg/l); filtered through diatomaceous earth filter; final pH adjustment to 8 before discharge.

The performance of the batch system in reducing the level of total metals in the wastewater discharge is presented in Table 5. As shown, the pH of the wastewater is raised to 11 before NaHS is added. Experimentally, it was found that the sulfide addition would reduce the dissolved metal concentration to equally low levels at a pH of 8.5. Removal of fluorides present in the plant's wastewater, however, required elevating the pH to 11.

The continuous and batch SSP systems described in this section are located in segregated waste treatment areas. Despite careful control of the wastewater pH and sulfide addition rate, the H_2S odor in the area was a nuisance. To reduce the ambient level of H_2S, the open-top treatment tanks where the sulfide reagent is added to the wastewater were modified into closed-top, vacuum-evacuated tanks. In the batch system shown in Figure 9b, the final pH adjustment tank contributed to the odor problem and was modified similarly. The exhaust from these tanks, which contains a low level of H_2S, is vented outdoors. These changes, plus rigid control of pH and sulfide dosage levels, have resulted in an almost undetectable H_2S odor in the waste treatment area.

SSP Polishing Treatment System

Sulfide reagent demand for the SSP treatment system shown in Figure 9a is a function of the total metal concentration of the raw wastewater. Sufficient reagent must be supplied to convert all entering metals to metal sulfides. In treating wastewater containing high metal loadings, significant sulfide reagent cost savings can be realized by using SSP to polish the effluent after a conventional pH adjustment/clarification treatment sequence (Figure 10). The LSPF process evaluated in the pilot studies discussed earlier simulated the use of SSP as a polishing system. There are no commercially operated SSP polishing systems currently in operation.

In addition to reducing sulfide reagent consumption, using sulfide precipitation as a polishing system will reduce the variability of reagent demand. The reagent demand for the polishing system will be a function of wastewater flow and the concentration of metals in the overflow from the first-stage clarifier. The metal concentration in the wastewater at this point

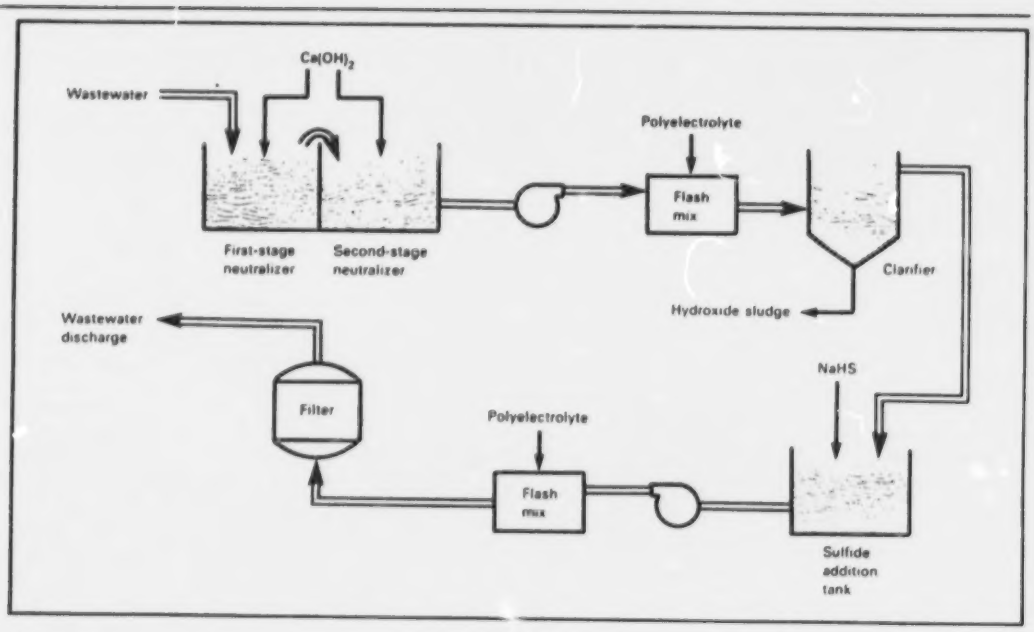


Figure 10.

SSP Polishing System

should not be subject to the wide variability that often characterizes the raw wastewater feed metal concentration. Without an automatic reagent addition control loop, dosing the wastewater with a predetermined amount of sulfide reagent would be considerably more reliable in a polishing treatment application.

The plant operating the treatment system shown in Figure 9a evaluated the use of SSP as a polishing treatment to reduce the variability of sulfide reagent demand. It was found that clarifying the wastewater before adding the sulfide reagent resulted in the formation of poor-settling particles that were difficult to remove from the wastewater. The current treatment sequence, in which the sulfide reagent is added in the second-stage neutralizer, removes precipitated metal more effectively. It was concluded that the presence of the precipitated metal hydroxides and lime solids in the wastewater entering the second-stage neutralizer provided nucleation sites, which promoted the coagulation of the precipitated metal sulfides.

An SSP pilot study reports success in forming metal sulfide particles that were easily removed from the wastewater despite precipitation in a solution lacking nucleation sites. The researchers found that conditioning the colloidal metal sulfide precipitants with a cationic coagulant to increase the particle size and then adding an anionic flocculant to link the particles produced large, fast-settling particles when flocculated. In the pilot study discussed previously, the sulfide polishing process precipitated metals as sulfides after the wastewater had been clarified to remove suspended solids. The study indicated that the metal sulfide solids were removed effectively by filtration.

The additional equipment requirements of a polishing treatment system include a second mixing tank to add the sulfide reagent and a second solids separation unit (using either a clarifier or a filter) installed downstream of the metal hydroxide clarification step. A second polyelectrolyte addition system also may be required to enhance the efficiency of the metal sulfide solids separation step.

Hydroxide System Modifications for SSP

Augmenting a hydroxide precipitation wastewater treatment system

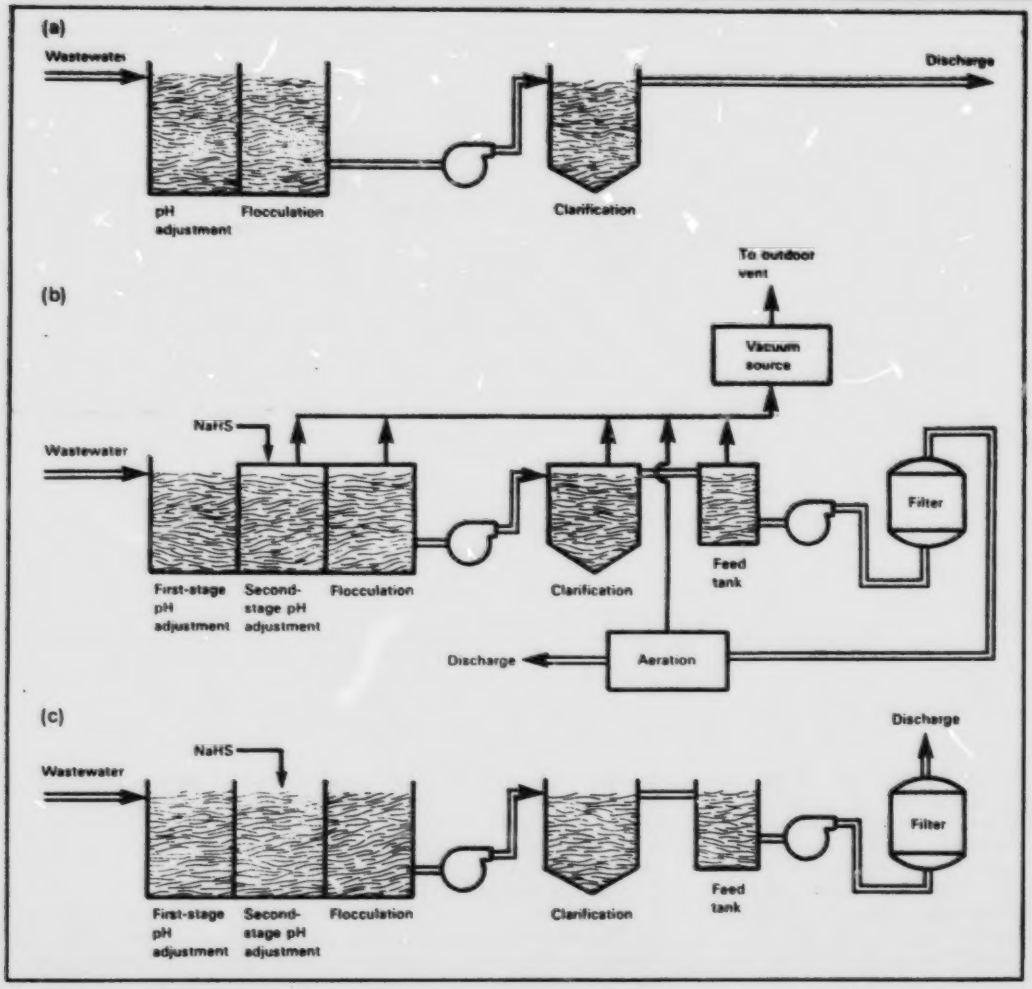


Figure 11.

Conversion of Hydroxide Treatment System To Use SSP: (a) Hydroxide Precipitation System, (b) SSP System, and (c) SSP System With Automatic Control of Sulfide Residual

with SSP to achieve a lower level of metals in the effluent can be a cost-effective means of achieving compliance. The cost of using soluble sulfide treatment will be significantly affected by the reliability and dependability of using the specific-ion sulfide reference electrode to control the sulfide reagent addition. If the residual sulfide concentration can be maintained consistently at a level of 0.3 to 0.5 mg/l in the wastewater, it should not be necessary to modify existing treatment tanks to eliminate sulfide odor in the work area. Because the reliability of the control system has not been established, two alternative approaches emerge for converting a hydroxide system to use SSP.

With no automatic control of the level of residual sulfide in the wastewater, converting the conventional hydroxide precipitation system (Figure 11a) to an SSP system (Figure 11b) requires

several process modifications. The modifications, which are discussed in the following paragraphs, include:

- NaHS reagent feed tank and feed pump
- Second-stage neutralizer/soluble sulfide treatment tank
- Clarifier enclosure and vacuum evacuation
- Control system
- Sand filter or other polishing filtration unit
- Aeration system

The NaHS feed tank should have a closed top with a vent connecting to an exhaust system. In installations where venting any odor is considered a public nuisance, the vent can be connected to a scrubber system. Using a scrubber eliminates the discharge of any odor, whereas simply venting outdoors eliminates any hazard to the worker during reagent preparation. The feed pump should be a positive displacement pump with a variable stroke to facilitate the metering of reagent into the system.

The second-stage neutralizer/soluble sulfide treatment tank is used for adding the sulfide reagent to the wastewater. The tank also provides improved pH control to ensure that the sulfide reagent does not come into contact with acidic wastewater. The tank contents should be agitated. The tank should be sized to provide a minimum retention time of 20 min, and it should be equipped with a pH control loop and alkali neutralizing reagent feed system. To minimize any H_2S odor associated with the treatment, the tank should be totally enclosed and vacuum evacuated.

To convert the conventional hydroxide precipitation system to an SSP system, it is also necessary to totally enclose and vacuum evacuate the clarifier.

A control system is needed to avoid mixing of the sulfide reagent with low-pH wastewater. An instrumentation loop that interrupts the wastewater feed to the sulfide treatment tank if the pH of this stream falls below set-point is one way of minimizing the potential hazard. Low-pH conditions also should sound an alarm and interrupt the sulfide feed to the system. This type of control will result in the need for surge volume upstream of the sulfide treatment tank to store the volume buildup until the pH is brought back above the set-point.

A sand filter or other polishing filtration unit that removes suspended solids in the clarifier overflow to very low levels is recommended for any treatment system that must achieve very low levels of metals in the effluent. The significance of reducing the solubility of a metal pollutant by means of sulfide precipitation will be lost unless the level of suspended solids, which include insoluble metals, is also controlled at a low level.

An aeration system may be needed to oxidize residual sulfide before wastewater discharge. If wastewater is discharged into a sewer system, precautions must be taken to ensure that the discharge does not contain high levels of sulfide. Discharge of wastewater containing significant quantities of sulfide could be hazardous to individuals working in a poorly vented sewer system. No specific limit exists for direct discharge of sulfide, but its presence contributes to the biochemical oxygen demand (BOD) of the wastewater. The easily oxidized sulfide compounds can be treated in an air-sparged tank with a retention time of approximately 30 min. If indoors, this tank also should be totally enclosed and vacuum evacuated.

For a process using automatic control of the sulfide reagent addition (Figure 11c), the required modifications to convert the hydroxide system to an SSP system would include the following:

- NaHS reagent feed tank and feed pump—identical to the tank and pump required for the previous case, except the feed pump is actuated by a signal from the sulfide reagent control system to maintain a constant residual sulfide concentration in the wastewater
- Second-stage neutralizer/soluble sulfide treatment tank—for addition of the sulfide reagent to the wastewater, but in this case the residual free sulfide ion concentration is maintained at a level below 0.5 ppm by means of a sulfide ion control loop
- Control system to avoid mixing of the sulfide reagent with low-pH wastewater
- Sand filter

The second-stage neutralizer/sulfide treatment tank and the downstream process tanks will not need to be enclosed and vacuum evacuated if careful control of pH (between 8 and 9.5) and sulfide ion concentration is maintained. Control of sulfide ion concentration also should eliminate the need to aerate the wastewater before discharge. The other elements of the sulfide system shown in Figure 11—first-stage pH adjustment, polyelectrolyte conditioning, and clarification—are common to hydroxide precipitation systems.

For batch treatment SSP systems, a two-tank system for alternately collecting and treating the wastewater would be required. The treatment sequence for a batch system was presented earlier. If the residual level of sulfide cannot be controlled, aeration of the wastewater after chemical treatment may be required in addition to enclosing and vacuum evacuating

the tanks during treatment. The wastewater could be aerated in the treatment tank before flocculation (if required) and solid/liquid separation.

Retrofitting a hydroxide system to use soluble sulfide polishing would require a mixing tank to add the sulfide reagent to the wastewater downstream of the existing clarifier and a second solids separation unit. Because the solids generation rate in the soluble sulfide polishing step should be low, a sand or mixed-media filter should be suitable for removing the suspended solids from the wastewater before discharge.

Polyelectrolyte conditioning and flocculation may be required between the sulfide reagent addition tank and the solids removal filter. Without instrumentation for reliable control of the residual sulfide concentration, the sulfide reagent mixing tank and downstream equipment would need to be enclosed and ventilated, and aeration of the effluent might be required.

Table 6.

Equipment Cost Factors for SSP Treatment Systems

Equipment component	Installed cost ($1,000),[a] by wastewater flow rate (gal/min)		
	30	60	90
Sodium hydrosulfide feed tank and metering pump	3.3	3.3	3.3
Automatic sulfide reagent addition control	3.5	3.5	3.5
Low-pH prevention control loop	1.5-2.0	1.5-2.0	1.5-2.0
Second-stage pH adjustment and sulfide reagent mixing tank:			
Open top	18	22	24
Totally enclosed and vented	23	28	30
Suspended solids polishing filter	24	33	41
Aerator	4	7	9

[a]March 1979 cost basis. Installed costs of different components are presented. Engineering and design costs, site preparation, and equipment freight charges are not included.

SSP Cost Estimating

Improving the performance of a hydroxide precipitation system through the use of SSP will require investment capital to modify the treatment system and will increase the cost to operate the system.

There is some uncertainty in predicting the extent of the modifications needed to convert a hydroxide system to use SSP. Demonstration of the reliability of automatic control of the sulfide reagent feed is needed to eliminate this uncertainty. Table 6 presents the costs (including hardware and installation) of the different equipment components that may be required:

- NaHS feed tank and metering pump
- Automatic control of sulfide reagent addition
- Low-pH prevention control loop
- Mixing tank
- Suspended solids polishing filter
- Aerator

The cost for a sodium hydrosulfide feed tank is based on a 400-gal (1,514-l), closed-top, carbon-steel tank that has a removable lid, exhaust vent, and appropriate nozzles. The diaphragm metering pump is rated to deliver 0 to 20 gal/h (0 to 76 l/h).

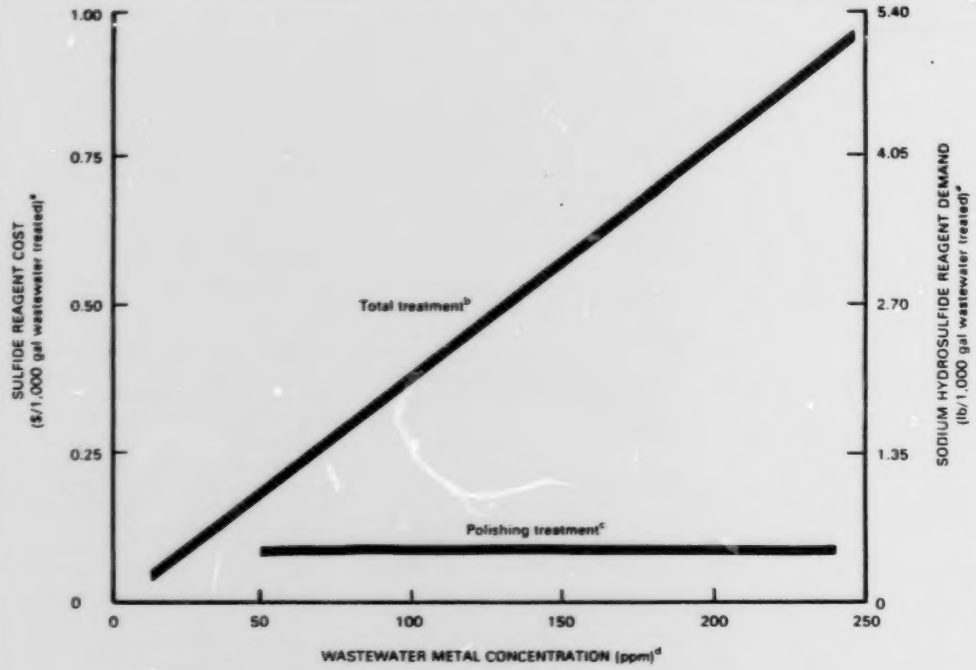
A specific-ion sulfide reference electrode pair automatically controls the sulfide reagent feed pump. A control loop prevents low-pH conditions in the sulfide treatment tank by automatically shutting down the wastewater feed pump and sulfide reagent feed pump if the wastewater pH falls below the control set-point. The cost presented assumes the prior existence of a pH probe and a surge volume to hold the diverted flow.

Second-stage pH adjustment and sulfide reagent addition occur in an agitated tank sized for 20-min retention of wastewater. Costs are given for both an open-top and a totally enclosed and vented tank.

The suspended solids polishing filter costs presented are for dual mixed-media filters, skid mounted and sized so that one filter can process the maximum flow during backwash. The unit is equipped with a blower for low pressure air scouring, a backwash storage tank, and a pump to bleed the wash back into the treatment system.

The aerator cost is based on an enclosed, vacuum-evacuated tank sized for 30-min retention of wastewater and equipped with an air sparger.

Higher operating costs—for operating labor and treatment reagents—will result from incorporating SSP into an existing treatment system. Additional operating labor will be required to prepare sulfide reagent and to maintain and operate the additional equipment components. Additional expense will result from consumption of sulfide reagent. The consumption rate will depend on the volume of wastewater treated and the



[a]Based on NaHS (72% flake) at $370/ton.

[b]Total treatment at 2 times the stoichiometric reagent demand.

[c]Polishing treatment at 4 times the stoichiometric reagent demand and a total metal hydroxide solubility of 10 ppm.

[d]Includes all metals that form sulfides, based on metal with molecular weight of 62.5 (average of Ni, Cu, and Zn).

Figure 12.

Soluble Sulfide Reagent Cost

required dosage. The dosage per volume of wastewater treated will be a function of the wastewater metal concentration. Figure 12 presents the sulfide reagent cost per 1,000 gal (3,800 l) of wastewater treated as a function of metal concentration for an SSP system used to treat the total metal load as well as for polishing treatment.

Sludge generation rates will increase with the use of SSP compared with a conventional hydroxide treatment system because of improved metal removal, but the increase should be insignificant. For example, precipitating an additional 5 ppm of dissolved metals from a waste stream will increase the clarifier underflow rate by less than 1 gal of sludge per 1,000 gal of wastewater treated, based on an underflow concentration of 1 percent solids by weight. Also, the dewatering properties of sulfide sludges are believed to be superior to those of hydroxide sludges, although limited information is available to support this view.

If the pH of the neutralized wastewater is increased to minimize odor, more alkali will be consumed, causing an increase in cost. The increased cost of alkali should not be significant except for high-volume treatment systems. Use of a pH above 10 would necessitate a final adjustment to lower the pH to the acceptable discharge range.

Insoluble Sulfide Precipitation

A commercially available ISP wastewater treatment system was developed to provide a treatment process that offers the superior metal removal of sulfide precipitation systems without the unpleasant H_2S odor often associated with soluble sulfide systems. Since the first commercial demonstration of the process in 1978, additional installations have become operational. The process is patented, and its use requires payment of a licensing fee to the patent holder. This section describes the process, presents performance data on three currently operating systems, and evaluates use of the process for treatment of electroplating wastewaters.

Process Description

Process Equipment Components. A hydroxide neutralization/ISP treatment system for control of pH and precipitation of heavy metals is depicted in Figure 13. In this system, the hexavalent chromium is reduced to its trivalent state by the sulfide and ferrous ions present in the mixer/clarifier, thus eliminating the need for a separate chromium reduction unit. With the exception of chromium and iron, all other heavy metals in the wastewater precipitate as sulfides. The key elements of the system are:

- pH control
- Mixer/clarifier
- Reagent addition to mixer/clarifier
- FeS feed rate control
- Sand filter

Effective metal removal by sulfide or hydroxide precipitation requires that the pH of the wastewater be controlled within the neutral to slightly alkaline range. Although the dependence of metal solubility on pH is not critical for sulfide precipitation systems, it still affects metal removal (see Figure 3). It is more important to eliminate the danger of the FeS slurry coming into contact with acidic wastewater; FeS is soluble in acidic solutions, and mixing it with low-pH wastewater would result in the emission of toxic H_2S fumes in the work area. The risk is minimized by installing a recycle control on the feed to the mixer/clarifier. If the pH of the feed stream drops below 7, valves automatically reroute the feed back to the second-stage neutralizer. For this reason, a surge volume, shown as V_s in Figure 13, is required to store the accumulated wastewater until the control set-point is reestablished.

The mixer/clarifier shown in Figure 13 serves two purposes. First, it provides the solid/liquid contact volume between the wastewater and the FeS slurry necessary to maintain the wastewater sulfide-ion concentration at its saturation point. As illustrated in Figure 6, both mixing time and sludge blanket density in the solid/liquid contact zone affect metal removal. Second, it clarifies the effluent of suspended solids.

To achieve low concentrations of dissolved metals, which are characteristic of metal sulfides, the liquid residence time in the solid/liquid contact zone of the mixer/clarifier must be sufficient for the metal precipitation reaction to reach completion. Proper agitation in the contact zone will enhance the degree of reaction completion achieved as well as promote particle growth of the precipitated metal sulfides. The formation of large, rapid-settling particles facilitates removal of the solids by clarification.

Reagent addition to the mixer/clarifier is controlled by a flow-measuring device that monitors the feed to the mixer/clarifier and sends a signal to a counter, which computes the cumulative flow. The additions of fresh FeS and polymer are controlled to provide a set quantity of each when

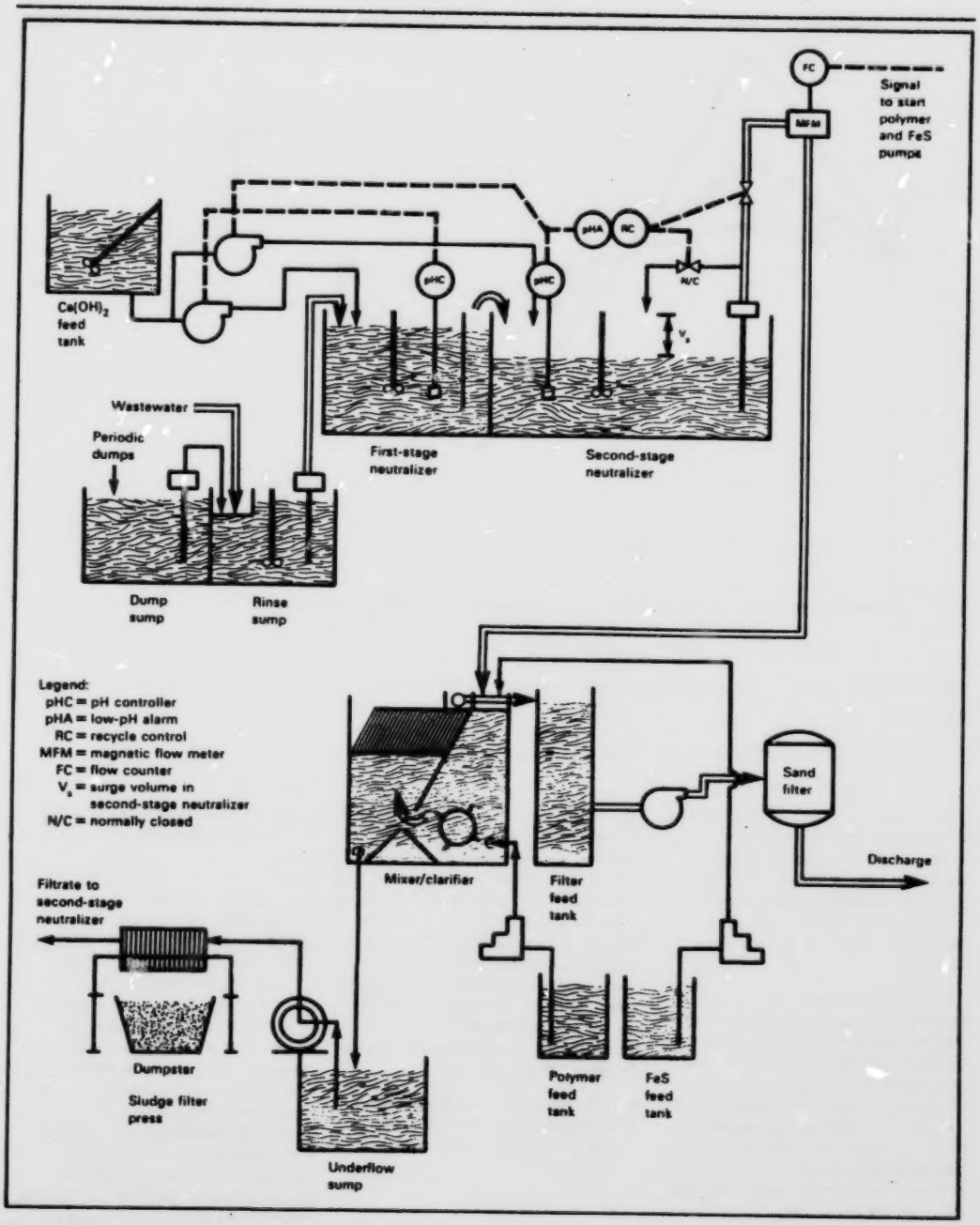


Figure 13.

Sulfex™ ISP Treatment System

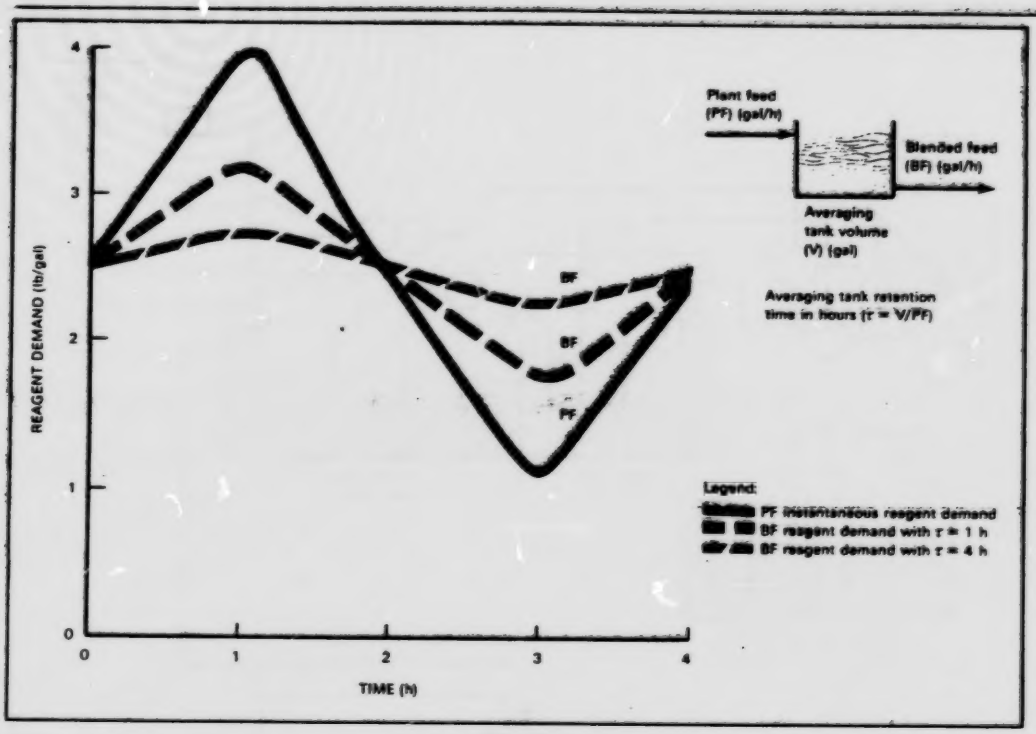


Figure 14.

Impact of Averaging Tank Volume on Reagent Demand Variability

the counter records a set volumetric throughput. The dosage rate is determined for both reagents by performing a series of jar tests. A sample is taken from the second-stage neutralizer and tested to determine the required addition of FeS.

Jar tests are conducted on approximately four samples to determine the lowest FeS dosage that provides optimum metal removal. Because polyelectrolyte demand should be proportional to the demand for FeS, it is fed at a constant ratio of the demand for FeS. Jar tests normally are conducted once or twice per shift to determine the required addition rate.

The FeS feed rate control loop automatically adds a preset amount of reagent each time an increment of wastewater enters the mixer/clarifier. The amount of reagent added is set manually based on the results of the jar tests. The inability to adjust the FeS reagent dosage automatically in response to changes in reagent demand complicates operation of ISP treatment systems. To compensate for the lack of automatic control, two features must be considered in design of the system:

- FeS reagent demand averaging
- Maintaining an inventory of unreacted FeS in the mixer/clarifier

Reagent demand averaging requires the elimination of sharp deviations in wastewater flow rate and pollutant concentration entering the treatment system. Flow variability normally is eliminated by providing a surge volume upstream of the treatment process and treating the wastewater at a constant average rate. The variability of pollutant concentration can be reduced by use of an averaging tank—an agitated tank that stores and blends the treatment system feed before processing. The impact of averaging tank volume and retention time on reagent demand variability is presented graphically in Figure 14. As shown, with 1 hour of retention time in upstream process tanks, the

variability of the mixer/clarifier (blended feed) reagent demand is equal to 54 percent of the plant feed reagent demand variability; with 4-hour retention time in upstream process tanks, the mixer/clarifier reagent demand variability is reduced to 15 percent of the plant feed variability. The graph presents an idealized situation of reagent demand fluctuating around a constant average demand. In actual practice, however, the deviations may be long term and may not average out to a constant demand rate. The relationship between retention time in upstream blending tanks and demand fluctuations is a key to operating any treatment process that does not adjust reagent supply to changes in demand automatically.

Maintaining an inventory of unreacted FeS in the mixer/clarifier is needed to provide the sulfide reagent when reagent demand exceeds supply. Because demand fluctuations are inevitable, an inventory of reagent is essential to consistently achieve maximum removal of metals. The quantity of FeS stored in the mixer/clarifier is proportional to the quantity of solids maintained in the unit and to the concentration of FeS in those solids.

A sand filter is included in the system to ensure that the wastewater discharge contains a minimum concentration of suspended solids. To meet strict metal discharge requirements, the level of dissolved and insoluble metals in the effluent discharge must be reduced to a minimum. For both sulfide and hydroxide precipitation systems, a sand filter ensures that upsets in the treatment system causing turbidity in the clarifier overflow will not jeopardize effluent quality.

FeS Reagent Consumption. As shown in Figure 6, precipitation of dissolved metals to the low solubility level characteristic of metal sulfides normally requires 2 to 4 times the stoichiometric amount of FeS. The ratio of the amount of reagent added to the stoichiometric demand establishes the equilibrium concentration of FeS in the sludge blanket solids. The FeS added in excess of the stoichiometric demand provides the inventory of unreacted reagent that is consumed when reagent demand exceeds supply.

The concentration of FeS in the sludge blanket as a function of the ratio of reagent addition to stoichiometric reagent demand is shown in Figure 15. The quantity of reagent consumed as a function of this ratio also is shown. Because the underflow rate is set to balance the solids loading rate, the concentration of FeS in the sludge blanket also determines the amount lost in the sludge underflow.

By defining the volume of the solid/liquid contact zone and the density of the sludge blanket in this zone, the amount of FeS stored can be approximated. The larger the quantity of unreacted FeS maintained in the blanket, the greater the ability of the system to compensate automatically for increases in reagent demand. The FeS supply can be increased by:

- Increasing the FeS reagent feed rate
- Designing larger solid/liquid contact volume into the system
- Maintaining the maximum sludge blanket solids concentration in the solid/liquid contact volume that is compatible with good clarification in the settling zone of the mixer/clarifier

The first two methods of increasing the FeS inventory have economic penalties: reagent cost and sludge volume rise as dosage is increased, and the initial cost and space requirements increase as larger mixing volume is designed into the system. Therefore, maintaining a dense sludge blanket in the mixing zone is the most efficient way to achieve good reagent use and to provide the inventory of FeS needed for reagent demand increases. In practice, this requires monitoring the blanket level and adjusting the sludge drawoff rate to match the solids accumulation rate in the system.

Operating Procedure. The ISP system shown in Figure 13 required a full-time operator during one shift and approximately 2 to 4 hours of operator attention during other shifts. Operator duties are as follows:

- Once each shift, a sample of mixer/clarifier feed is removed from the second-stage neutralizer for jar testing to determine the required FeS addition rate.
- Based on the jar test results, the FeS and polyelectrolyte addition control system is set to feed the needed quantity of reagents each time a set feed increment has entered the mixer/clarifier.
- The timer that controls the sludge blowdown is adjusted to reflect any change in the solids loading rate. (This relates to the jar test performed in the first step.)
- The level of solids in the mixer/clarifier is monitored periodically (normally every 1 or 2 hours) by performing a settling test on samples removed from the mixing zone of the mixer/clarifier. The sludge blowdown rate is adjusted to maintain the maximum solids concentration in the

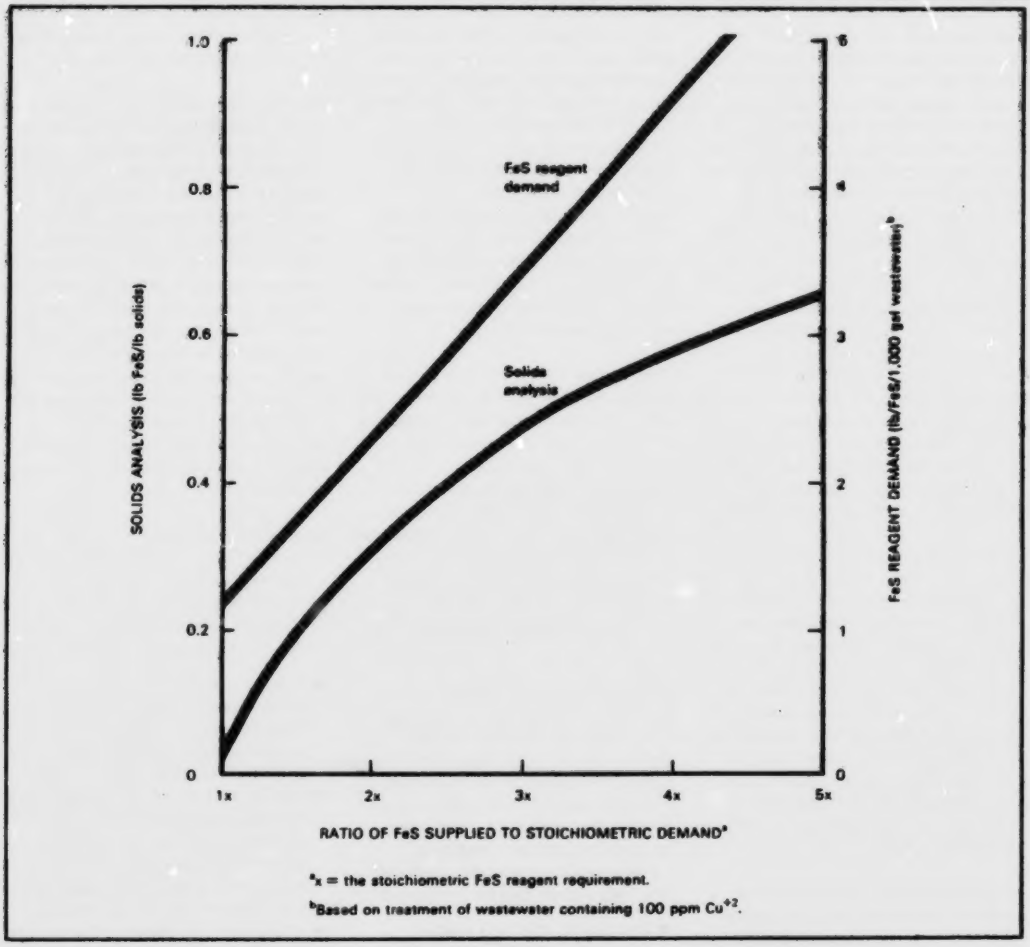


Figure 15.

Sludge Blanket FeS Concentration and Associated Reagent Demand

mixing zone that is compatible with low levels of turbidity in the clarified effluent.

Other operator duties generally required for operation of this system and most treatment systems include:

- Preparation of treatment reagents—in this case, reagents include lime slurry, Sulfex™ reagent (Figure 16), and polyelectrolyte
- Operation of sludge dewatering filter
- Periodic back-flush cleaning of the sand filter
- Periodic calibration of pH probes
- Collection of samples required for discharge permit
- Regularly scheduled lubrication of system elements

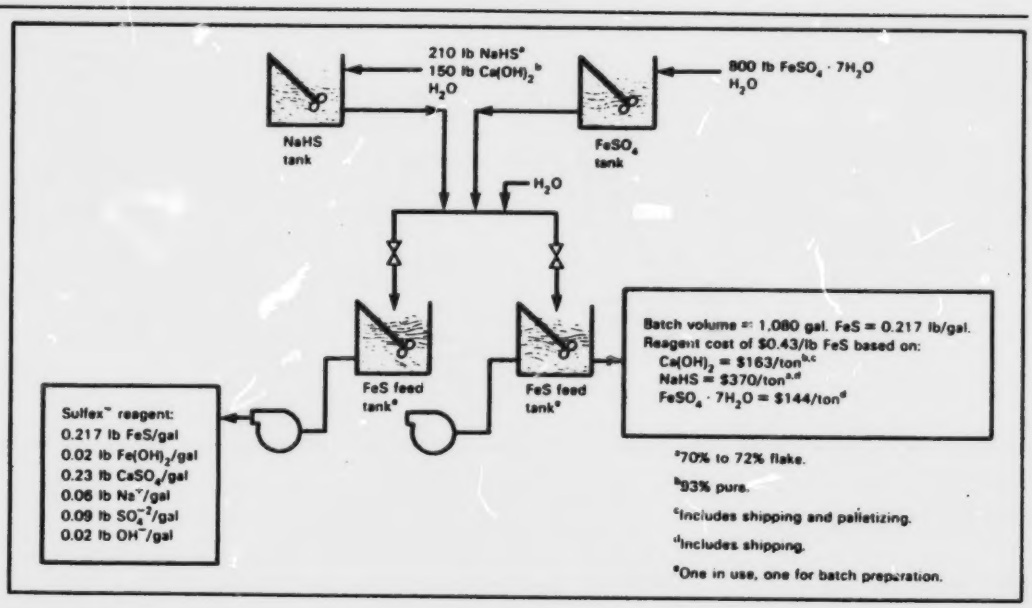


Figure 16.

FeS Feed System

ISP Polishing Treatment System

The FeS reagent demand for the system shown in Figure 13 is a function of the total metal load entering the mixer/clarifier. Sufficient FeS must be added not only to precipitate the dissolved metals but also to convert the precipitated metal hydroxides to metal sulfides. For treatment systems with a high mass flow of metals, FeS consumption will be high and considerable waste solids (a combination of metal sulfides, metal hydroxides, and unreacted FeS) will be generated. For these applications, the reduction in reagent consumption and solid waste disposal charges may justify using ISP to polish the clarified overflow after a conventional hydroxide precipitation/clarification treatment sequence (Figure 17).

In this polishing system, the FeS demand is based on the metals contained in first clarifier overflow. If hexavalent chromium is present in the wastewater, it will be reduced in the second-stage mixer/clarifier and precipitated along with the dissolved metals. Two advantages of this approach, compared with the system shown in Figure 13, are reduced FeS reagent demand and reduced sludge generation, which is a function of metal loading and reagent consumption. Another advantage is that the concentration of metals in the first-stage clarifier overflow will not be subject to the wide variation that often characterizes the wastewater feed metal concentration. The metal hydroxide equilibrium solubility will determine the concentration of dissolved metals in the overflow; this concentration will establish reagent demand. Again, because reagent supply is not adjusted automatically for changes in demand, this feature increases reliability. The concentration of hexavalent chromium, which is unaffected by the hydroxide treatment, will still be subject to variation, but the variability should be reduced because of the larger volume of upstream process tanks in a polishing treatment system.

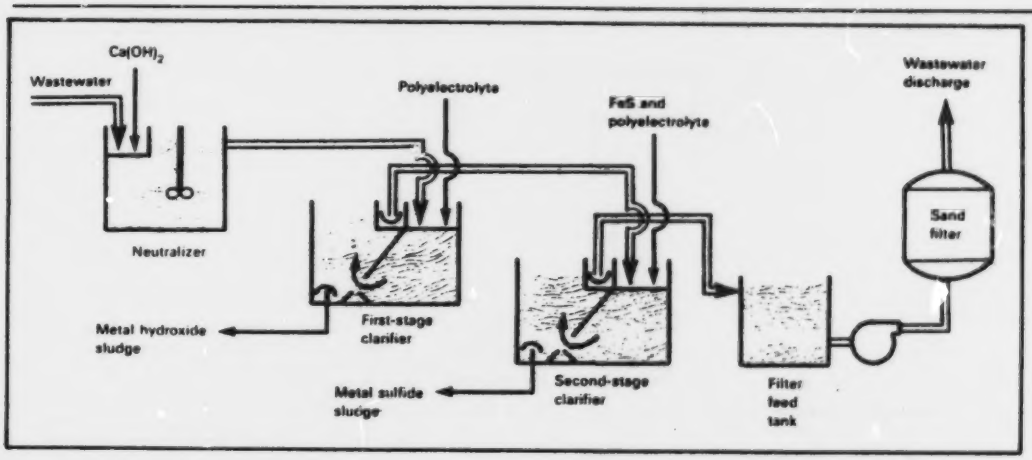


Figure 17.

ISP Polishing System

Identification of the optimum system—polishing sulfide precipitation or treatment of the total metal load—requires determining whether the operating cost savings of the polishing system offset the additional cost of a second mixer/clarifier and polyelectrolyte feeder.

Table 7.

Plant A Discharge Permit Requirements

Item	Discharge limits[a]			
	Mass (lb/d)		Concentration (ppm)	
	Average[b]	Maximum[c]	Average[b]	Maximum[c]
Suspended solids	35.3	53.0	NA[d]	NA[d]
Total copper	0.89	1.77	1.0	1.5
Total nickel	0.89	1.77	1.0	1.5
Total chromium	0.89	1.77	1.0	1.5
Hexavalent chromium	0.089	0.177	0.05	0.10

[a]Required pH level is between 6.0 and 9.5.

[b]Monthly average of daily 24-hour composite samples.

[c]Highest daily 24-hour composite in the month.

[d]Not applicable.

ISP System Performance

Three plants currently use the Sulfex™ system to remove heavy metals from wastewater discharge. All three systems were placed in plating shops where no wastewater treatment systems existed. Two of the plants (Plants A and B) treat the total metal load with FeS, whereas the third (Plant C) employs ISP as a polishing step after hydroxide precipitation/clarification.

Plant A performs copper, nickel, and chromium plating (both electroplating and electroless plating) of plastic components. The heavy metals in the wastewater are complexed with a variety of chelating agents. During the pilot evaluation, it was apparent that hydroxide precipitation would not remove the metals to the levels required in the discharge permit (Table 7). After a pilot evaluation showed that ISP could achieve the required discharge limitations, the firm hired a vendor to design a treatment system using this technology. The vendor guaranteed that the system would meet all discharge regulations.

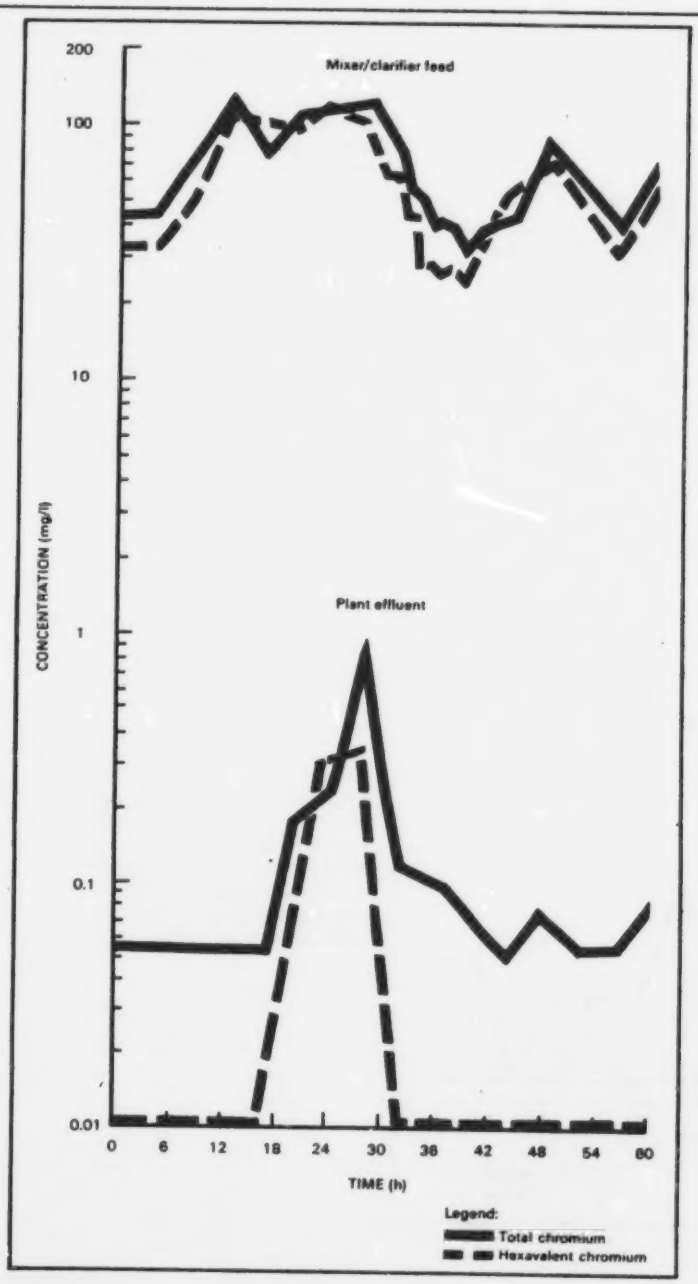


Figure 18.

Plant A's Performance in Removing Chromium

The system was designed to treat 40 gal/min (151 l/min) of wastewater and is essentially identical to the system shown in Figure 13. The performance of the system in removing copper, nickel, total chromium, and hexavalent chromium (Cr^{+6}) during a 60-hour test period is shown in Figures 18 and 19. Figure 20 shows the corresponding sample point locations.

The performance in chromium removal shows a deviation from normal removal efficiency between hours 16 and 28 that corresponds to an increase in the level of hexavalent chromium in the mixer/clarifier feed during hours 8 through 28. By comparing the stoichiometric FeS demand with the quantity supplied and the associated mixer/clarifier removal efficiency (Figure 21), it is obvious that the FeS feed was not increased sufficiently to compensate for the increased demand. Consequently, the level of unreacted FeS in the sludge blanket was gradually depleted, and at hour 16 insufficient FeS was present in the blanket to achieve the normal high level of removal. This condition persisted until hour 28. The FeS stored in the sludge blanket maintained the high removal efficiency between hours 8 and 16, despite a low FeS reagent supply/demand ratio.

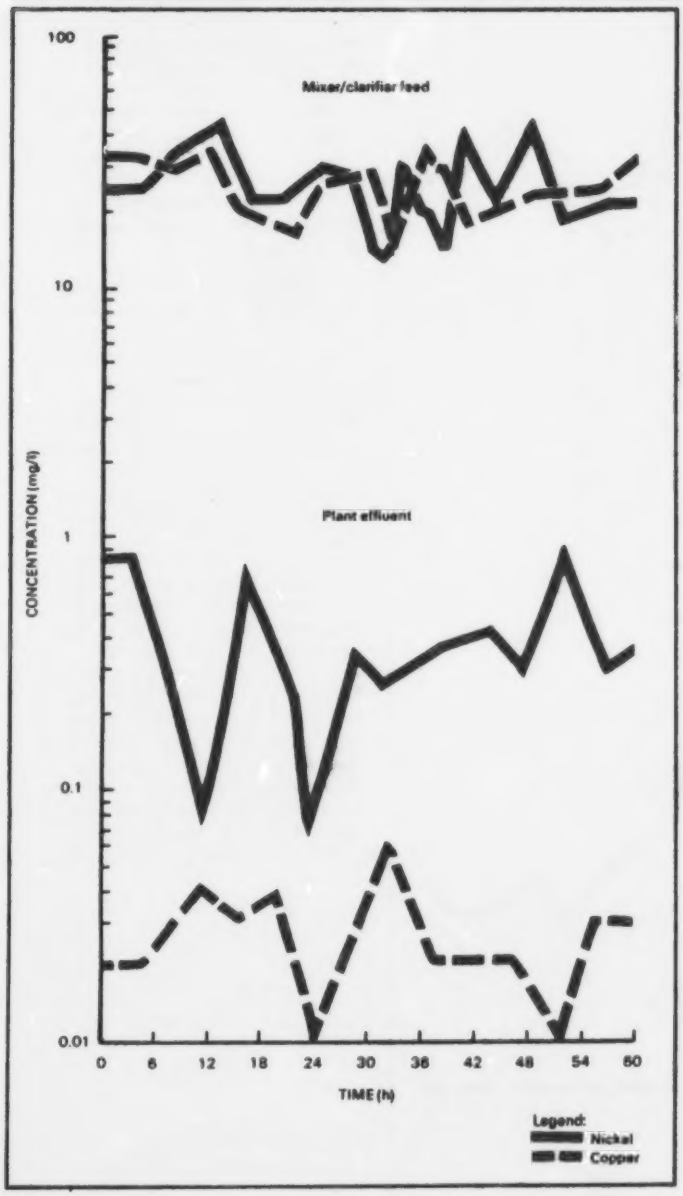


Figure 19.

Plant A's Performance in Removing Nickel and Copper

Figure 21 shows that optimum removal efficiency for the chromium is achieved with an FeS dosage of approximately 3 times the stoichiometric demand. Stoichiometric demand was determined by laboratory analysis of mixer/clarifier feed samples. The removal efficiencies for nickel and copper were relatively constant and showed no discernible trends over the dosage ratios encountered during the test period.

Based on an FeS dosage rate of 3 times the stoichiometric demand and the observed consumption of other treatment reagents, the cost of treatment chemicals and sludge generation factors for the ISP system at this facility are shown in Table 8.

Plant B manufactures carburetors for the automotive industry. Wastewater from the metal finishing portion of the process contains varying quantities of chromium (hexavalent and trivalent), zinc, and iron in solution with phosphates, organic chelating agents, and assorted chemicals used in the process baths. The wastewater is treated in a neutralization/ISP/clarification treatment sequence similar to that shown in Figure 13. Then it is mixed with the remainder of the wastewater from the plant and is discharged to the city wastewater treatment system.

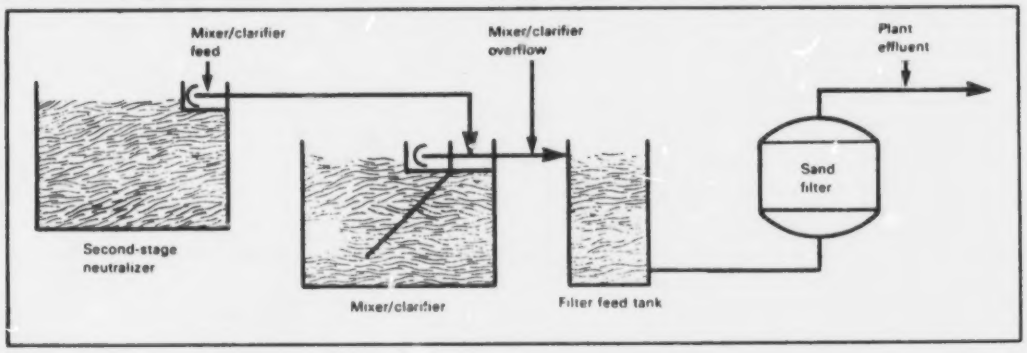
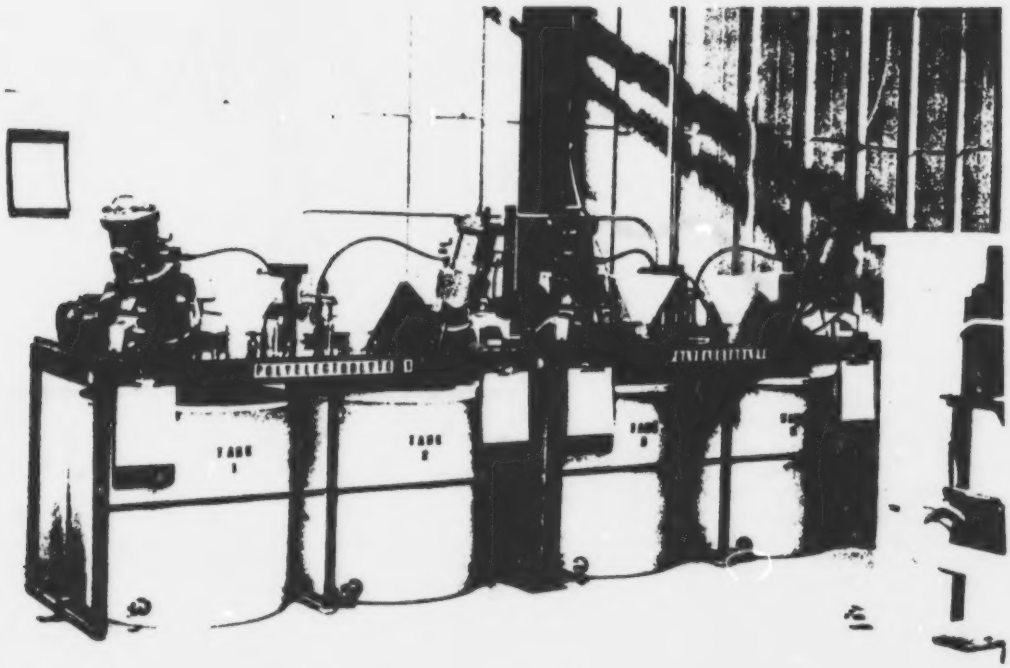


Figure 20.

Sample Points



Anionic and cationic polymer feed systems

The wastewater flow rate to the system averaged 20 gal/min (76 l/min). The performance of the system during a 2-day test in removing chromium (total and hexavalent), zinc, and iron from the wastewater is shown in Figures 22 and 23. The same sample location designation used in Figure 20 applies. Figure 24 defines the ratio of FeS supply to stoichiometric demand for the same test period. The ratio varied from 3 to 5 times the stoichiometric demand during the test period. The quality of the effluent, which contained lower pollutant levels than those specified in both local and State guidelines, showed no discernible trends within this range of reagent supply/demand ratios.

The cost of treatment chemicals and the sludge generation factors for the ISP system at this facility are shown in Table 8. Chemical costs were approximately $1.77/1,000 gal of wastewater treated.

Plant C uses the ISP process to polish the clarified overflow from a conventional hydroxide precipitation/clarification treatment sequence. The system treats approximately 15 to 18 gal/min (57 to 68 l/min) of wastewater from a programed, barrel-dip, zinc-phosphatizing plating line. The system is similar to the one shown in Figure 17; it has a second mixer/clarifier and polymer feed system, installed after the second-stage neutralizer, to remove the precipitated metal hydroxides and phosphates. Dual polyelectrolyte feed systems are needed because an anionic polymer is used in the hydroxide removal clarifier and a cationic polymer is used to enhance the settling of the precipitated metal sulfides. The sludge production and FeS consumption are reduced considerably compared with a system

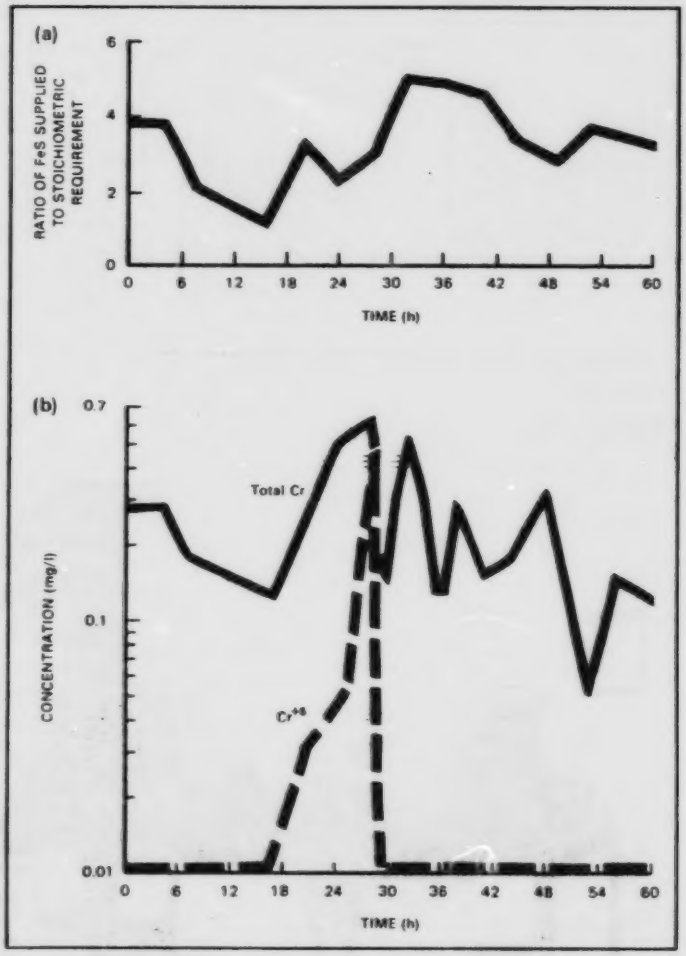


Figure 21.

Impact of FeS Supply/Demand Ratio on Reduction of Hexavalent Chromium at Plant A: (a) FeS Supply vs. Stoichiometric Requirement and (b) Mixer/Clarifier Overflow Chromium Concentration

Table 8.

Wastewater Treatment Process Characteristics for Plants A, B, and C[a]

Characteristic	Value		
	Plant A	Plant B	Plant C
Wastewater:			
Average flow rate (gal/min)	39	21	16
pH:			
Feed	2.0-4.0	4.5-6.0	2.5-3.0
Effluent	9.0-10.0	8.5-9.5	7.5-8.5
Average feed concentration (ppm):			
Nickel	31	NA	NA
Copper	28	NA	NA
Hexavalent chromium	76	27	0.07
Total chromium	88	39	8
Zinc	NA	48	24
Iron	NA	1.4	127
Phosphorus	NA	NA	289
Treatment chemicals:			
Lime:[b]			
lb/h	8.8	2.0	8.1
$/h	0.28	0.06	0.60
Calcium chloride (for phosphate removal):[b]			
lb/h	NA	NA	17.0
$/h	NA	NA	1.70
Cationic polymer:[b]			
lb/h	0.1	0.17	0.02
$/h	0.14	0.23	0.04
Anionic polymer:[b]			
lb/h	NA	NA	0.01
$/h	NA	NA	0.03
Ferrous sulfide			
lb/h	12.5[c]	4.5[d]	0.30[b]
$/h	5.37[c]	1.94[d]	0.11[b]
Total chemicals ($/h)	5.78	2.23	2.48
Chemical cost ($/1,000 gal)	2.47	1.77	2.58[e]
Sludge generation factors:			
Dry solids generation:			
lb/h	23.7	7.2	16.4
First stage	NA	NA	16
Second stage	NA	NA	0.4
lb/1,000 gal wastewater	10.1	5.7	17[e]
Underflow volume (gal/h at 0.75% solids)	380	114	262
Filter cake volume (gal/h at 30% solids)	7.9	2.4	5.3

[a]All three plants use an ISP process to remove metals from wastewater, but Plant C uses ISP as a polishing system.

[b]Observed rates.

[c]Based on 3 times the stoichiometric requirement.

[d]Based on 4 times the stoichiometric requirement.

[e]Without the presence of phosphates, treatment cost equals $0.81/1,000 gal, solids generation equals 6.4 lb/1,000 gal.

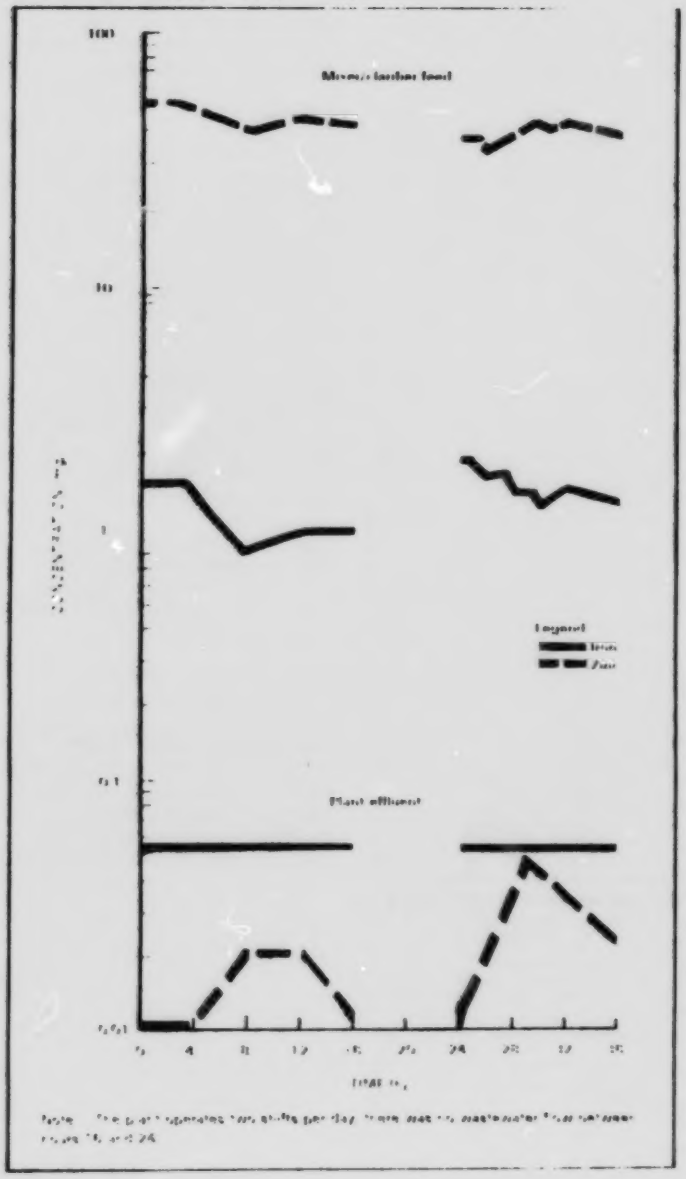
Note —1979 cost basis, NA = not applicable.

treating the total metal load with sulfide precipitation. Less than 5 percent of the waste solids removed from the system are attributed to the sulfide precipitation step.

Table 8 presents the chemical consumption and sludge generation rates for Plant C. Treatment of the phosphates in the wastewater accounts for a large percentage of the treatment cost, and the phosphate solids constitute the bulk of the sludge generated. The chemical cost associated with removal of the heavy metals contained in the wastewater was estimated at $0.81/1,000 gal. Without the presence of phosphates, the solids generation rate would equal 6.4 lb/1,000 gal (0.76 kg/m^3) of wastewater.

Table 9 presents the pollutant concentrations in Plant C's raw waste and effluent discharge and shows the effluent quality required by the discharge permit.

In this polishing application, FeS is fed into the second-stage mixer/clarifier to yield a concentration of approximately 40 ppm in the wastewater. The dosage rates for the insoluble solids systems treating the total metal load for Plants A and B are approximately 640 ppm and 430 ppm, respectively.



Note: The plant operates two shifts per day, from 8:00 to wastewater flow between hours 16 and 24.

Figure 27

Plant B's Performance in Removing Iron and Zinc

Hydroxide System Modifications for ISP

The metal removal efficiency of a hydroxide precipitation system can be improved by incorporating ISP into the system. Sulfide precipitation can be used either to convert the metals to metal sulfides before the clarifier or as a polishing system to precipitate dissolved metals from wastewater after the insoluble metal hydroxides have been removed by clarification.

Equipment Requirements. The key component of an ISP system is the solid/liquid contact chamber where the wastewater is mixed thoroughly with the insoluble sulfide contained in the sludge blanket. Three design criteria must be addressed in specifying the power of equipment:

- Liquid residence time in the mixing zone
- Sludge blanket volume and density
- Mixing efficiency

Figure 28 is a schematic of the mixer/clarifier designed specifically for this application. In the systems currently using ISP, the unit is sized to provide approximately 1 hour of liquid residence time in the mixing zone. Because the mixing zone volume is equal to the solids retention volume, a large inventory of unreacted FeS can be maintained in the unit. The agitator is designed to maintain a dense, fluidized sludge in the mixing zone. Sample ports are located in the different zones of the unit to check the sludge density. The unit also has a timed sludge drawoff valve that can be set to balance the blowdown to the solids accumulation rate automatically.

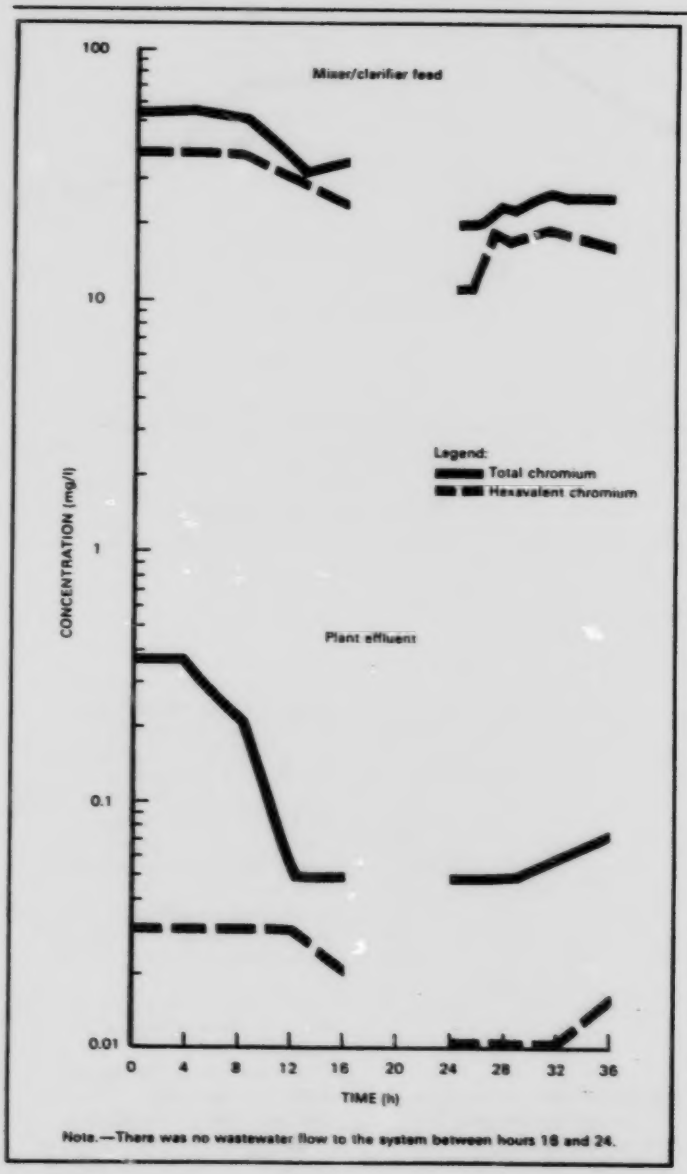


Figure 23.

Plant B's Performance in Removing Chromium

Other elements needed to augment a treatment system with ISP include:

- FeS reagent preparation tanks, reagent storage, and feed pumps
- A reagent feed control system that matches reagent dosage to wastewater flow rate
- A control loop to interrupt the wastewater feed during low-pH conditions

In converting a hydroxide system to use sulfide precipitation, the addition of a polishing filtration system to remove residual suspended solids from the clarifier overflow could significantly reduce effluent metal concentrations. Meeting strict effluent metal discharge limits will require an effluent with low levels of both suspended and dissolved metals.

Treatment System Evaluation. The cost advantages of using ISP as a polishing system must be weighed against the higher equipment costs and space requirements of a second clarifier. It might be more cost effective for plants with small metal loadings to incorporate ISP upstream of the existing clarifier and thus avoid the expense of a second clarifier.

Retrofitting a hydroxide treatment system that already has a flocculation zone to enhance the settling properties of the precipitated metals before clarification can be accomplished simply and with minimum investment. Many existing systems include a flocculation chamber either in a separate vessel or as part of the clarifier itself. As shown in Figure 26, sulfide precipitation can be incorporated

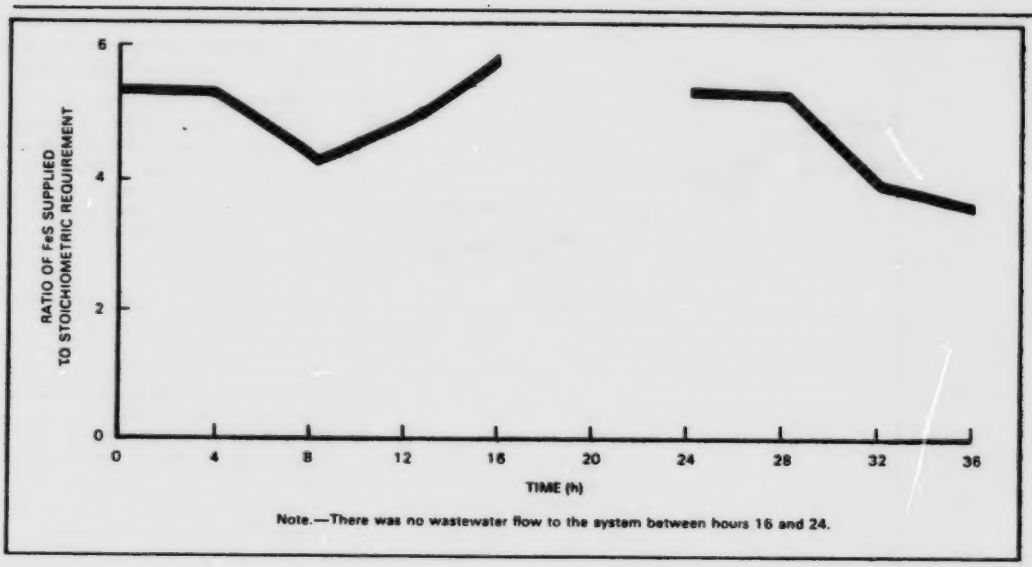


Figure 24.

FeS Supplied vs. Stoichiometric Requirement at Plant B

Table 9.

Influent and Effluent Wastewater Characteristics for ISP Polishing System

Item	Wastewater analysis		
	Influent	Effluent	Permit requirements[a]
pH	2.9	8.5	6.0-9.5
Phosphorus (mg/l)	289	0.3	<1.2
Total suspended solids (mg/l)	320	6	<23
Total chromium (mg/l)	8	<0.10	<0.6
Hexavalent chromium (mg/l)	0.07	<0.02	<0.06
Nickel (mg/l)	0.77	<0.1	<0.6
Zinc (mg/l)	24	0.12	<0.6
Iron (mg/l)	127	0.60	<1.2

[a]Monthly average of daily composite samples.

into this type of treatment system by installing:

- An FeS reagent addition system and feed control system to feed FeS into the flocculation chamber in proportion to the volume of wastewater processed
- A sludge recirculation loop (if not already existing) to recycle solids from the clarifier underflow back to the flocculator
- A low-pH feed interrupt control loop to stop the feed to the flocculator if the pH of this stream falls below the set-point

Pilot tests must be performed to determine if the residence time, agitation, and blanket density in the flocculation chamber are conducive to effective metal removal. Figure 6 defined the different variables for evaluation by pilot testing or jar testing. Deficiencies in the flocculator residence time, mixing efficiency, and the like can be tolerated, although they generally result in increased reagent consumption.

An approach for treatment systems that do not have flocculation zones is either to add a flocculator or to replace the existing clarifier with the mixer/clarifier designed for this application (Figure 25). The most reliable approach to using ISP as a polishing system would be to install a mixer/clarifier downstream of the existing clarifier.

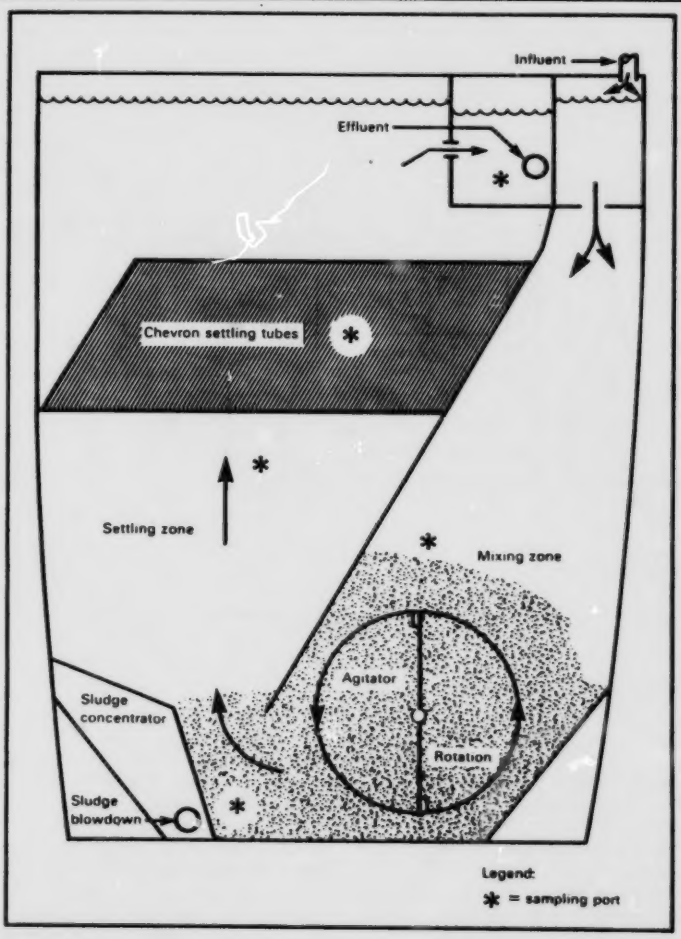


Figure 25.

Cross Section of Mixer/Clarifier

ISP Batch Treatment Systems. Batch treatment systems currently are not demonstrated for ISP. As with continuous treatment systems, batch treatment using ISP would require contact between the wastewater and a dense sludge blanket to achieve maximum metal removal. Consequently, a large volume of solids would be needed for each batch, necessitating storage of the settled sludge after batch treatment. Figure 27 shows a possible configuration of an ISP batch treatment system and the associated treatment sequence. The major process components of the system are:

- Two tanks equipped with mechanical agitation
- A precipitation tank
- Reagent storage and feed systems to add the lime (or caustic), FeS, and polymer

The two agitated tanks alternate as the wastewater collection tank and pretreatment tank. Pretreatment is required to neutralize the acidic wastewater before mixing it with the metal sulfide sludge. A precipitation tank is needed to bring the wastewater into contact with the FeS slurry and to provide storage volume for maintaining an inventory of sludge solids in the system. Gentle agitation is required to suspend the sludge solids during mixing and to promote particle growth of the precipitated solids.

ISP Treatment Costs

Operating Costs. The following costs associated with using ISP are in addition to the operating costs of

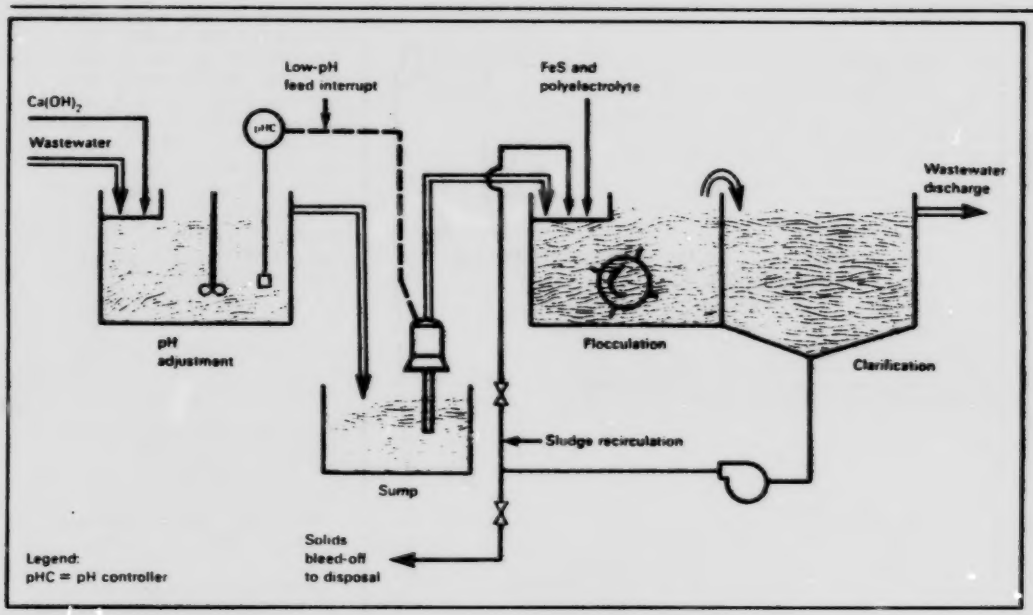


Figure 26.

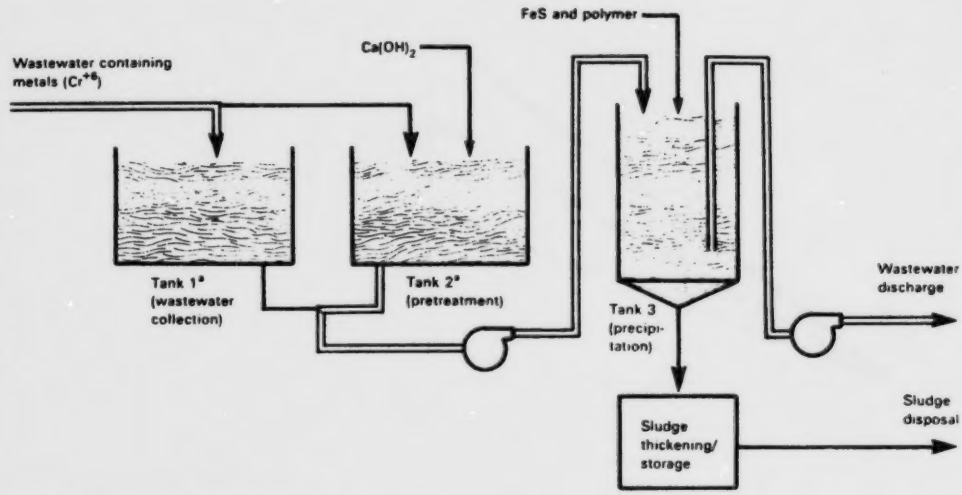
Retrofit of a Hydroxide System With Insoluble Sulfide Treatment

a conventional hydroxide precipitation system:

- Reagent costs for FeS and polyelectrolyte
- Labor cost of additional operational duties described earlier
- Disposal cost of any additional solid waste generated
- Licensing fee charged by the patent holder to use the process

Reagent costs for FeS depend on the quantity of metals to be precipitated (or, in the case of hexavalent chromium, the quantity to be reduced chemically) and the ratio of reagent needed for effective removal to the stoichiometric reagent requirement. Figure 28a shows the FeS consumption rates and reagent cost for various metal concentrations in the wastewater and typical ratios of reagent demand to stoichiometric requirement. The wastewater metal concentration is defined as the metals other than iron that will form sulfides. To compute reagent consumption rates, it was assumed that the metals have a "plus 2" valence and a molecular weight equal to the average molecular weight of copper, nickel, and zinc. Although determination of the optimum dosage ratio requires testing, wastewaters with no heavy metal complexing agents generally require 1.5 to 2 times the stoichiometric reagent requirements, whereas wastewaters containing complexed heavy metals will require 3 to 4 times the stoichiometric reagent dosage. Figure 28b presents the FeS reagent demand and cost for wastewater treatment over a range of hexavalent chromium concentrations.

At the three plants currently operating, labor requirements for the ISP systems varied only slightly. Each plant employed a full-time operator for one shift and required 2 to 6 hours of operator attention on other shifts.



*Tanks 1 and 2 alternate in process function.

Note.—Treatment sequence: When Tank 2 is filled to capacity, incoming wastewater is diverted to Tank 1. The pH of the wastewater in Tank 2 is adjusted to 8.5. A sample is removed from Tank 2 and analyzed by jar test procedure to determine required FeS dosage. The wastewater in Tank 2, along with the required amount of FeS and polymer, is charged into Tank 3. The wastewater/sludge mixture in Tank 3 is agitated for 1 hour. Agitation is stopped and the solids are allowed to settle. A sample of the clarified wastewater is analyzed to check water quality. The wastewater in Tank 3 is decanted and discharged. A portion of the settled sludge is discharged to sludge disposal to maintain a constant sludge inventory.

Figure 27.

Batch Wastewater Treatment Using ISP

The ISP systems generate considerably more sludge in treating a volume of wastewater than the conventional hydroxide precipitation scheme. The additional sludge results from precipitation as hydroxides of the ferrous and ferric ions liberated as the sulfide reagent is consumed and from the excess FeS that is used in treatment. Figure 29 compares the solids generation rates for ISP systems with those for treatment systems using hydroxide precipitation for metal removal and sulfur dioxide (SO_2) for chromium reduction. The graph also shows solid waste disposal charges, assuming the sludge is disposed of at 25 percent solids by weight and at a cost of $0.10/gal. For plants with different sludge disposal cost formulas, the disposal cost can be calculated by multiplying the cost indicated in Figure 29 by the ratio of the actual disposal cost to the assumed rate of $0.10/gal.

Owing to the high cost of sludge disposal—normally from $0.05/gal to $0.20/gal—it is cost effective to invest in mechanical dewatering equipment to reduce the sludge volume. At the three plants currently operating, recessed plate filter presses were installed

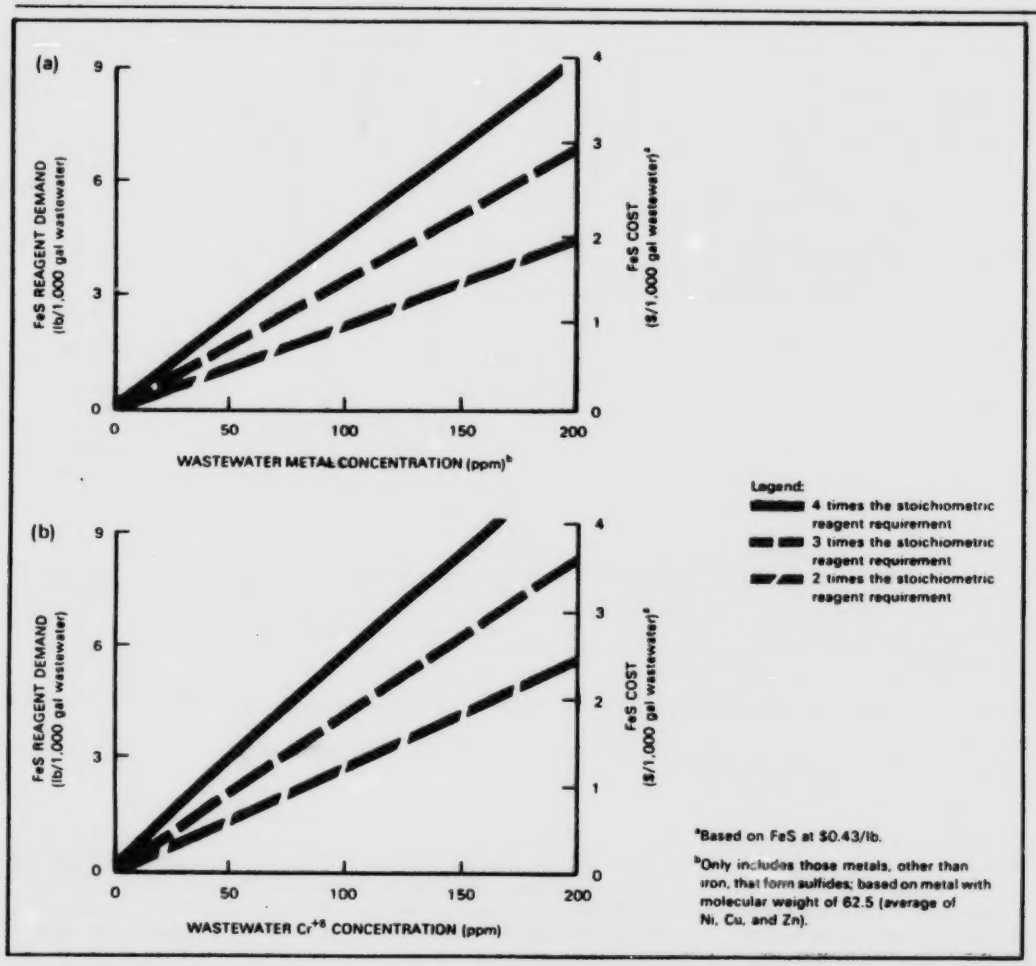


Figure 28.

FeS Consumption and Cost Factors for: (a) Precipitation of Metals and (b) Hexavalent Chromium Reduction

to dewater the sludge before transport to the disposal site. The presses dewatered the underflow from less than 1 percent solids by weight to 25 to 30 percent solids by weight.

Total sludge generation for both hydroxide and sulfide systems will be somewhat higher than the rates shown in Figure 29. The additional solids are caused by the presence of lime solids, suspended solids in the wastewater feed, and insoluble byproducts resulting from neutralization. For treating waste streams to remove heavy metals, the additional solids should be approximately the same for

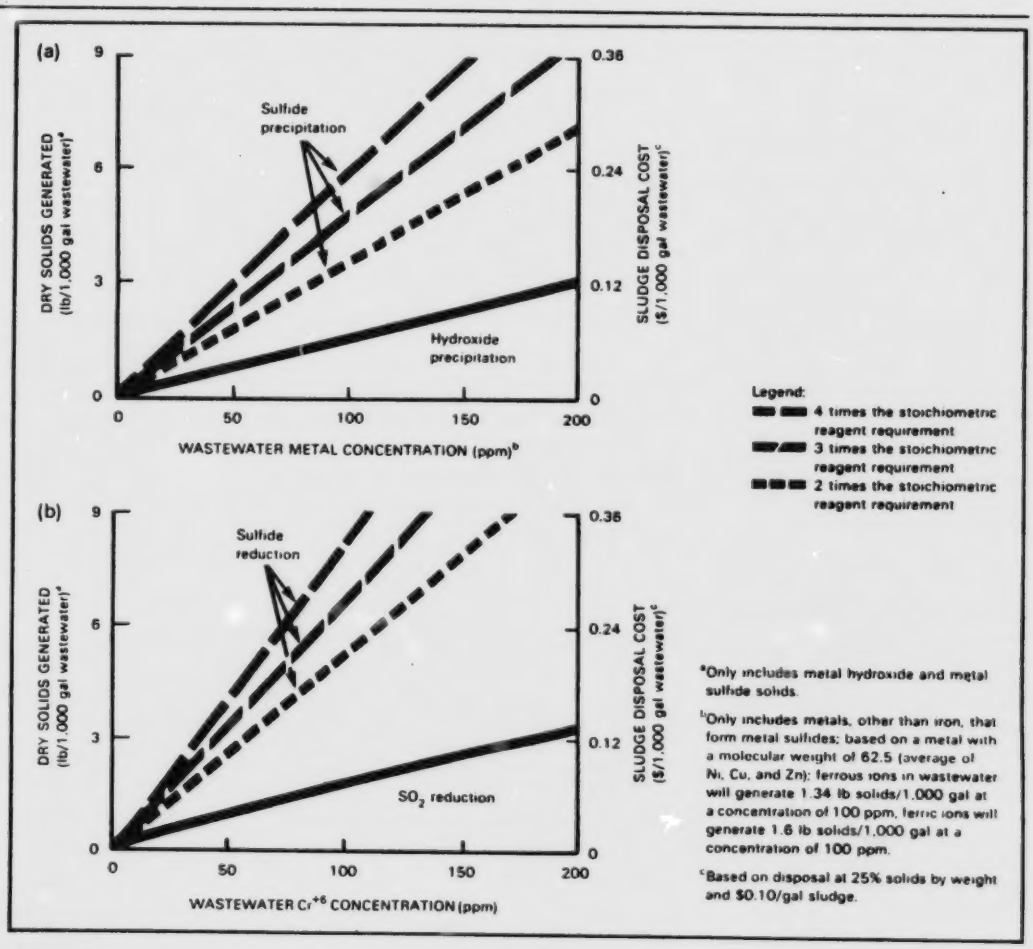


Figure 29.

Sludge Generation Factors for: (a) Precipitation of Metals and (b) Hexavalent Chromium Reduction

insoluble sulfide and hydroxide systems. For chromium reduction, SO_2 reduction systems often require the wastewater to be acidified, and the quantity of alkali for subsequent neutralization is larger than that required with sulfide reduction. Consequently, the additional lime required for neutralization with SO_2 reduction will result in more lime solids in the sludge.

Licensing fees for the use of ISP to treat wastewater are charged annually and are determined by the flow rate of wastewater treated. This fee is small, however, compared with other costs typically associated with wastewater treatment.

Equipment Costs. The actual total installation costs for the three ISP treatment systems described earlier are presented in Table 10. All three systems were installed in plants that had no existing treatment systems. The systems in Plants A and B are similar to the one illustrated in Figure 13. The costs presented also include duplexing of many of the pumps and reagent storage tanks, a control panel, and additional instrumentation not shown on the flow diagram. Plant C is a sulfide polishing system similar to the one shown in Figure 17. The installed cost of this system includes the additional equipment required by a polishing system—a second clarifier (to separate the insoluble compounds resulting from hydroxide neutralization) and a second polyelectrolyte feed system.

Much of the equipment in an ISP system is common to hydroxide systems. Cost data on wastewater treatment equipment for the metal finishing industry are presented in the EPA report, *Economics of Wastewater Treatment Alternatives for the Electroplating Industry.* Converting a hydroxide system to use ISP in many cases will require only the installation of a mixer/clarifier downstream of the existing clarifier and a feed system to meter the FeS and polyelectrolyte into the wastewater.

Table 11 presents the cost (including installation and hardware) of installing the following ISP process

Table 10.

Installation Costs for Three Sulfex™ ISP Treatment Systems

Cost component	ISP system cost ($1,000)		
	Plant A	Plant B	Plant C
Installation costs:			
Process equipment	175	92	NA
Underground tanks	36	48	NA
Shipping and installation	29	22	NA
Additional building space	20	NA	NA
Startup expenses	3	NA	NA
Engineering	NA	17	NA
Other	NA	1	NA
Total	263[a]	180[b]	156[c]
Current installation costs[d]	303	196	169

[a]ISP system design flow = 40 gal/min; installed in September 1977.

[b]ISP polishing system design flow = 35 gal/min; installed in April 1978.

[c]ISP polishing system design flow = 15 gal/min; installed in March 1978.

[d]Costs escalated to March 1979 based on Chemical Engineering Plant Cost Index.

Note.—NA = not available.

Table 11.

Equipment Cost Factors for ISP Treatment System Components

Equipment component	Installed cost ($1,000)
Mixer/clarifier:	
30-gal/min wastewater flow rate	18
60-gal/min wastewater flow rate	22
90-gal/min wastewater flow rate	24
Ferrous sulfide reagent preparation and feed system:	
5-lb/h FeS feed rate[a]	16
10-lb/h FeS feed rate	20
15-lb/h FeS feed rate	24
Polymer feed system	4-6
Control loops:	
Reagent addition system	4-5
Low-pH feed interruption control	1.5-2.5
Suspended solids polishing filters:	
30-gal/min wastewater flow rate	24
60-gal/min wastewater flow rate	33
90-gal/min wastewater flow rate	41

[a]For lower feed rates, less automated systems are available for approximately $12,000.

Note.—March 1979 cost basis. Costs are basic installed costs of different components. Engineering and design costs, site preparation, and equipment freight charges are not included.

SOURCE: Equipment vendors.

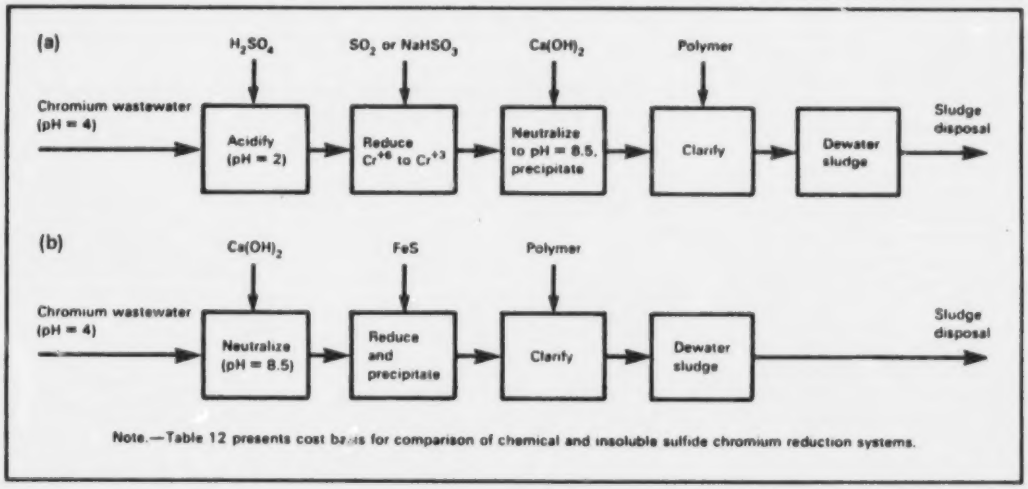


Figure 30.

Comparison of Chromium Reduction Treatment Sequences: (a) Chemical and (b) Insoluble Sulfide

equipment components in an existing treatment system:

- Mixer/clarifier
- FeS reagent preparation and feed system
- Polymer feed system
- Control loops
- Suspended solids polishing filters

The installed costs presented for a mixer/clarifier are for a preassembled, skid-mounted component requiring only piping and electrical connections for installation. The FeS reagent preparation and feed system includes two FeS feed tanks with low-level alarms, two reagent pumps, a mixing tank, and a transfer pump; the costs are for skid-mounted, preassembled units, constructed of carbon steel (see Figure 16).

The costs presented for the polymer feed system are based on a system with two plastic polymer feed tanks and two positive displacement pumps with adjustable stroke. The skid-mounted, preassembled components are equipped with a low-level alarm and dilution water-mixing apparatus. Costs are given for two control loops: a reagent addition control system with a magnetic flow meter and flow counter (to match the addition of FeS and polymer with wastewater volumetric throughput) and a low-pH feed interruption control. The costs for suspended solids polishing filters are for dual mixed-media filters, skid mounted and sized so that one filter can process the maximum flow during backwash. The filters are equipped with a blower for low pressure air scouring, a backwash storage tank, and a pump to bleed the wash back into the system.

Cost Comparison of Conventional Chemical Reduction and ISP Chromium Reduction. Replacing a conventional chromium reduction system with reduction by FeS can be advantageous. In some cases, an operating cost benefit will result. Another advantage of reducing chromium with FeS is that the hexavalent chromium wastewater does not need to be segregated for individual treatment; it can be treated in the common neutralization/precipitation treatment sequence. Figure 30 defines typical treatment sequences for reduction of chromium by chemical means and using FeS. The FeS treatment

process eliminates the need to lower and raise the pH of the wastewater and results in a significant saving in acid and alkali reagent. Table 12 presents treatment and sludge disposal costs for the two chromium reduction systems shown in Figure 30. The chemical consumption factors assume that lime consumption is twice the stoichiometric amount required to neutralize the wastewater and precipitate the dissolved metals. The excess lime is needed to overcome buffering normally encountered when neutralizing waste streams. It is further assumed that lime solids equal to 50 percent of the mass of lime used in neutralization are present in the sludge. These lime solids result from precipitation of insoluble byproducts in the neutralization reaction as well as from the tendency for some portion of the lime used not to dissolve and add to the sludge volume. Consequently, the lime required in the chemical reduction treatment sequence to raise the pH from 2 to 8 results in considerable sludge generation.

Figure 31 compares the cost of treatment chemicals and sludge disposal for the two chromium reduction systems shown in Figure 30 over a range of hexavalent chromium concentrations in the wastewater. A cost savings can be realized for FeS reduction compared with conventional chemical reduction. For wastewaters requiring twice the stoichiometric FeS dosage, a treatment cost advantage exists over treatment of wastewater containing less than 50 ppm Cr^{+6} by SO_2 reduction and that containing less than 100 ppm Cr^{+6} by $NaHSO_3$ reduction. For FeS reduction systems requiring twice the stoichiometric dosage rate, a savings in solid waste disposal costs also would be realized for treatment of wastewater containing less than 150 ppm Cr^{+6}. At higher FeS dosage requirements, such as 4 times the stoichiometric demand, chromium reduction using FeS is more economical for treatment of dilute chromium waste streams.

It is important to point out that the preceding comparisons are based on typical operating conditions and reagent costs; a comparative analysis for a specific plant should use actual operating data (e.g., reagent consumption and sludge generation).

Table 12.

Cost Basis for Comparison of Chemical and Insoluble Sulfide Chromium Reduction Treatment Systems Shown in Figure 30

Parameter	Cost[a]			
	Treatment[b]		Sludge disposal[c]	
	$/lb Cr^{+6}	$/1,000 gal wastewater	$/lb Cr^{+6}	$/1,000 gal wastewater
Chemical reduction:				
Sulfur dioxide	0.43	0.57	0.16	0.12
Sodium bisulfite	0.82	0.68	0.16	0.12
Insoluble sulfide reduction:				
Ferrous sulfide at dosage equal to 2 times stoichiometric requirement	1.58	0.03	0.21	0.01
Ferrous sulfide at dosage equal to 4 times stoichiometric requirement	3.12	0.03	0.33	0.01

[a]Total treatment cost is based on both mass of chromium reduced and volume of wastewater treated.

[b]Based on lime at $0.035/lb, sulfur dioxide at $0.15/lb, sodium bisulfite at $0.20/lb, sulfuric acid at $0.05/lb, and ferrous sulfide at $0.43/lb.

[c]Based on disposal at 25 percent solids by weight at a cost of $0.10/gal sludge.

Note.—1979 cost basis. Sulfur dioxide and sodium bisulfite consumption is equal to 2 times the stoichiometric requirement at a hexavalent chromium (Cr^{+6}) concentration of 50 ppm. Lime consumption is equal to 2 times the stoichiometric requirement for unbuffered waste streams. Lime solids are 50 percent of lime dosage and contribute to sludge volume.

Cost Comparison of ISP Polishing and Total Metal Treatment. Converting all metals in a waste stream to metal sulfides via sulfide precipitation uses considerable FeS and results in a large volume of waste solids. Separation of the precipitated metal hydroxides from the wastewater before polishing with sulfide precipitation can reduce both reagent consumption and solid waste generation. In a polishing application, the FeS reagent demand is a function of the dissolved metal concentration in the wastewater after hydroxide precipitation/clarification. Conversion of a sulfide precipitation system

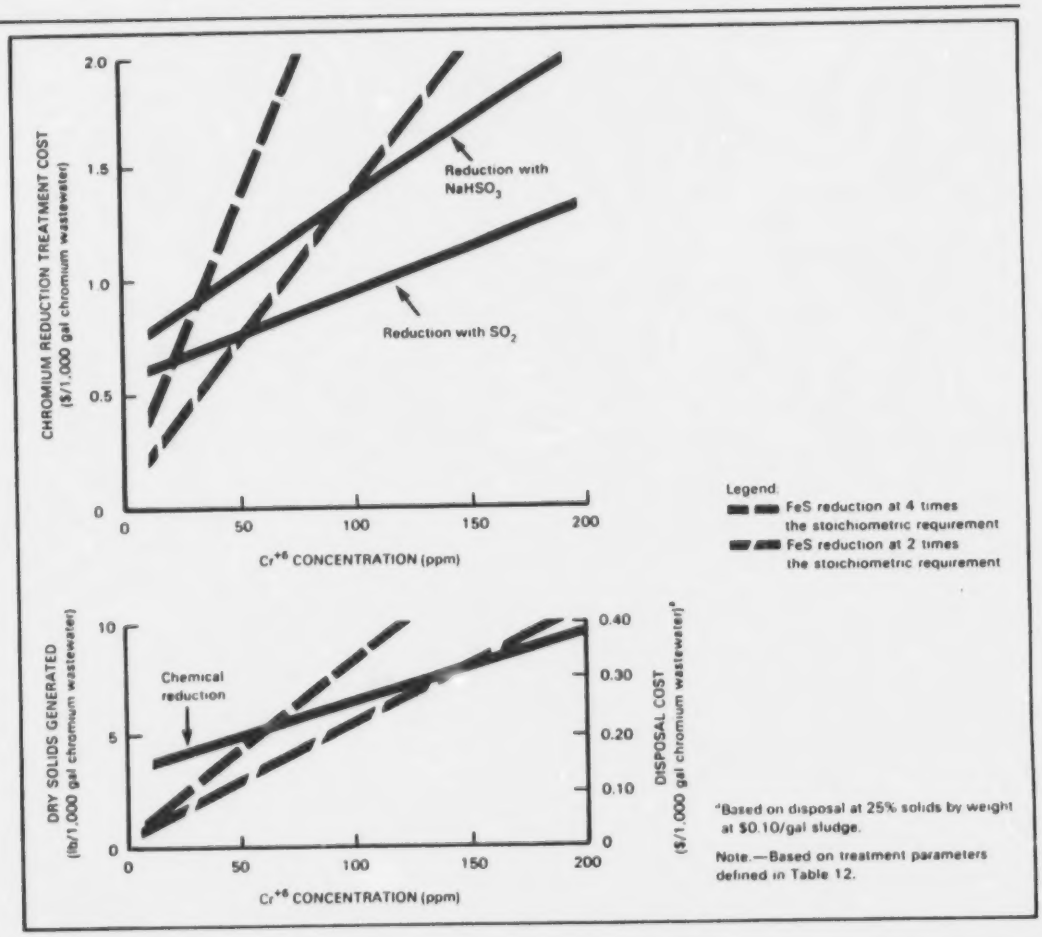


Figure 31.

Costs of Treatment Chemicals and Sludge Disposal for Chemical and Insoluble Sulfide Chromium Reduction

to a polishing system requires installation of a second clarifier and polyelectrolyte feed system to separate the precipitated metal hydroxides from the neutralized wastewater before adding the sulfide reagent.

The reagent consumption and solid waste generation factors associated with treatment of the total metal load were presented in Figure 28. To estimate reagent requirements for a sulfide polishing system, it is necessary to determine the concentration of the metals in the wastewater after hydroxide neutralization/precipitation/clarification. Reagent consumption ranges between 1.5 and 4 times the stoichiometric demand for polishing systems. Compared with the reagent consumption factors presented in Figure 28, the sulfide precipitation polishing system at Plant C required an FeS dosage rate of 40 ppm in the wastewater. Note, however, that this system did not have a significant level

Table 13.

Potential Benefits for Use of ISP Polishing System at Plant A

Item	Value	
Wastewater characteristics:		
Average flow rate (gal/min)	39	
pH:		
Feed	2-4	
Effluent	9-10	
Average feed concentration (ppm):		
Nickel	31	
Copper	28	
Hexavalent chromium	76	
Total chromium	88	
	Current system	Polishing system
Treatment chemical costs ($/h):		
Lime[a]	0.28	0.28
Polyelectrolyte[b]	0.42	0.35
Ferrous sulfide[c]	5.38	3.57
Total	6.08	4.20
Cost savings	NA	1.88
Sludge generation factors:		
Dry solids generation (lb/h):		
First stage	NA	6.2
Second stage	NA	13.1
Total	23.6	19.3
Sludge cake volume (gal/h at 30% solids)	7.9	6.4
Disposal cost at $0.19/gal sludge ($/h)	1.50	1.22
Disposal cost savings ($/h)	NA	0.28
Net savings: treatment chemical cost savings plus disposal cost savings ($/h)	NA	2.16
Annual savings based on 6,000-h/yr operation ($/yr)	NA	13,000

[a]Observed rates.

[b]Design rate.

[c]Based on 3 times the stoichiometric requirement.

Note —1979 cost basis. NA = not applicable.

of hexavalent chromium in the wastewater; hexavalent chromium is not removed by hydroxide precipitation, and reagent demand for chromium reduction will be the same for sulfide polishing or sulfide precipitation systems.

Plant A uses ISP for total treatment of the metals in the wastewater. Table 13 presents the costs of wastewater treatment using ISP as a polishing step compared with its use to precipitate the total metal load at Plant A. The major cost saving results from reduced FeS consumption; the required FeS dosage is reduced by separation of precipitated metal hydroxides before the addition of the sulfide reagent.

Based on the savings indicated in Table 13, a profitability analysis of the investment required to convert to a polishing system is presented in Table 14. The $26,000 investment required for the conversion would have an average

Table 14.

Economics of Converting Plant A ISP Treatment System to ISP Polishing System Operating 6,000 h/yr

Item	Value
Installation costs ($):	
Equipment:	
40-gal/min mixer/clarifier	18,000
Polyelectrolyte feeder	5,000
Total equipment installation	23,000
Additional installation: estimated freight, site preparation, and miscellaneous	3,000
Total installation costs	26,000
Additional annual operating costs ($/yr):	
Labor (100 h/yr at $8/h)	800
Supervision	0
Maintenance (6% of investment)	1,600
General plant overhead	800
Utilities:	
Electricity	200
Water (polymer feeder)	200
Total operating costs	3,600
Annual fixed costs ($/yr):	
Depreciation (10% of investment)	2,600
Taxes and insurance (1% of investment)	260
Total fixed costs	2,860
Total operating and fixed costs ($/yr)	6,460
Annual savings ($/yr):	
Chemicals	11,280
Sludge disposal	1,680
Total annual savings	12,960
Net savings: annual savings minus operating and fixed costs ($/yr)	6,510
Net savings after taxes, 48% tax rate ($/yr)	3,380
After-tax average return on investment (%)	13.0
Cash flow from investment: net savings after taxes plus depreciation	5,980
Payback period: total investment/cash flow (yr)	4.3

Note.—1979 cost basis.

after-tax return on investment of 13 percent.

The costs of FeS reagent and solid waste disposal for ISP systems and sulfide polishing systems are compared further in Figure 32 for each 1,000 gal (3,785 l) of wastewater treated at various metal concentrations. The solid waste disposal cost estimate assumed disposal of the sludge at 25 percent solids by weight at a cost of $0.10/gal of waste and that both sludges would dewater to the same level. The FeS reagent cost for the polishing system was derived from a required FeS dosage rate of 40 mg/l of wastewater. Figure 32 presents the difference in cost, rather than total treatment costs, of sulfide reagent and solid waste disposal for sulfide precipitation and sulfide polishing systems. Other costs associated with treatment should be similar for both systems.

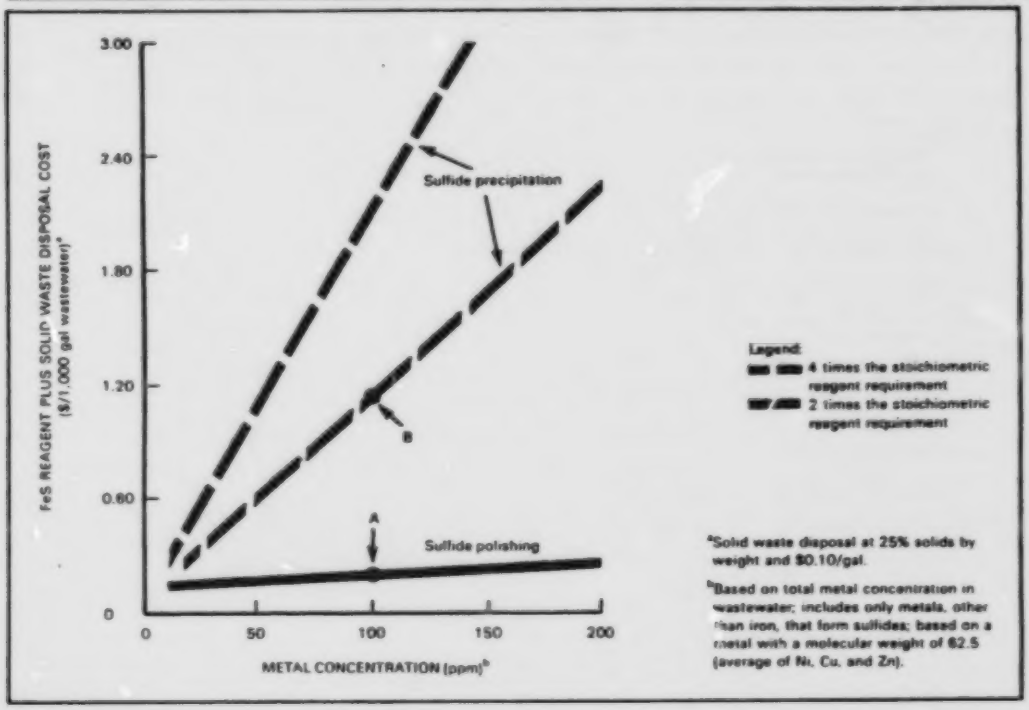


Figure 32.

Treatment Cost of ISP vs. Insoluble Sulfide Polishing

A polishing system can achieve significant savings at higher wastewater metal concentrations. As an example, Figure 32 reveals that a system treating 3,000 gal/h (11,340 l/h) with a metal concentration of 100 ppm and requiring twice the stoichiometric amount of FeS would save $2.80/h—(B minus A) × 3,000 gal/h. At the same flow rate and metal concentration, the savings would be $5.70/h if the wastewater required 4 times the stoichiometric amount of FeS.

Using the savings shown in Figure 32, Figure 33 presents the return on investment for installing the additional treatment hardware needed for a polishing system over a range of metal concentrations and wastewater flow rates.

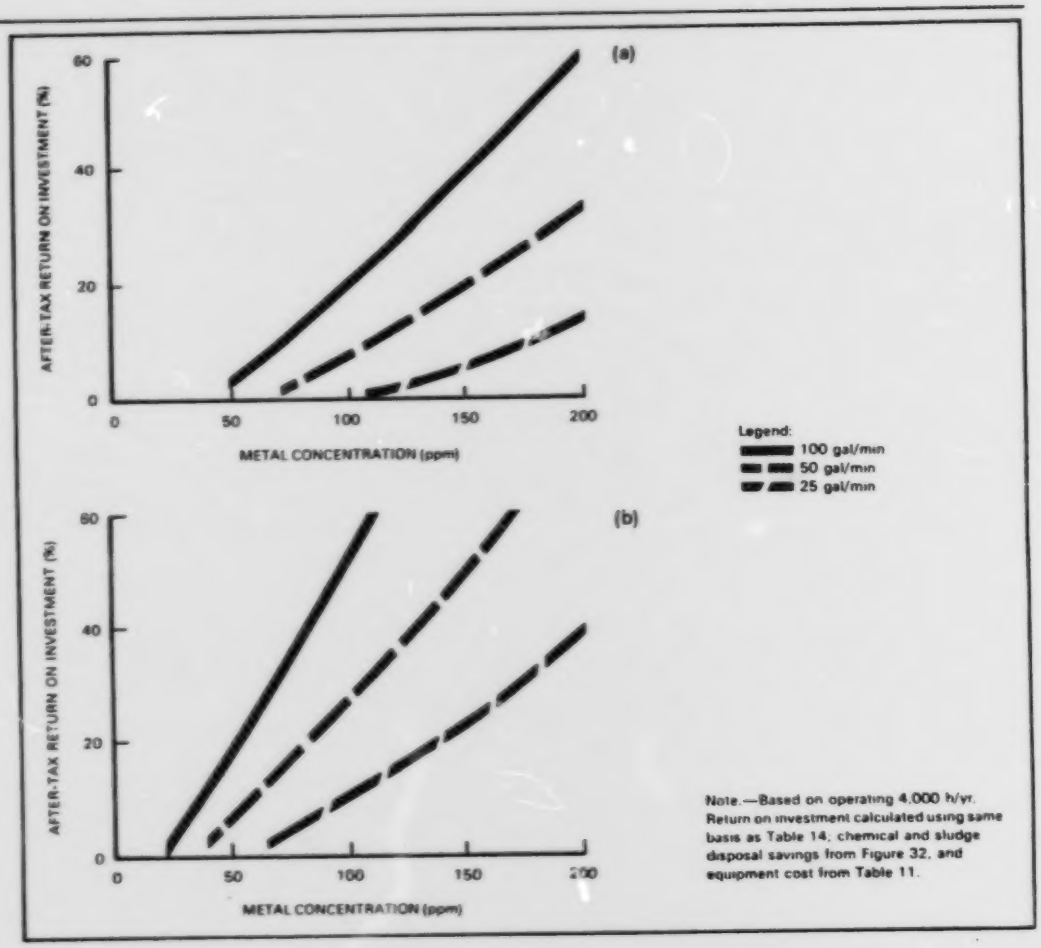


Figure 33.

Return on Investment of Additional Capital Required for Insoluble Sulfide Polishing System: (a) Treatment Requiring Two Times the Stoichiometric FeS Requirement and (b) Treatment Requiring Four Times the Stoichiometric FeS Requirement

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Dissolved Heavy-Metal Removal by Insoluble Starch Xanthate (ISX)

Case-history studies demonstrate that very low residual-metal concentrations can be achieved in the treated effluents.

R. E. Wing, U.S. Department of Agriculture, Peoria, Ill. 61604

ISX (insoluble starch xanthate), one of the simplest, most effective ways to reduce heavy metals in industrial wastewater, was originally developed at the U.S. Department of Agriculture, Northern Regional Research Center, Peoria, Illinois [1-7], under a grant from the Environmental Protection Agency. After internal ISX product research and development, Pollution Technology Systems of Garland, Texas announced formula changes that allow for mass-production capabilities, optimum heavy-metal uptake capacity, and the solution to shelf-life stability problems.

In January of 1980, ISX was introduced by Pollution Technology Systems as a commercially available product. ISX is allowing several industrial users to meet their present and future Public Owned Treatment Works (POTW), or Direct Discharge Statutory Water Quality Heavy Metal Limitations.

ISX offers industry a low-cost product requiring minimal capital investment for application of the treatment of industrial process and wastewater effluents. It is a highly cost-competitive product when compared to other known methods for final polish of process or effluent discharge water containing less than 10 mg/liter of heavy-metal ion contaminants in singular or complexed form.

ISX is a cereal grain-based product that is chemically cross-linked to make it insoluble in water and then xanthated to form an anionic polymer. When added to spent industrial process water containing dissolved heavy-metal cations, ISX exchanges sodium and magnesium ions upon contact for the heavy-metal cations.

Several case-history reports will follow, to show some of the ways ISX is being used to successfully remove toxic heavy metals from industrial process waters, thus allowing these industries to achieve the proposed Best Available Technology (BAT) and Best Practical Technology (BPT) discharge limits [8-9].

CASE HISTORY I

In 1980-1981, a large southeastern Company found it necessary to upgrade their waste-treatment plant in order to maintain compliance with their water quality-based direct discharge permit for heavy metals. (Table 1 defines the Company's operations.)

All process wastewaters are segregated in the manufacturing facility, then flow 400 meters to the segregated holding basins at the waste-treatment facility (Figure 1). Cyanide destruction occurs at pH = 10.5 with chlorine. After an approximate 90-minute contact time, the pH is lowered to 9.0 with additional chlorine to complete the destruction of cyanate to carbon dioxide and nitrogen.

Chromium (VI) is reduced to chromium (III) by the addition of sulfuric acid and SO_2. The reduction takes place at

TABLE 1. MANUFACTURING OPERATIONS

1. Printed circuit board fabrication
2. Aluminum and zinc die casting
3. Zinc plating
4. Chromium (VI) plating surface preparation
5. Copper-tin plating
6. Plastic injection molding
7. Chemical polishing and cleaning
8. Precious metal plating

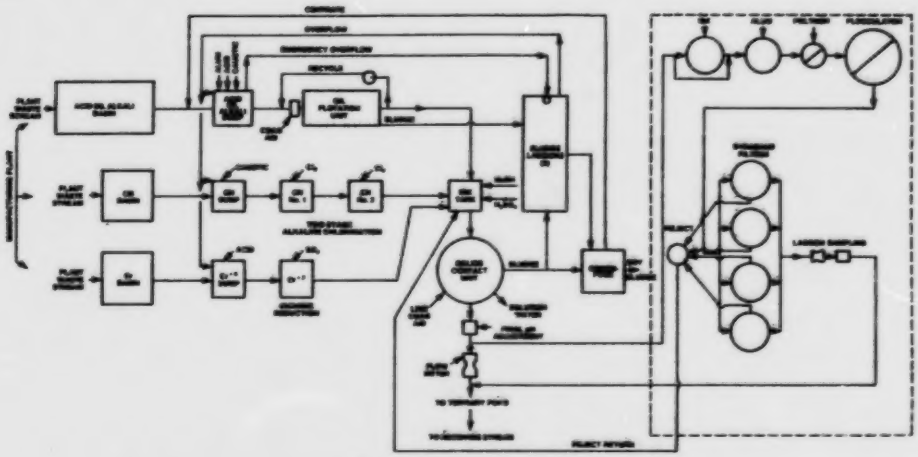

Figure 1. Waste-treatment facility.

pH 2.5 with a contact time of approximately 90 minutes. The alkaline/acid/oil waste stream is initially treated with alum to remove emulsified oil in a dissolved-air flotation (DAF) unit. All wastewaters from the three holding basins flow to the mix tank after initial treatment. The average initial copper concentration is 30-40 mg/liter unless plating-tank dumps are made, which will increase the copper and other metal concentrations from 100 mg/liter to as high as 1,000 mg/liter. The initial pH of around 6.0 is adjusted to 9.5-10 with caustic (25%) in the mix tank (40,000 liter). The wastewater then flows to the solids contact unit (300,000 liter lamella clarifier). Before the waste-treatment plant was upgraded in 1981, lime (227 kg/day) and an anionic polymer (3.6 kg/day) were metered into the contact unit to increase the pH and aid in solids formation settling. Now only 45 kg lime is required (pH = 10.5).

As the wastewater (1325 liter/min) leaves the clarifier the pH is adjusted to 7.0-8.0 with sulfuric acid (94%) and the copper concentration ranges from 0.5-5 mg/liter. Before 1981, the wastewater went to a holding pond before discharge to a tertiary pond, then on to a creek. Now, the water flows to the ISX contact tank prior to four continuously backwash sand filters.

ISX (23 kg) is premixed with water (1438 liter) in a 1500 liter tank. ISX (15.8 g/per min or 3 liter/min) is metered into the ISX contact tank. The ISX treated water gravity flows to the alum tank. Initial lab studies showed that alum was needed for better floc formation. However, under actual conditions, the alum addition is not necessary. Therefore, considerably less sludge is generated.

As the wastewater gravity flows to the polymer tank, cationic polymer (1 mg/liter) is added from the polymer premix tank (1.9 kg/1900 liter). The wastewater is pumped to a flocculator tank for conditioning before it flows through the four parallel sand filters.

The wastewater is analyzed every two hours for copper and other metal contact, usually (0.3 mg/liter), as it flows to the holding pond (Figure 2). The backwash from the sand filters is continuously returned to the mix tank and/or the clarifier.

The State discharge limit to the creek is 136 g (average) of any metal per day with a daily maximum of 272 g/day.

PLOT PLAN

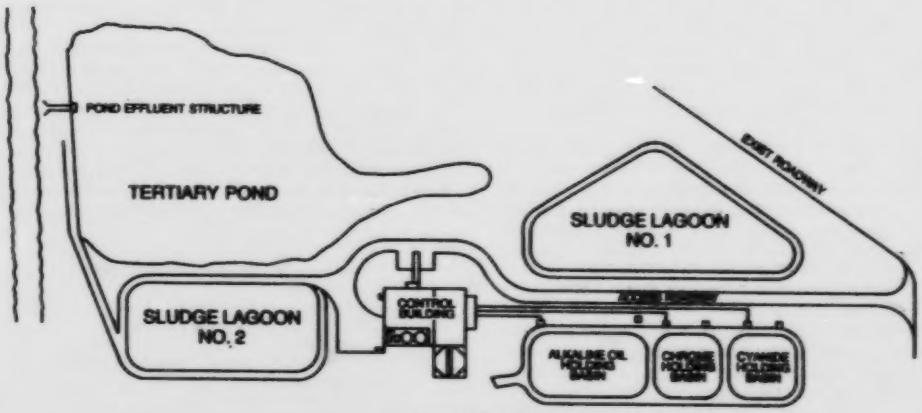

Figure 2. Plot plan.

Daily flows of 1.5 million liter/day with metal concentrations of approximately 0.08 mg/liter allow the company to meet its applicable discharge limits.

The sludge from the clarifier goes to one of two sludge lagoons. Periodically, it is pumped to the centrifuge following treatment with cationic and anionic polymer, and dewatered to 15% solids. The sludge is firm to the touch and is hauled to a Class 1 landfill. Company investigations are presently underway to delist the sludge.

Table 2 shows capital-cost information.

TABLE 2. CAPITAL-COST DATA

Total waste treatment plant	$2,500,000
1981 2.6 × 10⁶ liter/day capacity increase (Includes engineering, construction and capital-equipment installation)	$ 700,000
ISX Related	$ 22,000
2—Tanks—1500 liter	
2—Mixers	
2—Metering pumps	
1—Crane	
1—pH Controller	
Control-panel portion	
Walk-in refrigerator box	
Work paltform	
ISX slurry tank and mixer	
Acid-metering pump	

CASE HISTORY II

A Connecticut electroplating company, doing copper, chrome, and nickel plating, uses ISX on a precoated filter for a final polish. All plating processes have individual dead rinses, followed by two counter-flow rinses (Figure 3). Wastewaters are segregated for cyanide destruct with hypochlorite and chrome reduction with metabisulfite. All rinses, 410 liter/min, flow to a common sump for pH neutralization to 9.0 with caustic. The neutralized rinse water is transferred to combined holding and surge tanks (45,000 liter each), where it is continuously fed through two ISX (34 kg each) precoated filters for removal of metal hydroxides and heavy-metal cations. ISX treated water is returned to holding tanks for 90 percent rinse water recycle (Table 3).

The ISX precoat is changed weekly. The sludge is hauled to a Class 1 landfill. All dead rinses are treated within the system on a weekly schedule. Recycling water has dramatically reduced water and sewage surcharge costs (90 percent). End-product quality control has been improved by the use of more stable rinse-water temperatures and known conditions, independent of climatic and source-water variations.

TABLE 3. TREATED WATER

Metal	Initial Conc.,* mg/liter	ISX Treated Conc., mg liter
Cr^{+3}	0.8	0.02
Cu^{+2}	7.0	0.02
Ni^{+2}	2.5	0.10

* Prior to ISX treatment

CASE HISTORY III

A Texas company uses ISX to remove residual cadmium before wastewater discharge. The rinse water (20 liter/min) is neutralized to pH 9 with caustic. The wastewater is then processed through a clarifier with upflow through an ISX sludge blanket. The treated effluent (Table 4) is discharged to a POTW after suspended solids removal with bag filters. The ISX usage is 6 kg every two weeks.

CASE HISTORY IV

A large Illinois communications equipment manufacturer recently upgraded its waste-treatment facility by installing an ISX metering system (capital cost = $2,000). All

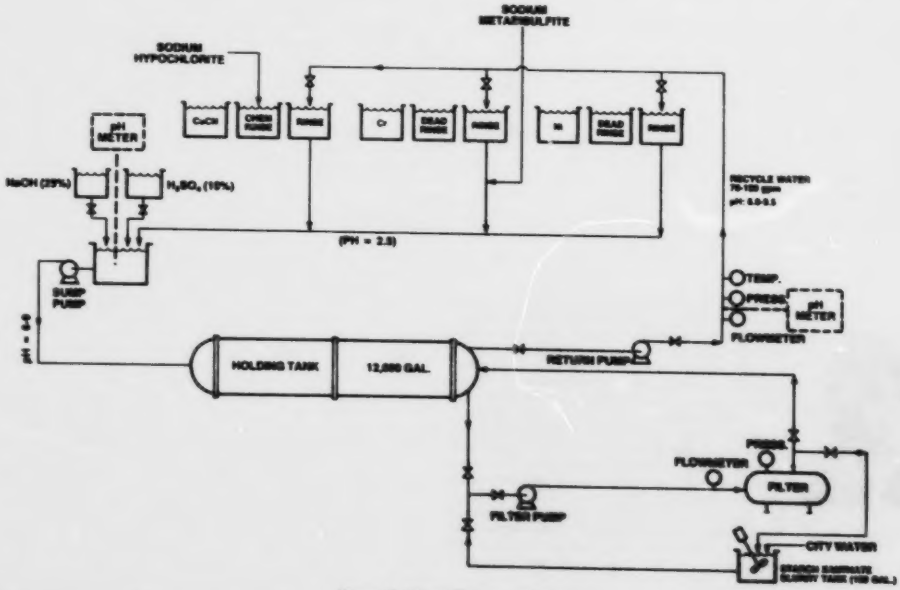

Figure 3. Waste Treatment Diagram.

TABLE 4. TREATED EFFLUENT

Metal	Initial Conc.,* mg/liter	ISX Treated Conc., mg/liter
Cd^{+2}	5.0	0.01

* Prior to ISX treatment

TABLE 5. TREATED EFFLUENT

Contaminant	Initial Conc.,* mg/liter	ISX Treated Conc., mg/liter
Cu^{+2}	6.0	0.5
Pb^{+2}	4.2	0.2
F^-	16.0	1.5

* Prior to ISX treatment

process waters (950 liter/min) are not segregated in the manufacturing plant, so the presence of complexing and chelating agents did prevent heavy-metal discharge limits from being achieved.

Process waters are neutralized to pH 9.5 with caustic, and ISX (154 mg/liter) in a water slurry is metered into the treatment system. A 45-minute contact occurs before solids removal on diatomaceous-earth precoated filters. The treated effluent (Table 5) is discharged to a POTW. Fluoride removal is an added benefit using ISX.

CONCLUSIONS

The cited examples show that ISX can be used in several different ways to achieve very low residual metal concentrations in treated effluent for discharge or reuse. Table 6 shows additional ISX treatment results that are being achieved by a cross-section of industrial categories. In addition to application in metal-finishing wastewaters, ISX is presently being evaluated for vanadium removal in boiler wastewaters from public utilities and as a selective flocculant in the recovery of sulfide-bearing ores.

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TABLE 6. CASE HISTORY RESULTS WITH ISX

Industrial Application	Flow Rate liter/min	ISX mg/liter	Dissolved Heavy-Metal Average Concentration, mg/liter					
			Cu^{+2}	Cd^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}	Cr^{+3}
Aerospace	100	140						
Initial			0.12	0.44	2.7			1.86
ISX Treated			0.05	0.02	0.18			0.23
Brass Works	400	135						
Initial			6.5					
ISX Treated			0.2					
Electronic	1750	30						
Initial			1.25			0.50		
ISX Treated			0.05			0.02		
Printed Circuit Board	750	315						
Initial			6.0			4.2	4.0	
ISX Treated			0.05			0.6	0.01	
Oil Field Equipment	20	60						
Initial				5.0				
ISX Treated				0.01				
Electroplating	500	Pre-coat						
Initial			7.0		2.5			0.8
ISX Treated			0.02		0.10			0.02

Robert E. Wing obtained his B.A. in chemistry from Millikin University and his Ph.D. in chemistry from Southern Illinois University-Carbondale. He joined the Northern Regional Research Center in 1968 as a research chemist and has been working on the development of starch-based products for industrial applications. During the last 10 years he has developed several starch-based products which have found use as heavy metal scavengers in water pollution control. He has also developed several treatment processes effective for heavy metal removal from printed circuit and plating on plastic rinse waters. He is a member of the American Electroplaters Society, American Chemical Society, and Sigma Xi and a part-time instructor at Bradley University. He has authored or coauthored 60 scientific papers and has 6 patents.

Insoluble Starch Xanthate(ISX) has been proven to be one of the simplest and most effective ways to reduce heavy metals in industrial wastewaters. The product was originally developed by the U.S. Department of Agriculture under a grant from the Environmental Protection Agency.

ISX is a cereal grain based product that is chemically cross-linked to make it insoluble in water and then xanthated to form an anionic polymer. When added to industrial process waters containing undesirable levels of dissolved heavy metal cations, ISX exchanges sodium and magnesium ions upon contact for the heavy metal cations. ISX containing the entrapped heavy metal cations is then removed from the treated process water by gravity precipitation or filtration.

The ion exchange efficiency of ISX and its capacity for heavy metal ion exchange is determined from the specific chemical composition of ISX and the related molecular weight and valence of a given heavy metal element or combination of elements. Table 1 identifies the documented heavy metal capacity of ISX under typical conditions.

TABLE 1
ISX CAPACITY RATIOS

HEAVY METAL ION		ISX RATIO
Ag^{+1}	Silver	6.5 : 1
Au^{+1}	Gold	3.5 : 1
Cd^{+2}	Cadmium	12.0 : 1
Co^{+2}	Cobalt	23.0 : 1
Cr^{+3}	Chromium	40.0 : 1
Cu^{+2}	Copper	21.0 : 1
Fe^{+2}	Iron	24.0 : 1
Hg^{+2}	Mercury	7.0 : 1
Mn^{+2}	Manganese	25.0 : 1
Ni^{+2}	Nickel	23.0 : 1
Pb^{+2}	Lead	6.5 : 1
Sn^{+2}	Tin	12.0 : 1
Zn^{+2}	Zinc	21.0 : 1

ISX is effective over a pH range of 3-11 with maximum effectiveness at approximately a pH of 9.

Copper complexes (EDTA and Quadrol as examples) are most effectively removed at a pH of 3. Hexavalent chromium (VI) removal occurs at a pH below 3 and subsequent neutralization to pH 8.

The treated water is clear and free of turbidity with improvements shown in both BOD and COD. With proper application ISX treated water can be recycled for added cost savings.

Results obtained from laboratory bench scale treatment of industrial process waters with ISX are shown in Tables 2 and 3.

TABLE 2
ISX REMOVAL OF INDIVIDUAL HEAVY METAL CATIONS FROM PROCESS WATERS

METAL	INITIAL CONC., mg/liter	ISX, g.	RESIDUAL CONC., mg/liter
Au^{+1}	53.94	0.32	0.016
Au^{+3}	30.00	0.50	0.010
Cd^{+2}	56.20	0.64	0.012
Co^{+2}	29.48	0.64	0.090
Cr^{+3}	26.00	0.64	0.024
Cu^{+2}	31.77	0.32	0.008
Fe^{+2}	27.92	0.32	0.015
Hg^{+2}	100.00	0.64	0.001
Mn^{+2}	27.47	0.64	0.015
Ni^{+2}	29.35	0.64	0.160
Pb^{+2}	103.60	0.64	0.035
Zn^{+2}	32.69	0.32	0.029

Process wastewater solutions (1,000 ml) containing the noted individual heavy metals were treated with the indicated amount of ISX at an initial pH of 3.7. The solutions were thoroughly mixed for positive contact and adjusted to a final pH of 9.0. Following filtration the remaining heavy metal in aqueous solution was determined by atomic absorption analysis.

TABLE 3
ISX REMOVAL OF COMBINED HEAVY METAL CATIONS FROM PROCESS WATERS

METAL	INITIAL CONC., mg/liter	RESIDUAL CONC., mg/liter
Cd^{+2}	5.62	0.001
Co^{+2}	2.95	0.010
Cr^{+3}	2.60	0.026
Cu^{+2}	3.18	0.005
Fe^{+2}	2.79	0.001
Hg^{+2}	10.00	0.0007
Mn^{+2}	2.75	0.010
Ni^{+2}	2.93	0.050
Pb^{+2}	10.36	0.031

A process wastewater solution (1,000 ml) containing the noted mixture of heavy metals was treated with 320 mg of ISX at an initial pH of 4.6. The solution was thoroughly mixed for positive contact and adjusted to a final pH of 8.9. Following filtration the remaining heavy metals in aqueous solution were determined by atomic absorption analysis.

Pollution Technology Systems ISX users (Table 4) represent industries selected from a general cross section of applications located throughout the United States. These industries range from Aerospace, Brass Works, Electronic, Printed Circuit Board, Oil Equipment to Electroplating. The companies all have varying degrees of Federal, State or local environmental effluent discharge requirements or internal objectives to meet. Case history in-process applications of ISX show heavy metal cation removal effectiveness approaching 99 percent. These users of ISX are able to economically meet or exceed the most stringent local, state or federal wastewater discharge permit requirements.

ISX is a highly versatile product requiring minimal, if any, capital investment for application. It can be used for batch treatment, slurried into a continuous flowing process stream or used as a filter precoat. It is especially effective when used as a final polish to remove 10 mg/liter or less of heavy metal cations from industrial process wastewaters for water recycle or effluent discharge. ISX is ideally suited in overcoming wastewater treatment conditions that result from the different solubility characteristics of metals as a function of pH or in the presence of metal complexing agents such as ammonia, EDTA, tartrate and Quadrol.

TABLE 4
CASE HISTORY RESULTS WITH ISX
DISSOLVED HEAVY METAL AVERAGE CONCENTRATION, mg/liter

INDUSTRIAL APPLICATION	FLOW RATE liter/m	ISX mg/liter	Cu^{+2}	Cd^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}	Cr^{+3}
Aerospace	100	140						
Initial			0.12	0.44	2.7			1.86
ISX Treated			0.05	0.02	0.18			0.23
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ISX Treated			0.05			0.6	0.01	
Oil Field Equipment	20	60						
Initial				5.0				
ISX Treated				0.01				
Electroplating	500	Pre-Coat						
Initial			7.0		2.5			0.8
ISX Treated			0.02		0.10			0.02

Figure 1 represents the case history application of **ISX** in an electronic manufacturing facility as a final polish for copper removal prior to treated effluent discharge into a natural waterway. **ISX** is metered into the process stream at a rate of 30 mg/l to satisfactorily treat approximately 450,000 gallons of process wastewater daily.

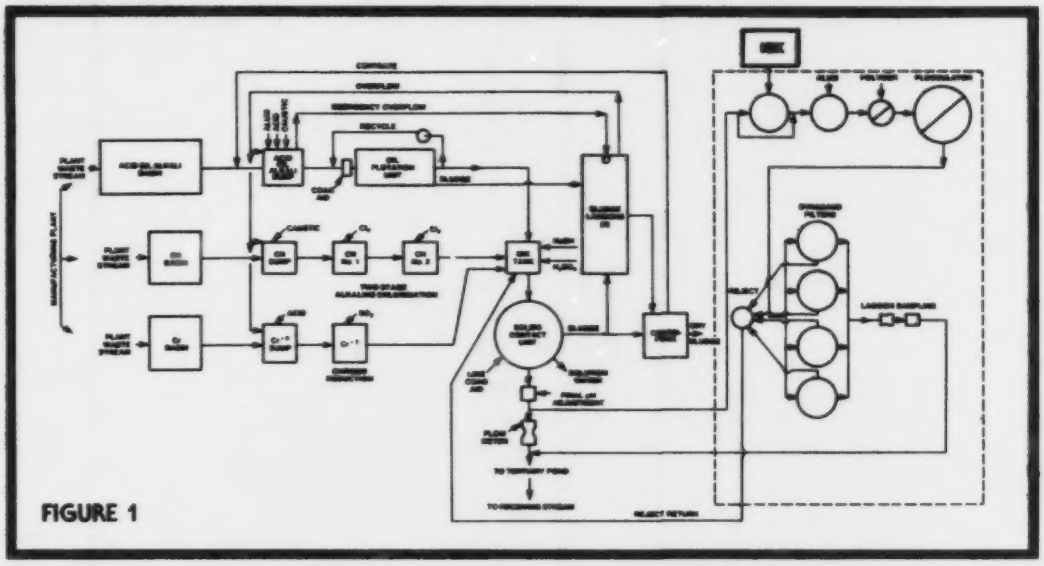

FIGURE 1

Figure 2 represents the case history application of **ISX** in a job shop electroplating facility where a 90 percent water recycle is accomplished. **ISX** is used as a filter precoat to remove heavy metals from approximately 50,000 gallons of process rinse water for recycle daily.

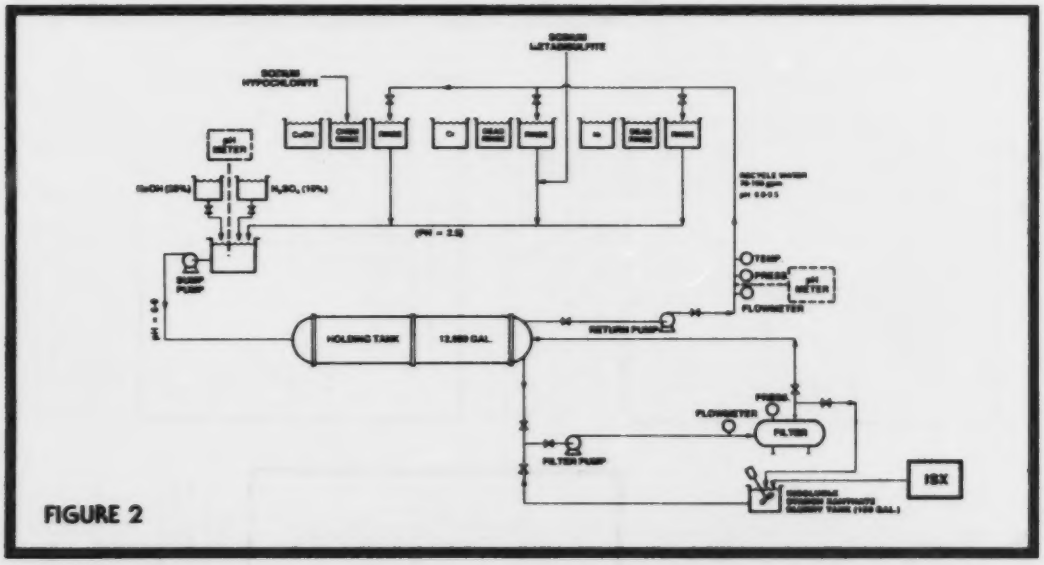

FIGURE 2

Pollution Technology Systems' **ISX** is a yellow powder of 20 micron nominal size. It is available in 25 and 250 pound net units. The product is shipped and stored under refrigeration for optimum shelf life.

Pollution Technology Systems is prepared to discuss ways in which **ISX** could be adapted to individual requirements. If you feel that **ISX** is suitable for your needs, we would be pleased to assist you in the adaptation of this technology. Please contact us for further information.

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PTS 1-80

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Removal of Heavy Metal Pollutants from Wastewater Streams

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Manufacturing operations of many industries, such as automotive, plating, printing, and metal-finishing, generate wastewater containing heavy metal components (chromium, nickel, zinc, copper, lead, etc.). These metals generally, if present in any appreciable amount, are toxic to aquatic life, exert a cumulative deleterious effect on receiving streams, lower or destroy the efficiency of biological waste treatment systems, and can, in many instances, represent a threat to human health. For these reasons, regulatory agencies have promulgated rather severe restrictions on the allowable heavy metals content of industrial waste outfalls. The trend is toward even more stringent limitations in the future; proposed guidelines contain requirements that approach the quality of potable water, with allowable contents of some heavy metals in the microgram range. If these guidelines become a reality (and, likely, they will), conventional methods now in use for the treatment of wastewaters containing heavy metals will become marginal for satisfying the low levels of contaminants allowed. This situation will require the development of more efficient and, undoubtedly, more sophisticated methods for heavy metal removal from wastewaters.

The anticipated need for improved heavy metal removal methods provided sufficient interest to undertake an evaluation and development program to identify those methods whose performance most likely would satisfy the projected wastewater quality criteria. In the course of this study, two methods, previously developed to some degree by others and potentially capable of meeting the future quality characteristics of heavy-metal wastewater treatment, were evaluated; additionally, a third method, based generally on one of the two methods initially studied, was conceived and subjected to preliminary evaluation study. This latter method for the removal of heavy metals from wastewater streams appears to have considerable promise in meeting quality requirements and for commercial application in alleviating the pollutional problems associated with heavy metals.

REMOVAL OF HEAVY METALS

Interest in treatment of heavy-metal wastewaters has been evidenced in recent technical literature. Several excellent reviews have been published, as well as many descriptions of specific problems associated with heavy metals treatment. The recent concern and interest in mercury removal has perhaps accelerated the investigative work in this field, and, with the prospect of more restrictive control of the entire heavy metals spectrum, more comprehensive consideration is being given to the entire family of heavy metal components.

For example, Cadman and Dellinger[1] review a total of 26 different methods that, technically at least, are applicable to the removal of heavy metals from wastewaters. They cover the more common methods, such as precipitation as hydroxides and sulfides, ion exchange, and extraction, as well as some of the more unusual and specialized treatments, among which are ion removal by a rotating electrode, paper chromatographic separation, radiation and magnetic field treatment, and biological ion removal. The results cited by Cadman and Dellinger apparently, for the most part, are from carefully-controlled laboratory tests or from very specialized mini-scale applications. They provide no evaluation of the performance that might be expected of these methods in commercial practice.

Argo and Culp[2] reviewed in detail the more common methods of heavy metal removal that could logically be applied to sanitary wastewater reclamation so that the treated wastewater could be utilized as an injection barrier for the prevention of sea water intrusion in the southern California area. These included chemical treatment, mixed-media filtration, and carbon adsorption. In part 2 of their paper, Argo and Culp reported the results of a pilot-plant investi-

gation of these methods for removal of heavy metals from a trickling filter effluent. It was found that the combined treatment of lime coagulation and settling, mixed-media filtration, and activated carbon adsorption was especially effective in reducing the concentrations of cadmium, hexavalent chromium, zinc, and copper in the biologically-treated influent. Other heavy metal components were removed to a lesser degree or were present in the influent in such low concentrations that a reliable evaluation could not be made. It was observed, as might be expected, that the removal efficiency was dependent on the concentration of heavy metals in the influent. The problems that increased metal content of the treatment sludges might cause was not discussed.

Cheremisinoff and Habib[3] in a two-part plenary account on heavy metal removal from wastewater covered: 1) nature, sources, and uses) 2) toxicity and toxic effects; 3) analytical methods for detection; and 4) removal techniques. The reports concentrate on cadmium, chromium, lead, and mercury because of their widespread industrial use, their toxicity, and their possible frequent occurrence in wastewater effluents. Ion exchange and hydroxide precipitation were the major routes suggested as appropriate for the removal of these metals; however, little quantitative data is presented as to the performance of these various methods.

Dean et al.[4] described the use of chemical precipitation methods, electrodeposition, cementation, solvent extraction, reverse osmosis, ion exchange, and activated carbon adsorption for heavy metal removal. While they mention application to many of the heavy metals, the review is particularly directed to the recovery of copper from waste effluents.

Esmond and Petrasek[5] have reported the fate of various metals in a municipal activated sludge pilot plant study involving biological/physical and biological/chemical/physical (AWT) sequences. The results indicated that substantial amounts of metallic constituents were removed by either method of treatment; influent concentrations were quite low and variable, however, and poor removal efficiencies were evident for such metals as lead, nickel, copper, cadmium, barium, and arsenic. The results would seem to discourage the use of waste pickle liquor as a source of iron salts in municipal waste treatment, notably in those applications where a high quality effluent is required.

Pugsley et al.[6] have described the removal of heavy metals from mine drainage waters by sulfide precipitation methods employing *p*H adjustment and either sulfide-containing reagents or a sulfate-reducing bacteria, *Desulfovibrio desulfuricans*. While further work was indicated, sulfide precipitation afforded low residual metal values and appeared to be a viable method of treating these discharges.

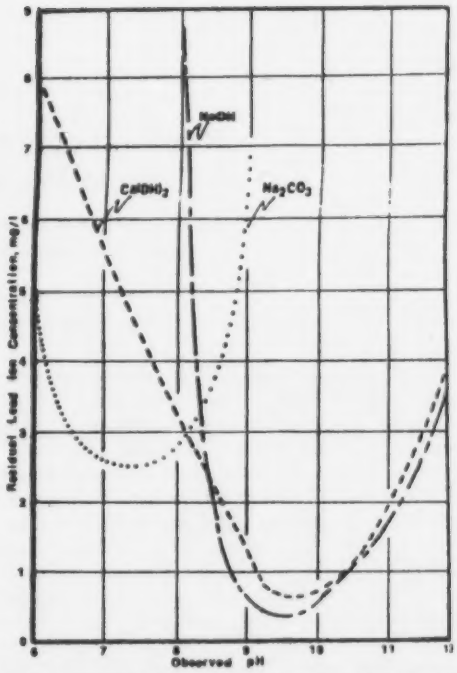

Fig. 1. Removal of Lead by Precipitation as a Function of Observed *p*H (Rohrer[7]).

More recently, Rohrer[7] investigated a number of chemical precipitants for removal of lead from wastewaters. The precipitants included lime, caustic soda, soda ash, trisodium phosphate, and combinations of these compounds. The results of his work are indicated generally in Fig. 1. With the exception of trisodium phosphate, residual lead levels with the individual reagents were in excess of 0.2 mg/liter; trisodium phosphate was effective to a residual level of 0.1 mg/liter. Based on typical regulatory agency requirements of residual lead contents of 0.05 to 0.1 mg/liter in industrial waste effluents, none of the individual precipitants seemed capable of consistently satisfying the limitations. Rohrer found that the most effective and economic combination was a trisodium phosphate-caustic soda mixture that was capable of reducing lead values to about 0.02 mg/liter. Figure 1 illustrates the rather narrow *p*H range where precipitate solubilities remain at a minimum when using mixtures of caustic soda-soda ash, lime, and soda ash as precipitants. These narrow ranges of operative *p*H require close maintenance of *p*H control points to provide consistent low level values of lead content.

With caustic soda, residual lead concentrations are minimal over a wider *pH* range.

Anderson and Weiss[5] patented a sulfide precipitation process that claims to avoid the generation of hydrogen sulfide and, through a coprecipitation mechanism with an additive compound, results in more complete removal of the pollutant ion than can be achieved by sulfide precipitation of the pollutant alone. In the process, a sulfide ion and a heavy metal ion that forms a sulfide having a higher equilibrium sulfide ion concentration than the sulfide of the heavy metal pollutant to be removed are added to the aqueous solution to be treated. As the sulfide of the added heavy metal is more soluble than the sulfide of the pollutant, the heavy metal pollutant ions are precipitated in preference to the added heavy metal ions. The added heavy metal ions also act as a scavenger for excess sulfide ions, thus preventing the formation of hydrogen sulfide and complex sulfide ions. In addition, the added heavy metal promotes coprecipitation of insoluble mixed metal sulfide compounds that leads to lower pollutant concentration in the effluent. A typical reagent pair suggested was sodium hydrosulfide (NaHS) and ferrous sulfate ($FeSO_4$). Using this procedure, residual concentrations of zinc, nickel, chromium, cadmium, copper, and iron of 0.05 mg/liter or less were claimed with simulated waste solutions.

Wing[6] described a novel method for removing heavy metals from wastewater employing starch xanthate produced from a highly cross-linked insoluble starch. This method was claimed to be highly effective in reducing heavy metal contents to the microgram level by forming an insoluble xanthate complex with the heavy metals present, thus permitting separation from the aqueous phase. It was suggested that a cyclic process could be used, including regeneration and reuse of the starch substrate and recovery of the removed metals. Wing's data were mainly collected during the treatment of relatively small volumes (50 mliter) of simulated wastewater solutions; copper, cadmium, chromium, mercury, and iron contents were reduced to below 0.01 mg/liter and nickel, lead, and zinc to below 0.05 mg/liter. Residual silver and manganese levels in the treated wastewater were somewhat higher than the levels attained with the other metals.

BACKGROUND OF THE PRESENT STUDY

The present experimental study was undertaken to evaluate available heavy metal removal methods that had 1) the potential for removal of heavy metals, particularly lead, to low residual levels (i.e., less than 0.050 mg/liter) and 2) the potential to be practically incorporated into high-volume industrial wastewater treatment applications. The study of the available literature had generally indicated that hydroxide precipitation methods would not be suitable because of their inability to satisfy the low levels of residual metal contents desired. In addition, the results of such processing were generally available. Sulfide precipitation methods seemed capable of perhaps satisfying quality criteria for the treated wastewater, but, historically, these methods have been plagued by operational problems, such as hydrogen sulfide evolution, that have limited their commercial application. If some of these operational problems could be eliminated, then perhaps a better climate for industrial application would result. The starch xanthate process was of interest because of its apparent ability to produce residual concentrations of heavy metals within the range of interest in the present work. Two general approaches, thus, sulfide precipitation and starch xanthate treatment, as exemplified by Anderson and Weiss and by Wing, respectively, seemed to fit the requirements of the evaluation program. These two approaches had been the subject of some experimental study by others, and the results appeared promising for industrial use. The exploratory experimental program thus was directed initially to the evaluation and applicability of the sulfide precipitation and the starch xanthate methods of heavy metal removal.

Bench-scale experimental work was undertaken with single-component (lead-bearing) simulated wastewater solutions and with multi-component simulated and actual wastewater solutions. Simulated wastewater solutions were employed to determine the general effect of pertinent parameters and to establish a nominal range of optimum performance. The results then were confirmed and expanded with actual multi-component wastewater samples. Laboratory glassware was used as reaction and sedimentation vessels throughout the studies, and sample volumes used throughout the program ranged from 0.5 to 20 liters. In general, standardized jar-treatment procedures were used throughout the work, with reaction contact being made under gently agitated conditions. The major variables studied were reaction time, temperature, amount of reagent, and, in some cases, sequence of reagent addition.

The experimental tests were evaluated by the level of residual metals in the treated solution. Analysis of the solutions for metal content was accomplished by atomic absorption spectrometry using a carbon arc vaporization chamber.

SULFIDE PRECIPITATION TESTS

The sulfide precipitation process proposed by Anderson and Weiss provided excellent technical per-

formance with both simulated and actual wastewater samples with respect to the residual heavy metal levels in the treated wastewater. Lead, zinc, copper, chromium, and iron contents all were reduced to below 0.05 mg/liter, employing two to three times the stiochiometric amount of sulfide precipitant (NaHS and $FeSO_4$). In some instances, lead and copper levels were less than 0.01 mg/liter. While some evolution of hydrogen sulfide was noted during the various tests, it was effectively eliminated by minor modifications in the manner in which the reagents were added to the reaction vessel.

As is common with many precipitation processes, sulfide precipitation of heavy metals produces substantial quantities of residual sludge. In some respects, particularly with regard to subsequent oxidation, solubilization, and leaching of the contained metal values, the sulfide sludges are more difficult to dispose of than are hydroxide precipitates. Because of dilution with extraneous materials, such as lime, it is not normally practicable to consider recovery and reuse of the contained metal values.

Primarily because of the sludge production noted in the sulfide precipitation process, it was concluded that this method would not yield a permanent and positive solution to the removal of heavy metals from industrial wastewaters. While it was capable of producing effluent qualities that would satisfy projected limitations and could be used as a stop-gap measure if necessary, its long-term use would undoubtedly be characterized by problems in sludge disposal and the improbability of any ultimate metal recovery from the residual sludges. Its utility from a widespread industrial usage standpoint appears to be severely limited.

STARCH XANTHATE TESTS

Technical performance of the starch xanthate heavy metal removal method as described by Wing likewise was excellent insofar as the levels of residual metal contents were concerned. The use of starch xanthate that had been prepared in the laboratory from highly cross-linked starch and dried prior to contacting with simulated and actual wastewater samples produced residual lead contents well below 0.05 mg/liter (ranging down to about 0.01 mg/liter). Residual copper contents at the same conditions were about 0.06 mg/liter. The results of these tests indicated that the starch xanthate process was capable of attaining extremely low levels of lead and copper in the treated wastewater.

On the other hand, the characteristics of the precipitated starch xanthate residue, while quite small in amount as compared to the degree of sludge production in more conventional heavy metal removal processes, were not particularly favorable. Sedimentation of the suspended material was found to be slow, and often the supernatant liquid was turbid and cloudy. On filtration, the suspended material and residue formed a homogenous and cohesive mass on the filter that impeded the rate of filtration and could only be removed by scraping. The filter cake was sticky and gummy (vis-a-vis typical starch suspensoids) and had a moisture content of 60 to 80% water. Its properties would make it difficult to handle on a commercial scale. The required steps of removing the precipitated metal, re-xanthating the spent starch, drying the re-xanthated starch, and recycling to the process would present a number of formidable problems in an industrial application.

The starch xanthate process was claimed to have an inherent capability to increase the *p*H of the contacted wastewater. While the use of starch xanthate with the simulated wastewater solutions (*p*H 6.5 to 7) resulted in residual lead contents below 0.050 mg/liter, the *p*H of the solutions did not change appreciably. In further tests, adjustment of the *p*H to 8 with lime or caustic made for somewhat better and more consistent results.

DEVELOPMENT OF THE CELLULOSE XANTHATE PROCESS

Prior to and during the bench-scale study of the starch xanthate process, the usefulness of some of the characteristics of the xanthate approach were recognized. The capability of removing heavy metals to an extremely low level, sufficient to meet projected limitations with a high degree of reliability, was a primary asset. The problem of disposal of large amounts of residual sludge seemed to be amenable to solution because of the small amount expected to be produced and the opportunity to recover metal values and to recycle process reagents appeared promising. These characteristics would mitigate many of the objections so often advanced with respect to contemporary conventional metal-removal methods.

On the other hand, the evaluation program did show that the starch xanthate process possessed some disadvantages. The major deficiency was the nature of the starch xanthate-metal complex precipitate or residue formed following contact with the wastewater effluent, which would cause handling problems in commercial application. A somewhat less important, but nevertheless critical, factor was the lack of history of the commercial production of starch xanthate—considerable development and process complication would be necessary to ensure the availability of starch xanthate as a process reagent.

Consideration then was given to modification of

the xanthate approach in order to improve its utility for commercial application. It was theorized that if, in fact, the xanthate portion of the starch xanthate

Table I.
Metal Removal from Wastewater with Cellulose Xanthate

Form Used	*Dosage, ppm*	*Waste type**	*Treated water, mg/liter*
Cotton xanthate (laboratory)	4,000	A	Pb: 1.410
Towel pulp xanthate (laboratory)	2,000	B	Pb: 0.096
	4,000	B	Pb: 0.054
	8,000	B	Pb: 0.039
Towel pulp xanthate (laboratory)	2,000	B	Pb: 0.015
Comm. xanthate (washed)	400	C	Pb: 0.095 Zn: 0.015 Fe: 0.440
	600	C	Pb: 0.035 Zn: 0.010 Fe: 0.250
	1,000	C	Pb: 0.026 Zn: 0.019 Fe: 0.060
Comm. xanthate (washed)	200	D	Pb: 0.015 Zn: 0.030 Cu: 0.140
Comm. xanthate (as rec'd)	90	D	Pb: 0.009 Zn: 0.030 Cu: 0.190 Fe: 0.430
	100	D	Pb: 0.009 Zn: 0.025 Cu: 0.100 Cr: 0.075 Fe: 0.360
	200	D	Pb: 0.012 Zn: 0.025 Cu: 0.070 Fe: 0.270

*Wastewater types:
A Simulated wastewater; 6 mg/liter Pb
B Simulated wastewater; 12 mg/liter Pb
C Simulated wastewater; 0.8 mg/liter Pb, 0.33 Zn, 4.5 Fe
D Industrial wastewater; 3.9 mg/liter Pb, 1.0 Zn, 1.9 Cu, 0.3 Cr, 32.0 Fe

molecule represented the active site for metal immobilization, then any xanthate should be as equally effective for metal removal. The xanthates were reviewed to define those that might be more suitable than starch xanthate as far as materials handling and dewatering properties were concerned.

Cellulose xanthate, primarily because of its fibrous nature and secondarily because of its commercial production as an intermediate in viscose manufacture, appeared to possess the characteristics that would eliminate some of the difficulties encountered with the use of starch xanthate. In order to confirm its possible use, bench-scale evaluation of its performance was undertaken.

Jar tests were employed to study the parameters associated with the use of cellulose xanthate. The procedure involved contacting samples of simulated and actual wastewaters containing lead and other heavy metals with cellulose xanthate, either prepared in the laboratory or obtained commercially, under various conditions. Sample volumes of from 0.5 to 5 liters were used throughout the program, contacting was made under standardized conditions with gentle agitation, and solids separation was made by a combination of sedimentation and vacuum filtration.

Laboratory-prepared cellulose xanthate was made from cotton and paper towel stock by reacting the cellulose substrate with carbon disulfide and caustic soda. Metal removal in these first tests with laboratory-prepared cellulose xanthate were erratic, probably reflecting nonuniformity of xanthation of the laboratory-prepared material, as no investigation was made of optimum xanthation conditions. The results became more consistent after commercial xanthate was received and used in the evaluation program.

Table I shows the results of metal removal tests from samples of wastewater with the various forms of cellulose xanthate. The initial *p*H of the simulated wastewaters was about 6.9 and that of the industrial wastewater was about 3.5. The *p*H was adjusted in both cases to about 8 with lime slurry or with caustic prior to the contacting step. As can be seen, at a xanthate dosage of 90 ppm, residual values of lead and zinc in the industrial wastewater are quite low, 30 μg//liter or less. At the same xanthate dosage, copper and iron contents were acceptably low. Contact times of 30 min. were used in these tests; additional work indicated that this could be decreased to less than 15 min. with no significant decrease in metal removal. Temperature was found to have little effect, and the use of a coagulant polymer provided only a slight improvement in results.

With comparison to starch xanthate residues, the handling and dewatering of the cellulose xanthate-metal complex residue were significantly improved. The residue settled rapidly, leaving a clear supernatant, and the fibrous nature of the residue enhanced fast and efficient filtration. No data were generated during the evaluation study as to the actual difference in filtration rates between the starch and cellulose xanthate residues; visual observation, however, would indicate improvement of an order-of-magnitude scale.

Detailed capacity or loading studies were not undertaken. The adsorptive capacity of the cellulose

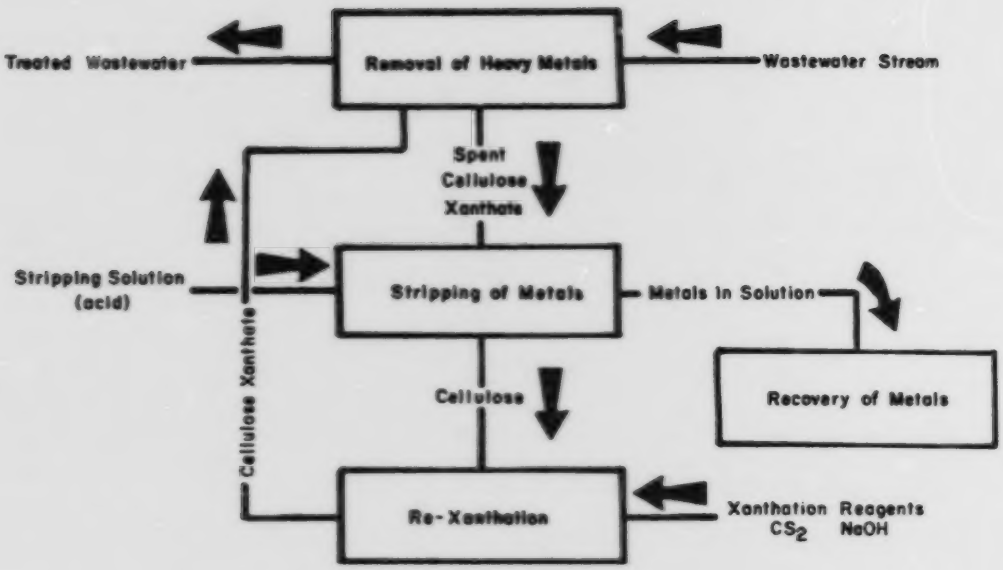

Fig. 2. Flowsheet of Cellulose Xanthate Process for Heavy Metal Removal.

xanthate would be expected to be a function of the degree of xanthation as indicated for the starch xanthate process. With the commercial cellulose used in this study (whose degree of sulfur substitution was not determined), it appears that a loading similar to that provided by starch xanthate should be possible before any significant deterioration of performance is encountered. This factor will require further study and development.

Data on the starch xanthate process indicate an inherent ability of the starch xanthate to adjust the *p*H of the wastewater to a value consistent with acceptable discharge criteria. This is ascribed to the presence of bound alkali in the xanthate product, which can be decreased by excessive washing of the material. In any case, this self-adjustment of the *p*H was not noted in the present study with cellulose xanthate. Many of the cellulose xanthate samples were washed thoroughly before use. It was necessary, therefore, to use external *p*H adjustment with lime slurry or with caustic to a final *p*H above neutral (*p*H 8) to insure consistent results. With the simulated wastewaters, whose initial *p*H was relatively high (6.5 to 7), the amount of lime or caustic required was negligible and did not contribute to sludge formation. With actual wastewater samples, the initial *p*H was much lower (3.5), and correspondingly more lime or caustic was required for *p*H adjustment. In the case of *p*H adjustment with lime, sludge formation was significant in such cases and complicated recovery of the spent xanthate. In most cases with the actual wastewater samples, *p*H adjustment was made with caustic so that sludge formation could be avoided.

Further work is needed to define more clearly the *p*H adjustment aspects of cellulose xanthate treatment so that external adjustment might be eliminated. It is apparent, however, that if external *p*H adjustment of low-*p*H wastewaters does prove necessary, the use of an insoluble base (lime) for such adjustment is undesirable because of sludge formation and the attendant complications involved with the recycling of the cellulose xanthate substrate.

COMMERCIAL APPLICATION OF THE CELLULOSE XANTHATE PROCESS

Figure 2 shows a simplified version of the commercial application of the cellulose xanthate process for heavy metal removal. The major steps indicated are wastewater contacting with the cellulose xanthate and removal of the heavy metals content, stripping of the metals from the cellulose by acid extraction, and re-xanthation of the cellulose substrate. There are several ways that these steps can be carried out. Batchwise operation, in which a quantity of cellulose xanthate is pulped with the wastewater stream, can

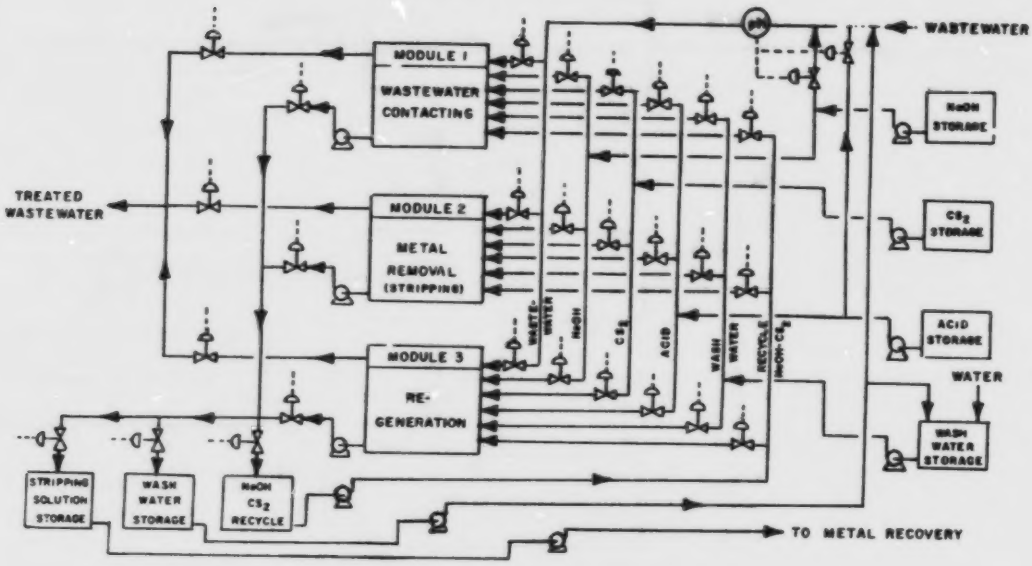

Fig. 3. Conceptual Commercial Application of the Cellulose Xanthate Process for the Removal of Heavy Metals from Wastewater.

be used, and after sufficient contact the residue can be separated by sedimentation or filtration, stripped of its metal content, re-xanthated, and returned to the process for additional treatment of wastewater. However, the physical characteristics of cellulose xanthate, particularly its fibrous nature, offer opportunities for potentially more desirable methods of operation. The fibrous nature of cellulose xanthate should allow the fabrication of porous mattes or elements having sufficient structural strength and stability to permit use in a flow-through reaction vessel that would allow application without the necessity for physical handling of the cellulose xanthate or substrate. This would permit the successive operations of wastewater contacting, metal stripping, and re-xanthation to be accomplished in place within the reaction vessel without the necessity of removing the cellulose xanthate or cellulose substrate after stripping from the reaction vessel. This concept is shown in Fig. 3.

In this instance, a porous cellulose substrate is contained in each of the three parallel reaction vessels where the steps of wastewater contacting, metal stripping, and cellulose re-xanthation are accomplished concurrently. By suitable arrangement of piping and control valves, the operation can be made continuous; automation can be provided so that unattended operation is possible.

No work has been undertaken on the extraction of metal values from the spent xanthate, recycle of the re-xanthated cellulose, or recovery of the metal from the stripping solution. Such effort will need to be made prior to full realization of the potential of the process. Analogous with the starch xanthate process, however, the metals could be removed by acid-stripping of the spent xanthate and would be available in a relatively concentrated solution for subsequent metal recovery. Possible routes to metal recovery include such conventional methods as electrolysis, cementation, or precipitation. Alternatively, if metal recovery is not to be accomplished, precipitation could be employed to immobilize the metals; this could probably be accomplished easier with the concentrated solution than with the entire wastewater flow. Obviously, metal recovery would seem the most desirable from an ultimate disposal standpoint even though, in most cases, the economic value of the recovered metals might not be a significant factor.

Consideration could also be given to the use of the cellulose xanthate process as a "polishing" operation subsequent to other methods of metal removal, where these methods are not capable of attaining the required low levels of contaminants in the effluent wastewater. As a matter of fact, it might be advantageous to combine a less efficient pretreatment method but one that facilitates metal recovery or minimizes sludge production with the cellulose xanthate treatment and to depend on the latter to reduce

the residual metal content to acceptable levels. There exist many possible combinations of this sort that would be possible, depending to a large extent on the specific characteristics of the wastewater and the environment in which it is generated.

CONCLUSIONS

While additional development work is required to refine many areas of the cellulose xanthate process for heavy metal removal, this preliminary evaluation has indicated that it does have the potential for effective treatment of industrial wastewaters. It has the most important capability of achieving low levels of residual metal content in the treated effluent, and specifically, lead, that will satisfy projected water quality criteria. For this purpose, it can be considered either as a replacement for or a supplement to the more conventional methods of heavy metal removal that may be marginal in providing the low levels of residual metals necessary. It offers this and also the potential of minimizing the excessive production of hard-to-handle residual sludges.

The cellulose xanthate process should be readily adaptable to a closed-cycle concept where recycle, recovery, and reuse of both reagents and products can be accomplished. Its operation would appear to be both simple and reliable and consistent with a high degree of automation, thus affording a less labor-intensive system than conventional methods of metal removal.

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Indications are that insoluble starch xanthate can reduce cadmium from around 1 ppm to less than 0.2 ppb in minewater-type effluents.

CHELATION FOR METAL REMOVAL

Although no information on how the process works has been made available and no cost data has been released, the results described by HOLBEIN, et al. (1984) inserted below indicate a process which is capable of removing metals to a very low level on the one hand (e.g., chromium VI) or being very specific in its removal of one metal (e.g., Hg) in the presence of other metals.

More information on applications and potential uses may be available from:

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DEVOE-HOLBEIN TECHNOLOGY: NEW TECHNOLOGY FOR CLOSED-LOOP SOURCE REDUCTION OF TOXIC HEAVY METAL WASTES IN THE NUCLEAR AND METAL FINISHING INDUSTRIES

BY

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ABSTRACT

Increased volumes and varieties of toxic heavy metal wastes from a number of industries, coupled with higher emission standards and dwindling waste repositories, have necessitated the introduction of greatly improved technology for the safe and effective handling of heavy metal laden wastes. Present and future requirements of toxic metal source reduction technology are best summarized by the terms "Concentrate and Contain"; concentrate, meaning improved efficiency of metal recovery and contain, meaning production of a metal waste form which can either be recovered and reused or transformed to a stable state where toxic metals remain imobile. This paper describes new technologies, the DeVoe-Holbein Technology, which provides highly efficient and effective means of waste metal closed-loop source reduction of aqueous heavy metal wastes from both nuclear and non-nuclear industries.

The DeVoe-Holbein technology consists of a novel series of synthetic compositions and various processes for their use. The compositions are highly efficient at metal recovery (typically achieving 99.99% source reduction) are selective for individual or groups of metals, allow high flow throughputs, are mechanically and chemically robust and stable and are completely regenerable with small volumes of regenerant.

Case studies are presented to illustrate how this new technology can be applied to the closed-loop recovery of mercury, chromium and radioactive fission products such as cesium and strontium. In addition, examples are shown to illustrate the effective recovery of metal finishing wastes such as cadmium, zinc, copper, cobalt, nickel and lead.

INTRODUCTION

Aqueous wastes laden with toxic heavy metals are generated by a large number of industries ranging from metal finishing operations to the nuclear industry. Such wastes pose an ever increasing threat to the environment. While the nuclear industry has handled waste problems by preventing the release of radioactive metallic wastes to the environment, the increasing volumes of such wastes together with the very long term time requirements for containment have necessitated improved methods for waste volume reduction and more stable storage forms for long-lived radioactive wastes.

Traditional methods of dilution and discharge of heavy metal wastes from metal finishing are now regarded as unacceptable. A number of technologies for the extraction of heavy metals from metal finishing wastes have been employed (1) Thus, hydroxide lime or sulphide precipitations of heavy metals have seen wide useage. However, these technologies generate large volumes of concentrated wastes which must be disposed of, in for e.g. landfill sites. Restrictions are now occurring in some locations as to the amounts of such relatively mobile and toxic waste which can be placed in landfills. In addition, precipitation methods often do not bring effluent residual metal concentrations to levels low enough to meet the emission standards. Other more efficient extraction technologies for plating wastes include ion exchange technology. However, regeneration of ion exchange materials can generate fairly large volumes of metal-laden waste which is mobile and therefore requires further treatment.

Surprising similarities can therefore be observed in the present and future requirements of new technologies for the treatment of aqueous wastes containing toxic metals in both the non nuclear and nuclear industries. These requirements are embraced by the terms concentrate and contain; concentrate, meaning improved efficiency of metal extraction and contain, meaning producing a waste form which can be recovered and re-used or transformed to a stable state where the toxic metal remains imobile. This paper describes recently developed technologies which meet these requirements.

NATURE AND DEVELOPMENT OF DEVOE-HOLBEIN TECHNOLOGY

DeVoe-Holbein technology consists of a family of new synthetic compositions and the processes and technology related to their use. The origins of this technology stem from the basic research of Drs. DeVoe and Holbein, both biochemists who specialized in metal metabolism in biological systems.

All living cells have requirements for a number of metals

in their nutrition such as Fe, Ni, Co, Cu, Zn, Mn, Mg, Na and K. Throughout evolution, living cells have developed specialized chemical mechanisms to ensure that they successfully obtain their required metals but at the same time do not allow toxic levels of these metals to accumulate inside the cells. Similar mechanisms are used to sequester various non essential but highly toxic metals such as Cd, Hg, and Pb, which can often appear in a cell's environment. DeVoe and Holbein used the biological metal extraction and recovery mechanisms as model systems to create synthetic mechanisms which would accomplish similar high efficiency metal extraction and recovery but without employing living cells. This work was initiated in 1980 and has progressed rapidly and continuously. As a result of this entirely new approach, a series of novel compositions has been developed.

Each composition was designed to achieve the necessary selectivity while in the presence of other competing ions. All the compositions share the general features of high extraction efficiency (typically 99.99% efficient), complete regenerability with small volumes of regenerant (typically 0.5 to 2 bed volumes of regenerant), high mechanical and chemical stabilities (no swelling or compaction even at high flow rates of 50 bed volumes per hour or abrupt changes in pH), and freedom of release of toxic components. The DeVoe-Holbein technology has been successfully applied to a number of challenging problems from the nuclear and non nuclear industries both in the laboratory and in the field (see below). Application of this technology has emphasized the achievement of closed-loop recovery of waste metals. In addition, the compositions themselves, after their useful lifetime of numerous loadings and regenerations, can be economically utilized as raw materials in the manufacture of other products of existing commercial value.

PERFORMANCE CHARACTERISITICS OF DEVOE-HOLBEIN COMPOSITIONS

DeVoe-Holbein compositions are particulate chemical compounds made to a number of particle size specifications. Most studies with the compositions have employed fixed bed columns of various sizes and diameters. Thus, small scale laboratory testing has employed small glass cylindrical columns with bed volumes ranging from 3 ml to 7 L, whereas, a two column prototype water treatment plant built in Holland to test flows up to 4,000 L per hour incorporated 140 L fixed beds. Figure 1. illustrates the principle testing scheme common to the various testing scales.

Efficiency of Metal Capture

Efficiency of metal capture of any system will directly influence the level of residual metal in the treated effluent stream. DeVoe-Holbein compositions all display very high metal

Figure 1.

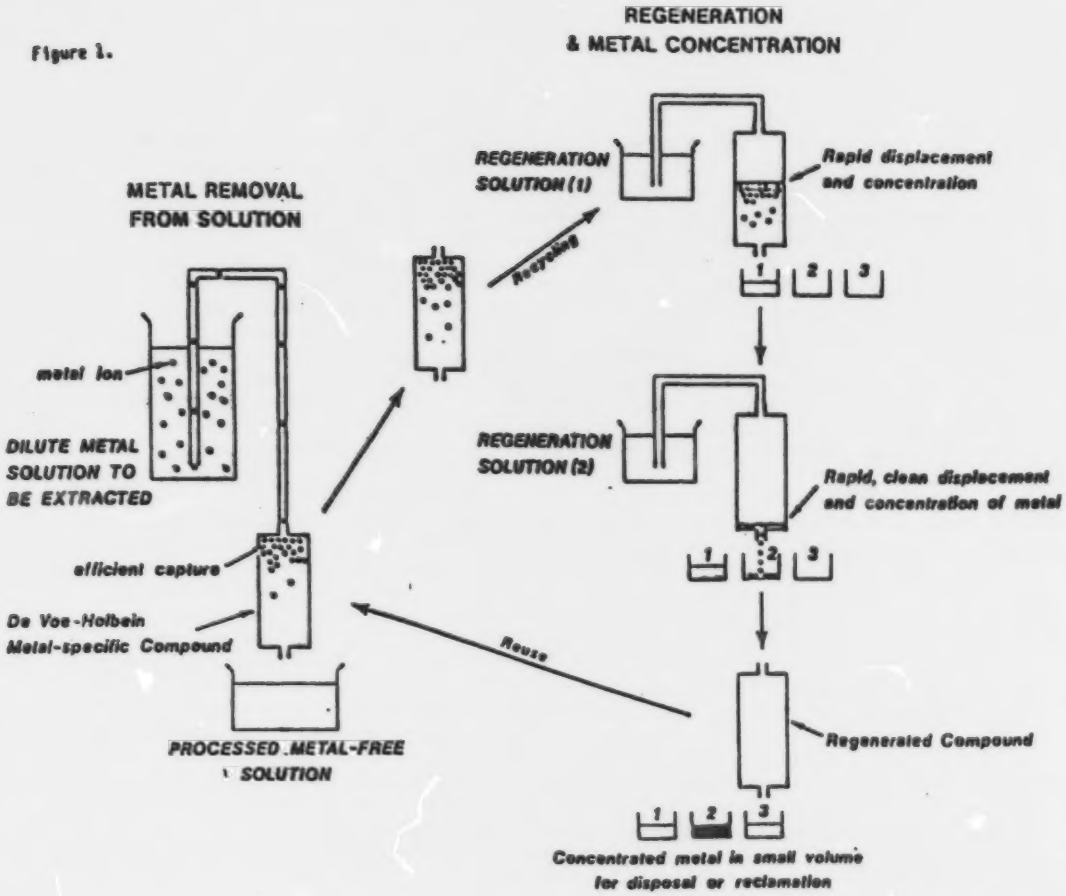

REGENERATION
& METAL CONCENTRATION
METAL REMOVAL
FROM SOLUTION
REGENERATION
SOLUTION (1)
Rapid displacement
and concentration
Recycling
metal ion
DILUTE METAL
SOLUTION TO
BE EXTRACTED
REGENERATION
SOLUTION (2)
Rapid, clean displacement
and concentration of metal
efficient capture
De Voe-Holbein
Metal-specific Compound
Reuse
PROCESSED METAL-FREE
SOLUTION
Regenerated Compound
Concentrated metal in small volume
for disposal or reclamation

TABLE 1

The Efficient Capture of Some Toxic Heavy Metals of Importance to the Hydrometallurgical and Metal Finishing Industries by DeVoe-Holbein Composition

Toxic Metals	DeVoe-Holbein Composition	Influent Concentration	Effluent Concentration [a]	Capture Efficiency % [b]
Cadmium	DH-516	674 ppm	< 1.0 ppb	≥99.99
Chromium	DH-524	694 ppm	< .01 ppm	≥99.99
Copper	DH-520	38 ppm	< 1.0 ppt	≥99.99
Lead	DH-501	42 ppm	<42. ppb	≥99.99
Mercury	DH-573	12 ppm	< 1.0 ppb	≥99.99
Nickel	DH-507	0.10 ppm	< 1.5 ppt	≥99.99
Zinc	DH-508	6.5 ppm	< 0.8 ppb	≥99.99

TABLE 2

The Efficient Capture of Some Metals of Importance to the Nuclear Industry by DeVoe-Holbein Compositions

Toxic Metal	DeVoe-Holbein Composition	Influent Concentration	Effluent Concentration [a]	Capture Efficiency % [b]
Cobalt	DH-502	1.2 ppm	< 20 ppt	≥99.99
Cesium	DH-566	7.8 ppm	< 2.0 ppt	≥99.99
Iron	DH-506	34 ppm	< 34 ppb	≥99.99
Strontium	DH-566	526 ppm	< 1.0 ppb	≥99.99
Thorium	DH-502	139 ppm	< 0.14 ppb	≥99.99
Uranium	DH-506	24 ppb	< 1.7 ppb	≥99.99

Notes: Table 1 and 2

[a] Effluent concentration at or below normal detection limits using either radioactive tracer or atomic absorption spectrophotometric determinations.

[b] Capture efficiency determined as % reduction in influent concentration; values are greater or equal to those shown due to detection limits of effluent metal concentration

capture efficiencies both in the laboratory when tested with laboratory-formulated metal effluents and in the field when tested with actual metal-laden waste waters of variable make-up. Table 1 illustrates the high capture efficiencies obtainable in the laboratory with test metal solutions of importance to metal finishing and hydro-metallurgical operations. The very high efficiencies of capture of metal result in treated effluents with extremely low metal concentrations. This is highly desireable when recovering highly toxic metals such as Hg, Pb or Cr from waste waters and mandatory when treating radioactive metallic wastes with long-lived high energy radionuclides, such as Cs, Sr and Co. These high capture efficiencies have also been obtained in the treatment of actual waste waters containing variable amounts of target and competing metals (see Industrial Applications). Table 2 illustrates the similar high metal capture efficiencies obtained with metals of importance to the nuclear industry.

The DeVoe-Holbein compositions, in general, exhibit their high capture efficiencies up to the capacity of the particular compound, with a sharp breakthrough occurring after saturation of the composition. A typical breakthrough curve is shown in Figure 2 where the DeVoe-Holbein DH 520 has been used for Cu removal from a relatively concentrated metal solution. In addition, high efficiencies are obtained at low (1 bed volume per hour) and high (50 bed volumes per hour) flow rate. The capacity at saturation of a composition for a metal depends on the composition and the metal in question, with capacities generally falling in the range of 5 grams of metal to 30 grams of metal per kilogram of composition (per cycle of use). The number of regenerations obtained over the life of the composition is relatively high (see below) and, thus, substantial amounts of metal can be recovered (see industrial applications) with the DeVoe-Holbein compositions.

Selectivity of Metal Capture

Most of the DeVoe-Holbein compositions display high levels of selectivity for the metals or group of closely-related metals for which they were designed. Selectivity is assessed in the laboratory by using identical columns of a particular composition to treat solutions of different metals, all at the same concentration, temperature and flow rate. A series of breakthrough curves for the different metals is thus obtained and the volume passed before breakthrough of a given metal is directly related to the specificity of the test composition for the metal. Figures 3 and 4 display the slectivities of two different DeVoe-Holbein compositions for various metals. The selectivity of composition DH 506 for iron and its lack of specificity for Cd can be observed in Figure 3. Composition DH 501 on the other hand does not select Co, Fe or Cd but is highly selective for Cu (Figure 4). Similar results demonstrating individual or group selectivities have been obtained for other DeVoe-Holbein compositions. Selectivity and specificity of a particular

composition are somewhat functions of the pretreatments used with the particular composition and the conditions under which the metal solution or waste water are treated. Thus, in many instances selectivity and specificity can be altered (broadened or narrowed) to meet specific requirements of metal extraction.

Another test for specficity demands the capture of a test metal from a complex solution containing a number of other metals. Figure 5 demonstrates the ability of DeVoe-Holbein composition 506 to selectivity remove iron from artifical sea-water. Here, one can observe the radical differences observed between the highly selective DeVoe-Holbein composition and the currently used selective ion exchange resin and strong cationic exchange resin. The latter either quickly became saturated with competing cations from the solution or were highly interfered with by competing cations due to their lower selectivities.

Selectivity of DeVoe-Holbein compositions for metals can also be observed in many other cases (see for e.g. mercury removal from complex solutions in industrial applications, below).

FIGURE 2

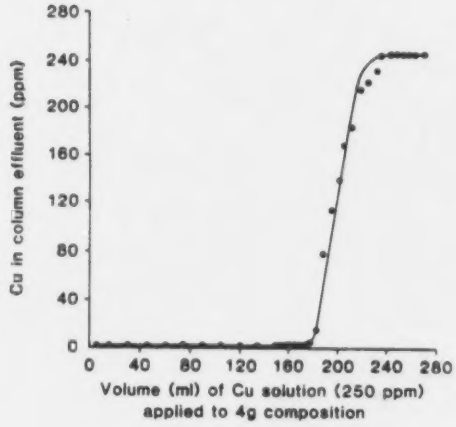


FIGURE 3

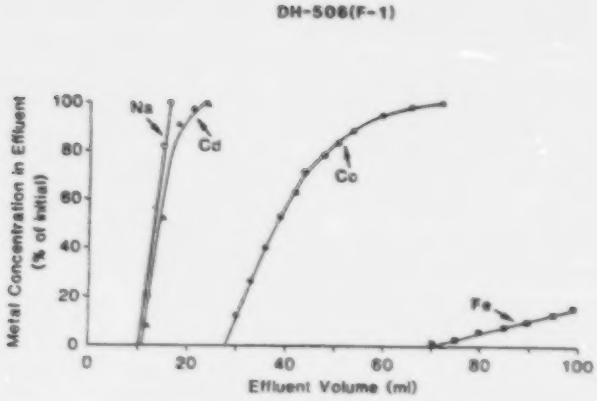


FIGURE 4

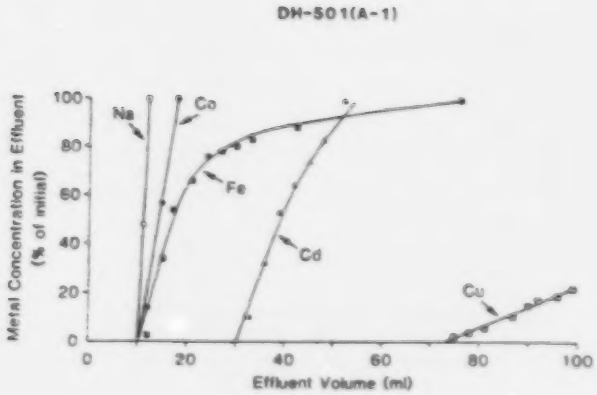
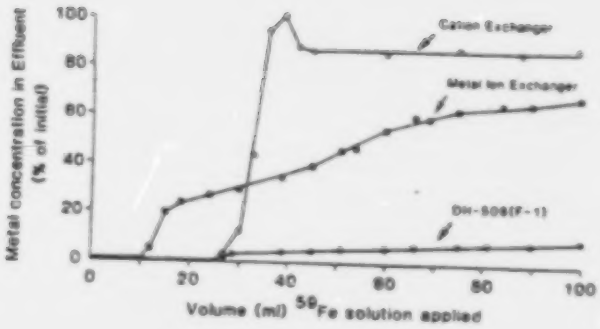


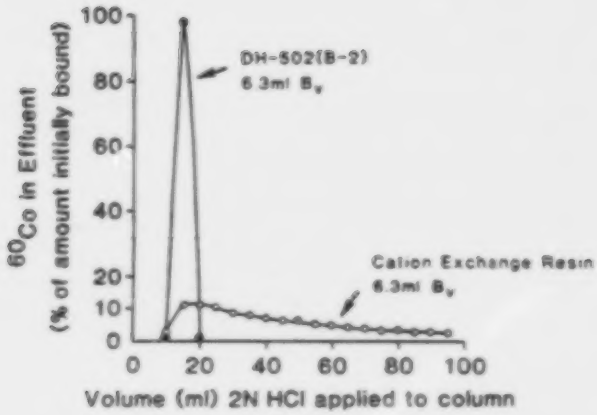
FIGURE 5



Regenerability

Regenerability of a metal capturing resin or compostion is of great importance in almost all applications involving the recovery of toxic metals from waste waters in the non-nuclear industries. Regeneration of the ion exchange resins commonly employed for such applications can present problems, due to the large volumes or regenerant required to remove the bulk of the bound metal. This creates a secondary problem of treatment and disposal or recovery of relatively dilute metal from large volumes of relatively expensive regenerant.DeVoe-Holbein compositions are fully regenerable and, typically, small amounts of regenerant are required to displace the bulk of the bound metal. A comparison in regeneration ease between a strong cationic exchange resin and a DeVoe-Holbein composition is shown Figure 6. In this test, identical size beds of both materials were used, they were both used to capture similar amounts of cobalt (60 Co was used as a tracer to aid the quantitation in the regenerant effluent) and both were regenerated with 2N HCl. It should be noted that all the Co was removed from the DeVoe-Holbein composition in a single bed volume of regenerant but incomplete removal of cobalt was observed with the cation exchange resin even after many bed volumes of regenerant had been passed over the column.

FIGURE 6



Studies with a variety of DeVoe-Holbein compositions, at different scales and employing bed volumes between 3 ml and 140 L have demonstrated a general ease of regeneration of the compositions. Virtually 100% of the bound metal can be collected from the saturated compositions in volumes of regenerant between 0.5 and 2.0 bed volumes. In a full scale test using the pilot water treatment plant with one 140L composition column operating, influent cadmium at 2500 ppm in waste water was successfully extracted to produce a processed effluent with less than 0.01ppm Cd. Approximately 80% of the composition-bound Cd could be displaced in 15% of one bed volume of regenerant and virtually 100% was displaced with two bed volumes of regenerant. The ease of the regeneration of the DeVoe-Holbein compositions therefore affords some great advantages in the closed-loop recovery of metals. Small volumes of regenerant containing concentrated recovered metal are readily amenable to either primary metal re-use, waste immobilization or secondary metal re-use.

Other Characteristics

The DeVoe-Holbein compositions, because of the primary substrates employed in their manufacture, are resistant to relatively harsh treatments of acids and bases, abrupt changes in pH and flow rate and high dose exposure to radiation. Their mechanical stabilities allow high flow throughputs, with up to 50 bed volumes per hour, while still permitting high efficiency metal capture in a stable bed. The physical and chemical qualities of the DeVoe-Holbein compositions are of paramount importance in applications in the nuclear industry. Compositions, laden with highly radioactive metals, can either be regenerated to achieve high volume reduction factors or can be incorporated directly in the loaded form into waste transformation schemes, principally vitrification of the laden composition. This can be done using either existing vitrification technology or with a new vitrification process specifically designed for the DeVoe-Holbein compositions (see below).

INDUSTRIAL APPLICATIONS - CASE STUDIES

Mercury Recovery from Incinerator Scrub Water

Mercury remains one of the most toxic heavy metals to all life forms. This is due not only to its outright toxicity in low concentrations but also due to the ease with which it is transformed in the environment to more mobile and toxic forms. As a result, very high standards are in place throughout the world to ensure minimal release of mercury to the environment. However, mercury is still widely used in a number of industrial processes and appears in waste waters. Mercury containing batteries are widely used in a number of consumer electronic devices. As a result, there is a growing amount of municipal waste containing spent mercury-laden batteries. In Japan, municipal waste is often incinerated with flue gases being water scrubbed. This generates large volumes of waste water containing substantial (7 to 15 ppm) Hg. DeVoe-Holbein International N.V. has been working with a major Japanese water treatment company on this important problem .

The best available technology up until this study for this problem has involved conventional sulphide precipitation as the primary treatment method of the mercury waste water. The major disadvantages reported for this treatment are threefold. Sulphide precipitation is relatively difficult to control in attempts to maximize Hg precipitation. Even at best, sulphide precipitation does not produce treated effluents with low enough mercury concentrations. In addition, the large volumes of mercury-laden precipitate are relatively labile and mobile when disposed of in for e.g. landfill sites. The incomplete effectiveness of the sulphide

precipitation primary treatment dictates a secondary treatment scheme. This has been attempted with currently-available chelating resins. However, these have not been regenerable. Thus, the polishing resins are disposed of by incineration, i.e. the mercury is once again mobilized up the incinerator stack. Therefore, it can be seen that the conventional technology applied to this problem falls far short of providing a closed-loop source reduction of the mercury.

The DeVoe-Holbein composition DH-573 which had been developed for Hg capture and shown effective in the laboratory (Table 1) was examined for its utility for this problem. Samples of incinerator srub water without prior treatment and containing between 7 and 12 ppm Hg were brought to the laboratory for analysis and test work. Table 3 shows a partial analysis of this waste water before and after treatment with composition DH-573. Two important results can be appreciated from this data. First, the wastewater is relatively rich in a number of cations, including Hg, but composition DH 573 removed only Hg from this waste water. The second point is the complete removal of Hg from the waste water by a single passage through a column of DH-573. Figure 7 shows the ICP (Inductively coupled plasma emission spectrometry) spectra for the untreated and treated waste waters in the region for Hg detection (194.23 mm). More sensitive analysis, using atomic absorption spectrophotometry with cold vapour analysis for Hg, has shown that this waste water when treated with composition DH-573 contains Hg at residual concentrations below one ppb, the detection limits for the most sensitive available equipment. Studies, using the effluents from the currently employed sulphide precipitation which contain Hg at approximately 0.1 ppm, have shown a similar high efficiency and specific removal of Hg to below the limits of detection. The relatively large outputs of a typical incinerator scrubbing system (150,000 L)per day demand that any column treatment scheme be able to meet high throughputs, preferably using high flow rates. This is another limitation encountered with the currently employed polishing resin as relatively low rates (less than 10 bed volumes per hour) must be used for Hg polishing. The DeVoe-Holbein composition DH-573 effects equally high Hg removal efficiencies at flows between lo and 30 bed volumes per hour (the highest as yet tested) (Table 4.)

The DeVoe-Holbein composition DH-573 was also found to have a capacity of approximately 4.0 grams of Hg per kilogram of composition (approximately a 1 L bed of composition) and, most importantly, the composition was found to be completely regenerable (see Table 5). The full lifetime of this composition in this application is not yet known. However, the relatively corrosive primary incinerator scrub water did not at all affect the composition over five recyclings. Studies in the laboratory have shown DeVoe-Holbein compositions to be useful for at least 300 recyclings. DH-573 composition in preliminary tests was also found efficient at Hg removal at 80° C, the exit temperature of the waste water from the scrubbing system.

TABLE 3

SPECIFICITY OF DEVOE-HOLBEIN COMPOSITION 573 FOR MERCURY REMOVAL

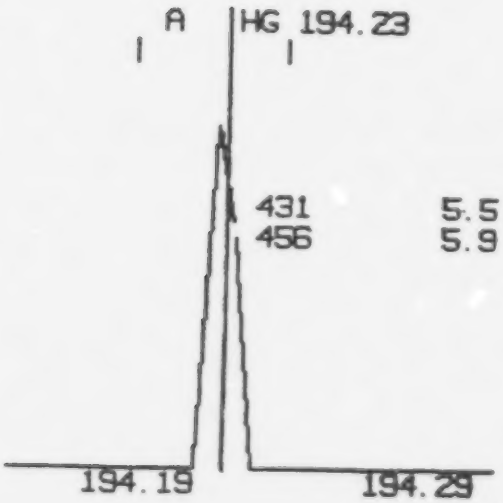
Analysis of Incinerator Waste Water before and after Treatment

Element	Concentration ppm * Before Treatment	After Treatment
Mg	2.8	2.7
Na	63,800.	64,000.
Sr	0.17	0.16
B	9.6	8.1
Si	33.7	34.2
Ca	2.0	2.2
Hg	7.2	0.0

* ICP analysis of filtered A-1 sample before and after treatment with composition 573. Fe originally present was removed by filtration.
Hg peaks shown below.

FIGURE 7

Before Treatment



After Treatment

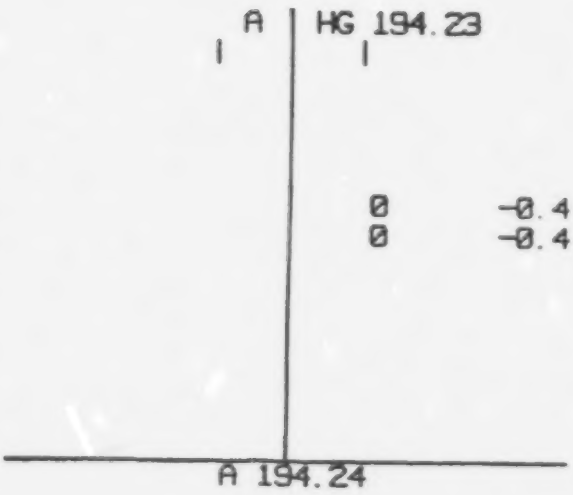


TABLE 4

Effect of Flow Rate on Hg Removal Efficiency with DH-573

Flow Rate Bed Volumes Per Hour	Influent Hg	Effluent Hg	Hg Removal Efficiency
10	11 ppm	≤1 ppb [a]	≈ 100%
20	8 ppm	≤1 ppb	≈99.99%
30	11 ppm	≤1 ppb	≈99.99%

[a] detection limits for Hg

TABLE 5

Regenerability of DH-573 for Hg Removal From Waste Water

Regeneration Number	Bed Volumes Passed to Breakthrough	Capacity Hg mg/kg Composition	Efficiency Of Regeneration	Bed Volumes of Regenerant Containing 100% Displaced Hg
1	≥230	≈4000	100%	≈2.0
2	≥230	≈4000	100%	≈2.0
5	≥230	≈4000	100%	≈2.0

The regenerant solution contains high concentrations of Hg. Studies have shown that this can be treated simply to generate reduced metallic Hg which can be collected readily Therefore all the Hg removed by this technology can be recovered in a form suitable to be returned to industry, thus closing the cycle for this toxic metal.

The DeVoe-Holbein technology, involving composition DH-573 for Hg removal, shows great promise for either primary treatment of Hg laden incinerator waste water or a greatly improved polishing treatment for sulphide precipitation effluents. Steps have now been taken to conduct full-scale field testing on site at a municipal incinerator facility in Japan.

Chromium (VI) Recovery from Plating and Boiler Wastes

Chromium is widely used in a number of metal finishing and plastic finishing operations. In addition, chromium is added to boiler systems for corrosion control. Therefore, chromium is commonly found in a number of industrial waste waters. Chromium VI is considered to be much more toxic in the environment than is chromium III and the emission standards reflect this fact. Chromium waste waters are usually handled by hyroxide precipitation with a prior reduction of Cr VI to Cr III in the case of chromate wastes. Two major problems attend this treatment scheme. The first is the large volume of Cr hydroxide wastes which must be disposed of as solid waste. This is a relatively labile waste form and the Cr can later be mobilized from the waste by natural processes and exihibit its toxicity. The second problem relates to the completeness to which Cr VI can be reduced and to which Cr III can be precipitated. Such treatments in practice often generate effluents with significant residual Cr VI or Cr III. Chromium can also be captured on conventional ion exchange resins but some resins are not regenerable and regeneration produces relatively large volumes of Cr laden waste in a mobile form.

Table 6 shows the make-up of three different chromium containing waste waters which have been analyzed and evaluated for treatment with DeVoe-Holbein technology. Example 2 is the effluent from conventional chromium reduction and precipitation of waste water from the aircraft industry. It should be noted that the residual 3,8 ppm Cr VI in this effluent is too high for normal discharge. The various effluents shown in Table 6 also contain a variety of other ions noteably calcium and magnesium which would interfere with conventional cation exchange resins should the Cr VI be reduced for capture by such resins.

DeVoe-Holbein composition DH-524 has been found to be exceptionally useful for the complete extraction of Cr VI from various waste waters, including those detailed in Table 6 (see Table 7). Very high extraction efficiencies and capacities

TABLE 6

PARTIAL ANALYSES OF DIFFERENT CHROMIUM WASTE WATERS

Element[a]	1. Boiler Blowdown Water (ppm)	2. Chrome Plating Waste Effluent[b] (ppm)	3. Cooling Tower Bleed (ppm)
Chromium (VI)	694.3	3.8	7.6
Sodium	432.	14.2	57.4
Calcium	155.3	88.4	176.4
Magnesium	64	6.8	42.1
Silicon	5.2	10.6	35.2
Strontium	0.8	0.3	0.9
Zinc	9.9	0.1	0.8
Boron	0.4	-	0.3
Iron	-	-	0.5

[a] Elemental analyses carried out by Inductively Coupled Plasma Emission Spectrometry

[b] Waste water following conventional chemical reduction and precipitation of chrome plating rinse water.

TABLE 7

Recovery of Cr from Various Waste Waters With DH-524

Type of Waste Water	Influent Cr VI ppm	Treated[a] Effluent Cr VI ppm	Cr Removal Efficiency %	Capacity mg CrVI per kilogram Composition	Regeneration[c] Efficiency
1. Boiler Blow Down	694.3	N.D.[b]	>99.99	≈20,000	100%
2. Plating Waste precipitator effluent	3.8	N.D.	>99.99	≈20,000	100%
3. Cooling Tower Bleed	7.6	N.D.	>99.99	≈20,000	100%

[a] Flow rate of 20 bed volumes per hour in a fixed bed of DH 524

[b] N.D. not detectable by atomic absorption spectrophotometry

[c] 100% of bound Cr displaced in approximately 3 bed volumes of regenerant. Fully regenerable over 15 cycles of use so far tested.

were found for this composition with these various waste waters. The composition was also found to be fully regenerable and result in small volumes of concentrated chromium waste. This chromium can either be returned for further use in the industry which generated it or it can be readily employed in secondary uses. The ceramics industry is an excellent example for secondary use. Chrome is a common colorant for glass and ceramics. DeVoe-Holbein has developed a technology employing chrome regenerant wastes and spent DH compositions where both are introduced into the ceramics industry as acceptable and useful raw materials. This closes the loop on both chrome waste and spent DH compositions, once they have served their useful lifetime of many regenerations.

Cesium and Strontium Recovery from Nuclear Wastes

Nuclear wastes consisting of various concentrations of metals at various radioactivities in water are generated both during the normal operation of nuclear power generating facilities and in the fabrication and reprocessing of nuclear fuels. Thus, various fission products including Cs and Sr are found in a range from relatively low amounts and activities in clean water systems used to store nuclear fuel to relatively high concentrations and activities in the wastes generated fron nuclear fuel reprocessing. Cs and Sr are considered important wastes from the points of view of their toxicities in biological systems and their long decay times. This has demanded safe long term storage forms for such wastes which can be met most effectively by concentration and containment. It has remained difficult to extract small but highly radioactive amounts of these metals from dilute wastes (e.g. fuel bay storage water) and to separate higher amounts of these when present in complex wastes containing a variety of other non-radioactive cations and anions at high concentrations (e.g. reprocessing wastes).

DeVoe-Holbein technology has been evaluated both in the laboratory and in the field for its ability to extract and concentrate Cs, Sr and Co from a variety of nuclear wastes. Table 8 details the analysis of two separate nuclear waste waters. Note the very low amounts of metal as radioactive Sr, Cs and Co in the waste water lagoon sample. However, significant radioactivity is associated with these metal contents. Extremely high capture efficiencies are necessary to remove these small amounts of metals.

DeVoe-Holbein composition DH-566 was found useful for the high efficiency extraction of Sr, Cs and Co from dilute wastes represented by the waste water lagoon and fuel bay storage/primary loop samples (Table 9). Substantial volume reduction factors were obtained by the column processing of these wastes with composition DH-566, while producing a treated waste effluent with no detectable amounts of ^{90}Sr, ^{137}Cs or ^{60}Co. The captured radioactive metal can be off-loaded in less than one bed volume of

TABLE 8

PARTIAL ANALYSES OF SYNTHETIC FORMULATIONS OF DIFFERENT AQUEOUS NUCLEAR WASTES

Element	Lagoon Waste Water ppm	Fuel Bay Storage Primary Cooling Water ppm
Boron	-	2000
Sodium	106	-
Potassium	-	-
Calcium	30	-
Magnesium	6	-
Iron	0.8	-
Copper	10.6	-
Rubidium	-	-
Lithium	-	4
Nickel	-	0.001
Chromium	-	0.0004
Ammonium	-	0.3
Strontium	0.1(^{90}Sr= 22μCi/L)	0.00002 (^{90}Sr=1.72μCi/L)
Cesium	0.00073 (^{137}Cs=63μCi/L)	-
Cobalt	0.00000885 (^{60}Co= 10μCi/L)	-

TABLE 9

Recovery of Various Radioactive Metals from Different Nuclear Wastes with DeVoe-Holbein Composition DH-566

Waste Sample	Radio Nuclide	Influent[a] Activity	Effluent Activity	Capture Efficiency	Volume[e] Reduction Factor
Lagoon Waste Water	^{90}Sr	22μCi/L	0[b]	100%	250
	^{137}Cs	63μCi/L	0[c]	100%	600
	^{60}Co	10μCi/L	0[c]	100%	1000
Fuel Bay Storage/ Primary Loop Water	^{137}Cs	1.7μCi/L	0[d]	100%	1500

[a] Fixed beds employing flow rates of 10 to 50 bed volumes per hour were used.

[b] Not detectable by scintillation spectrophotometry

[c] Not detectable by gamma spectrometry using a NaI detector

[d] Not detectable by gamma spectrometry using a Ge/Li detector

[e] Volume Reduction Factor = Volume processed: Volume regenerant obtained for a single cycle of capture and regeneration.

regenerant or the loaded composition, due to its chemical nature, can be vitrified directly to produce a safe, imobile, long-term concentrated waste form (see below). This is highly desirable with waste such as ^{137}Cs and ^{90}Sr due to their long half-lives for decay (approx. 30 years).

Fuel reprocessing wastes containing very high amounts of the two major fission products ^{137}Cs (3.25 Ci/L) and ^{90}Sr (0.25 mCi/L) in the presence of large amounts of non-radioactive ions such as Na (30,000 ppm) have also been evaluated in the laboratory. This is accomplished by formulating samples with predominantly non radioactive Cs and Sr to avoid undue exposure to these isotopes. DeVoe-Holbein composition DH 566 has also been found useful in capturing Cs and Sr from such wastes. Capture efficiencies of approximately 99.9% and volume reduction factors of 10 have been achieved. This is highly significant due to the very high Na content of these wastes. This technology therefore appears to hold great promise for the concentration (volume reduction) and separation of highly radioactive ^{137}Cs and ^{90}Sr from such high level wastes.

Other Applications

DeVoe-Holbein technology has demonstrated its utility for the handling of a number of other waste streams not elaborated on in this report. Compositions have been found effective for the efficient capture of a variety of metals from plating and other waste streams including Cd, Zn, Cu, Ni, Co, Ag, Pb, U and Th. Some of these applications have been the subjects of other past (2) and upcoming (3) reports.

COMMERCIAL DEVELOPMENT OF DEVOE-HOLBEIN TECHNOLOGY

The DeVoe-Holbein technology, including the compositions, methods of use and regeneration, and a double encapsulation vitrification technology are protected by a number of pending patents throughout the world. DeVoe-Holbein International N.V. holds the world-wide rights to the technology and is commercializing various aspects of the technology through its various subsidiaries and joint ventures. Research and applications development are carried out at Laboratories in Dorval, Canada and Den Haag, Holland. North American Nuclear Corp. is commercializing nuclear applications in North America. DeVoe-Holbein/John Brown B.V., a joint venture company with John Brown Engineers and Constructors is commercializing certain aspects of the technology for the non-nuclear industries in both Europe and North America. DeVoe-Holbein International N.V. is working under an agreement with C. Itoh and Company of Japan in the commercialization of various aspects of the technology.

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2) DeVoe, I.W. and B.E. Holbein. 1983, New Technology for the high affinity capture of radioactive metals from Water. Proceedings, 4th Annual Conference of the Canada Nuclear Society. Volume 2: I25 - I43.

3) Neirinck, L.G., D. Brener, C.W. Green, E.N.C. Browne, B.E. Holbein I.W. DeVoe, R. Ek. 1985. Novel compositions for high efficiency and specific removal of heavy metals from metal finishing and other waste streams. Paper to be presented at the 6th AES/EPA Conference on Pollution for the Metal Finishing Industry.

LIQUID-FILLED MEMBRANES

Liquid-filled membrane technology is not yet at a point where it can be applied on a commercial scale by any means, but it holds a significant potential for the removal of metals, particularly where selectivity is needed.

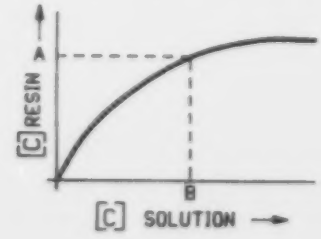
Several groups are actively engaged in research into liquid-filled membrane technology in the U.S.A., South Africa, and Israel. Although not yet applicable to acid mine drainage treatment, mention is made of the technology here to remind sponsors to keep an eye on this emerging technology.

Liquid-filled membranes work in much the same way as ion exchange resins in that metals are adsorbed from the liquid phase onto the membrane. The membrane may be an ion exchange type material similar to resins, or it may be a support for a solvent extraction organic phase, so membranes may function as solid/liquid or liquid/liquid ion exchange systems. The great advantage of liquid-filled membranes is that whereas the one side of the membrane is exposed to the feed pulp or solution, the other side may be exposed to the strip solution which continuously elutes the loaded resin membrane in the case of the liquid/solid IX mode and elutes the liquid film in the case of the liquid/liquid mode.

Because the adsorbant media is constantly being eluted, the loading on it never approaches equilibrium, and the adsorption system operates in a region where equilibrium favors adsorption even though there may be a high concentration of the recovered metal in the strip solution.

For normal IX and SX systems, several stages are needed to be able to bring the concentration of the adsorbed species down to a low level due to equilibrium considerations. Ion exchange resins loaded with metal values cannot remove metals from feed solution below a concentration that is in equilibrium with the partially loaded resin. That is, if resin loaded to [C]resin=A is brought into contact with a solution with concentration less than [C]solution=B, then metal will desorb from the resin to the solution and contactor concentrations of the metal ion in question cannot be reduced below B by that particular resin loaded to A.

CHELATION



Since in the liquid-filled membrane system metal values are constantly eluted from the system, adsorption in one contactor can proceed all the way down the equilibrium curve to very low concentrations.

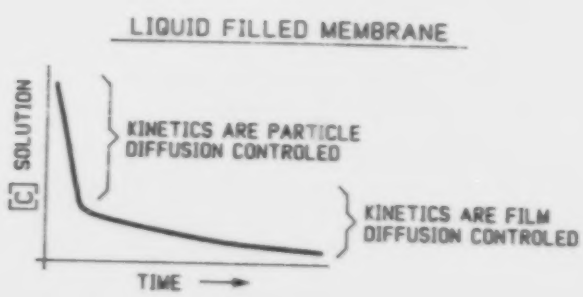
Other advantages of liquid-filled membranes are:

1) Very expensive selective reagents can be applied in small amounts since extractant reagent consumption is said to be very low. This opens the way to using very selective crown-chelating ethers, for example.

2) In systems where the membranes are attached, a single contactor can be equivalent to an infinite number of stages where perfect mixing in each stage is assumed for conventional fluid bed IX systems.

3) Because metals are eluted at the same time as they are adsorbed, the size of the system can be reduced considerably. That is, a very much smaller surface area of membrane should do an equivalent job to that of a large amount of resin or organic phase SX.

Based on early testwork and IX theory, it has been found that adsorption at high concentrations is particle diffusion kinetics controlled and at low concentration ranges, it is film diffusion kinetics controlled. Consequently, whereas liquid-filled membranes should work very well at relatively high concentrations in the feed solution, very large surface areas are needed to achieve a reasonable transfer rate of metal ions from feed solution to the membrane.



Early tests on uranium and copper recovery by BEND RESEARCH of Bend, Oregon, for the U.S. Bureau of Mines demonstrated this fact when using sheet membrane surfaces. This led to the development of 0.025" i/d hollow membrane fibers which provide a larger surface area and in their case, a process for recovering hexavalent chromium from metal

finishing operations which is designed to treat more concentrated effluents which are reduced to 10-20 ppm Cr.

Research and development work into liquid-filled membranes is known to be undertaken by:

Polymeric Crown Ethers - Compounds

Dr. A. Warshawsky	Weizmann Institute Rehovot, Israel
Dr. Jorgenson	Brigham Young University Provo, Utah
Professor Marr	Technical University of Graz Graz, Austria
Professor Johan Smit	Dept. of Chemical Engineering Christian University of O.F.S. Potchefstroom, OFS South Africa

Liquid-filled Polymer Filament Modules -

Dr. Harold K. Londsdale Dave Kamperman	Bend Research, Inc. 64550 Research Road Bend, Oregon 97701 (503) 382-4100

The BEND RESEARCH filaments have a 0.025 inch inside diameter, and feed solution flows through the inside with stripping taking place on the outside. Modules are about 3 feet long and 5-6"Ø, and the system operates under a low pressure. The commercial units were still in the final stages of development as of January, 1985.

Plastic Membranes for Liquid-Filled Membranes -

Celgard Membrane:	Celanese Corp., Inc. Charlotte, North Carolina Don Taft Ed Barnes
	Celanese R & D Summit, New Jersey Harry Taskier

Stein Hall SA (Pty) Ltd.
Post Office Box 520
Meyerton 1960
South Africa
(01612) 2-2340
Martin Hattingh, Managing Director

The Celgard membrane is designed to have up to 70% porosity, and most of the R&D work for development of a liquid-filled membrane process is being conducted in South Africa in conjunction with Professor Johan Smit of the Potchefstroom University.

It is emphasized again that liquid-filled membrane systems are not yet available on a commercial scale. Some workers in this field have indicated that crown-ether extractant liquid-filled membranes tested to date are relatively low flux units and, although very selective, have not been developed beyond an academically interesting phenomenon for that reason.

BIOLOGICAL OXIDATION FERROUS TO FERRIC

Biological oxidation of ferrous to ferric ions enabling iron to be precipitated as a hydroxide has been encountered as follows:

- Natural bogs in a West Virginia coalfield.
- The Portabog experiment by USBM.
- Suspended growth system of Thiobacillus Ferroxidans attached as a covering film to particulate bentonite.
- Use of rotating biological contactor-supported bacteria to convert Fe^{2+} to Fe^{3+}.

KLEINMANN, et al. (1983) described a portable bog experiment in which acid mine drainage was treated successively in five sections of loosely packed acid-conditioned sphagnum moss and one section of course limestone. The moss tolerated pH down to 2.3 and when the influent salt load decreased to less than 150 mg/l, the rate of acidity removal decreased. Apparently the portabog did not completely simulate results in a mature natural bog which has a deeper anaerobic zone.

KLEINMAN (1984 personal communication) showed slides of a natural bog containing sphagnum moss and cattails in West Virginia into which acid mine drainage from an adjacent coal spoil bank flows.

Within ten feet of the edge of the bog, the pH has increased to pH 4, and iron has precipitated and flocculated as ferric hydroxide. The mechanism for oxidation of the

ferrous ions and for the pH increase was not altogether explained. The USBM personnel are very interesting sources of information:

U.S. BUREAU OF MINES
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Dr. R. L. P. Kleinman
Patricia M. Erickson

THEIS, et al. (1982) described a method for oxidizing ferrous to ferric iron in acid mine drainage through the use of a suspended growth system of thiobacillus ferroxidans attached in a film to individual particles of bentonite and operated as a sequencing batch reactor. It was claimed that such biological oxidation followed by limestone neutralization is less expensive, safer, requires a lower pH, has a smaller solids buildup and avoids the danger of overtreatment while being very flexible.

Several experiments have been undertaken to oxidize ferrous ions in solution to ferric using bacteria attached to rotating biological contactors. It is believed that the HOMESTAKE MINING COMPANY has undertaken similar tests, but no published data was found. NOIKE, et al. (1983) examined bacterial activity in acid mine drainage containing 640 ppm Fe^{2+} and 4,500 mg/l SO_4^{2-}. It was found that acidophilic Fe oxidizing bacteria from the receiving waters have the greatest activity at about 30°C and pH 2.

The rate of oxidation of Fe^{2+} increases exponentially between 20°C and 30°C as retention time increases, and the activity of the acidophilic Fe-oxidizing bacteria decreases greatly at ten degrees. The number of bacteria attached to the surface of a rotating biological disc was found to increase as the ferrous Fe loading increases.

A considerable amount of work has been undertaken by the Pennsylvania State University on the use of rotating biological contactors for the treatment of acid mine drainage.

UNZ and WICHLACZ (1982) determined that transformation of Fe^{2+} in rotating biological contactors for the partial treatment of acidic coal mine drainage is capable of achieving Fe^{2+} oxidation efficiencies of 90% while sustaining a resilient population of chemolithotrophs over a wide range of temperature, pH, and mass Fe^{2+} loadings. Performance of the system was shown not to be adversely affected by sudden alterations of abiotic variables over the range typical in the natural environment. It was found that the microbial composition of the mine drainage environment consists of diverse acidophilic chemo-organotrophic bacteria in addition to the chemolithotrophs. Interrelations which may exist between the two microbial groups need to be identified to exclude the possibility that combined heterotrophic-autotrophic activities are the major biological force in the generation of acidic mine drainage.

Earlier work by Pennsylvania State University was described by OLEM and UNZ (1980, 1980A) in which a prototype rotating biological contactor was evaluated under conditions simulating actual treatment of acid mine drainage. Under all conditions, continuous microbiological oxidation of Fe^{2+} to Fe^{3+} occurred. At mine water temperature as low as 0.4°C, Fe^{2+} was found to occur albeit at a reduced rate.

Pilot scale (0.5 m diameter) and a prototype (2 m diameter) RBC's were investigated as a means of oxidizing ferrous ions in six heterogeneous mine waters at three coal mines in Pennsylvania and West Virginia. Continuous biological oxidation of ferrous ions was achieved at natural mine temperatures ranging from 0.4°C at Hawk Run, Pennsylvania, to 29°C at Crown, West Virginia. At 0.4°C, the oxidation rate of Fe^{2+} was 10-20% of that achieved at 10°C. At 10-29°C, oxidation efficiency of Fe^{2+} was about 80%. At Crown, West Virginia, the oxidation of Fe^{2+} with the 0.5 m RBC was unaffected by influent pH values in the range 2.18-5.50.

Fe^{2+} oxidation was, on average, 10% less efficient for a minewater treated under similar operating conditions with the 2.0 m RBC than with the 0.5 m RBC.

Neutralization of RBC effluent and separation of precipitated iron sludges is necessary to produce water of suitable quality to be discharged to a stream. Both Fe oxidizing and heterothrophic bacteria existed in a gelatinous matrix on the RBC disc surfaces which were operated at a test site at Hollywood, Pennsylvania.

Additional information has been requested from:

DR. RICHARD F. UNZ
Dept. of Civil Engineering
Pennsylvania State University
212 Sackett Building
University Park, PA 16802
(814) 863-2940

DR. HARVEY OLEM
Water Quality Dept.
Tennessee Valley Authority
248, 401 Building
Chestnut Street
Chattanooga, TN 37401
(615) 751-7322

RBC manufacturers are generally interested in expanding the applications of their equipment but, for the most part, do not have much experience outside the municipal waste water treatment industry. They are currently willing to supply test units of various sizes to demonstrate or test new applications:

WALKER PROCESS CORP.
840 North Russell Avenue
Aurora, IL 60506
(312) 892-7921
Telex: 720-430
Art Schlitt, Product Manager

WALKER PROCESS CORP.
Post Office Box 652
Austin, MN 55912
(507) 433-7345
Christopher Thissen

ENVIREX, Inc.
Post Office Box 1067
Waukesha, WI 53186
(414) 547-0141
Biological Treatment Group:
J. Wittmann
New Business Development:
Rich A. Sullivan

TED MILLER ASSOCIATES
Colorado Agents for Envirex, Inc.
2140 South Ivanhoe
Denver, CO 80222
(303) 758-3912
Debbie Miller

In general RBC's are applicable where:

1) The organism grows on a fixed media.

2) The organism can slough from the media after it completes its life cycle.

Walker Process supplies test units in two sizes:

- 6'Ø media with 4 modules, each 3' wide with a total of 22,000 ft^2 constructed in a steel tank which hooks up for inflow and outflow.

- A 3'Ø media unit which is 2' wide for bench scale pilot testing.

UNZ, et al. (1979) reported that supplementation of a synthetic feed solution with acid mine drainage water enhanced the oxidation of Fe^{2+} by Thiobacillus ferrooxidans in small scale RBC's, although the active ingredient was not known. At temperatures much below 10°C, the oxidation rate was reduced substantially, but at 25°C, the oxidation was not much different from that at the 10°C control. In the pH range 2.2-5.2, efficiencies were usually over 80%.

BIOLOGICAL SULFATE REMOVAL

Biological oxidation of thiosulfate has been attempted at NEW BRUNSWICK MINING AND SMELTING near Bathurst, N.B., in Canada. These experiments with activated sludge and pebble beds are reported not to have indicated an economically attractive or practical process for this particular case. The aim at Brunswick Mining was to oxidize thiosulfate so that the acid generated could be neutralized before the effluent leaves the property, rather than sulfate removal.

Sulfate removal may become necessary to meet effluent discharge regulations in some parts of the U.S.A. where 250 ppm $SO_4^=$ has been included in proposed effluent discharge regulations. The motivation for such a low level is not known, but such a proposed standard is referred to by HOLM and SIMPSON (1981). In South Africa on the Witwatersrand, regulations are being considered which will limit point source discharge TDS levels, possibly at 250 mS/m which is around 2000 ppm TDS. Sulfate forms a significant part of the TDS load of such effluents even after neutralization.

The possibility of removing sulfate biologically is worth further investigation because the alternative--desalination by reverse osmosis and evaporation or electrodialysis--is relatively capital and operating cost intensive.

The reduction of sulphates in natural waters through the agency of filamentous algae attached to rocks and pebbles is well established and was in fact the subject of a presentation to the French Academy of Sciences by M. E. Plauchud. Living filamentous algae in the presence of calcium sulfate yield H_2S.

Since 1886, it has been known that bacterial action produces H_2S from sulfates, or, in the presence of gypsum, iron oxide and a source of carbon, the products are likely to be $CaCO_3$, FeS, CO_2, and CH_4. Experimental results to this effect were reported by F. HOPPE-SEYLER (1887).

In 1882, ETARD and OLIVER found that some bacteria, the Begiattoa which are common in lakes and the sea, especially around sulfurous waters, contain sulfur granules in their protoplasm. When the same bacteria are grown in solutions free from sulfates, the sulfur granules disapeared, forming again when the bacteria were grown in a solution of calcium sulfate.

Filamentous blue algae of the genus Oscillaria and green algae of the genus Ulothrix were also found to decompose sodium and calcium sulfates with formation of sulfur and hydrogen sulfide.

The Dutch bacteriologist, W. M. BEYERINCK (1895), recognized the very considerable importance in nature of bacterial reduction of sulfates which he correctly suggested was

the cause of the high H_2S content of Black Sea water. He also predicted that the absence or extremely low levels of sulfates in the deeper layers of soil in certain parts of Holland was due to sulfate-reducing bacteria which has also subsequently been verified.

BEYERINCK isolated an organism, Spirillum desulfuricans, which has since been named Microspira desulfuricans which rapidly reduces sulfates under anaerobic conditions to H_2S.

As a result of bacterial reduction of sulfate in the salt water canals of the Dutch coastal tract, this water is often high in H_2S, and the canal bottoms are often coated with muds which, to a thickness of many meters, are blackened by iron sulfide with only a few mm of light-colored muds overlying the black mud. VAN DELDEN (1903-1904) ascribed the H_2S generation to an organism which he named Microspira aestuarii.

M. desulfuricans is intolerant of salt water, and M. aestuarii is intolerant of fresh water although both are tolerant of brackish water to 1.5% NaCl. Both are strictly anaerobic, and the presence of organic food in the culture media is essential for sulfate reduction.

Optimum temperature for the growth of M. aestuarii is 25-30°C. The organism will take oxygen from not only sulfates, but also sulfites, thiosulfates, and to a limited extent from nitrates. Where oxygen was present, sulfur was found due to the decomposition of H_2S. $2H_2S + O_2 = 2H_2O + 2S$.

ELION (1924-1925) discovered another bacterium named Vibrio thermosulfuricans that flourishes best at 55°C and appears to grow more rapidly than Microspira desulfuricans and M. aestuarii. Growth rate diminishes both above and below the optimal temperature. Media innoculated with Vibrio thermo-sulfuricans showed profuse growths overnight. Sulfate reducing bacteria have been found in river muds, brackish canal muds, sewage, soils, lake sands, dune sands at depths to 37 m, black muds of the ocean bottom to depths of 16 fathoms, and bottom muds of the Black Sea to depths of 2,118 m where conditions are highly anaerobic with pressures as high as 3,000 psi.

According to tests by ALLEN, CRENSHAW and JOHNSON (1912), when copper sulfate is present with calcium sulfate, the possibility of bacterial action is eliminated through the creation of aseptic conditions. The level of copper that can be tolerated was not quantitatively established.

The above details were extracted from a summary by BASTIN (1920's) and clearly indicates that several bacteria reduce sulfates and, depending on conditions, yield $CaCO_3$, H_2S, and CH_4 or $CaCO_3$, H_2O, S, and CH_4. This phenomenon is potentially useful in the removal of sulfates from solutions or in precipitating heavy metals in polishing ponds.

STARKEY (1956) pointed out that inorganic sulfur compounds including H_2S, $S_2O_3^{=}$, polythionates, $SO_3^{=}$, and elemental S are produced by micro-organisms in the aerobic and anaerobic transformation of organic and inorganic compounds of sulfur or reach waters in waste materials. These can be oxidized by three groups of autotrophic bacteria, namely photosynthetic sulfur bacteria, colorless sulfur bacteria with large cells sometimes producing filaments and colorless bacteria of the genus Thiobacillus. Various heterotrophic microorganisms including bacteria, aclinomycetes, and filamentous fungi also oxidize some of the sulfur materials. Each of these mechanisms is described, but the important aspect is that whereas some bacteria reduce sulfates, other microorganisms can reverse the reactions.

STARKEY (1956) mentions several additional bacteria that reduce sulfate or incompletely reduced sulfur compounds such as sulfite, thiosulfite, tetrathionate, and elemental sulfur; for example, the genus Pseudomonas was found to reduce thiosulfate to sulfide. He suggests that the most important sulfate reduction process is that affected by the specific sulfate-reducing bacteria known as genus Desulfovibrio, the most common of which is referred to as Desulfovibrio desulfuricans.

Sulfate-reducing bacteria are strictly anaerobic and use the sulfate as the hydrogen acceptor, and sulfite, thiosulfate, and tetrathionate can be used in place of sulfate. Various organic materials can be used as hydrogen donors including organic acids, alcohols, amino acids, and carbohydrates, following the typical reactions:

$$2\ CH_3\ CHOHONa + MgSO_4 = 2\ CH_3\ COONa + H_2S + CO_2 + MgCO_3 + H_2O$$

$$4H_2 + CaSO_4 = H_2S + Ca(OH)_2 + 2H_2O$$

The sulfate reducing bacteria have been implicated in anaerobic corrosion of iron and steel. This corrosion is rapid and is not self-stifling as is rusting where the adherent oxide film protects the underlying metal. Sulfide coating of the metals (or concrete) are then attacked by bacteria such as Thiobacillus ferroxidans or Thiobacillus sulfoxidans which generate relatively concentrated sulfuric acid at the localized surface which corrodes the metal or concrete surface. An example of where this is observed is described in the trip report on the ROSSING URANIUM MINE in Namibia where corrosion is associated with jarosite scale in pipelines carrying sulfate-rich reclaimed tailings solution.

WAKAO, et al. (1979) tested sulfate reducing bacteria in a mixed bacterial population as a means of removing $SO_4^{=}$ from acid minewaters from the abandoned Matsuo Sulfur and Pyrite Mine in Iwate Prefecture, Japan. Batch and continuous flow systems were tested using sawdust as the basic culture medium. Vigorous $SO_4^{=}$ reduction and neutralization of the acid mine water occurred in the batch cultures supplemented with organic nutrients peptones, Na-formeate, Na-lactate, or Na-pyruviate. SO_4 reduction worked only above

pH 4 and was tested in the range 4-5.2. pH seems to have been increased through the activity of other heterotrophic microflora. Neutralization of the acid mine water to pH 4 by SO_4-reduction was possible in the continuous flow system if organic nutrients usable by the bacteria were supplemented and the flow rate of the effluent property controlled.

Although the organic nutrients selected and the use of sawdust as a growth medium does not appear very practical for large-scale commercial applications, WAKAO, et al. (1979) have demonstrated that, in principle, biological processes have a potential application in the removal of sulfates from acid mine drainage. More information has been requested from:

DR. NORIO WAKAO
Agriculture Faculty
Awate University
Morioko 020 Japan

Given the recent extension in application of biological processes for the treatment of mine and mill effluents, it is believed that bacterial processes hold significant potential for reducing sulfate levels from neutralized AMD. It is emphasized that this is still in the concept stage with no practical cases known to date.

BRIERLEY and BRIERLEY (1981) refer to sulfate reducing bacteria Desulfovibrio and/or Desulfotomaculum being present in minewater ponds at a uranium mine in New Mexico and found that these may have a role in the removal of uranium, selenium, and possibly molybdenum from solution.

SPISAK (1979) saw metallurgical effluents of the nonferrous industries to represent a growing challenge to microbiological research. New environmental protection effluent discharge limits cannot be met by conventional chemical treatment, and he regards biochemical approaches as being one of the few methods that may be able to achieve the emerging objectives, especially for removing arsenic, for example, from smelter scrubber bleed solutions.

Sulfur compound removal was identified by SPISAK (1979) as being complex and important, particularly for copper smelter-refineries from which "a plethora of sulfur problems" in the form of sulfur dioxide, acidic tailings streams, sulfate saturated effluents, and sulfate containing dusts combine to create some serious environmental compliance barriers. These streams are often highly acidic at pH 1.0-2.0 in acid mine drainage, for example, and at pH 9-10.0 in ammonia-type hydrometallurgical process discharge streams from solvent extraction. He refers to work at the University of Arizona by CORK and CUSANOVICH (1978) which indicated a mutualistic relationship between Desulfavibrio desulfuricans and Chlorobium thiosulfatophilum in which sulfate is reduced to sulfide and subsequently re-oxidized to elemental sulfur. The sulfate source in this work was a solvent extraction raffinate derived from an oxidative ammonia leach

process employed by THE ANACONDA CO. for the processing of copper sulfide concentrates. Conventional treatment of this ammonium sulfate is to add calcium hydroxide and live steam for the purpose of recovering ammonia and fixing the sulfate as gypsum. This method does not address the problem of eventual disposal of the low-grade gypsum product.

A bacterial system that combines sulfate treatment and the production of potentially valuable by-product sulfur could be of significant advantage, but the inherent complexity of a mutualistic bacterial system was considered to be a potential stumbling block for a commercial process.

Some of the potential economic problems arising from the work of CORK and CUSANOVICH (1978) include the dependency of Desulfovibrio desulfuricans on sodium lactate as a reductant source. Although the bacteria efficiently reduce $SO_4^{=}$ to H_2S rapidly, the use of lactate as a substrate would be prohibitively expensive.

Sewage or pulp wastes could be employed as carbon sources, but problems would arise concerning additional impurities and rate considerations.

Oxidation of H_2S to elemental sulfur by Chlorobium thiosulfatophilum is not difficult because these bacteria are photosynthetic, and they excaete sulfur outside the cell. The use of cell culture to produce a final product, sulfur, presents complex problems of physical separation which add both cost and complexity to any proposed treatment scheme.

SPISAK (1979) shows a schematic representation of a bio-process for sulfur based partially on the work of CORK and CUSANOVICH (1978).

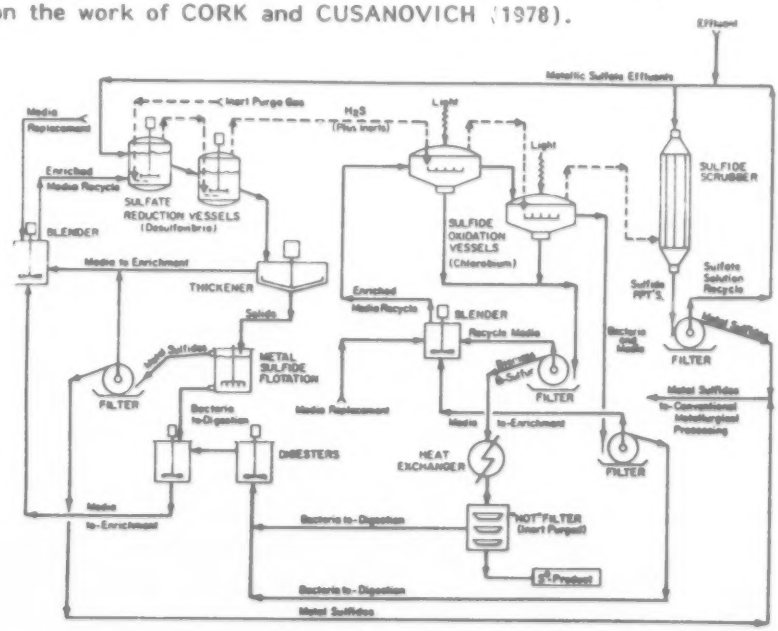


FIG. 3. Bio-Process sulfur recovery.

A sulfate effluent stream is slowly fed to a series of reduction reactors containing Desulfovibrio desulfuricans. An inert purge gas carries away H_2S generated to a series of photosynthetic reactors where Chlorobuim thiosulfatophilum generate elemental sulfur. The remaining sulfide gas proceeds to a metal sulfate scrubber where its discharge would be transported to a conventional metallurgical process.

Settled residues from the sulfide oxidation vessels would be continuously bled to a filter where the bacterial matter and sulfur would be separated from the media solution. This solid material then reports to a heat exchanger under inert atmosphere, and the sulfur is melted and filtered away from the biomass. The cooled filtrate is the final sulfur product while the biomass goes on to a digester for nutrient recycle. Additionally, a continuous bleed of cells from the oxidation reactors is maintained in order to hold a stable population in the reactors. These cells would be moved to digesters while the media would be enriched and recycled.

Likewise, a continuous bleed of cells and metal precipitates would be drawn from the sulfate reduction reactors and partially dewatered. The resultant solids would undergo conventional hydrometallurgical flotation in which metal sulfides are treated with surfactants and, using air sparging, are floated from the rest of the residue. These metal sulfides would then be dewatered and transported to a conventional metallurgical process while the remaining bacteria are sent to digestion for media enrichment. The products of these several stages of biomass digestion must be acceptable as nutrients to the Desulfovibrio reactors or the economic advantages of such a flowsheet would be lost.

From the above concept description, it is clear that the sulfur recovery flowsheet would be relatively complex and expensive but would yield a valuable by-product while recycling most of the needed energy internally. Considerable R&D and pilot scale development work would be needed to make this process suitable for consideration on a commercial scale. SPISAK (1979) has succeeded in demonstrating the technical potential for such a process within a metallurgical environment.

John F. Spisak prepared the above paper while employed by THE ANACONDA CO. He can now be reached at:

JOHN F. SPISAK
Anschutz Mining Company
555 Seventeenth Street, #2400
Denver, CO 80202
(303) 573-7954

BIOLOGICAL METAL REMOVAL PROCESS

Biological metal removing processes involving plants, algae, and/or bacteria have already been discussed in connection with passive AM[illegible]ment or polishing.

This method represents a significant potential horizon but requires significant further research and development.

ALGAE

SHERRITT and LESTER (1979) reviewed the removal of heavy metals and neutralization of acids in mine wastewater by algae and bacteria.

Several successful projects have been undertaken to remove metals and organics in polishing ponds as described above under passive treatment systems, and it is believed that a new biological polishing pond is to be installed at RIO TINTO ZINC's zinc refinery at Avenmouth, England.

DR. A. K. BARBOUR
RTZ Services Ltd.
York House
Bond Street
Bristol BS1 3PF
England

A leading proponent of the use of engineered biological polishing ponds for base metal mill effluents is:

DR. BOBBY G. WIXSON
Director and Professor of
Environmental Health
Center for International
Programs and Studies
Rolla, MO 65401
(314) 341-4208
(314) 341-4483

A summary of this work is provided by GALE and WIXSON (1979).

It is important to regard bogs and marshes as an ecological system consisting of plants, algae, and bacteria, all of which can be used to advantage. Multidisciplined knowledge is needed to define all the parameters to allow such systems to be optimized and engineered. It is important to determine the effect of an algae or plant on direct metal removal, but it is more important to understand the net ecological effect including putrification of dead biomass, bacterial processes, etc. in the complete ecosystem.

JENNETT, SMITH, and HASSETT (1983) presented a summary of "Factors Influencing Metal Accumulation by Algae." This review refers mainly to studies around the New Lead Belt of Missouri which has been the subject of intense study.

JENNETT, et al. (1983) seeked laboratory-derived information on the factors influencing heavy metal accumulation by algae which is only one side of the coin, albeit an important

one. An interesting observation is that most of the metal removed by algae can be recovered by a rinse with 0.01 M EDTA or 0.1 N HNO_3 which suggests that surface adsorption is the principle mechanism for removal of metals by algae from an effluent stream. Also, the ability of algae to remove metals was found to be generally in the following order starting with the highest to the lowest: mercury, lead, cadmium. Neither zinc nor arsenic was significantly removed at any pH by the algae during a three-hour exposure.

The authors of this paper on algae accumulation of metals all work at Syracuse University, New York.

Russian investigators, KOVAL'SKIY and VOROTNITSKAYA (1965), reported that algae are involved in the translocation of uranium in a lacustrine environment. The alga, Chara, could concentrate uranium in lakewater up to 1,000 times. Uranium in the Chara eventually passes to the lake muds since uranium concentrations in the mud correlated directly with the amounts of the element associated with the Chara. Chara is a calcareous algae and is encrusted with crystalline hydrous carbonates. It is possible that uranium associated with Chara may be liebergite $Ca_2UO_2(CO_3)_3\ 9H_2O$ according to KOVAL'SKIY and VORATNITSKAYA (1965). Chara has been attributed to removal of uranium from minewater by BRIERLEY, et al. (1980).

BRIERLEY and BRIERLEY (1981) concluded, however, on the basis of a four-year study on site at a treatment facility for minewater from two mines, No. 35 and No. 36 of Kerr McGee Nuclear Corp. at Ambrosia Lake near Grants, New Mexico, that:

1) The concentrations of soluble uranium, selenium, and molybdenum were not diminished in minewaters by passage through the series of impoundments which constituted the minewater treatment facility. Uranium concentrations were reduced, but this was due to the passage of the water through an ion exchange column.

2) Particulate concentrations of the minewater were reduced at least ten-fold by passage of the waters through the impoundments. Since uranium, selenium, and molybdenum were associated with suspended particles, reduction in the concentration of total suspended solids reduced the concentration in the final effluent.

3) The ponds were well oxygenated. This was probably due to their shallow depth and the growth of algae.

4) The pH remained near neutral during all collections which would indicate that the major soluble species would be molybdate, uranyl carbonate, and selenite (and possibly selenate at higher pH values).

5) Temperature remained above 10°C in winter suggesting that plant and microbial life could remain active even in winter because the volume of water was large enough to lessen large temperature fluctuations.

6) Phosphate and nitrate were present in high enough concentrations to support limited algal and microbial activity.

7) Sediments were anonic and enriched in uranium, molybdenum, and selenium. The deposition of particulates and the formation of insoluble compounds were proposed as mechanisms for sediment enrichment.

8) The predominant algae of the treatment ponds were the filamentous Spirogyra and Oscillatorea and the benthic alga, Chara.

9) Adsorptive processes resulted in the accumulation of metals in the algae cells.

10) Laboratory study indicated that Spirogyra was more active than Chara in the removal of uranium and molybdenum from solution.

11) The algae appeared to act as bio-filters for accumulation of particulate pollutants in the ponds.

12) The retention of uranium and molybdenum in sediments following the death and decay of the algae was dependent on the maintenance of reducing conditions.

13) The pond sediments had large numbers of sulfate-reducing bacteria Desulfovibrio and/or Desulfotomaculum.

14) Stimulation of sulfate reduction by the bacteria resulted in retention of molybdenum, selenium, and uranium in sediments.

15) Estimation of algae productivity and removal of uranium and molybdenum by the algae indicated that both stimulation of algal productivity and the increase in pond size are necessary for the system to be effective in the removal of trace contaminants.

16) Anaerobic biological reactors show promise for use in the removal of U, Se, and other pollutants in uranium mine wastewater.

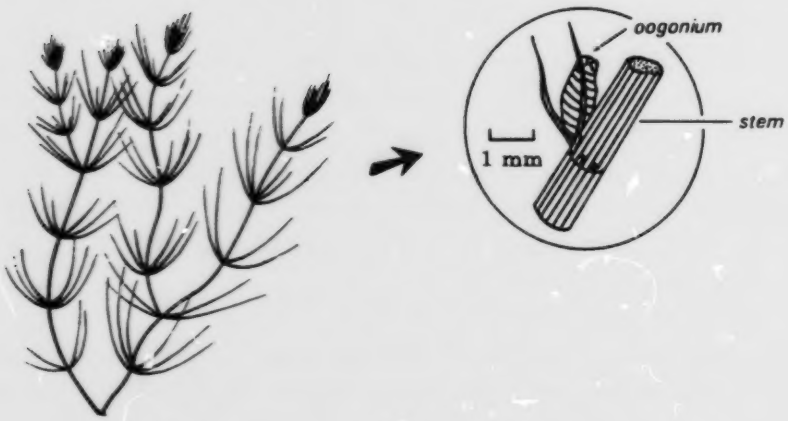
17) Studies must be continued to optimize biological reactor column design and nutrient source.

The BRIERLEY and BRIERLEY (1981) report contains an excellent description of relevant chemistries of uranium, molybdenum, and selenium and of literature searches of biological mechanisms for the removal of these metals.

In 1984, testwork in the propagation and use of benthic alga Chara for removal of metal contaminants including uranium was started in the Elliot Lake district at RIO ALGOM LTD. and DENISON MINES LTD. This work is being undertaken by:

BOOJUM RESEARCH LIMITED
26 Geneva Avenue
Toronto, Ontario M5A 2J8
(416) 922-9002
Dr. Margaret Kalin

CHAROPHYCEAE



WATER HYACINTHS

NATH (1982) included a mention of the usefulness of the water hyacinth in treatment wastewaters in tropical or warm temperate climates. This plant does not grow in water that is 50°F or colder; their optimum growth temperature being 70 to 86°F. The water hyacinth selectively filters out heavy metals (Cd, Hg, Ni, Pb, and Ag) and can adsorb and metabolize nutrients in sewage effluents according to WALTERS (1976), MIDDLEBROOKS and REED (1981), and PARKINSON (1981).

In sewage treatment water, hyacinths have been harvested for use in methane generation and as feed rations for beef cattle. The economics of harvesting this aquatic plant were

not yet resolved in 1982, and plants harvested from industrial wastewater treatment lagoons cannot be processed into animal feed because of the presence of toxic metals.

More information may be available from:

RAVI L. NATH
Chief Environmental Engineer
Fluor Mining & Metals, Inc.
10 Twin Dolphin Drive
Redwood City, CA 94065
(415) 595-6000

SPISAK (1979) referred to a common New Zealand lake weed, Ceratophyllum, which is effective in arsenic removal from effluents which would be dried and ashed. It is reported by CHAPMAN, et al. (1974) that certain algae indigenous in some New Zealand Lakes can contain up to 2% arsenic of their dry weight. These organisms, Ceratophyllum demursum and Largosiphon major, are capable of assimilating large amounts of arsenic and continuing to grow.

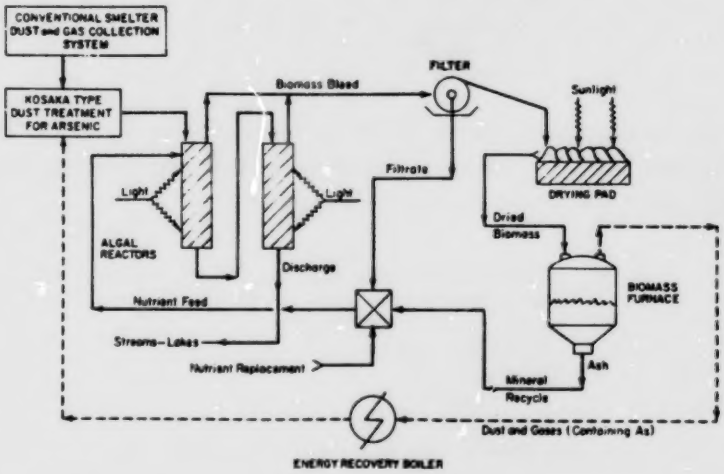
The rate of arsenic uptake by these weeds is phenomenal. In a series of experiments designed to kill off fouling algae in New Zealand, arsenic salts were dumped into a Waikato river-fed lake to a concentration of 5 mg/l. The rate of algal assimilation reduced the quantity of arsenic present in the water by 80% per day according to FISH (1963) until a stable concentration of 6 micrograms/l was achieved. Application of this assimilation rate to a copper smelter effluent containing 1 mg As/l would achieve 40 micrograms/l in a two-day period.

SPISAK (1979) proposed a supplemental arsenic scrub circuit for treatment of scrubber bleed streams which consists of a series of high surface area to volume ratio, light penetrable reactors to accept the arsenic bearing effluent. The reactors would contain a 5% by weight algal solution where a total system of water plus algae would consist of 26,000 kg. The 5% wet weight fraction of algae would represent 1,300 kg of plants which would be capable of assimilating a total of 2.6 kg of arsenic. With an effluent feed at 300 l/min at 1 mg As/l at neutral pH, and assuming 1 g arsenic assimilation per 100 dry grams algae per day, approximately 430 kg algae must be harvested per day to balance the daily imput of 0.43 kg arsenic per day. A daily harvest of 430 kg would remove all the influent arsenic and allow for a 50% plant mass regeneration per day.

The two photosynthetic reactor vessels containing a total of 1,300 kg of algal plants in 24,700 kg water would constitute the arsenic assimilation phase of the process.

The daily 430 kg biomass bleed would be filtered on a drum filter for dewatering. The filtered liquor would proceed to a small mixup vessel where growth nutrients would be replenished and recycled to the reactors. The filtered algae would proceed to a drying pad, and the dried biomass then incinerated in air at a temperature exceeding 300°C to

insure vaporization of the As_2O_3. Hot gases would pass through the heat exchanger of a waste heat boiler for energy recovery and then, carrying the condensed arsenic would proceed to a Kosaka-type dust treatment process thus closing the loop as illustrated. This discharge liquor from the algal reactors would average 40 ppb arsenic/l and would therefore be suitable for discharge.



Supplemental arsenic scrub circuit for treatment of a Kosaka-type effluent.

SOURCE: SPISAK (1979)

SPISAK (1979) provided an equipment list and a capital and operating cost estimate for the arsenic removal system which for a plant producing 60 metric tons of copper per day. He worked out a cost of U.S. ¢0.09/lb Cu produced, and capital costs in 1978 were around $834,000.

BACTERIA

Numerous accounts of metal removal through bacterial action have been noted in nature, and several attempts to create economically attractive processes for the treatment of mine and mill effluents have been made.

MUDDER and WHITLOCK (1984) and WHITLOCK and MUDDER (1984) describe pilot plant tests and a large commercial scale bacterial treatment of a mine and mill effluent at HOMESTAKE MINING COMPANY's gold recovery operations at Lead, South Dakota. This is the first known use of bacterial treatment for mine and mill effluent treatment. Although designed primarily around the removal of cyanide, thiocyanate, and ammonia, other metals including copper, arsenic, and gold are removed from solution. In this case, nutrients are added to the effluent stream which is treated using rotating biological contactor supported bacteria--Pseudomonas paucimobilis. More information on the practical

aspects of operating this plant are likely to emerge in the near future, and some additional detail is provided from published sources in Appendix I.

HOMESTAKE MINING COMPANY
Post Office Box 875
Lead, SD 57754
(604) 584-1020
Terry Mudder,
Chief Environmental Engineer
James L. Whitlock
Chief Chemist

Several other examples have been found where bacteria take part in a mechanism for metal removal, and one company in particular has been developing technology to make these processes practical and useful to the mining industry.

ADVANCED MINERAL TECHNOLOGIES, INC.
Post Office Box 1339
Socorro, NM 87801
(505) 835-0207
Corale L. Brierley
President
George M. Goyak
James A. Brierley

A process, AMT-Bioclaim, has been developed based on a biological phenomenon for the recovery of metals from dilute concentration wastewaters containing between 10 mg/l-100 mg/l metal. The system is primarily effective in the recovery of cationic species such as silver, lead, copper, and other common metals although cyanide complexed gold and silver can be accumulated in the process. Rapid recovery of metals is achieved over broad pH and temperature ranges. Recovery is little affected by the presence of many organic or inorganic metal complexing compounds. The process is designed for use in standard equipment designed for water treatment and metals recovery such as column and counter current pulsed bed reactors. Metals can be recovered from wastewaters generated from manufacturing industries, and the recovery of gold from leach solutions may also be possible. Following metal removal from solution, the metals can be recovered by a proprietory process with recycle of the metal-sorption agent.

BRIERLEY, BRIERLEY, and DREHER (1980) discuss several bacterial and algal phenomena in a series of ponds used to treat minewater from uranium mines at Ambrosia Lake near Grants, New Mixico. Sulfate reducing bacteria of the genera Desulfovibrio and Desulfotomaculum remove uranium, molybdenum, and selenium in various ways which accumulate in the pond sediment. Sulfide generation precipitated molybdenum and selenium whereas uranium is precipitated through a reducing effect. Filamentoris spirogyra and benethic Chara are predominant among the algae in the ponds, and the first was found to be more active than the latter in the removal of uranium and molybdenum. The algae appear to act as biofilters for accumulation of particulate pollutants and agents for adsorption and/or absorption of soluble pollutants. Additional

information may be available from Jim W. Kauffman, Kerr McGee Technical Center, Oklahoma City, or from Jim Cleveland, QUIVIRA MINING COMPANY, Grants, NM, 87020, (505) 287-8851.

In 1983, GORHAM INTERNATIONAL, INC. undertook a multi-client survey of metal extraction with microbes which examined metal extraction, concentration, and beneficiation processes using microorganisms and purified cell products.

GORHAM INTERNATIONAL, INC.
Post Office Box 8
Gorham, Maine 04038
(207) 892-2216
Telex: 94-4479

At least two companies offer bacteria cultures and enzymes for effluent treatment, presumably mainly for municipal treatment plants, and it is not known whether they stock bacterial streams of interest for metallurgical and minewater treatment. These vendors may well be sources of guidance on techniques, however:

SYBRON/BIOCHEMICAL TECHNICAL CENTER
Birmingham Road
Birmingham, NJ
(800) 257-9428

JADCO, INC.
5 Graeser Acres
St. Louis, MO 63146
(313) 562-1145
Richard Kinzie

RANDALL, et al. (1974) Removing Heavy Metal Ions from Water. U.S. Patent 3,925,192, December 9, 1975. Use of Formaldehyde Modified Peanut Shells and Hemlock Bark Drops Hg to 1 ppm, Ni to 0.1, Ag to 0.01 ppm, and Pb to 0.3 ppm.

CANMET in Ottawa, Ontario, is also conducting tests in which sawdust is used to raise the pH of AMD. More information as to the person responsible for this research can be found through:

CANMET
Energy, Minerals, Resources Canada
555 Booth Street
Ottawa, Ontario
Canada K1A 0G1
(613) 995-4124
Gordon Ritcey
Michael Campbell
A. Jongejan

First International Conference on

URANIUM MINE WASTE DISPOSAL

May 19, 20, 21, 1980
Vancouver, British Columbia, Canada

Chapter 27

REMOVAL OF SELECTED INORGANIC POLLUTANTS FROM URANIUM MINE WASTE WATER BY BIOLOGICAL METHODS

J.A. Brierley, C.L. Brierley, and K.T. Dreher

Department of Biology, and New Mexico Bureau of Mines and Mineral Resources, New Mexico Institute of Mining and Technology, Socorro, NM USA

ABSTRACT

Water from underground uranium mines located in the Ambrosia Lake district near Grants, New Mexico, U.S.A., is treated to reduce levels of uranium, selenium, radium and molybdenum. The treatment system consists of a series of ponds and an ion exchange plant. Bacterial and algal populations present in the pond system are considered agents which actively assist in removal of the pollutants present in the water. Pond-bottom sediments maintain a reducing zone and a large population of sulfate-reducing bacteria of the genera Desulfovibrio and Desulfotomaculum. Uranium, molybdenum, and selenium accumulate in the pond sediment. Stimulation of the microbial sulfate-reducing activity resulted in a decrease of soluble concentrations of these elements in laboratory systems. Predominant components of the treatment ponds' algal flora are the filamentous Spirogyra and benthic Chara. Laboratory study indicates that Spirogyra is more active than Chara in removal of uranium and molybdenum from solution. However field-collected algal samples of both of the genera contain uranium and molybdenum. Laboratory studies indicate that death and decay of the algae in association with pond sediment does not result in return of cell-bound uranium and molybdenum to the water. The algae appear to act as bio-filters for accumulation of particulate pollutants and agents for adsorption and/or absorption of soluble pollutants

INTRODUCTION

The mining of uranium ore may produce water from de-watering operations containing dilute concentrations of uranium, molybdenum, selenium, radium and other associated ions. This water presents a waste disposal problem, as the contaminants must be removed before the water can be discharged from a mining property. In addition, it is a potentially valuable source of economically important elements. Reclamation of mine wastewater can serve two purposes: removal of potential pollutants and concentration of resources. Several processes are available for soluble ion concentration including precipitation, ion exchange, solvent extraction and electrowinning. However, these systems are quite often ion specific and expensive when treating large volumes of water. An alternative system for resources concentration is based upon biological processes. Such a system has the potential for low cost, ion non-speci-

fic activity and efficiency in dealing with dilute solutions.

Microorganisms are effective agents in concentration of metals from solutions (see Kelly, Norris, and Brierley, 1979, a recent review of the topic). Norris and Kelly (1979) found yeasts to be more efficient than bacteria in gross removal and accumulation of nickel and copper. Bacteria will concentrate potassium, magnesium, manganese, iron and calcium (Eisenstadt, et al., 1973), and also produce complexing agents which selectively extract metals from dilute solution (Pollack, et al., 1970). There appear to be two mechanisms by which microbes concentrate metals: binding of metals to cell surface components and metabolism dependent intracellular accumulation (Gadd and Griffiths, 1978). Hatch and Menawat (1979) reported that the bacterium Sphaerotilus natans, found in waste sludges and polluted waters, will accumulate iron, magnesium, copper, cobalt, and cadmium in an external mucilage layer. The accumulation was a mass transfer limited process. Other physiological activities requiring metabolically active cells also lead to insolubilization. Uranium (VI) was reduced by cell extracts of Micrococcus lactilyticus using hydrogen as an electron donor. The extract could also reduce molybdate to molybdenum blues and selenium to selenate (Woolfolk and Whiteley, 1962). As microbes accumulate heavy metals, it is of concern whether these metals are released upon death and cellular lysis. Guthrie and Cherry (1979) found that accumulated heavy metals increase in sediments as the organisms die, but some of metals are returned to a system in organic detritus.

Systems utilizing bacteria or fungi have been proposed for removal of uranium from wastewater (Shumate et al., 1978; Shumate et al., 1979; Volesky and Tsezos, 1979). These processes were based upon biosorption using cell masses of the respective microbes. The fungus Rhizopus arrhizus accumulated 185 mg uranium per gram dry weight of cells (Volesky and Tsezos, 1979). A mixed culture of denitrifying bacteria decreased uranium in solution from 25 g/m^3 to 0.5 g/m^3 in just 8 minutes while accumulating 0.14 g uranium per gram of dry cells.

Algae have also been found active in biosorption of pollutants from aqueous solution. Marine algae growing near tailings of an iron ore mine concentrated iron, manganese, lead and zinc on cell-wall material (Wong et al., 1979). Marine algae also accumulate uranium, plutonium and polonium (Hodge et al., 1979). The algae collected the particulate form of the radioelements by an organic coating on their cell surface. Filip et al. (1979) used semi-continuous cultures and mixed algal flora (Chlorella, Scenedesmus, and Oscillatoria), for heavy metal removal from wastewater. The algae absorbed 70 to 90% of the cadmium and copper and 20% of the chromium; but the amount of chromium removed was substantial, as the chromium concentration in solution was high (250 g/m^3). However, cadmium and copper were released from algae after cell death. Gale and Wixson (1979) utilized algae to reduce the amount of particulate matter and heavy metals (e.g., lead, zinc, copper and manganese) in lead mining and milling effluents. A system using several types of microbes was proposed for heavy metal removal from lakes and streams polluted by mine and smelter wastes (Jackson, 1978). Algae may function in heavy metal accumulation and transport to bottom sediments. The metals can then be sequestered as metallic sulfides by bacterially produced hydrogen sulfide. In addition, the algae provide the organic substrate necessary for sulfate reduction by the bacteria.

The sulfate-reducing bacteria, Desulfovibrio and Desulfotomaculum, precipitate copper and mercury from dilute solutions (Ehrlich and Fox, 1967; Ilyaletdinov et al., 1977; Temple, 1964; Temple and LeRoux, 1964; Vosjan and Van Der Hoek, 1972).

Dockins et al. (1980) suggested that Desulfovibrio be used to control mining related pollution problems. It has been proposed that Desulfovibrio could be involved in deposition of uranium from solution (Jensen, 1958). The hydrogen sulfide produced by the bacteria reduces uranyl ion to uraninite. According to Taylor (1979), uranium enrichment is likely to be enhanced where reducing conditions occur in contact with water in which oxidizing conditions prevail (i.e., sediment-water interface).

The Kerr McGee Corporation has a treatment process for waste-water from two uranium mines in the Ambrosia Lake district near Grants, New Mexico, U.S.A. The system consists of several settling and algae ponds. The pond sediments concentrate uranium (1037 g/m^3), selenium (30 g/m^3), and molybdenum (160 g/m^3). The system has been effective in reducing the concentions in the water of the uranium (from 5.8 to 0.8 g/m^3), selenium (from 0.03 to 0.01 g/m^3), and molybdenum (from 2.3 to 0.8 g/m^3) (Brierley and Brierley, in press). This system is being evaluated to identify the biological agents which participate in removal of the pollutants and to determine the mechanisms which operate. The data reported in this paper represent a portion of the study.

MATERIALS AND METHODS

Field Site

The wastewater treatment system has been described previously (Brierley and Brierley, in press). The mine water passes through a series of settling ponds, and water from one mine is also treated with an ion exchange resin to remove uranium. Barium chloride is added for radium removal. The combined mine waters subsequently flow through three consecutive algae ponds prior to discharge.

Analyses

Uranium concentrations were determined by the TOPO procedure (Johnson and Florence, 1971). Molybdenum was quantitated by the method of Meglen and Glaze (1973).

Algology

Algae samples were collected in nonsterile polyethylene bottles and placed on ice for transport to the laboratory. The samples were either dried for metal analyses or transferred to $2.0 \times 10^{-2} m^3$ aquaria for laboratory culture. Shen's Medium (Shen, 1971), was used for algae culture. Algae populations were identified using the keys of Prescott (1954) and Smith (1950).

Removal of molybdenum and uranium from solution by algae was tested in short-term uptake experiments. Using 250-ml erlenmeyer flasks, 100 ml Shen's Medium at pH 7.8 were spiked with 2 g/m^3 molybdenum (added as $Na_2MoO_4 \cdot 2H_2O$) and 10 g/m^3 uranium (added as $UO_2SO_4 \cdot 3H_2O$). Duplicate flasks contained 1 g wet weight algal material either as whole cells or as particulate material produced by disintegrating the cells one minute in a Sorvall Omni-Mixer (Ferguson and Bubela, 1974). Flasks were incubated 24 hr in light before samples were collected by filtration through 0.4 µm "Millipore" filters and acidified with 1.5% (v/v) HNO_3.

Long-term interactions between water, algae and sediment were modeled in the laboratory using $2.0 \times 10^{-3} m^3$ growth tanks. An initial aliquot of 5 g wet weight algae was grown in $1 \times 10^{-3} m^3$ Shen's Medium spiked with 2 g/m^3 molybdenum and 5 g/m^3 uranium. After 13 days' incubation in light, containers were placed in the dark to promote decay of the algae. At that time, 150 g pond sediment were added to two containers of each algae and to two control containers without algae. Removal of metals was monitered by periodic sampling of the nutrient medium only, medium plus sediment, algae only, and algae plus sediment.

Analyses for metal content in field-collected algae were carried out

on samples of 0.1 g - 0.75 g dry weight which were dissolved overnight in 10 ml concentrated HNO_3 at 85°C, followed by addition of 5 ml 30% H_2O_2 and digestion at 125°C. Samples were filtered through 0.45 µm "Millipore" filters and brought to volume with distilled water. Blanks without algae were run as controls.

RESULT

Algal Populations

Dense mats of the macrophytic green alga Chara cover the pond floors. Diatoms and unicellular green algae are associated with Chara, particularly in summer. Populations of floating algae, which occur along the pond edges, include mainly Spirogyra and the blue-green Oscillatoria, while summer blooms are also comprised of filamentous algae tentatively identified as Rhizoclonium, Ulothrix, and the blue-green Lyngbya.

Uranium and Molybdenum Accumulation by Algae

Table 1 summarizes the results from analyses for molybdenum and uranium in algae samples collected during September, 1979 and January, 1980.

Table 1. Levels of Uranium and Molybdenum in Field-Collected Algae

Location	Algae	U g/m³		Mo g/m³	
		Sept.	Jan.	Sept.	Jan.
Pond 1	Spirogyra Oscillatoria Rhizoclonium	2195	1597	32	316
Pond 2	Chara	352	405	22	ND+
Pond 2	Spirogyra Oscillatoria	651	2915	27	268
Pond 3	Chara	1150	-++	ND	-
Pond 3	Spirogyra Oscillatoria	-	2565	-	117

+ no detectable levels
++ no samples collected

Samples were collected from the three ponds in order to compare metal levels in the macrophytic Chara and in the filamentous algae during the summer and winter seasons, since the ponds' populations varied over the year. Pond 1 contained no evident Chara, while pond 2 contained abundant populations of both Chara and several filamentous algae, particularly Spirogyra and Oscillatoria. Pond 3 contained predominately Chara in the summer and filamentous algae in the winter.

In general, levels of molybdenum and uranium were higher in the filamentous algae than in Chara. While both molybdenum and uranium levels varied widely among the samples, in a given algal sample the uranium content was an order of magnitude higher than the molybdenum. A comparison of values determined for Chara and for a mixture of Spirogyra and Oscillatoria in pond 2 illustrates both these points. Some seasonal variation can also be seen. January samples tended to have higher levels of uranium and molybdenum than September samples. There did not seem to be a correlation between the metal content of a sample and the pond from which the sample was collected.

Uptake of uranium and molybdenum on a short-term basis was studied in Chara and Spirogyra in 24-hour laboratory uptake experiments. Results of two representative experiments are given in Table 2. The ability of the two types of algae to remove metals from solution seems to correspond to the levels of the metals in field-collected specimens. Spirogyra, which had generally higher levels of uranium and molybdenum in the field, was able to absorb significantly higher amounts in the short-term up-

Table 2. Removal of Uranium and Molybdenum from Solution by Algae in 24-hour Uptake

	g/m³ U	% Removed	g/m³ Mo	% Removed
Control	10.1		2.2	
Whole Chara	8.2	19%	2.7	8%
Particulate Chara	8.1	18%	2.2	0%
Control	10.9		3.1	
Whole Spirogyra	7.9	28%	2.7	13%
Particulate Spirogyra	1.9	83%	2.4	24%

take studies. Chara, which contained low levels of molybdenum in the field specimens, showed no detectable absorptive capacity for Mo over 24 hours. Chara cells did absorb uranium over 24 hours, removing about 0.2 mg U per 0.2 g cells (dry weight) in both whole cell and omni-mixed preparations. While increasing surface area by cell-disintegration had no effect on absorption in Chara preparations, the effect on Spirogyra cells was evident for both molybdenum and uranium. Disintegrating cells increased molybdenum uptake 2-fold. Particulate Spirogyra removal of uranium amounted to 1.0 mgU per 0.1 g cells (dry weight). This value, corresponding to 10,000 g/m^3 in the exposed algae, is 10 times higher than in either whole or particulate exposed Chara.

While the whole cells used in the 24-hour uptake studies were living, the time course was too short to follow the effects of cell growth on uptake. Growing cultures were monitered in the long-term study summarized in in Table 3 and Table 4. Cultures of

Table 3. Removal of Uranium by Algae in Presence of Sediment

Day	Control		Chara		Spirogyra	
	U g/m^3		U g/m^3		U g/m^3	
0	5.8		5.8		5.3	
3	5.7		6.7		4.2	
7	3.3		5.3		3.5	
13	3.0		5.5		2.1	
		SA*		SA		SA
14	4.3	5.9	7.8	8.0	3.7	3.0
21	2.7	4.6	6.1	3.2	1.9	1.2
49	3.7	5.2	6.5	2.0	1.7	1.5
80	4.8	5.5	7.1	4.2	2.4	2.3

+ sediment added

Spirogyra and Chara were allowed to grow in light for 13 days. Although the initial amount of algae added was measured (1.1 g dry weight Chara or 0.4 g dry weight Spirogyra) no attempt was made to measure algal mass during the course of the experiment. New growth was observed in Chara cultures

Table 4. Removal of Molybdenum by Algae in Presence of Sediment

Day	Control		Chara		Spirogyra	
	Mo g/m^3		Mo g/m^3		Mo g/m^3	
0	2.0		1.9		2.1	
3	2.2		2.2		2.0	
7	2.2		2.2		1.9	
13	3.0		2.5		1.9	
		SA*		SA		SA
14	1.9	2.1	2.0	2.5	1.4	1.8
21	2.3	2.0	2.3	2.4	1.6	1.0
49	2.3	2.7	2.9	1.8	2.6	1.0
80	2.1	2.8	2.3	1.3	2.7	2.8

+ sediment added

over the 13 day period, while Spirogyra cultures grew rapidly for 4-5 days and then started to decay. All containers were placed in the dark after 13 days, and sediment was added to duplicate culture vessels in order to simulate conditions which would prevail in the field as algae die and sink to the bottom of the pond. The addition of sediment hastened decay of the algae in the dark. Since none of the cultures were bacteria-free, both sediment-containing and sediment-free cultures presumably had increased bacterial activity as decay proceeded. The sediments became black, which is indicative of bacterial sulfate-reduction activity. After 21 days in the Spirogyra cultures and after 49 days in the Chara cultures, the blackening of the sediment surface and presence of algae cells were no longer evident.

Removal of uranium (Table 3) was most pronounced in the Spirogyra cultures. While the presence of sediment did not seem to enhance removal of uranium from solution in comparison to Spirogyra alone, in comparison to the sediment control the algae increased the sediment's ability to retain uranium, with 2.3 g/m^3 remaining in solution in the Spirogyra-sediment cultures and 5.5 g/m^3 in the sediment control.

In the Chara cultures, growing algae had no effect on uranium removal, and

some release of U from the Chara seems to have occured after transfer to the dark (Table 3). However, as Chara decayed in the presence of sediment, levels of uranium fell from 8 g/m^3 on day 14 to 2 g/m^3 on day 49. Less decay of the algae after day 49 allowed re-establishment of an oxidizing zone at the sediment surface, which coincided with partial remobilization of uranium into solution by day 80.

No cultures showed irreversible removal of molybdenum, although Spirogyra cultures reduced molybdenum concentration substantially by day 21 (Table 4). However, molybdenum levels returned to initial values in solution. Chara sediment cultures showed reduction in molybdenum levels when compared to the control.

DISCUSSION

Both the analyses of field-collected algae samples and the evidence from laboratory uptake experiments (Tables 1 and 2) indicate a marked difference in the interaction of uranium and of molybdenum with the algae present in the pond system. Uranium accumulates to a much greater degree than molybdenum in both the filamentous and the macrophytic algae. This difference in accumulation may be due to the roles of the metals in the algal life cycle, or to different interactions between the metals and the algal cell surfaces. Molybdenum can be an essential trace element for algal growth (O'Kelly, 1974), so that it is possible that regulatory mechanisms exist in the cells for maintaining constant levels of the element. Chara in particular shows little variation in molybdenum levels. The field-collected filamentous algae contain higher levels, which may be due to absorption. The ability of Spirogyra to absorb molybdenum onto cell surfaces was demonstrated in the 24-hour uptake experiment. Uranium, in contrast, is generally considered an abiological element (Taylor, 1979), and its uptake is more likely to be governed by physical-chemical factors than by active cellular processes. The uranyl ion has an extremely high affinity for organic material (Jackson Jonasson, and Skippen, 1978), and absorption onto the negatively-charged algal cell surfaces probably accounts for the high levels of uranium in the pond algae. In a study of radionuclide accumulation by Chara species, Marchyulenine (1978) felt that the presence of calcium in the Chara cell wall, chiefly in the bound form of carbonate compounds, reduced the number of cation exchange sites on Chara as compared to other algae. This may be a factor in the lower affinity for uranium in Chara as compared to Spirogyra.

The seasonal variation in both uranium and molybdenum levels also suggests that absorptive processes are important in accumulation of the metals in the algal cells, since extent of absorption is influenced by the amount of metal available per unit of surface area and by length of exposure of the surface to the metal. The September collections represent quickly growing, high density populations; the January collections were taken from sparser populations which, due to the lower growth rate in winter, had a slower turnover time than the summer populations. Knauer and Martin (1973) found that levels of heavy metals were low in marine phytoplankton during periods of high growth rate (algae blooms) due to dilution of the amount of metal per unit mass of phytoplankton. In the case of the algae in the settling ponds, probably the more important factor is the increased length of exposure time to the metals for the winter populations. Hodge, Koide and Goldberg (1979) found that marine macroalgae absorbed uranium, polonium, and plutonium in direct relationship to exposure time.

The phenomenon of increased absorption of metals in dead over living cells has been observed in marine macroalgae for ^{65}Zn but not ^{137}Cs (Gutknecht 1965), in marine plankton for ^{65}Zl but not ^{32}P (Cushing and

Watson 1968), and in Chlorella regularis for UO_2^{2+} (Horikoski, Nakajima and Sakaguchi, 1979). Horikoski et al. (1979) suggested that the increased uptake of UO_2^{2+} in heat-killed Chlorella regularis was due to an increase in absorption sites on the disrupted cell walls rather than to an inhibition of cellular regulatory mechanisms, since whole cells treated with metabolic inhibitors absorbed UO_2^{2+} at the same lower levels as metabolizing whole cells. Absorbed UO_2^{2+} was associated with cell wall and cell membranes, and 81% of absorbed UO_2^{2+} was removable by EDTA washes. In the present study, the particulate suspensions of Spirogyra absorbed twice as much molybdenum and three times as much uranium as whole cells in 24-hours. The main effect of disrupting the cells is probably to increase surface area available for binding, although release of cellular constituents may also be a factor. The suspensions of Chara cells may not have been ground enough to increase the surface area significantly, since the Chara cell is much less fragile than Spirogyra. Ferguson and Bubela (1974) have suggested that fresh particulate algal material should be studied for metal complexing ability, since much organic material in aquatic systems may exist as dead, but not extensively decomposed, material. The ability of particulate suspensions of filamentous algae to concentrate Cu, Pb and Zn was considered by Ferguson and Bubela good evidence for the ability of algae to participate in the formation of metal-rich sediments.

In the pond system, the ultimate fate of uranium and molybdenum accumulated by either living or particulate algal material depends on the retention of the metals in organic-metal complexes and, perhaps more important, on the interactions between metals, algae, and sediment.

While evidence in this study and in those discussed above (Ferguson and Bubela, 1974; Cushing and Watson, 1968; Gutknecht 1965) indicates that dead algae material can absorb heavy metals, several studies on the accumulation of metals by living algae have noted substantial release of metals from algae as cells died (Filip, 1979; Jennett, Hassett and Smith, 1977; Laube, Ramamoorthy and Kushner, 1979). Laube et al. (1979) gave evidence in their study of Cd and Cu uptake by Anabaena that cell lysis released Cd and Cu as organic complexes. Whether such organically-bound metals could be reabsorbed onto sediment particles was not investigated. Filip (1979) observed that mixed algal cultures could remove 50-75% of the Cd and Cu in a wastewater treatment system, but that sand filtering increased removal to 98 to 100%. It is possible that the sand particles not only adsorbed metals ions from water but also stabilized the metals accumulated by the algae by an exchange of adsorbed material between algae and sand particles.

Algae cells come in contact with the sediment primarily as decomposing material. Studies on aerobic and anaerobic decomposition of a wide range of algae types indicate that both processes result in mineralization of about 60 percent of cell material, while the remaining faction persists as particulate material whose carbon content is similar to the starting material (Fallon and Brock, 1979; Foree and McCarty, 1970; Weir, 1978). This refractory material could be a source of organic material for long-term complexing of metals in sediment.

When sulfate levels are high in anaerobic decomposition, sulfate reduction accompanies decomposition of algae (Foree and McCarty, 1970). Taylor (1979) has pointed out that the production of hydrogen sulfide by sulfate-reducing bacteria may increase the absorption of uranyl ion by organic material in sediment, since iron and other sulfide-forming metals could be desorbed from the organic material

and increase the possiblity of uranium sorption.

The patterns of retention and release of uranium and molybdenum in the 80-day study using Chara and Spirogyra suggest that the maintenance of reducing conditions is critical in the sequestering of both metals in the sediment. In the model system, the period of algae decomposition was associated with increased bacterial activity and an enhancement of reducing conditions in the sediment-containing cultures. The cultures of algae without sediment probably decomposed mainly in aerobic conditions. The period following decomposition was characterized by release of molybdenum and uranium back into the water. The release of molybdenum was surprising, since sulfides which are formed during sulfate reduction can form highly insoluble molybdenum sulfide. It is possible that molybdenum was precipitated in the reduced Mo (IV) state but not as a sulfide, so that release occured as molybdenum re-oxidized. The Chara cultures contained twice as much material on a dry weight basis as Spirogyra, which may have contributed to the greater retention of molybdenum in the Chara sediment.

Algal material contributed to some extent to the retention of uranium in sediment. Evidently reduction of uranium to the insoluble U (IV) ion played a part in removing uranium, with absorption onto organic material also a possible mechanism. While Chara material alone was unable to affect uranium levels in the water significantly, the presence of the decaying algae in the sediment resulted in retention or uranium in the sediment. On the other hand, Spirogyra contributed to removal of uranium in algae cultures without sediment, possibly by absorbing uranium onto cell surfaces more effectively than Chara.

The mine-water of the study system contains 700 g/m^3 sulfate and a large population of sulfate reducing bacteria (2.5×10^2 g^{-1} dry weight) in the pond sediments (Brierley and Brierley, in press). The conditions present in the sediments, high sulfate concentrations, available organic matter from algae decomposition, and a reducing environment (Eh,-350mV) favor growth of Desulfovibrio and Desulfotomaculum. Laboratory experimentation has indicated that enhancement of growth and sulfate reduction by these microbes results in removal of uranium, molybdenum, and selenium from solution (Brierley and Brierley, in press). However, a recent report (McCready and Krouse, 1980) has indicated that the activity of sulfate reducing bacteria may also lead to mobilization of radium bound in sediments with barium sulfate. This observation needs further investigation to determine if the beneficial activity of these microbes in sequestering various pollutants may also have a deleterious aspect in regard to radium release.

The biological components of the wastewater treatment system effective in pollutant removal from mine water of two Kerr-McGee Corporation mines is a complex association among diverse microbial populations. The algae, Spirogyra, Oscillatoria, Chara plus others, concentrate soluble and particulate pollutants, and convert CO_2 and solar energy to reduced organic compounds which serve as substrates for the bacteria. Upon death, the algae settle to the pond bottom sediments where decomposition occurs by aerobic and anaerobic bacteria. Some unknown amount of the pollutants may be released and some amount sequestered in a recalcitrant organic fraction. The degradative activities of the bacteria will result in consumption of oxygen, with establishment of reducing conditions and production or fermentation products such as organic acids and alcohols. The fermentation products in turn serve as energy sources for Desulfovibrio and Desulfotomaculum which reduce sulfite to sulfide. The sulfide can then act as a reducing agent for hexavalent

uranium and precipitate other metals as sulfides.

There are other biological activities and physico-chemical processes which also lead to pollutant removal. The relative contribution of each active component to the system is yet to be established.

ACKNOWLEDGEMENTS

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DISCUSSION

Question - What is the pH of the mine water, algae-ponds and the laboratory-study system?
Answer - The mines'-water pH average 6.95 and 7.05. The pH of the algae-ponds averages 7.28 to 7.52. The pH was 7.8 for short term batch-reaction experiments. Algae cultures in the laboratory were initially pH 7.7 - 7.9; the pH increased to 8.0 - 8.2 during growth and decreased to 6.0 when Spirogyra died and decayed and pH 7.6 with decaying Chara. When sediment was present in the culture flasks the pH remained at 7.6.

Question - What is the effect of pH change on pollutant removal?
Answer - At low pH values hydrogen ion competes with cations for adsorption sites on cell-surface biopolymers resulting in decreased absorption. In conditions of pH above 5, uranyl-ion absorption may depend on presence of anions (e.g., $H_2PO_4^-$, $HPO_4^=$, HCO_3^-) which form complex ions with uranyl-ion not absorbed by cell surfaces. At low phosphate or bicarbonate concentrations, absorption of uranyl-ion is pH-independent above pH 5. In acidic environments (e.g., pH 3.5) the algae populations found active in the mine-water treatment system would not grow or function.

Question - What are the optimum conditions for sulfate-reducing bacteria (Desulfovibrio and Desulfotomaculum)?
Answer - The sulfate reducing bacteria can be found which tolerate extreme physical conditions. These microbes can grow at temperatures at or below 0°C to 70°C with optima of 25-30°C for Desulfovibrio and 35-55°C for Desulfotomaculum. The sulfate reducing bacteria can grow at all salinities from near zero to saturation. The Desulfovibrio are more tolerant of salt that the Desulfotomaculum. These microbes are strict anaerobes; the redox potential of the environment should be - 100 mV or less. pH 7 to 7.6 favors growth. Most sulfate-reducing bacteria have no special requirements for organic growth factors. The substrates apparently preferred as carbon sources are a few C_3- and C_4- fatty acids.

Question - What precent removal of the various pollutants occurs in the mine-water treatment system?
Answer - The field-site system reduces uranium 70% and selenium and molybdenum by 60%.

CONTROL OF HEAVY METALS IN LEAD INDUSTRY EFFLUENTS BY ALGAE AND OTHER AQUATIC VEGETATION

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ABSTRACT

The lead mining industry in Southeast Missouri, U.S.A. has successfully utilized algae and aquatic vegetation in tailings ponds or experimental stream meanders as a control method to remove heavy metals such as lead, zinc, copper and cadmium from mine-mill and smelter effluents. Research has indicated that the heavy metal removal has been accomplished through the physical trapping of suspended mineral particles and subsequent chelation to the numerous anionic sites within the cell wall resulting in the displacement of divalent or monovalent cations normally associated with the cell envelope. Some heavy metals may also be transported to the interior of the cell in membrane lined vessicles.

Laboratory studies on mixed algal cultures have demonstrated cation exchange capacities in excess of 640 microequivalents per gram (dry weight). The displacement of considerable quantities of normal cations by lead and zinc does not seem to cause physiological impairment and the amount of heavy metals tolerated was found to vary with the species studied.

The ability of algae and aquatic vegetation to utilize nutrients and remove heavy metals from mine-mill and smelter effluents are discussed with emphasis on their potential use by industry for the management and control of heavy wastes.

TEXT

The Missouri "New Lead Belt" in the U.S.A. continues to be the largest lead producing district in the world: 508,857 metric tons in 1978, or 87% of the total U.S. production. The location, development and impact of this industrial enterprise have been previously documented in the intensive interdisciplinary study funded by the National Science Foundation (Ref. 1).

The Buick Mine and Mill complex, owned and operated by AMAX Lead Tollers, Inc., is the largest lead mine in the world with annual production in 1978 of 167,421 metric tons of lead concentrate. It also produced 62,495 metric tons of zinc concentrate. At this mine, water is pumped from underground operations at a rate of 5.5 mgd, with 4 mgd being used in the surface milling operations. Excess mine water and mill wastewater (tailings) are piped to a large 425 acre-ft lagoon approximately 2 miles away, situated at the headwaters of Strother Creek.

After operations began, there was considerable alteration in the quantity and quality of water entering Strother Creek. Excessive accumulation of rock flour and nuisance algal blooms extended several miles downstream, and the rate and possible extent of environmental contamination by vagrant heavy metals were not known. Early studies conducted on Strother Creek showed that aquatic vegetation blooming throughout much of the year effectively scavenged suspended or dissolved

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heavy metals and other vagrant particulates. Submerged algae and rhizophytes were found to contain extraordinary amounts of heavy metals at collection sites in the vicinity of industrial tailings lagoons, decreasing in metal content at downsteram sites. Unfortunately, however, unsightly blooms of metal-laden vegetation often extended several miles downstream, stimulated by the release of abundant nutrients by industrial operations.

With the large volumes of mine-mill wastewaters and the availability of land AMAX chose not to recycle but, in an attempt to improve water quality of the receiving stream, constructed a system of artificial meanders and a final sedimentation pond below the main tailings lagoon (See Figure 1). These alterations, completed in 1972, provided a long, meandering, shallow stream bed, encouraging the growth of aquatic vegetation and removal of suspended particulates and nutrients prior to discharge to public streams. This wastewater treatment scheme has operated successfully for the past 7 years. The effectiveness of the treatment system is indicated in part by Figure 2 which shows lower concentrations of heavy metals observed in aquatic vegetation specimens collected downstream after installation of the secondary meander system. The number and severity of nuisance algal blooms observed in Strother Creek have been reduced dramatically. Benthic conditions in the public receiving stream have returned to pre-industrial levels so that stream quality closely resembles that observed in control Ozark streams.

Within the meanders and final settling pond, aquatic productivity is excellent. Stocking of these areas with catfish, bass, and bluegill has been very successful, much to the delight of area fishermen. Dominant producer organisms within the meanders include: Potamogeton, Typha (cattails), Cladophora, Rhizoclonium, Hydrodictyon, Spirogyra, and seasonal blooms of Oscillatoria. Typical consumers which abound throughout the treatment system include crayfish, tadpoles, frogs, bluegills, catfish, smallmouth bass, carp, and a variety of aquatic insects. Although absent in the upper meanders, snails are abundant in the final settling pond and discharge areas.

The mechanism by which aquatic vegetation binds heavy metals has been the subject of further investigation (Ref. 2). Some heavy mineral particles are obviously physically trapped by roots, stems and filaments of stream vegetation. Numerous anionic sites on and within cell walls of exposed vegetation participate effectively in a process of cation exchange with the heavy metals. Those available metal ions which possess greater charge density displace other normal cations of lesser charge density such as Na^{+}, K^{+}, Mg^{++}, and Ca^{++} commonly associated with cell walls, membranes and internal structures. Laboratory investigations have confirmed the displacement of approximately equivalent quantities of normal cellular cations as soluble lead salts are bound to surfaces of algal filaments and partially decomposed leaf litter. Even relatively insoluble mineral particles (galena) have been found to be dissociated at the surface of algal filaments and subsequently bound within the matrix of the adjacent cell walls. Saturation of living and autoclaved algae (Rhizoclonium, Cladophora, and Spirogyra) by applied lead solutions indicate cation exchange capacities (CEC) of over 640 microequivalents per gram dry weight. In comparison, partially decomposed leaf litter displayed CEC of approximately 1800 microequivalents per gram dry weight.

Despite elevated metal concentrations in sediment, stream vegetation and litter, no indication was found for biomagnification or concentration of heavy metals in stream consumer organisms, either within the meander system or further downstream (Ref. 3). Research indicates that lead bound to aquatic vegetation or debris apparently passes through the digestive tract of common herbivores, remaining predominantly with the

partially decomposed plant matter. Mucous membranes and chitinous coverings of aquatic consumers can compete in the process of cation exchange with heavy metals, though not as efficiently. Quantities of heavy metals associated with gills, skin, exoskeletons, and mucous membranes of consumer organisms abundant within the meander system apparently are quite tolerable.

Many of the potential problems associated with large-scale lead production are alleviated by the chemical and physical conditions imposed by the geologic regime and the hard, naturally alkaline stream waters of southeastern Missouri. Reduced solubility of heavy metals under these conditions is an obvious convenience and environmental protection in a region of intense mineral exploration. The abundant vegetation within the region, and especially in the vicinity of industrial operations undoubtedly plays a role in scavenging particulate matter and effectively binding potentially toxic heavy metals. This not only restricts and limits rates of lateral dispersion from areas of contamination, but also limits availability of toxic heavy metals to organisms, tissues and structures more physiologically sensitive.

Further studies are being conducted to evaluate the use of aquatic vegetation as a method of controlling heavy metals in industrial effluents on a broader scale.

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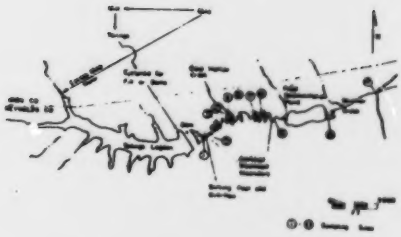

Figure 1. Schematic of Wastewater Treatment System at Buick Mine-Mill Complex.

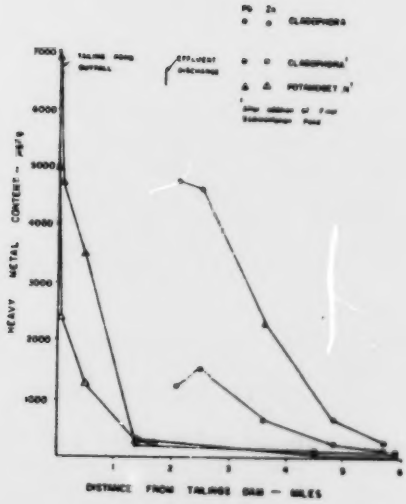

Figure 2. Lead and Zinc Concentrations in Aquatic Vegetation From Strother Creek.

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Agency

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Research and Development

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Project Summary

Factors Influencing Metal Accumulation by Algae

(all from Syracuse University)

J. Charles Jennett, J. E. Smith, and J. M. Hassett

Full Text (NTIS)
7 pages 7 references, incl.:
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Summary of 124 pages (same title) NTIS PB83-149377 (in Library) → 7 pages of references

Shallow beds of algae (algal meanders) have proved to be highly effective at removing heavy metals and organometallics from lead-zinc mine and mill wastes. A laboratory-scale research program was initiated to determine conditions under which algae were most effective at concentrating significant quantities of As, Cd, Cu, Hg, Ni, Pb, or An, for the purpose of potential application of the meander technology to new types of wastewater-metal problems.

Studies were performed on 20 species of algae to determine interactions of experimental variables affecting metal adsorption, species and strains of algae, type, form, and concentrations of metal, pH, culture age, micronutrient composition of culture medium, exposure to metal, and light intensity and exposure period. These numerous variables were studied by means of a rapid analytical technique, the Titertek™* supernatant collection system, to determine the adsorption of metal radionuclides.

Metal removal was observed to be fast (three hours), young growing cultures were seen to be most effective, and concentration factors $> 1 \times 10^4$ were observed. The pH had little effect on accumulation of metals except lead. Heavy metals could be stripped from algal mats with 0.01 M EDTA or 0.1 N HNO_3. Ca and Mg were not effective competitors for the binding sites of Hg, Pb, and Cd. Neither Zn nor As was bound significantly at any pH. Experimental and literature data indicate that algae remove certain metals economically from a variety of waters and that the meander system can be used to recover these metals for processing.

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This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Effluents from secondary lead smelters are a major source of heavy metals in the aquatic environment. These effluents are frequently low in pH and contain a wide range of heavy metals. The largest single heavy metal constituent is, of course, lead. Relatively large amounts of zinc, cadmium, arsenic, copper, and other toxic cations may also be found, along with a wide variety of anions often associated with these metals (chloride, sulfate, nitrate and chromate for example). Lead smelter effluents also contain toxic trace organics generated when batteries and other materials are crushed, and the heavy metals are removed from their plastic encasements. The fact that heavy metals are dangerous in the aquatic environment has been well documented in the literature.

To protect the environment, the discharge of heavy metals must be minimized. One approach is to apply the type of algal-meander treatment system cur-

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

rently in use for treating mine and mine-mill wastes at one site in the new lead-belt region in southeast Missouri—the world's largest lead mining region. A detailed laboratory study of the factors influencing heavy metal accumulation by algae is the subject of this investigation and an attempt has been made to evaluate the feasibility of using algal meanders to remove a variety of heavy metals.

Description of the Meander Process

In the Missouri algal-meander system, mine and mill wastes were treated in a standard tailings pond followed by a series of shallow meanders in which the growth of algae is encouraged. These algae grow, utilize the waste millings reagents and trap heavy metals, both particulate and dissolved, on their surface. When the algae mat breaks loose, it is then trapped in a settling pond at the end of the meander system. The pond is equipped with baffled weirs which prevent algal overflow into the receiving stream. Based on total heavy metals removed, the system is more than 99-percent effective. Dissolved heavy metals are also removed to levels well below U.S. Public Health Service drinking water standards. Past work has shown also that lead in its highly soluble acetate form is removed effectively by the algae.

To date, the algal-meander system has been used to treat only one waste, a combined lead-zinc mine and mill waste in the new lead-belt mining region. Since 1971, this region has been the site of a large interdisciplinary investigation, supported by the National Science Foundation, of environmental pollution by lead and other heavy metals. It was confirmed in 1974 that below the AMAX-Homestake Lead Tollers, Inc., mining mills, severe stream degradation and heavy metal buildup was occurring. The meandering system was built to a full operating scale and as a result the stream was returned to essentially pre-mining conditions. The history of this treatment system and the quality of the water in receiving streams has been well documented for lead and zinc. This technology, however, has not been applied to wastes containing other toxic metals. This has been largely due to the lack of information on the system's range of application and the newness of the technology. The ability of algae to concentrate heavy metals from their aqueous environment has been reported by radioecologists examining debris from nuclear tests, chemical geologists attempting to explain low-grade deposits of metal, and ecologists concerned with the self-purification of streams below mining operations. While these observations are clearly valuable, a more detailed knowledge of the interaction between algae and heavy metals could aid in understanding these processes. A systematic study of these interactions has been difficult because a wide range of variables affects metal accumulation by algae. These variables include the length of the exposure period, the type of metal, oxidation states, pH, salinity, and presence of organic pollutants. To understand the factors influencing metal accumulation by algae in the meander system, laboratory studies were initiated with pure cultures of representative species from other laboratories and from the algal culture collection at the University of Texas.

Conclusions

The ability of representative algae to concentrate large quantities of specific heavy metals was demonstrated by adapting the Titertek™ supernatant collection system (Flow Laboratories, Rockville, Maryland) for assaying radionuclides of heavy metals. This technique permitted the simultaneous study of several factors affecting heavy metal accumulation and provided a sufficient number of replicates for statistical analysis. Algal-metal combinations used in batch studies are presented in Table 1.

The removal and concentration of heavy metals from their aqueous environment by algae was first studied in detail in the 1950s and 1960s as part of the problem of the release of nuclear debris from weapons testing, and from reactor cooling water effluent. Scientists took advantage of the released isotopes, as well as newly developed analytical techniques, to study pathways of various elements in the environment. One early result of this work was the observation that certain isotopes were concentrated by biota to a much greater extent than the concentration of that isotope in water. From these observations came the concept of the concentration factor (CF) such that

$$CF = \frac{C}{C'}$$

where C and C' are the concentration of the radionuclide in the aquatic organism and in the aqueous medium respectively. The concept is also applicable to stable isotopes (Polikarpov, 1966).

Calculation of concentration factors for heavy metals revealed significant differences between species of the same genus and between strains of the same species (i.e., *Nostoc*). Some species regularly had concentration factors of 1×10^4. In general, young cultures exhibited very much higher concentration factors than old cultures. Most of the metal removed by algae can be removed by a rinse with 0.01 M ethylenediaminetetraacetic acid (EDTA) or 0.1 N nitric acid (HNO_3). This information suggests that surface adsorption sites are the principal repository for the metallic ions or particles.

The ability of algae to remove metals is generally in this order: mercury > lead > cadmium. Neither zinc nor arsenic was removed significantly at any pH during a three-hour exposure. The presence of chelating agents in the medium (such as EDTA) inhibited the removal of the heavy

Table 1. Algal-Metal Combinations Used in Batch Studies

		Cations							
Alga	*Age (days)*	*As(III)*	*As(V)*	*Cd*	*Cu(II)*	*Hg(II)*	*Ni(II)*	*Pb*	*Zn*
Chlamydomonas	12	+	+	+	+	+	+	+	+
Chlorella	12			+	+		+	+	
Spirogyra	12		+	+	+	+	+	+	
Ulothrix	12	+	+	+	+		+	+	+
Ulothrix	20	+			+		+	+	
Gleotrichia	12				+		+	+	
Gleotrichia	20	+							
Gleotrichia	40	+							
Nostoc *31*	40	+	+						
Nostoc *586*	12	+	+	+	+	+	+	+	
Nostoc *586*	20	+							
Oscillatoria	12	+	+	+	+	+	+	+	+
Oscillatoria	20	+							

metals. Calcium and magnesium were not effective competitors for the binding sites of mercury, lead, and cadmium. There was remarkably little effect of pH on metal accumulation in the range of pH 5 to 8, when young cells were employed. Lead was the principal exception because it was removed more efficiently at pH 4 to 5 than at other pH values.

The removals of lead and mercury from nutrient solution by algae are found to be rapid phenomena, usually accomplished in three hours or less at room temperature. If the cells were placed in buffer after the initial adsorption of lead, a limited, slow release of lead occurred for a few hours, perhaps while some surface polymer-lead complexes were released from dead or dying cells. Mercury was removed from solution in nearly identical fashion by two strains of *Nostoc* and showed little evidence of being released. In the control wells without algae there were reproducible losses of ^{203}Hg that occurred within the first 24 hours at pH 6. This may be related to reports in the literature claiming volatilization of mercury by algae.

Chlamydomonas (a green flagellated form) proved to be dramatically superior to all other species in its ability to remove lead. Concentration factors for the organism of 1.9×10^4 were noted. This organism showed essentially the same concentration factor for lead in the pH range of 4 to 9. In other experiments, *Ulothrix* and *Chlorella* had concentration factors for cadmium greater than 10^4.

The empirical successes of the algal-meander system for removing lead from surface waters can be explained in part by the concentration and sequestering of lead and cadmium on the surface of algal cells. Very little heavy metal was leached from these cells at pH 5 to 9 in the presence of divalent cations and other inorganic constituents of algal growth media.

Results

Algal Growth

Algal growth for 20 species provided a representative selection of algae for the experiments. Some species proved impossible to culture and others exhibited unusual rates of growth. Table 2 reveals that no growth was obtained from any form in soil-water media. The choice of African violet potting soil was probably unfortunate because this soil is high in humus. Success with this medium depends on the selection of a garden soil with a medium humus content.

A few algal forms were characterized by unusual growth rates. *Mougeotia* and *Zygnema* grew only slowly and to a low final biomass. *Nostoc* 31, *Nostoc* W and *Gleotrichia* exhibited a long lag phase. For each of these forms, inoculation was followed by about 15 days of apparent inactivity. After this period, growth to a useful final biomass was rapid. For these forms, then, no young culture data are available.

Batch Studies

The results of the batch studies are presented in Figures 1 through 8. The figures show the concentration of metals in the sample as a function of the time the samples were withdrawn from the culture. It should be noted that, for reasons of clarity, not all data points are shown on the figures.

Arsenic III—The data show no obvious trends in the removal of arsenic III. The highest removal (about 35%) was accom-

Table 2. Sources and Cultivation of Algae

Algae	Source*	Type	Growth on media† B	D	SW
A. *Baccillariophytes (diatoms)*					
Navicula pelliculosa	*UTEX 668*	*Pennate diatom*	-	+	-
B. *Chlorophytes (green algae)*					
Chlamydomonas *sp.*	*Dr. C. Kuehnert Syracuse University*	*Unicellular, 2 flagella*	+		
Chlorella pyrenoidosa	"	*Unicellular*	+		
Chlorotyllium *sp.*	*Dr. N. Lazaroff SUNY Binghamton*	*Filamentous*	+		
Kirchnerella *sp.*	"	*Colonial, enclosed in gelatinous matrix*	+		
Mougeotia *sp.*	*UTEX 758*	*Filamentous, planktonic*	+		
Scenedesmus obliquus	*UTEX 2016*	*Colonial, 4-8 cells, planktonic*	+		
Spirogyra *sp.*	*Dr. N. Lazaroff*	*Filamentous, planktonic*	+		
Ulothrix fimbrinata	*Dr. N. Lazaroff*	*Filamentous, benthic*	+		
Zygnema	*UTEX 923*	*Filamentous, enclosed by mucilaginous sheath*	+		
C. *Cyanophytes (blue-green algae)*					
Gleotrichia *sp.*	*Dr. Lazaroff*	*Colonial*	+		
Nostoc muscorum *A*	"	"	+		
Nostoc *F*	"	"	+		
Nostoc muscorum *H*	"	"	+		
Nostoc *L*	"	"	+		
Nostoc muscorum *W*	"	"	+		
Nostoc *31*	"	"	+		
Oscillatoria *sp.*	"	"	+		
Nostoc *586*	"	"	+		
Schizothrix calcicola	"	"	+		
D. *Mixed Cultures*					
Cazenovia Lake			+	+	
Onondaga Lake			+	+	

**University of Texas Culture Collection and Identification.*
†B = Bold's medium; D = diatom medium; SW = soil water medium.
+ = success
- = failure

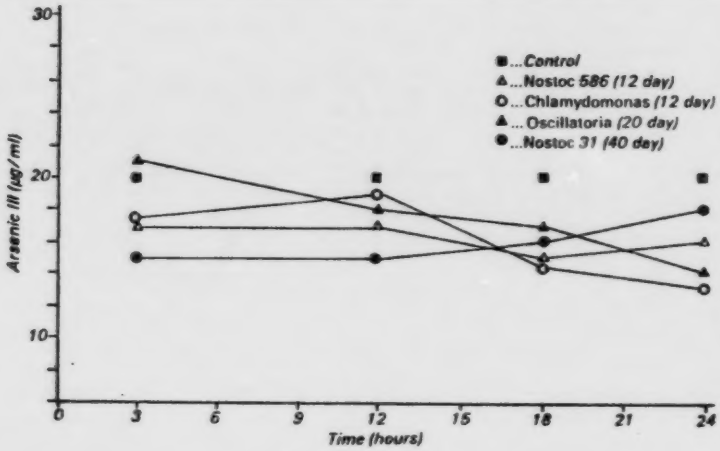

Figure 1. *Uptake of arsenic (III) by various algae.*

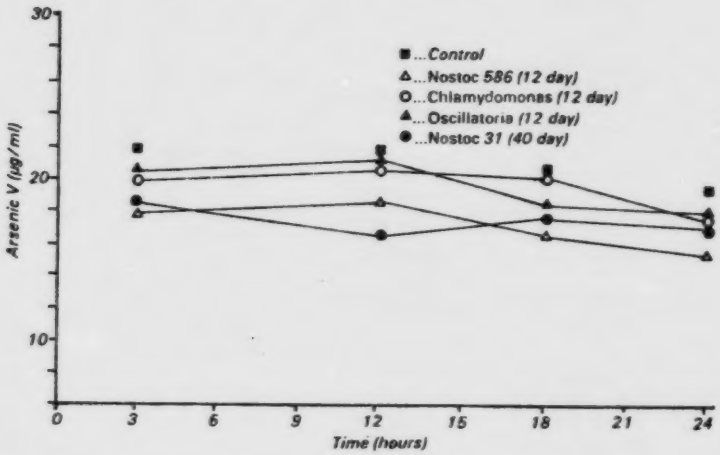

Figure 2. *Uptake of arsenic (V) by various algae.*

plished by *Chlamydomonas*, which also had the lowest biomass (0.12 mg/ml).

Arsenic V—There are no obvious trends in the removal of arsenic V. Most experimental values are too close to the control value to be considered significantly different. The lowest experimental value (16 µg/ml, compared to a control value of 20 mg/ml) was attained by *Nostoc* 586, which had among the highest biomass (0.40 mg/ml).

Cadmium—Cadmium was likewise not dramatically removed by the algae used in this part of the study. The lowest experimental values (about 10 µg/ml) were achieved by *Ulothrix*, which had the highest biomass (0.34 mg/ml). That the acid rinse for both *Ulothrix* and *Nostoc* 586 (with the next lowest experimental value) had high concentrations of cadmium indicates a surface adsorption mechanism for cadmium removal.

Copper—The highest removal of copper (about 30% compared to the controls) was attained by *Gleotrichia*, which had a biomass of about 0.14 mg/ml. This alga, though usually a dark brown mass of filaments, turned greenish on exposure to copper.

Lead—Lead appeared to be removed by all the forms studied in this experiment, with removal (compared to the 18-hour control) of from 15% for *Spirogyra* to about 87% for *Oscillatoria*. The green filamentous *Ulothrix* showed high values of lead removal, and the morphologically similar *Spirogyra* showed values little different from the controls, even though both algae had nearly identical biomasses. The high values of lead in the acid rinses suggest again a surface adsorption.

Mercury—The most dramatic removal of mercury was accomplished by *Nostoc* 586, which had an experimental value of 6 µg/ml as compared to the control value of 34 µg/ml after only three hours. Again the values of mercury in the acid rinses were high.

Nickel—Although all algae seemed to exhibit some removal of nickel (17% to 37% after 24 hours), no trends could be discovered from the data.

Zinc—The algae that seemed to accumulate zinc were *Spirogyra* (with 41% removal after 18 hours) and *Nostoc* 586 (with 37% removal during the same length of time). Again, the acid rinses of these two algae had high values of zinc, suggesting surface adsorption sites.

Discussion of Project Results

With the exception of zinc, these results show reasonably good agreement with the literature, with all concentration factors between studies agreeing within a factor of 2 to 3.

Previous studies also examined the kinetics of heavy metal accumulation by algae and in general show that uptake was an extremely rapid phenomenon. The results of the 24-hour experiments in this study clearly confirmed the earlier observations in this regard. The negative results for the cadmium experiments cannot be explained at this time.

One obvious manner in which the present study extends previous work is the calculation of concentration factors for species of algae previously unstudied. These data were obtained under identical conditions and record both intraspecific (in the case of *Nostoc*) and interspecific differences in heavy metal accumulation by algae. New data are provided on the effects of culture age, and initial pH

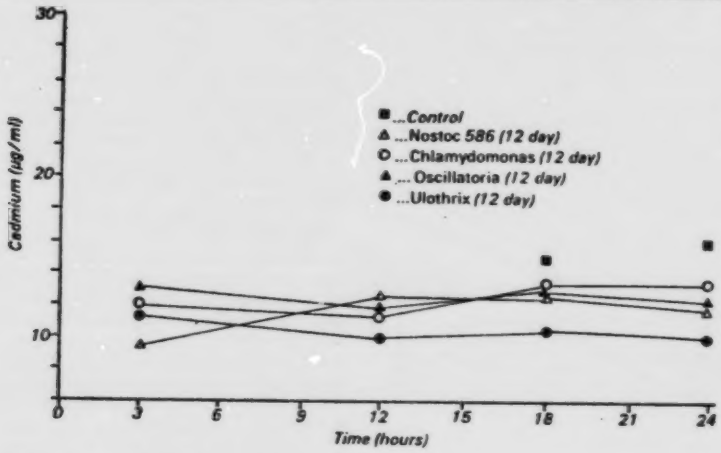

Figure 3. *Uptake of cadmium by various algae.*

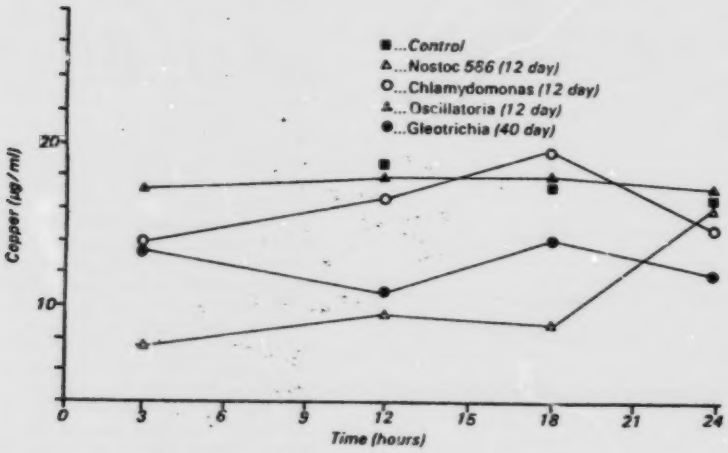

Figure 4. *Uptake of copper by various algae.*

during the labelling period, on the accumulation of heavy metals by algae.

The present study about doubles the number of algae for which concentration factors for cadmium have been determined. This is not only important to waste treatment applications, but also to environmental impact studies. Also noteworthy is the close agreement of concentration factors from the literature with those of this study, with CFs on the order of 10^3 common to both. What is not immediately apparent is the generally lower CFs for the blue-green algae. In fact, three 10-day old cultures of blue-green algae, *Nostoc muscorum* A, *Nostoc* H and *Schizothrix calcicola* did not remove cadmium significantly at any pH, while only one green algae, *Mougeotia*, showed such negative results. Although the total number of species examined is small, the present study suggests that green algae are somewhat more efficient at accumulating cadmium than the blue-green algae.

Concentration factors for lead are generally on the order of 10^3 to 10^4 for all algae studied. All the blue-green algae screened were successful at removing lead at least at one pH, while the diatom *Navicula pelliculosa* and the green *Chlorella* and *Scenedesmus obliquus* were successful at accumulating lead at any pH. *Chlamydomonas* proved to be the most efficient at removing lead from solution.

Mercury was again demonstrated to be concentrated avidly by most species of algae. Every organism screened in this study removed mercury at least at one pH, with concentration factors on the order of 10^3 and 10^4. Algae may be one of the most effective means for removing this element. Algae can reduce mercuric ion to elemental mercury which is subsequently volatilized to the atmosphere. The question might arise whether the same phenomenon occurred in these experiments, giving artifically high concentration factors. Although the possibility cannot be denied categorically, the short time scale of these experiments (three hours) and the quiescent conditions under which the plates were held would argue against loss of very much mercury to the atmosphere. This is especially true since most other studies employed aerated cultures and a time scale of several days. It has also been reported that the reducing factor(s) were extracellular. Since the algal cells in the present study were washed and resuspended in distilled water before introduction to the assay plates, the concentration of reducing factor(s) would be diminished, at least initially. However, the phenomenon of mercury reduction and volatilization by algae clearly deserves further study.

Another contribution of this work was the systematic study of the effect of pH on heavy metal accumulation. The studies cited from the literature were generally field observations, during which the pH of the surroundings varied naturally, or were laboratory studies where the culture media characteristically determined the pH of metal uptake, and therefore, uptake across a wide variety of pH conditions could not be determined. In general, those algae which are most proficient at removing metals will remove them over a wide pH range. For example, *Chlamydomonas* removes lead across a pH range from 4 to 9 at about the same efficiency (0.69-0.80) while the less effective alga *Mougeotia* removes lead only at pH 9 and

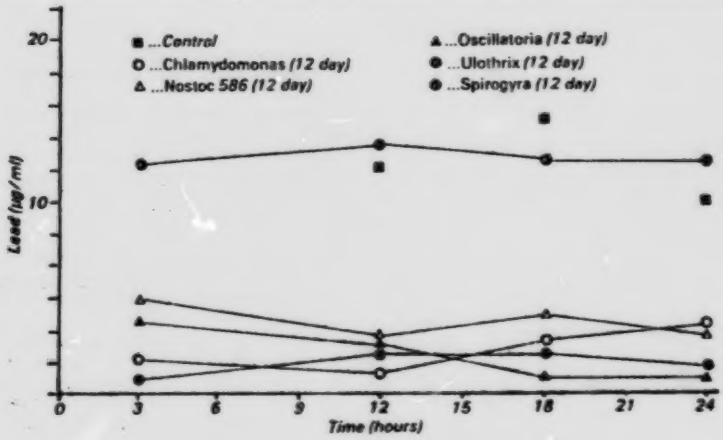

Figure 5. *Uptake of lead by various algae.*

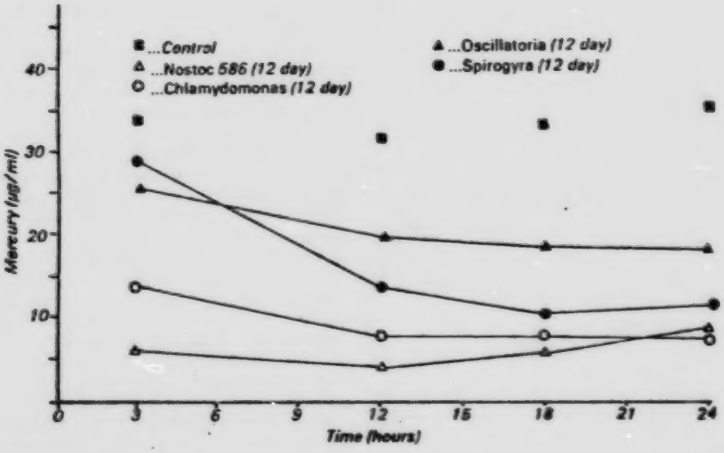

Figure 6. *Uptake of mercury by various algae.*

then only at an efficiency of 0.29. Clearly *Chlamydomonas* is more competent at removing lead from solution.

Other observations made during this study tend to confirm and extend suggestions made by earlier workers. It has been hypothesized that the flagella of *Platymonas subcordiformis* provided the sites for a significant fraction of the lead taken up by this algae. While this hypothesis was not specifically tested in the laboratory, the dramatic superiority shown by *Chlamydomonas* in removing lead, as compared to the other algae evaluated combined with the fact that *Chlamydomonas* was the only flagellated form used, argues for the importance of the flagella as sites of lead accumulation.

Perhaps one of the most important contributions of this work, however, was the adaptation and development of microtiter equipment, especially the Titertek™ supernatant collection apparatus, to the study of the problem of algal uptake of heavy metals. The technique and procedures developed during the course of this study have already provided usable data on a relatively limited number of variables. Future work will no doubt utilize the rapidity and sensitivity of the technique to accumulate more data covering a wider range of variables.

Recommendations

The remarkable ability of selected algae to concentrate heavy metals on their cell surfaces suggests that the use of intensive algal culture may be a very practical way to reclaim wastewater and/or recover useful quantities of metals. Several directions for future research and development are clearly indicated before this potential can be realized:

1. The glycocalyx—i.e., the mucopolysaccharide and protein capsule—surrounding all algae must be isolated from metal-avid species and further studied for its biochemical structure, exchange capacities, and biphasic physical properties. With these data in hand, it is practical to search for organisms with glycocalyces having desirable properties for the adsorption of metals.
2. If algal beds are to be maintained on a continuing basis, it will be necessary to follow the reproductive capacity of the organism(s) in the presence of excessive levels of metal. In fact, it may be necessary to devise schedules for metal adsorption that are followed by regeneration at low metal levels.

   The present meander technology depends entirely on the presence of naturally occurring wild algae, probably growing as a mixed flora. Since some of the species may have concentration factors in excess of 1×10^4 under certain conditions, and others may not concentrate metal at all, it appears profitable to encourage the former by selective algal farming. Simple enrichment culture techniques are feasible for the meander manager.
3. A screening operation should be devised with the objectives of finding natural or induced mutants that a) have accumulation coefficients one or more orders or magnitude greater than wild types, b) exhibit greater selectivity for a particular metal ion than the wild types, and c) tend to

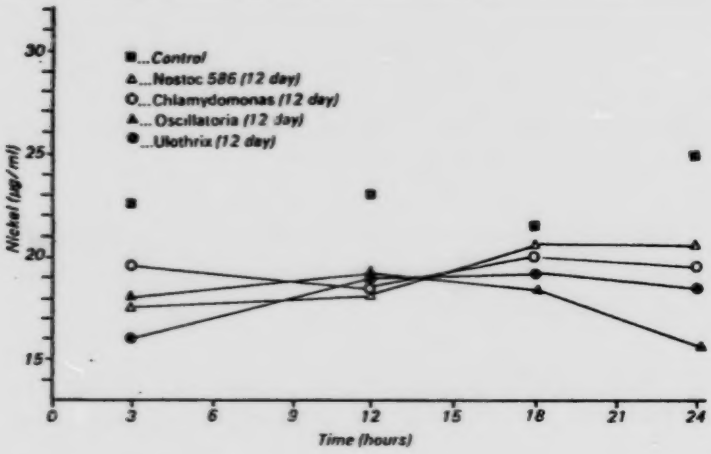

Figure 7. Uptake of nickel by various algae.

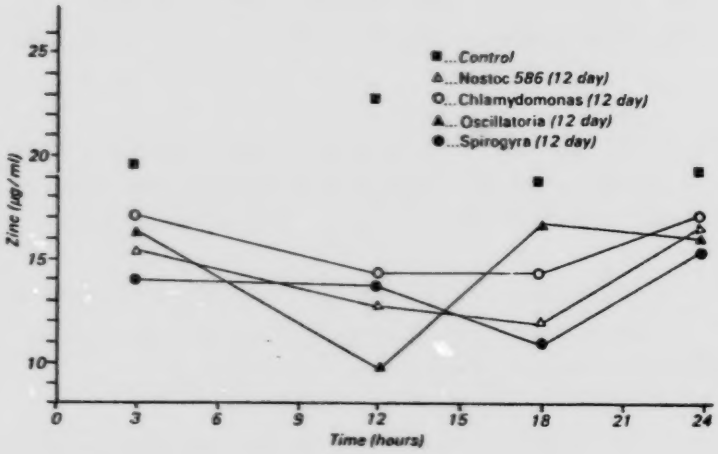

Figure 8. Uptake of zinc by various algae.

remain in their benthic form rather than in their free-floating form. The blue-green algae may be the better choice for this work because they are usually more metal-avid than green algae, and because they are haploid. The latter characteristic makes it easier to induce mutations and to select for variants than in diploid organisms.

4. Almost no data are to be found concerning the maintenance of beds of benthic algae on a continuous basis. Experiments are needed to learn the long-term consequences of heavy metal accumulation in such beds, to monitor detention and release of metals during chronic exposures, and to study the detachment of benthic cells coated with heavy metals.
5. Methods must be devised for systematically discharging metals, or for otherwise recovering them, from meander beds. Simultaneously, it must be determined whether or not it is feasible to recycle the algal cells as inoculum or feedstock after they have been stripped of metal by chemical washing.
6. Investigation of practical questions regarding the suitability of metal-stripped secondary sewage effluent for agricultural purposes must be examined. Conversely, the efficacy of sewage as a dependable nutrient source for algae has not been established. Certainly, the presence of oil, cyanates, solvents, etc., could be expected to interfere with the productive synthesis of the glycocalyx adsorptive surface.
7. The effects of light, temperature, and salt concentration have not been evaluated on a continuously operating meander. Quantitative data have not been collected on the optimum output of glycocalyx because the factors which stimulate it are essentially unknown.
8. Future work should determine whether or not an appropriate substitute can be found for the algal cells in the meander (aggregates or other surfaces coated with semi-purified glycocalyx, for example). This search might provide a renewable and/or strippable surface that would eliminate some of the vagaries associated with the maintenance of open algal cultures.

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Hugh B. Durham is the EPA Project Officer (see below).

The complete report, entitled "Factors Influencing Metal Accumulation by Algae," (Order No. PB 83-149 377; Cost: $14.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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CHAPTER 26

ALUMINUM Al

Aluminum is a light metal which is relatively abundant in the earth's crust. It is soluble in both acid and alkali and forms a gelatinous insoluble hydroxide at intermedate pH values. Considering its abundance in rocks and soils, it is surprising that so little is known about its environmental effects.

Aluminum analyses up to now have not been required in most effluent monitoring programs. Mine and mill discharge permits usually do not list limits for this metal either. Criteria of 100 ug/l have been proposed for the U.S.A. (EPA, 1972), Ontario (1978), and Quebec for fresh water and 200 ug/l for marine effluents (EPA, 1972).

There are no NPDES standards for Al in effluents discharged to surface waters. Public drinking water standards in Canada and the U.S.A. do not list Al, and 5,000 ug/l Al is the maximum permissable for livestock watering and irrigation according to the EPA (1972).

Some states (New York, for example) are proposing that Al should be monitored in effluents and reported even though it does not have to meet any specific limit at this point.

Limited attention has focussed on aluminum recently since there has been speculation that acid rain leaches it from soils and that some fish species find aluminum toxic and the cause of gill damage. Aluminum was implicated in the decrease of fish stocks in lakes whose pH levels declined as a result of inadequate buffering capacity to neutralize acid inputs. Aluminum mobilized by acid rain would drain into lakes and accumulate by precipitation until the pH of the lake decreased sufficiently to redissolve the precipitates and pose a threat to aquatic organisms. Also, aluminum has been identified in the brains of victims of Alzheimer's Disease--the disease of senility.

The importance of pH was reported by FREEMAN AND EVERHART (1971) who showed that Al toxicity is very pH dependent. BURROWS (1977) reviewed the chemistry, toxicity, and environmental prevalence of aluminum in the aquatic environment. The California Regional Water Quality Control Board, North Coast Region, Order No. 84-108 on waste discharge requirements for NORANDA Grey Eagle Mines, Inc. stipulates that no water shall be discharged into streams or other surface waters. Excess water disposed of through irrigation to a disposal site shall contain no more than 0.5 ppm Al.

Strangely enough, this metal that the California RWQCB considers in need of regulation is grouped as a heavy metal in their classification. The basis for this

Al (ug/L) ALUMINUM

Summary of North American Water Quality Criteria for Aluminum

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	--	--	<100 *	Undefined Tolerance Limits <100 Fish	--	--	500-1,000	--	--
MAX. PERMISSIBLE LIMIT		--	--	--	100 *	--	100	--	--	--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<200 .01 (96-hr LC50)	--	--	<200 *	--	--	--	500-1,000	--	--
MAX. PERMISSIBLE LIMIT		1,500	--	--	1,500 *	--	--	--	--	--	--
PUBLIC WATER SUPPLY		--	--	--	--	--	--	--	--	--	--
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	5,000	--	--	5,000	5,000	--	--	--	--	5,000
	IRRIGATION	5,000	--	--	5,000	5,000	--	--	--	--	500

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limitation for irrigation is not mentioned, and, unquestionably, it is much stricter than agricultural irrigation water standards.

PATTERSON (1979), in a review paper on industry sources and control of metals, lists Al as one of the regulated metals for coal and ore mining which was based on a directory of federal and state water pollution standards prepared by the same author for the Illinois Institute for Environmental Quality. PATTERSON (1979) also shows proposed levels of 0.6 mg/l Al for 30-day averages and 1.2 mg/l Al as the 24-hour maximum for Al within BPCT, BAT, and NSPS regulations.

LARSEN AND ROSS, formerly of the University of Denver, showed two acid mine drainage streams, namely the Idaho drainage tunnel with 10.00 ppm Al and the Montana drainage sample with 904 ppm Al. They indicate that aluminum is readily removed by the addition of lime which is the first step of their two-step process.. In the diagram shown in their paper, however, some Al seems to be left in solution by the time sulfide addition starts. Their diagrams indicate that Al is the first metal to be quantitatively removed as sulfide is added although presumably not as a sulfide.

At the EAST RAND PROPRIETORY MINES LTD. on the Witwatersrand, acid mine drainage pumped from underground at pH 4.5 contained 30 mg Al/l. In the seeded slurry reverse osmosis test this was reduced to 0.5 ppm Al in the product water.

It is known that the very acidic raffinate solutions generated from Witwatersrand ores can contain very high levels of Al (3-5,000 ppm), but these are undoubtably reduced during neutralization. Of some concern is the amphoteric nature of Al which seems to go back into solution readily if the pH of water in contact with the precipitate drops again. One non-Witwatersrand uranium mine also employing an acid leach yields a tailings pond decant solution with 625 ppm Al, and the tailings pond seepage after natural pH adjustment to pH 6.6 has dropped to 12 ppm Al. Aluminum forms soluble hydroxide complexes which means that at high pH levels, it is also rendered soluble; if such water is discharged, it will, on mixing with recovering waters, likely reprecipitate to some extent. Not very much seems to be known about the effects of aluminum in the environment or on the long-term health effects on humans of aluminum in the drinking water. Aluminum is, of course, routinely used for clarification of drinking water by municipalities as alum ($Al_2(SO_4)_3$).

WILMOTH AND SCOTT (1976) showed interesting data for unreferenced acid mine drainage and treatment thereof by several processes. It is interesting that alumina-lime-soda, a process in which aluminum is added to the effluent, actually achieves one of the lowest Al levels in the processed water.

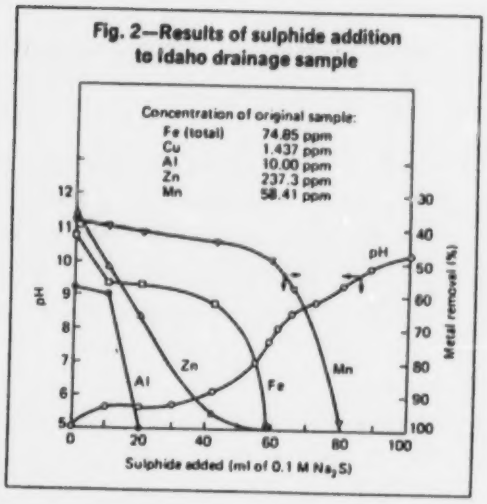

Fig. 2—Results of sulphide addition to Idaho drainage sample

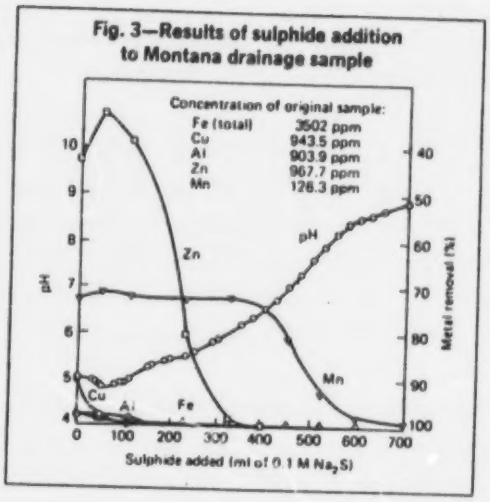

Fig. 3—Results of sulphide addition to Montana drainage sample

LARSEN & ROSS (1976)

Chemistry Analyses Illustrating Effluents from Various Processes to Treat AMD

Sample	*Cond*	*Acid*	*pH*	*Ca*	*Mg*	*Total iron*	*Fe^{2+}*	*Na*	*Al*	*Mn*	*SO_4*	*Alk*	*TDS*
Example One—Limestone Neutralization: Ferrous(A) versus Ferric(B) Using No Coagulants													
Raw feed A	4,000	610	5.2	360.	110.	270.	260.	480.	5.4	5.9	3,000	12.	4,200
Feed B (H_2O_2)	4,000	590	3.1	340.	95.	270.	0.	440.	8.2	5.9	2,500	0.	3,500
Effluent A	4,000	230	6.5	420.	90.	150.	150.	380.	1.0	5.8	2,400	88.	3,500
Effluent B	4,000	13	6.5	380.	70.	6.2	0.	370.	1.2	5.0	2,000	50.	2,900
Example Two—Limestone Neutralization with Extended Aeration, Sludge Recycle, and Coagulant Addition													
Raw feed	3,650	460	5.5	370.	110.	230.	220.	470.	12.	5.4	2,800	8.	4,000
Effluent	3,650	0	7.4	520.	110.	0.9	0.	440.	0.4	3.9	2,700	47.	3,700
Example Three—Lime Neutralization Comparing *p*H 8(A) versus *p*H 7(B) Using Coagulant Addition													
Raw feed	4,000	520	5.7	400.	130.	280.	260.	510.	9.8	6.4	3,200	23.	4,500
Effluent A	4,100	0	7.9	600.	120.	2.1	0.	500.	0.4	1.6	3,300	88.	4,700
Effluent B	4,100	0	7.0	620.	120.	10.	0.7	490.	0.6	4.9	3,300	50.	4,400
Example Four—Combination Limestone-Lime Treatment(A) versus Lime Treatment(B) Using Coagulants													
Raw feed	3,600	630	5.2	340.	100.	290.	270.	380.	15.	5.4	2,700	4.4	3,800
Effluent A	3,500	0	8.0	560.	83.	2.3	0.	370.	0.5	2.2	2,500	100.	3,500
Effluent B	3,500	0	8.0	560.	95.	1.4	0.	360.	0.2	1.2	2,500	110.	3,500
Example Five—Lime-Soda Treatment Where Effluent Hardness Is Less Than 100 mg/liter													
Raw feed	820	170	3.0	28.	18.	17.	—	1.8	13.	4.5	270	0.	350
Sed. eff.	930	0	11.	140.	1.1	0.8	—	1.8	2.7	0.2	240	100.	500
Softener eff.	1,000	0	10.8	41.	0.4	0.3	—	140.	2.5	0.05	220	110.	510
Recarb. eff.	790	0	9.2	33.	0.4	0.3	—	140.	2.4	0.06	220	74.	470
Example Six—Alumina-Lime-Soda Treatment													
Raw feed	—	700	2.8	8.	25.	100.	—	2.	40.	4.0	750	0.	950
Effluent	—	0	7.5	20.	10.	0.3	—	150.	0.2	0.04	250	—	450
Example Seven—Reverse Osmosis Treatment													
Raw feed	1,000	240	3.4	130.	90.	77.	64.	—	12.	12.	750.	0.	1,300
Waste brine	3,600	810	2.9	490.	310.	330.	250.	—	44.	24.	2,800.	0.	4,500
Effluent	17	32	4.5	0.5	0.6	0.5	0.5	—	0.2	0.08	2.2	0.	5
Example Eight—Ion Exchange Treatment (Design Values)													
Raw feed	—	240	3.4	130.	90.	77.	64.	1.0	12.	12.	750	0.	1,300
Cation eff.	—	800	1.9	13.	5.	6.	5.	3.	0.2	0.6	750	0.	800
Anion eff.		0	8.0	13.	1.5	1.2	1.0	20.	0.2	0.3	40	20.	110
Neu. eff.	—	0	7.5	20.	1.5	0.1	0.1	20.	0.2	0.04	50	30.	120

Note: All units are mg/liter except for conductivity (micromhos/cm) and *p*H. Alkalinity and acidity are expressed as $CaCO_3$.

Source: WILMOTH & SCOTT (1976)

CONCLUSIONS

- Not much is known about aluminum levels in mine and mill effluents. Aluminum was one metal that was overlooked by the PEDCO (1983) Evaluation of Management Practices for Mine Solid Waste Storage, Disposal, and Treatment.

- Most mine/mill effluent analyses do not include aluminum.

- Aluminum is acutely toxic to fish at low levels of around 0.1 mg/l or less, especially at low pH, and is likely to become more of a focal point as a result of studies on the acid rain problem. Aluminum may also be of concern for high pH effluents due to its solubility as a hydroxide complex.

- Seeded slurry reverse osmosis reduced aluminum levels in AMD treatment test from 30 mg/l to 0.5 mg/l.

- Aluminum is precipitated as a hydroxide at around pH 5.5-6. Pilot scale tests of a two-stage lime-sulfide process indicate that Al can be almost quantitatively removed by precipitation.

- More needs to be known about the effects of aluminum in recycled mine and mill process water on metallurgical processes.

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CHAPTER 27

AMMONIA

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INTRODUCTION

Ammonia is a pungent, colorless, alkaline compound NH_3 that is very soluble in water. It is a biologically active compound present in most waters as a normal biological degradation product of nitrogenous organic matter. It is, however, undisputably toxic to fish. Ammonia may also reach ground and surface waters through agricultural drainage after application of ammonia fertilizers and through discharge of industrial wastes containing ammonia as a by-product or wastes from industrial processes using ammonia as a reagent or for pH control. Considering the huge volume of sewage effluents containing around 10-20 ppm NH_3 (NALCO, 1979) and the millions of tons of ammonia fertilizer applied to the land surface annually, it is, at first impression, incongruous to find such tight regulations governing ammonia in minewater discharges.

AMMONIA IN MINING AND MINERAL PROCESSING

Ammonia enters minewater mainly through the use of explosives containing ammonia; e.g., AMFO, which are commonly used. Metallurgical plant effluents may contain ammonia due to its use as a reagent (e.g., in copper and nickel refining) or as a pH modifier (e.g., one copper-lead-zinc flotation plant in Ontario), through sewage plant effluents or even possibly through biological degradation of cyanide in gold mill tailings solutions. Ammonia is also introduced to some uranium mill systems as ammonium sulfate used to elute uranium from ion exchange resins and SX and as NH_4OH to precipitate uranium from the eluates.

Unquestionably, the use of ammonia in metallurgical plants has mostly been replaced by other reagents where appropriate because of the awareness of the damage that ammonia in effluents does to fish.

In the PEDCO (1983) report to the U.S. EPA on Evaluation of Management Practices for Mine Solid Waste Storage Disposal and Treatment, ammonia was analyzed in tailings pond decant and in water extractions from tailings. Quite variable concentrations of ammonia were found in minewater and tailings pond liquid.* In one case where 39.85 ppm NH_3 was found in tailings dam seepage + runoff, it has to be assumed that fertilizer on the

NH_3 (ug/L) AMMONIA (un-ionized) Summary of North American Water Quality Criteria for Ammonia

Compiled by NORANDA

WATER USAGE	EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9,**]	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE										
OBJECTIVE	.05 of the 96-h LC50	20	--	<20*	<20	20	--		--	--
MAX. PERMISSIBLE LIMIT	20	--	--	<20*	20	20 -1,500 100	--		--	--
PROTECTION OF MARINE LIFE										
OBJECTIVE	<10 .1 of the 96-h LC50	--	--	<10*	--	--	--		--	--
MAX. PERMISSIBLE LIMIT	<400	--	--	<400*	--	--	--		--	--
PUBLIC WATER SUPPLY	500	--	--	10	--	10 - 500	--		--	--
AGRICULTURAL WATER SUPPLY: LIVESTOCK WATERING	--	--	--	--	--	--	--		--	--
AGRICULTURAL WATER SUPPLY: IRRIGATION	--	--	--	--	--	--	--		--	--

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Environmental Protection Agency Ambient Water Quality Criteria not available for ammonia.
4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada 1979. Guidelines for Surface Water Quality. Vol.1. Inorganic Chemical Substances, Preamble.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Gouin, D. et Malo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9. British Columbia - Receiving water quality objectives not available.
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

tailings dam wall caused the very high value because liquid in the same tailings pond ran only 2.00 ppm NH_3.

REGULATED AMMONIA LIMITS IN EFFLUENT

According to the U.S. EPA (1976), the objective for ammonia in receiving waters is 0.020 mg/l as un-ionized ammonia for freshwater aquatic life.

Concentration of un-ionized ammonia varies depending on total ammonia concentration, temperature, and the pH of water according to the following tables. These firstly show the percent un-ionized ammonia in aqueous ammonia solutions and the concentration of total ammonia (NH_3 + NH_4^+) which contain an un-ionized ammonia concentration of 0.02 mg/l NH_3.

According to a NORANDA internal survey, a 1972 U.S. EPA document found that un-ionized ammonia of 400 ug/l or more may constitute a hazard to marine life while levels below 10 ug/l present minimal risk to marine biota.

The MINISTRY OF ENVIRONMENT (1979) of Ontario also set the objective of 0.02 mg/l unionized ammonia for protection of aquatic life.

It is of interest that the U.S. EPA (1981) Development Document for Effluent Limitations Guidelines and Standards for the Ore Mining and Dressing Point Source Category did not include ammonia.

-Concentrations of total ammonia (NH_3 + NH_4^+) which contain an un-ionized ammonia concentration of 0.020 mg/l NH_3(mg/l)*

Temperature (°C)	pH Value								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5....	160.	51.	16.	5.1	1.6	0.53	0.18	0.071	0.036
10....	110.	34.	11.	3.4	1.1	0.36	0.13	0.054	0.031
15....	73.	23.	7.3	2.3	0.75	0.25	0.093	0.043	0.027
20....	50.	16.	5.1	1.6	0.52	0.18	0.070	0.036	0.025
25....	35.	11.	3.5	1.1	0.37	0.13	0.055	0.031	0.024
30....	25.	7.9	2.5	0.81	0.27	0.099	0.045	0.028	0.022

*[Abstracted from Thurston et al. (1974)]

Percent un-ionized ammonia in aqueous ammonia solutions*

Temperature (°C)	pH Value								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5....	0.013	0.040	0.12	0.39	1.2	3.8	11.	28.	56.
10....	0.019	0.059	0.19	0.59	1.8	5.6	16.	37.	65.
15....	0.027	0.087	0.27	0.86	2.7	8.0	21.	46.	73.
20....	0.040	0.13	0.40	1.2	3.8	11.	28.	54.	80.
25....	0.057	0.18	0.57	1.8	5.4	15.	36.	64.	85.
30....	0.080	0.25	0.80	2.5	7.5	20.	45.	72.	89.

*[Thurston, et al. (1974)]

Source: U.S. EPA "Red Book."

PERCENTAGE OF AMMONIA UN-IONIZED IN DISTILLED WATER*

Temperature C	Percentage Un-ionized at Given pH								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5	0.01	0.04	0.11	0.40	1.1	3.6	10	27	54
10	0.02	0.06	0.18	0.57	1.8	5.4	15	36	64
15	0.03	0.08	0.26	0.83	2.6	7.7	21	45	72
20	0.04	0.12	0.37	1.2	3.7	11	28	55	80
25	0.05	0.17	0.51	1.7	5.1	14	35	63	84
30	0.07	0.23	0.70	2.3	7.0	19	43	70	88

*Prepared from data given in Sillen and Martell.**

Source: NWWA "Standard Methods," 16th Edition.

The South African Government Gazette (1962) Regulation No. R533 set a general effluent limit for "free and saline ammonia as 10 mg N/l and a special standard for discharges to certain listed troutbearing surface streams at 1 mg/l "free and saline ammonia" as N.

Ammonia limits set in permits for mines and mills visited in North America were often not specified or ranged from 1 to 30 ppm NH_3 expressed as N.

On February 7, 1984, the U.S. EPA published in 49 Federal Register, page 4551 and 4553, a summary of revisions to the "Guidelines for Deriving National Water Quality Criteria for the Protection of Aquatic Life and its Uses" wherein it was proposed that the "Final Acute Value" of 0.30 mg/l NH_3 derived in the "1983 Ammonia Criteria Document" should be divided by two for a criterion maximum concentration.

Motivation for this is that the final acute value (0.30 mg/l NH_3) is intended to protect 95% of a group of diverse species unless an important species is more sensitive. "However, a concentration that would severely harm 50 percent of the fifth percentile or 50 percent of a sensitive important species cannot be considered to be protective of that percentile or that species."

"Dividing the Final Acute Value by 2 is intended to result in a concentration that will not severely adversely affect too many of the organisms."

The American Mining Congress has argued that dividing the FAV for ammonia of 0.30 mg/l NH_3 by two is not clearly supported by any specific field data.

It is interesting that regulators are arguing about whether or not the maximum criterion should be 0.15 or 0.3 mg/l NH_3 as N when most permits either do not include ammonia or include it in a range from 1-30 mg NH_3/l which are 6-20 times higher than the proposed new maximum criterion.

In one case, the level must refer to the receiving stream concentration whereas, in the other, it refers to the ammonia level in the discharge stream itself.

Whereas it is not the intention of this report to review toxicity nor health effects of various contaminants, it appears that the proposed ammonia maximum level criteria will be subject to review for some time and that the proposed levels of 0.15 or 0.30 mg NH_3/l total would, if enforced, present a serious obstacle for minewater discharge from operatons that use ammonium explosives and sewage treatment plant effluents.

Ammonia in mine and mill effluents is an example of a case for, at most, site specific regulations. Since ammonia is harmful only to fish, effluent regulations on ammonia should only be applied where there is a sensitive aquatic environment to protect.

TYPICAL AMMONIA LEVELS IN DISCHARGES

Based on a casual survey of reported ammonia levels in mine/mill effluents, these range anywhere from 1 ppm to over 20 ppm NH_3. For instance, Quirke Lake in Ontario, which is part of a macro water recycling pattern serving the Elliott Lake Uranium Mines and Mills, ammonia runs around 22 ppm according to MALAIYANDI and SASTRI (1981). According to WHITLOCK and MUDDER (1984), minewater from HOMESTAKE's Lead, S.D., operations contains 5.0-6.0 mg/l NH_3 while the tailings decant runs at less than 1.0 mg NH_3/l.

ANALYSIS FOR AMMONIA

The American Water Works Associaton Handbook on "Standard Methods" is generally used as a source of analytical techniques.

WEATHERBURN (1967) described a method using phenol-hypochlorite which has been referred to in the literature.

AMMONIA IN MINEWATER PONDS DATA (mg/l)

PEDCO (1983) REPORT TO EPA

	Minewater Pond Liquid	Untreated Minewater	Tailings Pond Liquor	Pregnant Heap Leach Liquor	Spent Leach Liquor	Mill Waste Water	Tailings Seepage & Runoff
New Mexico Uranium Mines							
Mine No. 12	0.01						
Mine No. 13	0.15						
Mine No. 14	0.06						
Mine No. 15	0.30						
Wyoming Uranium Mines							
Mine No. 16	LT0.0030						
Mine No. 17	0.04						
Mine No. 18	0.23						
Mine No. 19	4.90						
Other Uranium							
Mine No. 20	LT0.0030						
Mine No. 26	1.32						
Mine No. 27	0.78	0.48					
Florida Phosphate							
Mine 1			LT0.01				
Mine 2		0.82	0.64				
Mine 3			LT0.05				
Mine 4			0.72/0.83				
Idaho Phosphate							
Mine 5			0.17				
Mine 7			8.10/0.45				
Other Phosphate							
Mine 9			LT0.01				
Mine 11			LT0.02				
Southwestern Copper							
Mine 28		LT0.05	1.56				
Mine 29			LT0.05				
Mine 30	LT0.05		1.06				
Mine 31			1.43	25.2			
Mine 32			12.8				
Mine 33			0.28	26.40	15.6		

	Minewater Pond Liquid	Untreated Minewater	Tailings Pond Liquor	Pregnant Heap Leach Water	Spent Leach Liquor	Mill Waste Water	Tailings Seepage & Runoff
Other Copper							
Mine 34		0.40	5.52				
Mine 36		LT0.02*			1.94		
Mine 37	0.16		LT0.02			2.40	
Mine 38	1.73		0.60			LT0.02	
Western Lead/Zinc							
Mine 39	1.94		18.1				
Mine 48		0.53					8.55
Eastern Lead/Zinc							
Mine 40	0.99		3.20				
Mine 41		2.70	5.22				
Mine 42		0.34	0.44				
Mine 43	0.08	0.27	0.60				
Missouri Lead/Zinc							
Mine 45	LT0.05		3.25				
Mine 46	18.10		2.36				
Molybdenum							
Mine 49		2.08				1.48	2.63
Mine 50	0.44	1.55	2.00				39.85
Mine 51		LT0.02*	LT0.05				
Nevada Gold and Silver							
Mine 52			3.2				
Mine 53			4.6				
Other Gold							
Mine 55	4.95		5.7				
Mine 56			6.30				
Mine 58			10.40				
Taconite/Iron Mines							
Mine 60		LT0.54	0.02				
Mine 61		0.83	LT0.02				
Mine 63			0.61				
Mine 64			0.04				

* Inactive Mine

MOTIVATION FOR AMMONIA REMOVAL

Ammonia may need to be removed from minewater or mill tailing decant water before it can be discharged as an effluent.

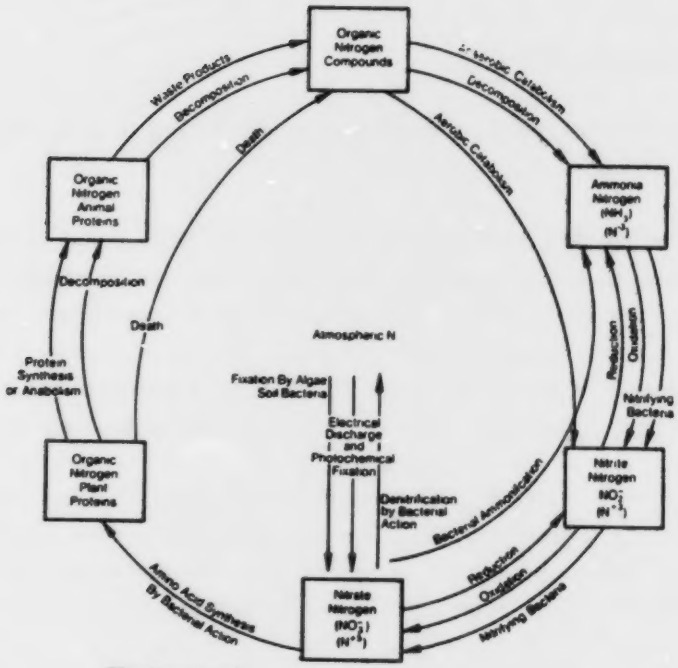
On the Witwatersrand, an interesting need for ammonia removal was encountered. The South African gold and uranium mines are very labor intensive and employ thousands of underground miners at each mine. These mineworkers are often housed in mine "compounds" which consume large amounts of water and are serviced by equally large sewage treatment plants. It was pointed out that a mine housing complex may well yield 2000 m^3/d of treated sewage effluent which is usually discarded to drainage.

Because of the shortage of water due to drought conditions, companies have been trying to find a way to use the treated sewage effluent to supplement mine cooling water, even possibly by spraying it into the ventilation ducts. By law, all water used underground in South African mines must be chlorinated to breakpoint as it is likely to be used for refreshment.

Because of organics present and ammonia levels, this would require excessively expensive chlorine consumption. Work is in progress to determine whether chloramines are an adequate disinfectant which would support changing the law to allow a more economical practice. Questions have been raised as to whether viruses are resistant to chloramine and the possibility of generating chlorinated organic compounds.

Some of the environmental problems associated with the various forms of nitrogen (including ammonia) are as follows:

- Nitrogen compounds are nutrients and may cause undesirable algal growths.
- NH_3 can be toxic to fish and other aquatic life.
- NH_3 and organic nitrogen in effluents can cause a dissolved oxygen demand in receiving waters.
- NH_3 is corrosive to certain metals.
- NH_3 can have detrimental effects on disinfection of water supplies.
- NO_3, an oxidation product of ammonia, can be a health hazard.



The nitrogen cycle.

Source: The Nalco Water Handbook.

METHODS FOR AMMONIA REMOVAL

Several methods are in use for removal of ammonia from effluents of various types. None of them have been applied specifically for the treatment of minewater or mill tailings decant water to the aurhor's knowledge. If ammonia must be removed from effluents, much can be learned from the sewage treatment industry. CULP, et al. (1978) provides one of the most informative descriptions of various ammonia removal processes:

- Ammonia Stripping
- Selective Ion Exchange
- Biological Nitrification-Denitrification
- Breakpoint Chlorination
- pH Change
- Desalination

Probably the best and least costly approach to ammonia removal from mill effluents is to avoid using ammonia at all. In many cases, metallurgical facilities have converted to non-ammonia systems--e.g., for elution of uranium from IX resins or for precipitation of

uranium from concentrated eluates. It is not known how economically feasible it would be for a mine to convert from ammonia-based explosives.

pH CHANGE

One example was found where ammonia was introduced to a large minewater holding pond via a small amount of sewage effluent. Due to bacterial action, CO_2 in the water was consumed which resulted in a pH increase such that the reduced ammonia limits could no longer be met. Rather than remove ammonia, it was found to be less expensive to add CO_2 to drop the pH. The table above indicates that by decreasing the pH from 9 to 6, the total ammonia level allowed without exceeding the 0.02 ppm NH_3 un-ionized limit increases from 0.070 ppm to 50 ppm.

AMMONIA STRIPPING

Ammonia stripping is described in detail by VAN VUUREN (1981) and CULP, et al. (1978).

Of the available methods for removal of nitrogen from wastewater, ammonia stripping is the simplest and easiest to control. There are two serious limitations which the designer must recognize:

1. Ammonia stripping does not work at ambient air temperatures below 32°F.

2. Calcium carbonate scale is likely to be deposited onto the stripping tower slats which results in a reduction of air circulation and droplet formation with loss of efficiency.

In warm climates, the temperature limitation does not apply, and in some locations in cold climates such as alongside a flowing river, nitrogen removal may not be required during winter. There are ways to eliminate or control scale.

Under the right climatic conditions and with provisions for scale prevention or removal, ammonia stripping is a practical, reliable method for nitrogen reduction. If nitrogen removal is necessary during freezing weather, then ammonia stripping can be used in warm weather and a supplemental method, such as ion exchange, employed during the cold seasons.

AMMONIA STRIPPING PROCESS

More than 90 percent of ammonia in most effluents is in the form of ammonia NH_3 or compounds from which ammonia is readily formed.

If certain conditions are met in the secondary treatment process of sewage, the ammonia will be converted to nitrate. CULP, et al. (1978) point out that it is cheaper to maintain the nitrogen as ammonia and to remove it in that form than to remove it as nitrate. The nitrificaton process can be eliminated by maintaining a relatively high organic loading in the secondary process.

Either ammonium ions NH_4^+, or dissolved ammonia gas NH_3, or both may be present as seen above in the tables. At pH 7, only ammonium ions in solution are present. At pH 12, only dissolved ammonia gas is present, and this gas can be liberated from wastewater under proper conditions. The equilibrium proceeds to the right at pH over 7. $NH_4^+ = NH_3 + H^+$.

Two major factors affect the rate of transfer of ammonia gas from water to the atmosphere:

1. Surface tension at air-water interface.

2. The difference in concentration of ammonia in the water and in the air.

Surface tension is at a minimum in water droplets when the surface film is being formed, and ammonia release is greatest at that instant. Little additional gas transfer takes place once a water droplet is completely formed; therefore, repeated droplet formation and coalescing of the water assists ammonia stripping.

To minimize ammonia concentration in the ambient air, rapid circulation of air is beneficial. Air agitation of the droplets may also speed up ammonia release.

The ammonia stripping process consists of:

1. Raising the pH of water to 10.8-11.5.
2. Formation and reformation of water droplets in a stripping tower.
3. Providing air-water contact and droplet agitation by circulating large quantities of air through the tower.

In designing an ammonia stripping tower, it is important to make sure that in solving a water pollution problem, an air pollution problem is not being created.

ENVIRONMENTAL FACTORS

Three potential environmental impacts need to be addressed if an ammonia stripping tower is to be proposed:

- Air Pollution
- Washout of Ammonia from the Atmosphere
- Noise

At an air flow of 500 ft^3/gal and at an ammonia concentration of 23 mg/l in tower influent, the concentration of ammonia in the stripping tower is about 6 mg/m^3. Since the odor threshold of ammonia is 35 mg/m^3, the process would not present an odor nuisance. Concentrations of 280-490 mg/m^3 can cause eye, nose, and throat irritation. 700 mg NH_3/m^3 can have an adverse effect on plants. 1700-4500 mg NH_3/m^3 or more is needed before animal or human toxicity effects start to occur.

Background levels of ammonia in the atmosphere vary from 0.001 mg/m^3 to 0.02 mg/m^3.

Concentrations of ammonia in rainfall washout approach natural background levels within about three miles of the tower. Most soils retain ammonia.

CULP, et al. point out that ammonia stripping towers can be noisy; the noise, however, can be controlled as follows:

Motors: Proper installation, maintenance and insulation.
Fans: Reduction in tip speed and installation of exhaust silencers.
Water: Shielding of the tower packing and air inlet plenum.

DESIGN

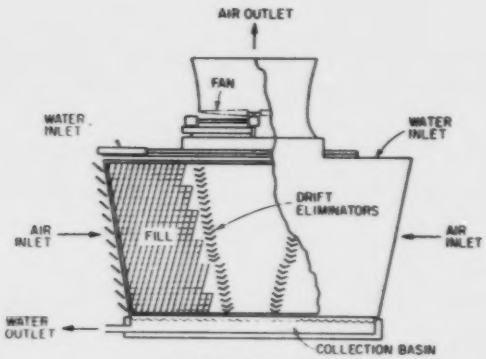
The major factors affecting design and process performance include tower configuration, pH, temperature, hydraulic loading, tower packing depth and spacing, air flow, and control of calcium carbonate scale.

There are two basic types of stripping towers now used in full scale applications: Counter current towers and crossflow towers. Counter current towers (the entire airflow enters at the bottom of the tower while water enters at the top and falls to the bottom) have been found to be most efficient. Crossflow towers have been found to be more prone to scaling.

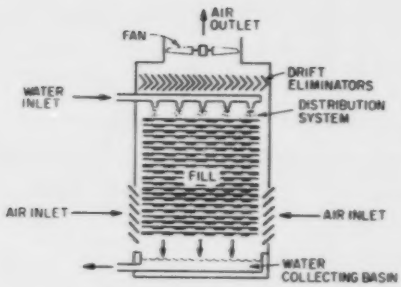
Often pH may be high already if, for example, for phosphorus removal upstream, pH had already been raised. If not, the costs of stripping will be higher if it must be brought about solely for ammonia stripping.

CULP, et al. (1978) provide details of many useful aspects to be taken into account in designing and operating ammonia stripping towers.

Performance of 87-92% of total nitrogen removal in this way is typical.



CROSS-FLOW TOWER



COUNTERCURRENT TOWER

Source: CULP, et al. (1978)

AIR FLOW

In general, 550 cfm/ft^2 is considered to be the practical upper limit for countercurrent towers, although in warm weather conditions, 300 ft^3/gal. will give 90% removal, and 500 ft^3/gal. will achieve about 95% removal.

Typical air design quantites for 90% removal are:

Orange County, California	400 ft^3/Gal
South Lake Tahoe	390 ft^3/Gal
Pretoria, South Africa	338 ft^3/Gal

The required air quantities are usually provided by a fan located on top of the tower. Two-speed fan motors may be used. Horsepower requirements for the fans are not great for these large quantites of air at a small (say one inch) pressure drop. For the 15 mgpd Orange County plant, total installed fan brake HP is 1,380.

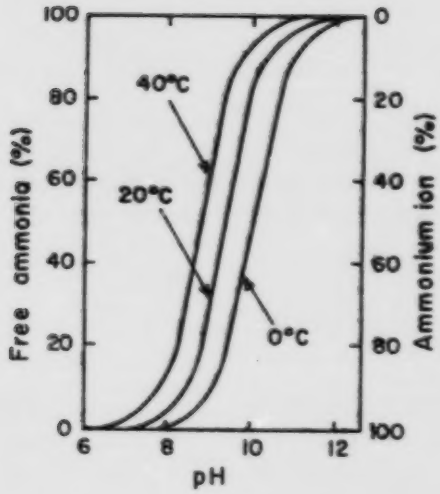
SCALE CONTROL

Scaling results from deposition of calcium carbonate from unstable high pH water flowing through the tower. Scaling potential can be minimized by using a high level of solids recycle in the clarification step after lime treatment. Another approach would be to eliminate the CO_2 from the air.

Portions of the tower packing on which scale is deposited are readily cleaned using high pressure hoses.

CULP, et al. (1978) mentions several different scaling experiences in actual plants. The use of a scale inhibiting polymer supplied by CALGON, NALCO, etc. also offers a means of scale control.

VAN VUUREN (1981) pointed out that environmental conditions, i.e. ambient air temperature, humidity, and the diurnal and seasonal temperature differences affect the performance of ammonia stripping. He also describes a relatively simple pilot plant. During periods of high humidity, the performance improved markedly. For example, during the Pretoria summer rainy season, removals of 90% and more were readily achieved. However, when low humidity air was used in winter at lower temperatures, the cooling effect was greater, and efficiency of the tower dropped to around 50%.



The effects of pH and temperature on the distribution of free ammonia and the ammonium ion in water.

Source: Van Vuuren (1981)

CULP, et al. (1978) also show how ammonia can be recovered from the exhaust gas if necessary.

Numerous ammonia stripping plants have been installed, and design data of a few are provided as examples:

South Lake Tahoe, California

Dimensions - 32 ft. x 64 ft. x 47 ft. high.

Design Data for Full Scale Ammonia Stripping Tower.

Capacity: Nominal, 3.75 mgd
Type: Cross flow with central air plenum and vertical air discharge through fan cylinder at top of tower.
Fill: Plan area, 900 sq ft
Height, 24 ft
Splash bars:
material, rough-sawn treated hemlock
size, ¾ x 1½ in.
spacing, vertical 1.33 in.
horizontal 2 in.
Air Flow: Fan, two-speed, reversible, 24-ft diameter, horizontal

Water Rate		Air Rate	
gpm	gpm/ft²	cfm	cfm/gpm
1,350	1.0	750,000	550
1,800	2.0	700,000	390
2,700	3.0	625,000	230

Tower Structure: Redwood
Tower Enclosure: Corrugated cement asbestos
Air Pressure Drop: ½ in. of water at 1 gpm/ft²

Design data and operational conditions for some cross-flow ammonia stripping towers

Parameter	Lake Tahoe[1,2]	Orange County[3]	Kansas City[4]
Nominal flow through plant, x 10^3 m^3/d	17	57	Pilot scale
Dimension of tower, m	9,6 x 19,2 x 7,2	62,0 x 18,5 x 7,6	1,2 x 1,5 x 3,5
No. of fans per tower	1	6	1
Diameter of fan, m	7,2	5,5	0,7
Details of packing	Splash bars	Splash bars (38 mm PVC)	Polypropylene grids 1,2 x 1,5 x 0,013
Hydraulic loading, $dm^3.m^{-2}.min^{-1}$	40 to 120	40	40 to 100
Air to water ratio by volume	1 850 to 4 100	2 960	750 to 5 600
Temperature of inflowing air, °C	-	32	5 to 26
pH of treated water	11,0	11,0	10,5 to 11,5
Initial ammonia concentration	-	15 to 30	9,5 to 12,0
Maximum ammonia removal, %	95	90	90 at pH to 11,5 at 26 °C

	Stander Plant Dasspoort, Pretoria	Windhoek Plant Namibia
Type	Upflow Tower	Upflow Tower
Total Effective Packing Area m^2	3056	5040
Hydraulic Loading $m^3\ m^{-2}\ min^{-1}$	110	65
Fans	4 @ 11.7KW	4 @ 15KW Original 4 @ 22KW Replaced
Air to Water Ratio by Volume	1,536	2,047 (22KW)
Percentage Ammonia Removal		
Winter	LT50	LT55 (22KW)
Summer	46-56	--

Detailed information on ammonia stripping plant thermodynamics and modeling are available in papers by ROESLER, et al. (1970), ROESLER, et al. (1971), and PERRY, but CULP, et al. (1978) state that most effective design is on an imperical basis.

Most leading water treatment companies would be able to design and build ammonia stripping units, and the following addresses could be helpful:

CULP, WESNER AND CULP
2461 Robin Lane
Cameron Park, CA 95682
(916) 677-1695
Russell L. Culp
George Mack Wesner
Gordon L. Culp

CULP, WESNER AND CULP
1777 South Harrison, #310
Denver, CO 80210
(303) 758-1721
Henry Benjes

NATIONAL INSTITUTE FOR WATER RESEARCH
Council for Scientific and Industrial Research
Post Office Box 395
Pretoria 0001
(012) 869211
Telex: 3-630 SA
Lucas R. J. Van Vuuren

SELECTIVE ION EXCHANGE

Conventional ion exchange resins are not selective enough to be useful for ammonia removal from water. However, clinoptilolite clay is selective for ammonia, and a process

has been developed as described by KOON and KAUFMAN (1971), BATELLE NORTHWEST (1971), and BATELLE NORTHWEST (1969).

Clinoptilolite is a zeolite which occurs naturally in several deposits in the western U.S.A., including near Hector, California. Recently, a deposit was discovered in Natal, South Africa, which is controlled by PRATLEY INDUSTRIES, Krugersdorp.

Clinoptilolite is selective for ammonium relative to calcium, magnesium, and sodium, and ammonia may be eluted from the adsorbent as well as stripped from the regenerant solution allowing both the clinoptilolite and the regenerant to be reused. Ammonium may also be recovered for reuse as fertilizer.

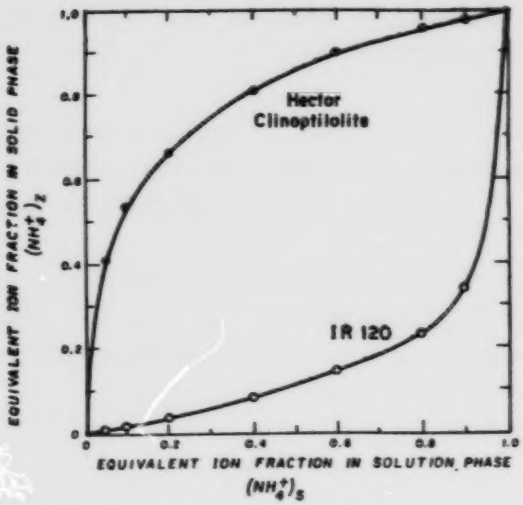
THE PROCESS

Wastewater is passed downward through a 4-5-foot bed of 20 x 50 mesh clinoptilolite granules until ammonia levels in the effluent exceed a desired point at which the bed is regenerated by passing a concentrated NaCl solution through the bed. Problems associated with brine disposal are overcome by removing ammonia from it rendering it suitable for reuse.

Basic ion exchange principles can be used to determine the capacity of clinoptilolite for ammonia, and BATELLE NORTHWEST (1971) provides an example of how to size a unit. CULP, et al. (1978) provide a simplified way of designing such a plant. CULP, et al. (1978) show the following comparison of the adsorption isotherm for HECTOR clinoptilolite and an ion exchange resin IR120. This shows that the favorable isotherm shape is greater than one for the clinoptilolite isotherm. Clinoptilolite is selective for ammonium relative to all common cations except potassium.

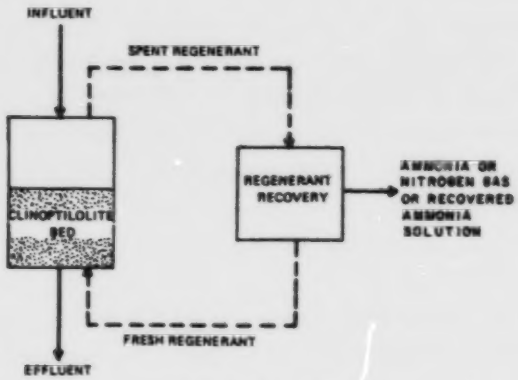
Total exchange capacity of clinoptilolite ranges from 1.6 to 2.0 meq/l. With typical cation concentrations encountered in municipal wastewaters, the capacity for NH_4^+ is around 0.4 meq/g.

NITROGEN REMOVAL



Isotherms for the reaction $(Ca^{2+})_z + 2(NH_4^+)_s = 2(NH_4^+)_z + (Ca^{2+})_s$ with Hector clinoptilolite and IR 120.

Source: CULP, et al. (1978)



Selective ion exchange process.

Source: CULP, et al. (1978)

CLINOPTILOLITE

Clinoptilolite is a zeolite consisting of a hydrated silicate matrix containing alkali and alkali earth metal ions. Clinoptilolite is commonly found in bentonite deposits in the western U.S.A. The Hector, California, clinoptilolite is in the sodium form. Not all

deposits produce a material that is strong enough to be used in columns. When crushed, screened, and attrition washed to remove clay, 20 x 50 mesh Hector clinoptilolite has a five-minute wet attrition rate of three percent according to MERCER (1969). The wet 20 x 50 mesh clinoptilolite has a specific gravity of 1.59 and a bulk density of 0.74-0.79 g/cm^3.

Clays and zeolites are often unstable towards acids and alkalis. Clinoptilolite is relatively resistant to acid and caustic solution although strong caustic solutions attack clinoptilolite but not in the concentrations used for ammonia removal and regeneration.

DESIGN FACTORS

Factors affecting process efficiency include pH, hydraulic loading rate, clinoptilolite size, pretreatment, wastewater composition, and bed depth. These are discussed by CULP, et al. (1978).

Optimum ammonium exchange occurs in the pH range 4-8. Below pH 4, ions compete for loading sites; above pH 8, ammonium converts to ammonia which does not load.

7.5-20 bed volumes/hour using 20 x 50 mesh clinoptilolite (0.95-2.7 gpm/ft^2) have been used with good results. Ammonium concentrations of 0.22-0.26 ppm NH_4^+ in the effluent after contacting clinoptilolite have been reported by KOON and KAUFMANN (1971). At rates beyond 20 BV/hour, the exchange kinetics suffer, and significant ammonium leakage occurs.

Based on 20 BV/hour, a 2000 m^3/d sewage effluent treatment would require a clinoptilolite adsorption contactor with a bed volume of 4.6 m^3 allowing 10% for regeneration.

Better kinetics can be achieved with finer sized clinoptilolite, but elutration losses will be greater, and CULP, et al. (1978) recommend the use of 20 x 50 mesh adsorbent.

Head loss at 15 BV/hour in a three feet deep bed (5.6 gpm/ft^2) is calculated at 2.1 feet with 20 x 50# adsorbent. A six-foot bed under the same circumstances would result in a head loss of 4.2 feet.

Bed depths of six feet were generally more efficient than three-feet depth at the same number of bed volumes/hour because the upflow velocity is much less for a three foot bed than a six foot bed, and at the lower velocity in a three-foot bed, some plugging may occur which reduces the efficiency. Full scale designs are reported to use four foot bed depths with a high degree of pretreatment (coagulation and filtration).

MULTIPLE COLUMNS VS. SINGLE COLUMN

The number of bed volumes treated per cycle can be increased with the same effluent quality using two or more columns in series according to standard ion exchange practice. Tests indicated that ammonium loadings can be increasd from 55 -58 percent of equilibrium capacity to 85% by using two columns in series, and average inputs at the Tahoe plant were increased from 150 to 250 BV/cycle. Because of added capital costs in a series system, all commercial-scale units up to 1978, anyway, used parallel single beds. Improved utilization of available exchange capacity was achieved by blending effluents from several parallel columns, each in a different stage of exhaustion.

To avoid excessive headloss, feedwater should have less than 35 mg/l suspended solids, and no problems are anticipated with organic fouling because biological growth is adequately removed during salt regeneration.

CULP, et al. (1978) report results of pilot tests for ammonia removal from three wastewaters with 12-16 ppm NH_4^+-N, and there was a marginal increase in bed volumes to 50% breakthrough point for feedwaters containing lower competing ion concentrations, e.g., about 10-25% greater. The 50% breakthrough point was reached typically after 300-400 BV.

Breakthrough curves for a single six-foot column of clinoptilolite operated at 6.5-9.7 BV/hour with 15-17 ppm NH_4^+-N in the feed stream indicate that about 150 BV could be used for design purposes for effluents requiring less than 2 ppm NH_4^+-N. Although the effluent, after 150 BV, is around 2 ppm NH_4^+, the average effluent to this point in the cycle is less than 1 mg/l.

Breakpoint chlorination would be more economical for removal of residual ammonia below 1 ppm NH_4^+-N, especially if the water is to be desinfected with chlorine anyway.

DETERMINATION OF IX CONTACTOR SIZE

Determination of the contactor size is found by testing the clinoptilolite capacity for ammonium adsorption from the characteristics of the feedwater which can be determined experimentally or estimated from a table provided in CULP, et al. (1978), page 334, if the ionic strength of the feedwater is known.

REGENERATION ALTERNATIVES

Using concentrated salt solution to regenerate the clinoptilolite loaded to breakthrough, the volume of ammonium laden, spent regenerant is about 2.5-5 percent of the throughput

treated prior to regeneration. By removing ammonium from the spent regenerant, regenerant can be recycled for reuse. Alternative ways to recover regenerant are:

Air Stripping
Steam Stripping
Electrolytic Treatment

Regeneration is in an upflow mode.

HIGH pH STRIPPING

Use a 5 g/l lime slurry to which 0.1N NaCl has been added. The volume of regenerant needed decreases with increasing pH, and the ammonium is converted to ammonia ready for removal from the regenerant.

High pH regeneration, however, leads to precipitation of magnesium hydroxide and calcium carbonate during the regeneration cycle which plugs the exchanger inlets and outlets and fouls the zeolite particules. This is overcome by using neutral regeneration in a closed loop.

NEUTRAL pH REGENERATION

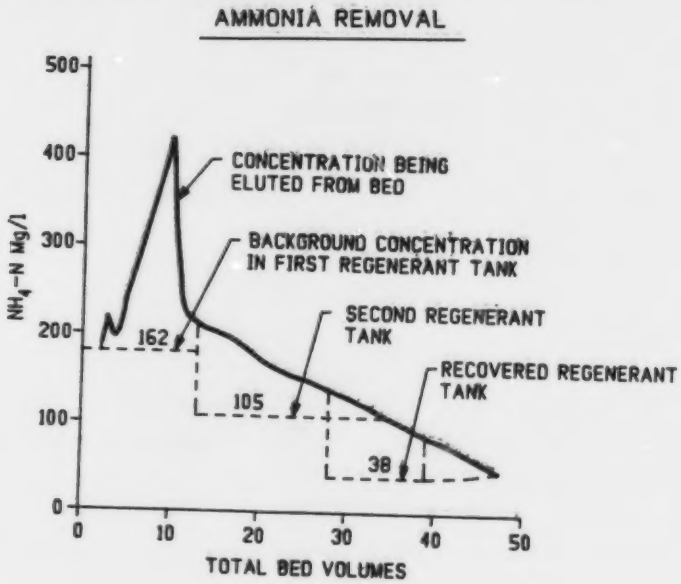
The 15 mgd Upper Occoquan regional plant in Virginia and the 6 mgd Tahoe-Truckee Sanitation Agency plants in California use a regenerant near neutral pH. The regenerant consists of two percent NaCl requiring 25-30 BV to reach equilibrium at a typical rate of 10 BV/hour. Provision is made for backwash at 8 gpm/ft^2 and a surface wash of the contactor prior to initiation of regenerant flow.

Air stripping of high pH regenerant removes ammonia from it until the NH_3-N is reduced to around 10 mg/l. Liquid flow rate to the stripper was typically 2 gpm/ft^2 with an air-liquid ratio of 150 ft^3/gal in a pilot plant. Severe scaling resulted which required overdesign in the commercial plant.

Air stripping of neutral pH regenerant containing two percent NaCl at near neutral pH solved the scaling problem in the zeolite contactor.

Ammonia can be recovered by passing the gases through an absorption tower containing sulfuric acid. Some detail of possible arrangements is provided by CULP, et al. (1978)

A typical elution curve after U.S. EPA (1975) is shown:



Stream stripping of ammonia to recover the regenerant is economical only for high pH regeneration and is used at the Rosemont, Minnesota plant.

A third alternative is to use electrolysis to generate chlorine from the salt in the regenerant at neutral pH which converts ammonia to nitrogen and hydrogen after soda ash treatment for calcium removal. Pilot tests indicate a consumption of 50 watt-hours per gram of ammonia or 4.7 kWh/1,000 gallons. Electricity required for air stripping is only about 10% of that for the electrolytic process.

OPERATING PLANT PARAMETERS

Operating parameters and performance data for two U.S. plants is provided in CULP, et al. (1978) for the Rosemont plant in Virginia reported by U.S. EPA (1975). Typical ammonia removal efficiencies are 90 percent at 10°C and 95% at 20°C which indicates the efficiency of this process.

It is known that work on the use of clinoptilolite ammonia removal is being undertaken in South Africa by:

NATIONAL INSTITUTE FOR WATER RESEARCH
C.S.I.R.
Post Office Box 395
Pretoria 0001
(012) 86-9211
Telex: 3-630SA

BIOLOLGICAL REMOVAL OF AMMONIA AND NITRATES

Nitrogen may be removed both as ammonia (nitrification) and as nitrogen (denitrification). Nitrification of ammonia takes place in a controlled aerobic environment, and denitrification takes place if the nitrified effluent is subjected to a period of anaerobiosis to allow saprophytic bacteria to utilize the nitrates as electron acceptors.

Nitrification and denitrification require simple equipment, and no liquid or solid by-products are created.

All of the biological system designs for nitrogen removal are based on a sequence of: 1) oxidation of carbonaceous materials; 2) oxidation of nitrogenous materials including ammonia; and 3) reduction of nitrates.

Nitrification is carried out by two groups of autotrophic bacteria, Nitrosomonas and Nirobacter, which must operate sequentially because Nitrosomonas can oxidize ammonia to nitrite, and Nitrobacter is limited to oxidation of nitrite to nitrate.

Nitrification processes fall into several categories:

Single stage in which the carbonaceous and nitrogenous oxidation steps are combined in a single reactor rather than first achieving the carbonaceous oxidation in a separate reactor.

Suspended growth - nitrification in a mixed reactor such as a conventional aerated tank.

Attached growth nitrification is accomplished by organisms attached to a growth media as in a trickling filter or rotating biological contactor (RBC).

Both suspended and attached growth systems are used for denitrification.

Several factors are important in the nitrification process and the design of a plant.

pH - pH should be somewhere around pH 8.0-8.5 to achieve a maximum nitrification rate. Acid pH will depress the rate of nitrification although acclimation is possible to pH 5.5. The nitrification process itself can depress the pH below optimum levels:

$$NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + 2H_2CO_3 + H_2O$$

7.14 mg of alkalinity (as $CaCO_3$) is destroyed per mg NH_4^+ nitrogen oxidized.

Temperature has a marked influence on nitrification attached growth systems; e.g., on an RBC, it can compensate for colder temperatures by accumulating thicker slime growths.

Dissolved oxygen - increased dissolved oxygen concentration greatly enhances the rate of nitrification, and the efficency of the air diffusion system has a marked impact on nitrification performance.

Ammonia concentration has little effect on the rate of nitrification until a level of 2.5 mg NH_4^+-N is reached below which the rate of nitrification decreases sharply.

Toxicity - several heavy metals, complex anions, and organic compounds are toxic to nitrification organisms, but a degree of accumulation is possible. Some of the toxins include:

Thiourea	
Zn	Cr
OCN^-	Ni
ClO_4^-	Ag
Cu	Thiourea
Hg	Amino Acids

Apparently, 10-20 mg/l of heavy metals can be tolerated because of low ionic concentrations at pH 7.5-8.0, but if precipitated metals that concentrate in the sludge should redissolve if the pH should fall, then the system could fail. High concentrations of ammonia or nitrite are also toxic to the nitrification process.

NITRIFICATION BY ATTACHED GROWTH SYSTEMS

Rock Trickling Filters

Nitrification is usually achieved only at low hydraulic loading rates and warm temperatures, and nitrification is difficult to maintain in a conventional rock trickling filter. Significant nitrification will not occur at loading rates in excess of 12 lb. BOD/1000 ft^3/day. Synthetic media is more effective for denitrification, partly because the surface area of synthetic media at 27 ft^2/ft^3 is about double that of 3" rock at 12-18 ft^2/ft^3.

Synthetic Media Trickling Filters

Combined carbon oxidation and nitrification can be achieved in a single-stage system using synthetic media towers. BOD loading is again the limiting factor which should not exceed 25 lb/1,000 ft^3/day.

Recycling is necessary to prevent the media from drying out, and this requires 0.5-1.0 gpm/ft^2. Recycling is also important to maintain a uniform flowrate.

Rotating Biological Contactors (RBC's)

RBC's may be used for single stage or two stage nitrification systems. These equipment items consist of a series of closely spaced discs (10-12 mØ) mounted on a rotating horizontal shaft with about 50% of their surface area immersed in wastewater. The discs are constructed of lightweight plastic, and, in operation, are covered by a 1/16-1/8 inch layer of biological slime. A very large surface area is packed into a small volume in RBC's which serve two purposes. First, they provide media for the growth of attached microbial growth, and they contact the growth with the water. Secondly, they aerate the water and agitate the suspended biomass in the wastewater resevior. Rotation speed is adjustable, and one company, ENVIROX DIVISION OF REXNORD, now makes a unit which is rotated by air that collects in cup-shaped collectors on the outside edge of the discs which seems to work particularly well.

RBC's can be used in series for nitrification followed by denitrification.

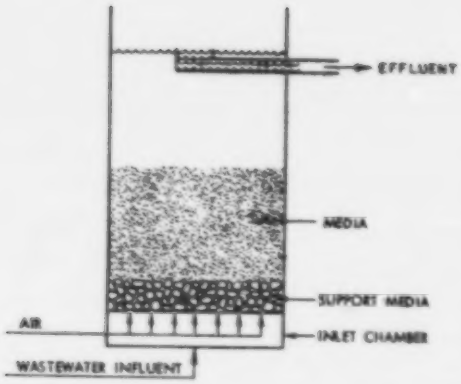
Submerged Filters

Submerged filters have been applied for nitrification. These consist of a bed of media on which biological growth occurs overlaying an inlet chamber with feedwater flowing upwards. Rather large detention times of, say, 60 minutes at 15°C are needed to denitrify 20 mg/l NH_3-N. Various ways have been devised to add air to the system. Preoxygenation produces effluents of similar quality to those from tertiary multi-media filtration.

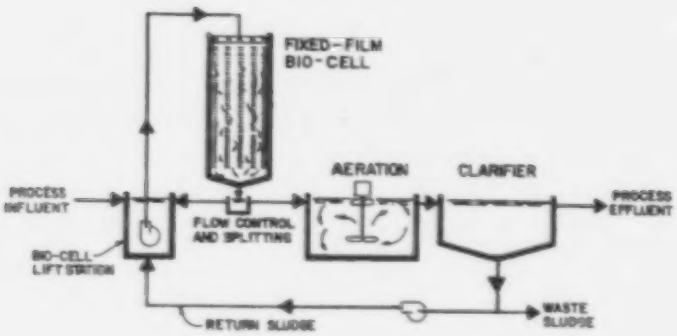
Activated Biofilters

The activated biofilter (ABF) process operates as a two-stage biological system which includes the following components:

1. Pump to lift return sludge plus influent feed to the top of the fixed film bio-cell.
2. A fixed film bio-reactor.
3. Flow control and splitting.
4. A short detention aeration basin.
5. Clarifier.
6. Return sludge facilities.



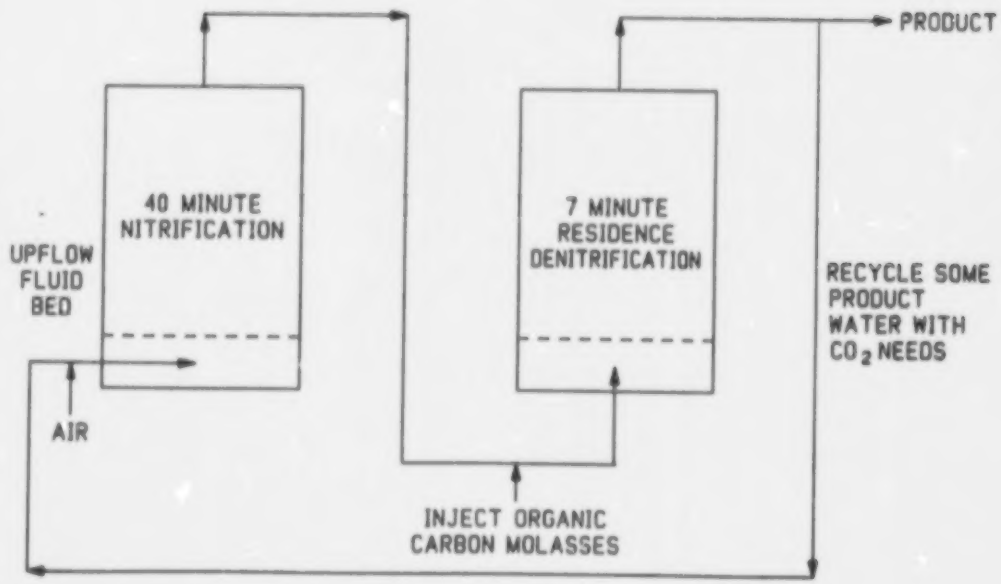
Schematic diagram of a submerged filter.



ABF process flow diagram.

Source: CULP, et al. (1978)

ENHANCED RATE BIOLOGICAL CONTACTOR



FLUID BED NITRIFICATION

The National Institute for Water Research of the CSIR, Pretoria, is involved in a paper study on how best to remove 20 mg NH_3/l in reclaimed water which would be a source of water for the large refrigeration plants on South African gold and uranium mines.

One possibility under consideration is the development of an upflow fluidized bed of sand to provide an activated sludge with media support for Nitrobacter pseudomonas. An organic source would be provided in the form of molasses or sewage sludge. The upflow fluid bed configuration was expected to give a tenfold rate increase.

Subsequent studies had indicated that the corrosion effects of ammonia at 20 mg/l were not very serious on the refrigeration tubes. Also, FLOCCATAN (PTY) LTD., the local subsidiary of CALGON CORP., can supply additives that would protect the copper/brass cooling tubes from ammonia corrosion.

Design criteria for biological ammonia removal processes are beyond the scope of this report but can be provided by any one of several leading municipal water treatment specialists.

For most mine and mill effluents, the conventional ammonia removal processes used in sewage treatment plants for tertiary treatment are unlikely to be applicable because of the lack of adequate organic cometabolites. Several sources of organic material could be investigated:

- Molasses
- Sewage
- Harvested Cattails and Other Marsh Plants

ALKALINE CHLORINATION

Ammonia can be destroyed chemically by chlorination. The initial reaction is the formation of chloramine, and, until all chloramine has been oxidized, no free residual chlorine is detected.

$$NH_3 + Cl_2 = NH_2Cl + HCl$$
$$2NH_3 + 3Cl_2 = N2 + 6HCl$$

Stoichiometrically, about 7 g Cl_2 is needed to oxidize 1g NH_3 to breakpoint, the point at which residual chlorine can be detected. Typical Witwatersrand treated sewage effluents, for example, require 10-12 g Cl_2 per g NH_3, and, according to NALCO (1979), ammonia

cannot always be destroyed in this fashion since many wastewaters contain organic materials that react with ammonia in preference to ammonia.

Chlorine gas reacts with water to form hypochlorous acid and hypochlorite:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-$$
$$HOCl = H^+ + OCl^-$$

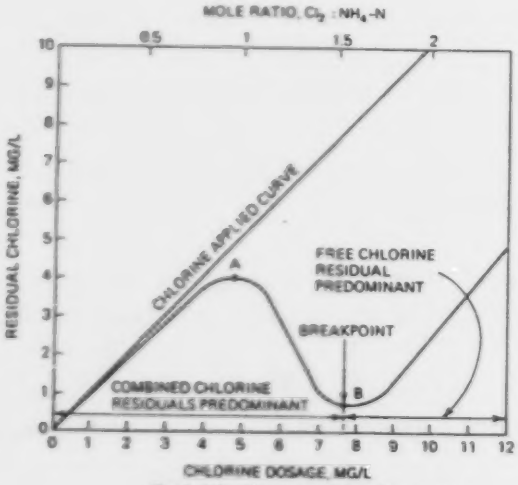
The distribution of hypochlorous acid HOCl and hypochlorite OCl^- varies with pH, and at pH 7.5, about 50% of the chlorine is in the form of HOCl and 50% in the form of OCl^-. As pH increases, the OCl^- concentration increases as HOCl decreases.

Ammonia reacts with hypochlorous acid in dilute aqueous solution to form chloramines:

$$NH_4 + HOCl = NH_2Cl \text{ (monochloramine)} + H_2) + H^+$$
$$H2Cl + HOCl = NHCl_2 \text{ (dichloramine)} + H_2O$$
$$HCl_2 + HOCl = NCl_3 \text{ (trichloramine)} + H_2O$$

Chlorine (Cl_2), hypochlorous acid (HOCl), and hypochlorite ions (OCl^-) are referred to as free chlorine residual, and the chloramines are called combined chlorine residual.

The combined chlorine residual increases as chlorine is added up to a mol ration of 1:1 (weight ratio 5 Cl_2:1 NH_4-N) shown as point A. Additions of chlorine above 5 mg/l per mg/l NH_4-N result in a decrease in the chlorine residual to a minimum, the "breakpoint" at a mole ration of about 1.5:1 (weight ration 7.6 Cl_2:1 NH_4-N) indicated as point B. At the breakpoint, all oxidizing chlorine is reduced, and all ammonia is oxidized. Further additions of Cl_2 result in free chlorine residuals.



Typical breakpoint chlorination curve.

The actual mechanism and reactions that occur during breakpoint chlorination of ammonia are not clearly understood, and some conclusions arrived at by PRESSLEY, et al. (1972) and PRESSLEY, et al. (1973) include:

1. Chlorine demand to reach breakpoint decreased and approached the stoichiometric amount for oxidation of NH_4^+ to N_2 (7.6:1) as the degree of wastewater pretreatment increased.

Cl_2:NH_4-N Wt. Ratio Required to Reach Breakpoint	Wastewater Source
10:1	Raw
9:1	Secondary Effluent
8:1	Lime Clarified and Filtered Secondary Effluent

2. Alkalinity of the wastewaters maintained the pH between pH 6.5-7.5. Concentrations of nitrate and nitrogen trichloride in this pH range were always less than 1 mg/l. Near complete removal of NH_4-N was obtained with only a slight reduction of organic nitrogen within two hours contact time.

3. Highly treated wastewater exhibited breakpoint performance similar to synthetic buffered waters.

EPA studies on synthetic waters (with 20 mg NH_4-N/l) have been reported by CULP, et al. (1978) to have shown the following:

- Breakpoint reaction was complete within one minute in the pH range 6-8.

- Minimum chlorine dosage required to reach breakpoint occurred in the pH range 6-7.

- The amount of nitrate produced at the breakpoint increased from about 1.5% of the NH_4-N at pH 5 to about 10% at pH 8.

- The amount of nitrogen trichloride produced at the breakpoint decreased from approximately 1.5 percent of the NH_4-N at pH 5 to about 0.25% at pH 8.

- Temperature variation of 5-40°C at pH 6.0 and two hours contact time did not change the required chlorine dose or the amounts of the products.

Two other factors need to be taken into account:

1) Use of Cl_2 produces acid. Oxidaton of one mole of NH_4-N produces four moles H^+. Stoichiometrically, it requires 14.3 g bicarbonate alkalinity (as $CaCO_3$) to neutralize the acid produced during oxidation of 1 g NH_4-N.

2) Chloride ion concentrations increase by at least 7.6 g Cl^- for each g NH_3 oxidized.

Sodium hypochlorite can be used in the breakpoint process instead of Cl_2 gas. Reaction of sodium hypochlorite in water will tend to raise the pH instead of lowering it:

$$NaOCl + H_2O = HOCl + Na^+ + OH^-$$

The breakpoint reaction with sodium hypochlorite is represented as:

$$1.5\ NaOCl + NH_4^+ = 0.5\ N_2 + 1.5\ NaCl + 1.5\ H_2O + H^+$$

Stoichiometrically, it requires 3.6 g bicarbonite alkalinity (as $CaCO_3$) to neutralize the acid formed during breakpoint chlorination of 1 g NH_4-N with NaOCl.

CULP, et al. (1978) provides ten pages of data on nitrogen removal capital and operating costs which were based, however, on 1978 U.S.A. parameters. These, however, provide some sort of relative idea of costs and are summarized below.

Comparative Costs (Capital, Operation and Maintenance) of Alternative Nitrogen Removal Processes. (¢/1000 gal)

	1 mgd			5 mgd			10 mgd		
	10 mg/l[a]	20 mg/l	30 mg/l	10 mg/l	20 mg/l	30 mg/l	10 mg/l	20 mg/l	30 mg/l
Single-stage nitrification[b]	5	7	9	4	5	6	4	5	6
Single-stage nitrification[b] and denitrification	31	39	45	16	21	25	14	19	23
Two-stage nitrification[b]	16	18	20	9	10	11	8	9	10
Two-stage nitrification[b] and denitrification	42	50	56	21	26	30	18	23	27
Breakpoint chlorination	18	32	44	10	17	26	7	14	20
Selective ion exchange	26	28	30	14	16	18	14	16	17.5
Ammonia stripping	14	14	14	10	10	10	8	8	8

[a]Incremental costs above conventional activated sludge required to nitrify.
[b]Ammonium nitrogen concentrations.

Source: CULP, et al. (1978)

BADENPHO AND PHOREDOX PROCESSES

The National Institute for Water Research, CSIR, Pretoria, has been developing a multi-stage phosphorous/nitrogen removal process for use in treatment of sewage effluents. These are integrated processes and would not be applicable for insertion at the end of a minewater or mill tailings decant stream for nitrogen removal.

However, where the intention is to convert a treated sewage effluent into a useful source of water for use in metallurgical processes, and/or for recycling and reuse for domestic purposes, and/or for discharge as an effluent meeting the NH_4-N and phosphorous limits, possibly these processes applied at the mine community sewage plant will solve both the problem of phosphate and nitrogen removal. The Kloof Gold Mining Co. Ltd. on the Witwatersrand sewage plant effluent has maximum 0.5 mg/l NH_4-N. It is possible that the Badenpho process is employed there, but this was not confirmed.

Description of these five-stage processes is beyond the scope of this report, but details are available from the National Institute for Water Research at the address shown above.

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CHAPTER 28

ANTIMONY Sb

Antimony is not a common problem in the operations visited either from an environmental point of view or from a process efficiency standpoint.

During the course of this investigation the only operations where provision has been made for antimony removal that can be recalled are the new gold recovery operations at Hemlo, Ontario, of NORANDA MINES LTD. and LAC MINERALS. It is mentioned in the chapter on Water Management in Gold and Silver Recovery, below, and at EQUITY SILVER MINES LTD., British Columbia.

This investigation did not take into account any antimony mines, mills, and mineral processing operations. Antimony seems to be a non-problem.

REGULATORY LIMITS

No regulatory limits exist for antimony in fresh or saltwater effluents.

ENVIRONMENTAL AND HEALTH EFFECTS OF ANTIMONY

Test data is very limited, but the U.S. EPA (1980) and ANDERSON (1950) found acute toxicity for Daphnia magna, which is a commonly used test organism because of its important role in the food cycle of fish larvae, to range from 9,000 to 19,800 ug/l as Sb. Chronic toxicity for Daphnia magna was found at 5,400 ug/l Sb.

Tests with fathead minnows (Pimephales promelas) using antimony trioxide in an embryo-larval toxicity test indicated that the highest concentration tested (7.5 ug/l) had no adverse effects and in a comparable test with antimony trichloride, a chronic limit of 1,600 ug/l was established for fathead minnows (U.S. EPA, 1980).

A 96-h LC50 for the sheepshead minnows (Cyprinodon variegatus) was between 6,200-8,300 ug/l with no lethal effects at 4,200 ug/l Sb on the myrid shrimp Mysidopsis bahea after 96 hours exposure (U.S. EPA, 1980).

It is concluded that:

1. Insufficient data on antimony toxicity is available to establish water quality criteria for the protection of aquatic organisms.

56 (ug/L) ANTIMONY

Summary of North American Water Quality Criteria for Antimony

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9]	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE				(2)		Undefined (with some notes)					
OBJECTIVE		--	--	<610	--	9000-80,000 (96-hr LC50) Fish	--	--		--	--
MAX. PERMISSIBLE LIMIT		--	--	--	--	20,000 (96-hr LC50) Daphnia	--	--		--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		.02x(96-hr LC50)	--	--	<200*	--	--	--		--	--
MAX. PERMISSIBLE LIMIT		200	--	--	<200*	--	--	--		--	--
PUBLIC WATER SUPPLY		--	--	145	0.2	--	--	--		--	--
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	--	--	--	--	--	--	--		--	--
	IRRIGATION	--	--	--	--	--	--	--		--	--

Compiled by NORANDA

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.

2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.

3. United States Environmental Protection Agency Ambient Water Quality Criteria not available for Antimony, EPA-440/5-80-020.

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11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

2. Acute toxicity in freshwater occurs at 9,000 ug/l and could occur at lower levels for aquatic species.

3. Chronic toxicity has been recorded at 1,600 ug/l, and some species may be more sensitive.

4. At levels in which antimony is most likely to be encountered in effluent receiving waters, it appears that antimony in mine and mill effluents is rarely of potential environmental concern.

5. Toxicity to freshwater algae at 610 ug/l has been noted in U.S. EPA, (1980), indicating that antimony levels may bear watching as an influence in biological polishing systems which include the use of algae.

OCCURRENCE OF ANTIMONY IN MINING AND MILLING WASTES

Antimony occurs as the antimony sulfide mineral stibnite in Hemlo gold ores at a level of about 0.02% Sb. Stibnite and sulfosalts containing antimony in association with silver and gold and base metals are not uncommon in "refractory" gold ores, and frequently antimony minerals occur in flotation concentrates that previously were roasted. During the roasting step, antimony and lead, if present, form glasslike compounds in the calcine which can interfere with the roaster bed and also are often blamed for gold losses in the subsequent leaching step.

Gold concentrates shipped to the government roasting plant at Kwekwe, Zimbabwe, frequently contain high levels of antimony for which a severe penalty is applied.

It is not yet known how antimony will affect gold recovery from refractory ores and concentrates by pressure oxidation or bio-oxidation processes currently being developed in preference to roasting ahead of cyanidation. Although antimony occurs in ore at HOMESTAKE's new McLaughlin mine, it is not listed as an element of interest in their operating permits.

Even at EQUITY SILVER MINES LTD., where the flotation concentrates before pressure leaching to remove antimony typically ran 0.16% in the Southern Tailing ore zone and 7.11% Sb in the concentrate, the acid mine drainage contains less than 0.1 ppm Sb before treatment.

PEDCO (1983) REPORT

Antimony in Mine-Mill Waste and Effluents (ppm)

	Untreated Mine Water	Minewater Pond Liquid	Tailings Pond Liquid	Minewater Pond Settled Solids	Minewater Pond EP Leachate	Low Grade Ore Solids	Low Grade Ore Leachate	Tailings Pond Solids	Tailings Pond Leachate	Waste Rock Solids	Waste Rock Leachate	Pregnant HL Liquor
Uranium, New Mexico												
Mine No. 12		LT 0.05		LT 98.040	LT 0.0320	98.040	LT 0.0320					
Mine No. 13		LT 0.05				194.420	LT 0.0500					
Mine No. 14		LT 0.05			LT 0.050	124.500	LT 0.0500					
Mine No. 15	0.0600			98.68	LT 0.032	106.800	LT 0.0500			141.770	LT 0.050	
Uranium, Wyoming												
Mine No. 16		LT 0.05		LT 98.04	0.16	123.900	LT 0.080			171.91	LT 0.050	
Mine No. 18	0.0380	LT 0.05		LT 98.04	LT 0.032	138.330	LT 0.050			351.05	0.0510	
Uranium, Other												
Mine No. 25						186.84	LT 0.050			180.87	LT 0.050	
Phosphate, Florida												
Mine No. 1	LT 0.032		LT 0.080					LT 98.04	LT 0.050	LT 98.04	LT 0.050	
Phosphate, Idaho												
Mine No. 5								LT 98.04	LT 0.160	131.020	LT 0.032	
Copper, Southwestern U.S.A.												
Mine No. 28	LT 0.050		LT 0.050			163.31	LT 0.032	LT 98.04	0.080			
Mine No. 30		LT 0.064	0.057					115.98	LT 0.032	183.640	LT 0.032	
Mine No. 31			0.220					171.20	LT 0.050	206.68	LT 0.032	4.300
Lead-Zinc, West												
Mine No. 38	0.190		0.180					LT 98.04	LT 0.032			
Lead-Zinc, East												
Mine No. 40		LT 0.050	LT 0.05	126.06	LT 0.080			LT 98.04	LT 0.080			
Molybdenum												
Mine 49	1.250		LT 0.032			131.60	LT 0.032	LT 98.04	LT 0.032	LT 98.04	LT 0.032	
Nevada Gold/Silver												
Mine 52			LT 0.050					152.60	LT 0.032	193.21	LT 0.032	
Mine 53			0.450			172.76	LT 0.050	144.40	LT 0.05	516.19	LT 0.05	

REMOVAL OF ANTIMONY

Antimony occurred in the Southern Tail ore deposit at a concentration of 0.158% and concentrated up to 7.11% Sb leaving 0.035% in the tailing. The concentrate was leached in hot caustic soda and NaHS to reduce the Sb level in the concentrate to below 0.3% Sb.

The leach liquor is filtered off the concentrate solids and the antimony recovered as sodium antimonate by an autoclave reaction for 1/2 hour at 150°C and 80 psi O_2 after which the solution is cooled in a flash tank at which point it contains about 8% sodium antimonate which is filtered on a belt filter with two stages of washing. The filtrate contains arsenic in a caustic thiosulfate solution. Sodium antimonate recovered in this way is sold as a by-product. More information is available in RANDOL (1983) and from:

EQUITY SILVER MINES LTD.
Houston, B.C.
(604) 845-7799
P. Brad Marchant

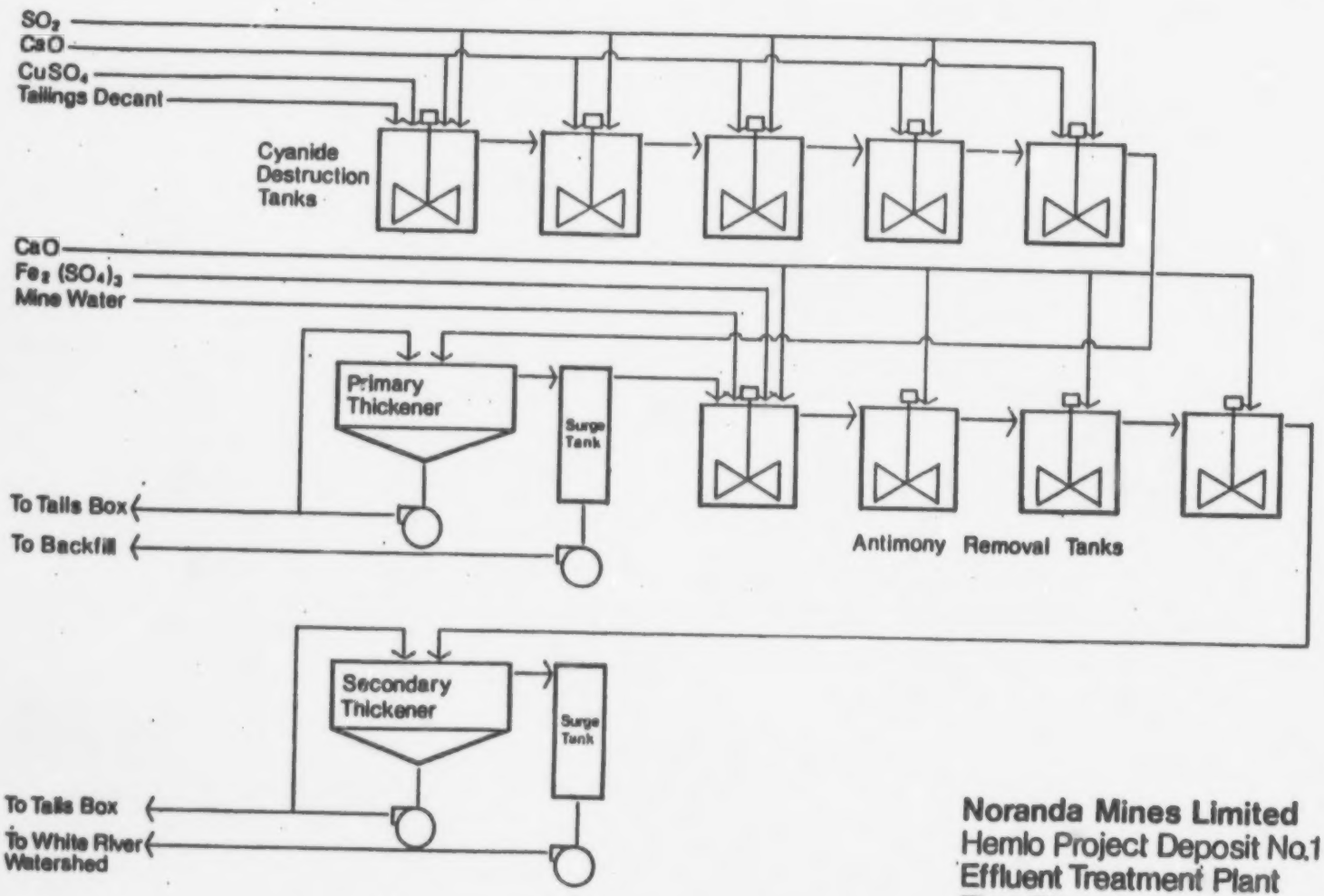
NORANDA MINES LTD. - HEMLO

The Hemlo gold ore is rich in pyrite and contains relatively large and variable amounts of environmentally undesirable metals. The average composition of Hemlo ore is approximately:

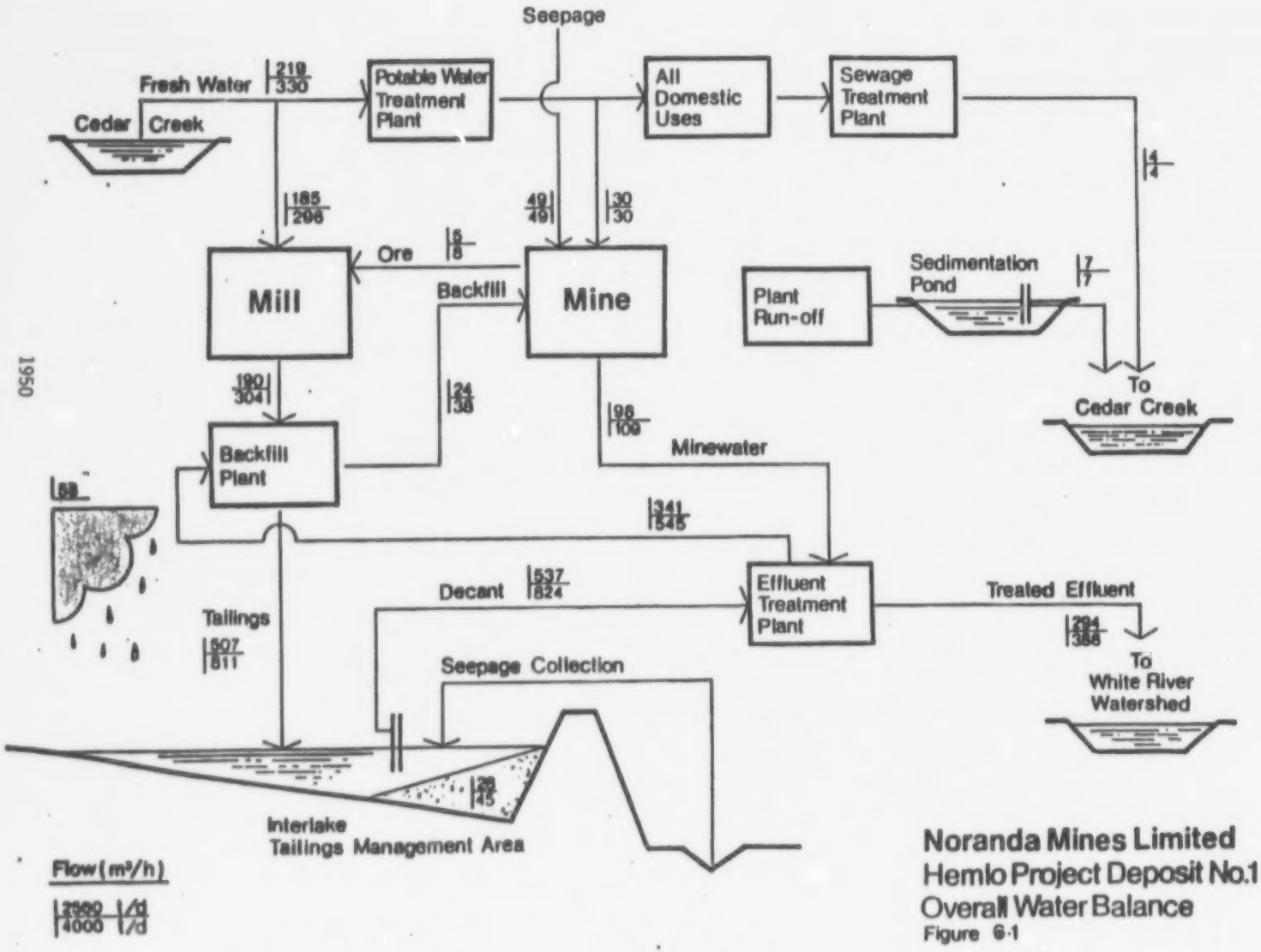
Gold	4-16 g Au/t
Silver	0-2%
Mercury	16 g Hg/t as Cinnabar
Molybdenum	0.03-0.04% MoS_2
Zinc	0.002% Sphalerite
Antimony	0.02% Stibnite
Arsenic	0.02% as Realgar

The metallurgical gold recovery circuit using straight-forward cyanidation has had to take into account ore characteristics as well as a very sensitive location adjacent to a provincial park on one side and an Indian fishing ground on the other.

Water management for the operation has required an integrated plan including a partially-lined tailings pond with seepage collection and return, mine backfill, tailings treatment to remove molybdenite with some of the arsenic, mercury, and antimony sulfides and finally, effluent treatment for cyanide and residual soluble antimony and arsenic removal. The effluent treatment plant flow diagram and how it fits into the overall mine-mill-tailings arrangement is shown in the following diagrams.



Noranda Mines Limited
Hemlo Project Deposit No.1
Effluent Treatment Plant
Flow Diagram



Noranda Mines Limited
Hemlo Project Deposit No.1
Overall Water Balance
Figure 6-1

1990

The addition of lime and ferrous sulfate to the effluent o/f after SO_2-Air cyanide destruction, metal precipitation, and thickening is projected to drop the soluble antimony level from 1-30 ppm (average 10 ppm) Sb to around 2.0 ppm. Antimony removal from the effluent is likely to be less of a concern than removal of metals such as mercury, copper, and arsenic.

Additonal information on the Hemlo effluent treatment process is available in NORANDA (1983) and from NORANDA MINES LTD. LAKEFIELD RESEARCH carried out the Hemlo effluent treatment testwork and may be free to discuss antimony removal processes.

NORANDA MINES LTD.
Post Office Box 45
Commerce Court West
Toronto, Ontario MSL 1B6
(416) 867-7306
Telex: 065-24231
Frank Frantisak

LAKEFIELD RESEARCH LTD.
Post Office Box 430
Lakefield, Ontario KOL 2HO
(705) 652-3341
A. M. (Bert) Wyslouzil

LAC MINERALS, HEMLO PROJECT

LAC MINERALS is developing a gold mine and mill at Hemlo, Ontario. No information on precisely how LAC MINERALS plans to treat their effluent or even the composition of their ore was obtained, although it is possible that it will contain a similar suite of undesirable contaminants.

It is believed that GOLDER ASSOCIATES has been responsible for the overall water management investigation for this project:

GOLDER ASSOCIATES LTD.
Mississauga, Ontario
(416) 625-0094
Don Welch
George Costa

It is also believed that testwork to evaluate effluent treatment processes for LAC MINERALS' Hemlo project has been carried out by WITTECK DEVELOPMENT, INC. which is one of the first test programs for a gold extraction plant that takes into account the effects of water recycling on water quality and metallurgical efficiency.

WITTECK DEVELOPMENT, INC.
2640 South Sheridan Way
Mississauga, Ontario L5J 2M4
(416) 823-7381
Telex: 06-982328
Peggy Witte, President

More information may also be available from the owners of the project who are supporting development of several innovative technologies:

LAC MINERALS LTD.
Post Office Box 1105
Kirkland Lake, Ontario P2N 361
(705) 567-3358
George Hope, Chief Metallurgist

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CHAPTER 29

ARSENIC

- Conclusions 1954
- Occurrence of Arsenic in the Environment 1954
- Regulatory Effluent Discharge Criteria and Limits 1955
- PEDCO. Report Data Summary - As in Gold Mill and Mine Wastes 1959
  - As in Liquid Effluent 1961
- Analysis of Arsenic 1964
- Environmental and Health Effects of Arsenic 1964
- Arsenic from the Gold Mining Industry 1965
  - Arsenopyrite Gold Ores 1965
  - Arsenic in Roaster Flue Dust Removal 1968
  - Experience in Arsenic Removal 1969
- Treatment Technology for Arsenic 1970
  - Summary of Arsenic Removal from Mine and Mill Effluents 1972
  - Summary of Arsenic Removal Processes - General 1975
- Arsenic in Gold and Silver Mine and Mill Effluents 1978
  - Gold Mine Effluents 1978
  - Silver Recovery Operations 1980
    - Equity Silver Concentrate Leaching 1982
      - Southern Tailings Bio-oxidation 1985
      - Acid Mine Drainage Treatment 1986
- Arsenic from Acid Mine Drainage 1987
- Arsenic from Copper and Lead Smelters 1988
- Arsenic Discharge from a Primary Copper Smelter by K. Schwitzgebel, R.V. Collins and R.T. Coleman (1979) 1993
- Arsenic in Uranium Mill Effluents 1997
  - Key Lake Mining Corporation 1997
  - Rabbit Lake Mining Corp. 1999
  - Removal of Arsenic from Aqueous Solutions, R. D. WEIR (1982 Patent) 2001
- Arsenic Precipitate Disposal 2005
- ROBINS and TOZEWA (1982) Arsenic Removal from Gold Processing Waste Waters the potential ineffectiveness of Lime 2007
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- Bibliography on Arsenic Removal Processes 2018

CONCLUSIONS

1. In some parts of the world effluent discharge regulations with respect to arsenic are extremely tight whereas in others, they are lax. Much more knowledge is needed about the toxicology and health effects of different arsenic species.

2. Arsenic can be removed readily from solutions down to relatively low levels provided it is oxidized to arsenic (+5) and that appropriate cations are present to make an insoluble precipitate.

3. Sludge stability is of concern as there is evidence that some precipitates resolubilize when they come into long-term contact with CO_2 from the atmosphere.

4. Arsenic control in the environment around mine-mill effluents requires an integrated program covering all aspects of mine-mill-roaster-tailings management.

5. The answer to long term stability of arsenic-bearing sludges lie in sludge disposal and stabilization or in making a more stable precipitate in the first place.

INTRODUCTION

Arsenic removal is important because of its acute toxicity not only to aquatic life but also to humans. Review of present day disposal methods may be needed because of questions as to the long-term stability of arsenic precipitate sludges.

Arsenic is a metal which forms toxic oxides, principally trivalent arsenite AsO_2^- and pentavalent Arsenate AsO_4^{-3}. The less stable arsenite is significantly more toxic to fish than pentavalent arsenic in arsenate. The oxidation state of the anion is believed to have a significant impact on the efficiency of processes to remove arsenic from solutions according to PATTERSON (1975).

Arsenic, like cyanide, enjoys an unfair degree of public and regulator paranoia compared with other contaminants from the mining and metallurgical industry.

OCCURRENCE OF ARSENIC IN THE ENVIRONMENT

Arsenic occurs in nature in deposits of arsenopyrite and sulfosalts in mineral deposits where it is commonly associated with iron, sulfur, antimony, silver, cobalt, nickel, and other base metals minerals. Natural weathering of rocks containing these minerals results in arsenic distribution to soils and groundwater in affected regions. Several plants are known to concentrate arsenic, and sporadic groundwater aquifers occur

As (ug/L) ARSENIC

Summary of North American Water Quality Criteria for Arsenic

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,8] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	--	--	50	<100	not detectable	--	Range As^{+5} 50 - 250 As total 100 -1,000	--	--
MAX. PERMISSIBLE LIMIT		--	--	440 (As^{+5})	--	100	10	10	--	10	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<10 .01 (96-hr LC50)	--	--	<50 *	--	--	--	As^{+5} 50 - 250 As total 100 -1,000	--	--
MAX. PERMISSIBLE LIMIT		50	--	--	--	--	--	--	--	--	--
PUBLIC WATER SUPPLY		100	50	2.2×10^{-5} -10^{-6}	50	50	N.D. (Objective) 50 (Limit)	10	--	10	10
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	200	(50)	--	500	200	--	10	--	--	50
	IRRIGATION	100	100	--	See Ref. 5	100	--	10	--	--	100

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.

2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.

3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Arsenic, EPA 440/5-80-021.

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10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.

11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

which are contaminated by arsenic to the extent that they are unusable--mostly in the western states.

High arsenic levels have been encountered in few municipal water supplies necessitating treatment for its removal. Many groundwater supplies in Central and South America contain excessive arsenic according to TRELLES and ARMATO (1950) and VINIEGRA and MARQUEZ (1965), and deep-well water in some desert areas in the U.S.A. contain in excess of 0.1 mg/l arsenic (BELLACK, 1972).

Arsenic in the form of arsenical compounds occurs in the wastewaters of the metallurgical industry, glassware and ceramic production, tanneries, dye, and pesticide manufacture. Other sources include the organic and inorganic chemicals and petroleum refining industry and the rare-earth industry (SKRIPACH, 1971). The manufacture of Paris Green and calcium-metaarsenate, both insecticides, in one instance produced a wastewater containing 362 mg As_2O_3/l according to CHERINSKI (1941). In recent years (PATTERSON, 1975), with the development of organo-arsenic compounds, many arsenic-based forms have declined in use. During the 1980's there has been a significant increase in the demand for arsenic oxide feed material, and this may to some extent be the result of the expanded use of an arsenic wood-preserving process--the one with a green finish. It is also used in hide preservatives, sheep dip, glass manufacturing, and electronic components.

In the mining industry, arsenopyrite is frequently associated with gold deposits in several gold belts of the world. Notable arsenopyrite gold regions include Kalgoorlie, Western Australia; the Ashanti Goldfields, Ghana; the Emperor Gold Mine, Fiji; several mines on the Canadian Shield including Campbell Red Lake, Giant Yellowknife and early CON operations in the Northwest Territories; the Barberton Gold Belt of the Eastern Transvaal; several mines in Zimbabwe including Dalny and the now exhausted Cam and Motor Mine; the Getchells deposit in Nevada; and several deposits in the Soviet Union as well as the Salsigne deposit in France. There are many more less famous arsenical gold occurrences in the world, and arsenic frequently occurs in small amounts in many non-refactory gold ores.

Arsenic sulfosalts occur with copper and silver sulfides at the Equity Silver Mine in British Columbia and with copper-gold concentrates at the El Indio Mine in Chile. Arsenic also occurs with cobalt in sulfide ores at sites such as the Blackbird Mine in Idaho and at Cobalt, Ontario, where cobalt and arsenic have been liberated by pressure oxidation.

Arsenic also occurs in lesser amounts with copper-lead-zinc ores and concentrates and becomes concentrated in roaster and smelter fluedusts often increasing in concentration due to recycling of dusts and water used in gas scrubbers. One such case is a lead smelter in Canada, where arsenic enters the system primarily with lead-bearing fluedusts.

Considering the price of lead and the cost of freight, the economics in today's economy of the use of some fluedusts in this way compared with pozzolonic disposal nearer the source of the fluedust is probably favorable in special cases only.

Arsenic also occurs in some uranium deposits, particularly the high grade deposits in Saskatchewan where is must be precipitated from effluents as at Key Lake.

REGULATORY EFFLUENT DISCHARGE CRITERIA AND LIMITS

Criteria

Fresh Water:

U.S. EPA, (1980)	440 ug/l	As^{3+} Maximum Permissable Concentration
Canada, (1979)	50 ug/l	Total As
Ontario, (1979)	100 ug/l	Total As Maximum Permissable Concentration
Quebec, (1977-80)	10 ug/l	Total As Minimum Permissable Concentration
South Africa, (1962)		
Special Standard	100 ug/l	Total As
General Standard	500 ug/l	Total As

Marine:

U.S. EPA, (1980)	Less than 508 ug/l As^{3+} may be harmful.

Public Water Supply:

U.S.A., (1980)	2.2×10^{-2} to 10^{-4} mg/l Maximum Permissable Level
Canada, (1979)	50 ug/l
Ontario, (1979)	50 ug/l
Alberta, (1977)	10 ug/l
South Africa, (1971)	
Recommended	50 ug/l
Maximum Allowable	50 ug/l

Typical total arsenic levels in effluents from mining and metallurgical operation permits range from 2 to 800 ug/l maximum average up to 160 ug/l maximum grab sample.

	Average	Maximum Daily
HOMESTAKE, McLaughlin NPDES (Zero Discharge)	0.05 ppm	0.10 ppm
Mount Emmons (Zinc)		0.05 ppm
KEY LAKE MINING	0.50 ppm	1.00 ppm
HOMESTAKE, Lead NPDES	0.38 ppm	
Cominco, Con Mine, Yellowknife, NW	0.50 ppm	1.0 ppm

	ARSENIC	
	Average	Maximum Daily
Giant Yellowknife, Yellowknife, NWT	0.80 ppm	1.60 ppm
ST. JOE, Monaca, Pennsylvania, Zinc Refinery	0.05 ppm	
NORANDA Grey Eagle, Californa Gold Mine (Zero Discharge)		0.002 ppm

It is concluded that:

1. Some discharge permits are well in excess of levels recommended as maximum to avoid damage to aquatic species.

2. Some regulations are excessively strict and were formulated on an unfirm scientific basis.

3. Permit requirements--e.g., for NORANDA Grey Eagle in California which is a zero discharge operation with a permit to dispose of excess water by irrigation--2 ppb As are ludicrous and might appear to be bureaucratic harrassment.

4. Arsenic discharge limitations for new operations in third world countries, e.g., Brazil, range from 0.1 to 0.2 mg/l depending on the state. It is expected that with maturity, the more developed countries may relax some excessively low-level arsenic requirements (e.g., 2 ppb) and that the third world countries, some of which are still lax and have just recently "discovered" environmental concerns, may first have to go through a similar phase of excessive overcompensation before they too mature.

Of interest in the PEDCO (1983) report are analyses of tailings pond solids and liquids as well as mine water pond liquid and settled solids for a wide range of mines in the U.S.A. The arsenic analyses are summarized in the table below.

It is observed that, in general, arsenic levels are low in these liquids, i.e., effluents and reclaimable recycle tailings water.

Also of interest is the fact that even where solids contain relatively high arsenic values either in settled tailings, wasterock, or minewater pond settled solids, the level of acetic acid-soluble arsenic and water-soluble arsenic is very low. Consider the following data for gold and silver mines tested by PEDCO (1983).

ARSENIC IN GOLD AND SILVER MINE AND MILL WASTE (mg/l OR ug/g)

	Waste (ug/g or mg/l)	Acetic Acid Leach U.S. EPA EP Test	Water Extract
Mine 52, Nevada			
Tailings Pond Liquid	0.089	--	--
Tailings Pond Settled Solids	219.000	0.0308	0.7348
Fresh Tailings	0.718	0.1011	--
Surface Mine Wasterock	26.800	0.0320	--
Inactive Surface Mine Wasterock	208.500	0.0302	--
Inactive Heap Leach Material	212.000	0.0057	0.0039
Mine 53, Nevada			
Surface Mine Wasterock	20.900	0.0268	0.0025
Seggregated Mine Waste Rock	94.500	0.0122	0.0049
Low Grade Ore	41.800	0.0025	0.0027
Fresh Tailings	14.800	0.0039	--
Tailings Pond Settled Solids	58.650	0.0074	0.0568
Tailings Pond Liquid	2.230	--	--
Mine 54, Nevada			
Inactive Low Grade Ore	0.847	LT 0.0232	LT 0.0040
Inactive Surface Mine Wasterock	0.852	0.0196	LT 0.0040
Inactive Heap Leached Material	113.710	0.0162	LT 0.0040
Inactive Heap Leached Material	69.860	0.2620	--
Inactive Tailings Pond Settled Solids	4.356	0.3685	0.0952
Inactive Tailings Pond Settled Solids	4.230	0.1260	--
Mine 55, Outside Nevada			
Tailings Pond Liquid	0.106	--	--
Fresh Tailings	56.800	0.0117	--
Tailings Pond Settled Solids	168.000	0.0082	0.0445
Mine Water Pond Liquid	0.0729	--	--
Underground Mine Wasterock	224.000	LT 0.0020	0.0145
	0.043		
Mine 56, Outside Nevada			
Inactive Tailings Pond Liquid	0.050	--	--
Inactive Low Grade Ore	714.000	0.0571	--
Fresh Tailings	229.000	0.0103	--
Underground Mine Waste Rock	102.000	LT 0.0005	LT 0.0030

ARSENIC IN GOLD AND SILVER MINE AND MILL WASTE (mg/l or ug/g) (Continued)

	Waste (ug/g or mg/l)	Acetic Acid Leach U.S. EPA EP Test	Water Extract
Tailings Pond Settled Solids	380.000	0.0188	LT 0.0032
Inactive Tailings Pond Settled Solids	394.000	0.0533	--
Underground Mine Wasterock	123.000	LT 0.005	LT 0.0071
Inactive Low Grade Ore	1,230.000	0.1030	0.7000
Mine 57, Outside Nevada			
Inactive Tailings Pond Settled Solids	1,900.000	0.0250	0.0098
Mine 58, Outside Nevada			
Tailings Pond Liquid	0.1024	--	--
Low Grade Ore	44.600	LT 0.0054	0.0048
Fresh Tailings	13.7500	0.0166	--
Surface Mine Wasterock	26.000	LT 0.0054	LT 0.0032
Surface Mine Wasterock	13.400	LT 0.0054	LT 0.0032
Tailings Pond Settled Solids	10.400	0.0349	0.0538
Inactive Surface Mine Wasterock	22.200	LT 0.0005	--

ARSENIC IN MINEWATER/TAILINGS DECANT SOLUTION

PEDDCO (1983)

(ug/g or mg/l)

	Untreated Minewater	Minewater Pond Liquids	Minewater Pond Settled Solids	Tailings Pond Liquid	Pregnant Heap Leach Liquor	Spent Leach Liquor	Inactive Spent Oxide Leach Liquor	Mill Waste Water	Tailings Pond Seepage Runoff
Uranium-New Mexico									
Mine No. 12		0.025							
Mine No. 13		0.027							
Mine No. 14		0.025	0.16						
Mine No. 15	0.036								
Uranium-Wyoming									
Mine No. 16		0.015	1.57						
Mine No. 17		0.001							
Mine No. 18	0.013	0.014	8.93						
Mine No. 19		0.055	16.90						
Uranium-Other									
Mine No. 20	0.030	0.031	11.20						
Mine No. 24			321.65						
Mine No. 26	0.0036								
Mine No. 27	0.069	0.047							
Phosphate-Florida									
Mine No. 1				LT 0.001					
Mine No. 2	0.002			LT 0.006					
Mine No. 4				0.006					
Phosphate-Idaho									
Mine No. 5				0.057					
Mine No. 7				0.048					

ARSENIC IN MINEWATER/TAILINGS DECANT SOLUTION (Continued)

PEDDCO (1983)

(ug/g or mg/l)

	Untreated Minewater	Minewater Pond Liquids	Minewater Pond Settled Solids	Tailings Pond Liquid	Pregnant Heap Leach Liquor	Spent Leach Liquor	Inactive Spent Oxide Leach Liquor	Mill Waste Water	Tailings Pond Seepage Runoff
Phosphate-Other									
Mine No. 9				0.000					
Mine No. 11				0.046					
Copper-Southwestern U.S.A.									
Mine No. 28	0.088			0.097					
Mine No. 28				0.085					
Mine No. 30		0.031		0.090					
Mine No. 31				0.104	4.226				
Mine No. 32				0.077					
Mine No. 33				0.067	2.152	2.112			
Lead-Zinc/Western U.S.A.									
Mine 34	0.109			0.064					
Mine 36	0.017						1.299		
Mine 37		0.498		0.078				0.833	
Mine 38		0.116		0.021				0.034	
Mine 39		0.974		0.006					
Mine 48	0.014								0.010
Lead-Zinc/Eastern U.S.A.									
Mine 40		0.003		0.002					
Mine 41	0.011			0.031					
Mine 42	0.009			0.062					
Mine 43	LT 0.001	0.001		0.002					

ARSENIC IN MINEWATER/TAILINGS DECANT SOLUTION (Continued)

PEDDCO (1983)

(ug/g or mg/l)

	Untreated Minewater	Minewater Pond Liquids	Minewater Pond Settled Solids	Tailings Pond Liquid	Pregnant Heap Leach Liquor	Spent Leach Liquor	Inactive Spent Oxide Leach Liquor	Mill Waste Water	Tailings Pond Seepage Runoff
Lead-Zinc/Missouri									
Mine 45				0.030					
Mine 46		0.006	9.945	0.027					
Molybdenum									
Mine 49	0.269			0.030					
Mine 50	0.032	0.016	2.000	0.005				0.021	0.051
Mine 51	0.041			0.071					
Gold-Silver/Nevada									
Mine 52				0.089					
Mine 53				2.230					
Gold-Silver/Other									
Mine 55		0.073		0.106					
Mine 56				0.043					
Mine 58				0.102					
Iron-Taconite									
Mine 60	0.024			LT 0.006					
Mine 61	0.011			LT 0.006					
Mine 63				0.050					
Mine 64				0.055					

ANALYSIS OF ARSENIC

Arsenic can be determined down to 0.002 ppm by atomic absorption spectrometry using hydride generation according to the EPA (1982), page 150.

A colorimetric method based on a color reaction with silver di-ethyl carbamate is reported to provide a detection limit of 1 ppb (0.001 ppm) and is described by AWWA 'Standard Methods.' This method is used routinely by Giant Yellowknife Mines, Yellowknife, NWT, with good results. Interferences are listed as Cr, Co, Cu, Hg, Mo, Ni, Pt, and Ag which supposedly interfere with the arsine generation step in the method, and the presence of antimony can also give a high reading because it too gives a red color reaction.

ENVIRONMENTAL AND HEALTH EFFECTS OF ARSENIC

Arsenic has for some time been a suspected carcinogen.

According to ROBINS (1984, personal communication), a population survey around the former Tacoma smelter indicated a correlation to lung cancer. On the other hand, intensive studies by the Canadian government into possible health effects of arsenic in Yellowknife, NWT, and other mining camps where arsenopyrite is roasted were inconclusive and showed no such evidence.

The environmental impact of arsenic was discussed at an international arsenic conference believed to have been held in the early 1980's in North America, but this document is not reviewed as health and environmental effects are not a focus of this investigation.

U.S. EPA (1980) and FERGUSON and GAVIS (1972) conclude that soluble inorganic arsenate (+5) predominates under normal conditions as it is thermodynamically more stable than arsenite (+3).

It has been pointed out by M. R. Speyer and L. Trudel of NORANDA RESEARCH that the majority of scientific papers on the environmental effects of arsenic are based on research conducted with arsenic in the (+3) form, and the EPA criteria are stated in terms of total recoverable trivalent inorganic arsenic.

Oysters are said to concentrate arsenic (a factor of 350 over a 112-day exposure period in one case) although it is believed that once metabolized, "organic arsenic" is not toxic to humans.

There is evidence that the LC_{50} bioassay test for marine fish ranged from 508 ug/l to 16,000 ug/l.

Trivalent arsenic is much more toxic than pentavalent arsenic, and it appears that most arsenic toxicity tests were based on trivalent arsenic. NORANDA RESEARCH found a 96-hour LC_{50} of 220,000-380,000 ug As^{V}/l for Atlantic Salmon. Even EPA (1980) data for a 96-hour LC_{50} test on Rainbow Trout for sodium arsenate of 10,800 ug/l turned out to have been performed with sodium arsenite according to HALE (1977).

It is reputed that after the Cam and Motor Mine arsenopyrite roaster shut down, health effects ascribed to the reduction of arsenic levels appeared. One possible explanation of this unconfirmed observation is that people living near the roaster had lost their immunity to certain bacteria that were killed by the high arsenic levels in the environment while the roaster operated.

Deep well waters in Taiwan containing up to 2.0 mg/l arsenic are believed to be the cause of an endemic illness called "black foot" disease and described by SHEN and CHEN (1964) and SHEN (1973).

ARSENIC FROM THE GOLD MINING INDUSTRY

Arsenic control at gold recovery operations can be generally divided into two categories--those where there is a high level of arsenic present as in arsenopyrite ores, and those where levels of arsenic in the ore are in trace amounts only.

ARSENOPYRITE GOLD ORES

By far the greatest source of arsenic in wastes that require management are generated by the roasting of refractory arsenopyrite gold ores.

The finely-ground ore is conventionally floated to yield an auriferous sulfide concentrate which is then roasted to make the gold amenable to cyanidation from the calcine. A two-stage roast is usually used in which arsenic is volatilized as an oxide and collected in varying degrees of efficiency from the roaster gas stream. The hot calcine is quenched in water and washed to remove unwanted base metals, including some residual arsenic, prior to cyanidation.

Arsenic enters the mine-mill water effluent system through several pathways:

1. Calcine washwater.

2. Drainage from the smelter area which can be contaminated by fallout from the roaster gasses.

3. Acid mine drainage from underground workings.

4. Seepage and runoff from mill tailings and wasterock.

5. Seepage and drainage from flue dust and leached calcine impoundments.

6. Leachate from calcine washwater precipitate sludges.

Historically, arsenical gold concentrates were roasted with minimal concern for arsenic removal from the roaster gases or effluents. Some of these have been in operation for half a century, and a considerable amount of arsenic has been destributed over a wide area around the site.

Roasting in the more recent generation of plants is carried out in fluid bed roasters which provide a much cleaner control of gases than was the case with the older Edwards roasters although undoubtably these could also be designed to avoid gas leakages. There are roasters operating today in some of the more remote parts of the world where there is virtually no attempt made to recover arsenic from the gas steam. In the U.S.A. today, there are no operating gold plants which operate roasters. In Canada, the remaining roasting plants have installed highly efficient gas cleaning systems for arsenic recovery. In Ghana, the prevailing wind direction is obvious as judged by the denudation of the jungle downwind from the plant.

The treatment of roaster gases from arsenopyrite roasters has been improved to such an extent that technology exists to remove arsenic to such low levels from the gas stream that arsenic emissions should no longer prevent the use of roasting as a metallurgical tool. More likely, it is the economics of SO_2 removal and the associated cost of disposing of the sulfuric acid generated. A very thorough statement of the state of the art in arsenic removal from roaster gases was prepared by MARCHANT and MEEK (1980) of the Industrial Environmental Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio, 45268.

One of the major breakthroughs in arsenic recovery from roaster gases is the successful use of Dralon baghouses to collect As_2O_3 after the gases have passed through a hot electrostatic precipitator for dust removal and then been cooled to condense the arsenic. The innovative "quench bend" for rapid cooling of the gases developed by HATCH ASSOCIATES and installed by DORR OLIVER in Australia seems to be important in avoiding problems in the baghouse due to arsenic condensation. Arsenic condenses at a temperature not that much higher than the condensation of water vapor in the gas stream which, of course, would generate sulfurous acid on the bag surfaces and make a mess of the baghouse. Consultants who are familiar with details of this aspect are:

D. W. ROSTRON
27 Pitcairn Avenue
Toronto, Ontario
Canada M4A 1P5
(416) 751-3477

VAN LEE
Fluosolids Department
Dorr-Oliver
77 Havemeyer Lane
Stamford, CT 06904
(203) 358-3200

KEN R. KELLETT
Dorr-Oliver Pty Ltd.
28 Spring Street
Chatswood, NSW 2067
Australia
(02) 412-1800

Baghouses for collection of arsenic troxide particles at around 150°C from the cleaned roaster gas are provided by:

FLAKT AUSTRALIA LTD.
124 Pacific Highway
St. Leonards N.S.W. 2101
(02) 439-8000
John Porter

Information on roasting and arsenic collection was provided in a chapter of the RANDOL Report "Innovations in Gold and Silver Recovery - Phase II" and by ROSTRON (1982), WRIGHT (1961), FOSTER (1963), MORTIMER and TAIT (1959), and GOODFELLOW et al. (?). The quench bend was described in the latter publication, and more information would likely be available from:

HATCH ASSOCIATES LTD.
21 St. Clair Avenue East
Toronto, Ontario
(416) 962-6350

ROBINS (1984) refers to a company in England that has developed a process to convert arsenic in hot roaster gases as arsenic sulfide which is much easier to separate from gas streams. This work has apparently been supported by BRITISH PETROLEUM, and a pilot plant is available for testing and demonstration. The company is:

REDLAC METALLURGICAL PROCESSES LTD.
148 Buckingham Palace Road
London SW1
England
(01) 730-7266

Apart from removal of arsenic from flue dusts, there is also a possibility that if sulfuric acid is generated to remove SO_2 from the gases, this will be contaminated by arsenic

which could limit the marketability of the acid. OHSAKO and YONEYAMA (1973) described one case where sulfuric acid contained 200-500 mg As/l.

ARSENIC FLUE DUST DISPOSAL

Arsenic control in roaster gas and in solid dusts generated is an important part of overall water quality management. Arsenic removal from the roaster gas is only one side of the problem, however. Once recovered, the dusts must be stored and disposed of safely. There is a wide range in methods employed for arsenic sludge and arsenic dust disposal.

The safest and most permanent disposal for arsenic dust is to sell it to an arsenic product manufacturer. This is, in fact, what some generators of arsenic do. For example, the government roasting plant at Kwekwe in Zimbabwe upgrades their arsenic dust and sells it to a user in South Africa. GIANT YELLOWKNIFE MINES LTD. sells some of the arsenic that is produced from their gas stream, and the operation at Salsigne, France, employs a novel shaft furnace to roast arsenopyrite concentrate which yields an arsenic flue dust of exceptional purity. The problem is that at both GIANT and the Zimbabwe roasters, very much more dusts are generated that there are markets for.

GIANT YELLOWKNIFE has developed one of the most innovative arsenic dust storage approaches. Arsenic dust is pneumatically pumped into specially prepared chambers in the underground workings which are in permafrost.

A giant truck-mounted vacuum cleaner is kept on hand to clean up any accidental arsenic spills and to reinject the collected dust into the underground storage. Provision is also made to store the dust in above-ground silos for shipping when there is a market.

At the Con Mine of COMINCO, which has long since ceased roasting arsenopyrite concentrates, a chemical plant has been installed to recover a very pure arsenic oxide product from dust generated over a decade ago and stored underwater in ponds. This approach has required a capital expenditure of $12 million and was partially motivated by the cost of alternative methods of disposing of the arsenic safely.

At the Fairview Mine, Barberton, South Africa, the only dusts collected are those that settle in a flume between the roaster and the stack. This dust is stored in an impoundment constructed from roaster coal ash. Seepage drains to groundwater and a nearby stream.

At ASHANTI GOLD MINES LTD. in Ghana, all arsenic is discharged with the roaster gas to the atmosphere leaving an unsightly scar in the remote jungle location.

Canadian and Australian operations are the most advanced in arsenic removal from roaster gases which has a positive impact on reducing arsenic levels in surface and groundwater in their surroundings. GIANT YELLOWKNIFE MINES LTD. is described in a trip report in Appendix I. There are no arsenopyrite roasters in the U.S.A., and there would be no state in which such a plant could be installed without the most exacting scrutiny.

BELL (1973) described how the abandoned Deloro Smelting and Refining site in Ontario led to arsenic contamination of the Moira River years after operations ceased due to groundwater migration from calcium arsenite ponds which had been covered over. This led to the owners being forced to stabilize the site more than a decade after the site had been abandoned. How arsenic dusts and sludges are disposed of is considered to be a critical aspect of arsenic control with respect to water quality and effluents from the plantsite both during and after the life of the operation.

EQUITY SILVER MINES, Houston, British Columbia, is believed to have shipped a calcium arsenate precipitate (after dewatering in a filter press) to a hazardous waste disposal site in Oregon which sounds like an expensive excercise.

EXPERIENCE IN ARSENIC PRECIPITATION/REMOVAL

WALTER J. KUIT
Cominco Ltd.
200 Granville Street
Vancouver, BC V6C 2R2
(604) 682-0611
Telex: 04-507730

DR. LORNE BALL
Group Leader-Chemical
Metallurgical Research
Cominco Ltd.
Trail, B.C.
(604) 364-4419

ROBERT G. ROBINS
School of Chemical Engineering
and Industrial Chemistry
The University of New South Wales
Kensington, N.S.W. 2033
Australia

KAZUTERU TOZAWA
Institute of Mineral Dressing and Metallurgy
Tohoku University
Sendai, Japan

MR. LYNN S. PRICE
Falconbridge Ltd.
Post Office Box 40
Commere Court West
Toronto Ontario M5L 1B4
(316) 862-7000

KLAUS SCHWITZGEBEL
Radian Corporation
8500 Shoal Creek Blvd.
Austin, TX 78758

JAMES V. ROUSE
Envirologic Services International
2425 South Colorado Blvd.
Denver, CO 80222
(303) 759-2611

P. BRAD MARCHANT
Equity Silver Mines Ltd.
Post Office Houston B.C.
Canada
(604) 845-7799

TREATMENT TECHNOLOGY FOR ARSENIC

PATTERSON (1975) and ROBINS and TOZAWA (1982) pointed out that limited information was available on the levels of arsenic in industrial wastes and on current wastewater treatment processes. Although this investigation was able to find some information on arsenic removal from several more recent mine-mill effluent treatment installations, the information gathered by PATTERSON (1975) for arsenic removal from drinking water may be useful since the methods for arsenic treatment of drinking water and metallurgical and mine effluents are similar.

ROBINS (1983, 1984, 1985); ROBINS and TOZAWA (1982), NISHIMURA, et al. (1983), and NISHIMURA and TOZAWA (1977) have made significant contributions to the better understanding of the solubilities and precipitation mechanisms of arsenic although they have done more to point out the long-term instabilities of arsenic precipitate sludges due to the action on them by dissolved CO_2 than they have to find a practical and usable solution to the problems of removing arsenic from mine-mill tailings effluent solutions and disposal of the precipitates. These authors showed that calcium arsenate and ferric arsenates are insoluble and form precipitates which are not stable. The implications of this are that arsenic, once precipitated and settled in a decant pond, may not remain stable for long as CO_2 from the atmosphere dissolving in the water covering the precipitate sludge will gradually convert some precipitates to calcium and ferric carbonate rendering the arsenic from the precipitate soluble. Most of their tests are performed on relatively pure laboratory solutions, and there are practical effluent disposal sites where their laboratory derived conclusions could readily be tested.

A lead smelter in eastern Canada (see Lead Smelter B in Appendix I) treats lead-bearing flue dusts containing arsenic. The recycling dusts introduce arsenic, cadmium, zinc, etc. to a scrubber system, and arsenic gets into the plant effluent stream. Conventional lime settling removes the base metals, and original plans called for precipitation of arsenic with iron. However, this has not worked quite as well as

planned, possibly because the iron is added after the lime or because the arsenic is in the trivalent arsenite (AsO_2^-) form as opposed to the pentavalent arsenite (AsO_4^{-3}) form which precipitates with iron. Pilot tests are underway to determine how chlorine or peroxide oxidation of the solution will improve the arsenic removal process.

GIANT YELLOWKNIFE MINES LTD. oxidizes cyanide using alkaline chlorination which also oxidizes arsenic in the effluent which is then precipitated with ferric sulfate. This is accomplished in two energetically agitated tanks followed by flocculant addition in a third reactor prior to discharge to a large decant basin where the precipitated arsenate settles as a reddish brown sludge.

EAST RAND GOLD AND URANIUM MINES LTD. (ERGO) generates arsenic in solutions used to quench and wash calcines after pyrite roasting. The pyrite is recovered by flotation from old tailings dams. The calcine wash solution is treated by adding iron-rich acidic solvent extraction raffinates followed by intense air agitation while adding lime--this reduces arsenic from 9.3 ppm to below 0.5 ppm. Undoubtably, the presence of small amounts of iron base metals in the calcine wash solution help to co-precipitate the arsenic.

The Con Mine gold cyanidation tailings are treated with sodium sulfide and ferrous sulfate at the tailings outlet to a large, shallow, segmented pond and when necessary, augmented by broadcasting over the decanted effluent pond surface prior to discharge.

SUMMARY: ARSENIC REMOVAL FROM MINE-MILL EFFLUENTS (mg/l)

	Type of Mine	Effluent Volume	Before Treatment Effluent pH	Other Contaminants	As Removal Process	Composition Influent	Composition Effluent	Sludge Disposal
GIANT YELLOWKNIFE, N.W.T.	Au arseno-pyrite roaster	1.4 Million m^3/yr	7.7	Fe, Cu, Zn, Ni, Cn	1) Lime addition to pH 10.5. 2) Cl_2 addition oxidizes Cn and As^{III} to As^{V}. 3) $Fe_2(SO_4)$ addition. 4) Flocculation. 5) Settling.	As_T 12.1 Cn_T 8.6 pH 7.7	As_T 0.14 ppm pH 8.5	Decant Pond
COMINCO Con Mine Yellowknife, N.W.T.	Au conventional leach as in ore and old tailings 650 stpd	700,000-900,000 m^3/yr	10.5-11.0 at tailings outlet	Fe, Ni, Sb	1) Add $FeSO_4$ and Na_2S to tailings. 2) Broadcast $FeSO_4$ and Na_2S.			Pond Decant
ERGO	Au tailings retreatment recovers Au, pyrite, U_3O_8	1025 m^3/h calcine thickener o/f pH 1 9,000,000 m^3/yr	pH 1	Fe, As, Cn	1) Calcine thickener o/f mixed with raffinite and lime. pH 1. 2) Vigorous aeration at pH 9.5-11.0.	As_T 97 mg/l	As_T 0.5 mg/l	

1972

SUMMARY: ARSENIC REMOVAL FROM MINE-MILL EFFLUENTS (mg/l) (Continued)

	Type of Mine	Effluent Volume	Before Treatment Effluent pH	Other Contaminants	As Removal Process	Composition Influent	Composition Effluent	Sludge Disposal
EQUITY SILVER, British Columbia	Silver		Acid AMC	Fe, Cu, Zn, As, $SO_4^=$	1) Lime precipitation in presence of lime. 2) Settling pond. 3) Precipitate mixed with tailings containing excess alkalinity.	Fe 600 Cu 50 Zn 35 Al -- Sb LT 0.1 As 15 Cd -- $SO_4^=$ 5000 Total Acidity 5000	LT 0.03 0.01 0.01 0.15 LT 0.01 0.002 0.005 2500 --	Mixed 4:1 with tailings slurry v/v.
KEY LAKE MINING	Uranium acid leach	5,000 m^3/d 1,750,000 m^3/yr	Acid	Co, Ni, As, U_3O_8, Ra	1) Lime neutralize in four air agitated pachucas. 2) Settle. 3) o/f mix with lime and $BaCl_2$ at pH 11 to precipitate $BaRaSO_4$, BaRa arsenate, and $Mg(OH)_2$. 4) Clarification.		As LT 0.01 Ba LT 0.04 Co LT 0.02 F 2.00 Fe 0.06 U 0.85	To subaerial tailings dam

SUMMARY: ARSENIC REMOVAL FROM MINE-MILL EFFLUENTS (mg/l) (Continued)

	Type of Mine	Effluent Volume	Before Treatment Effluent pH	Other Contaminants	As Removal Process	Composition Influent	Composition Effluent	Sludge Disposal
					5) Diatomaceous earth filters (no longer needed). 6) Acidify with H_2SO_4 to pH 7.			
GULF MINERALS, Rabbit Lake	Uranium Acid Leach	N/A	Acid	Co, Ni, As, Zr, Fe, H^+, Mo, SiO_2	SX Barrens treated separately. 1) SO_2 sparge to oxidize Fe^{2+} to Fe^{3+}. Lime addition maintains pH 1.3. 2) Lime addition to pH 4.5 to precipitate ferric arsenate. 3) Settling. Neutralization Circuit 1) Stage 1 pH 4.5 removes residual As. 2) Stage 7 pH 12.7-12.7 removes Ni.			To tailings.

SUMMARY OF ARSENIC REMOVAL METHODS

Treatment	Initial Arsenic mg/l	Final Arsenic mg/l	Percent Removal	Reference
Charcoal Filtration	0.02	0.06	70	Magnusen, et al. (1970)
Lime Softening	0.2	0.03***	85	Magnusen, et al. (1980)
Lime Softening	0.5	0.03***	95	Rosehart and Lee (1972)
Precipitation with Lime plus Phosphate	-	-	-	Nikolaev and Mazurova (1972)
-Do-	-	- ***	-	FMC Corp. (1980)
Precipitation with Lime plus Iron	-	0.05***	-	Skripach, et al. (1971)
Precipitation with Lime	-	1.00***	-	Nishimura, et al. (1983)
Precipitation with Lime and Tailings	15.0	0.002	+99	Equity Silver (1985)
Precipitaton with Alum	0.35	0.003-0.005	85-92	Logsdon, et al. (1974)
Precipitation with Ferric (Raffinate) (SO_2 Oxidized) and Lime				Rabbit Lake (1980)
Precipitation with Ferric Sulfate	0.31-0.31	0.003-0.006	98-99	Logsdon, et al. (1974)
Precipitation with Iron	-	-	-	Shabunin, et al. (1968)
Precipitation with Iron	-	-	-	Rosehart, et al. (1972)
Precipitation with Ferric Sulfate	25.0	5	80	Buswell, et al. (1943)
Precipitation with O_2 and Ferric Sulfate	12.1	0.14	99	Halverson and Ross (1984)
Precipitation with Lime, Ferric Sulfate	9.7	0.5 Max.	95	ERGO (1984)
Precipitation with Ferros Sulfate	-	-	-	Con Mine (1984)
Precipitation with Ferric Chloride	3.0	0.5	98	Irukayama (1964)
Precipitation with Ferric Chloride	0.58-0.90	0.0-0.13	81-100	Shen (1973)

SUMMARY OF ARSENIC REMOVAL METHODS (Continued)

Treatment	Initial Arsenic mg/l	Final Arsenic mg/l	Percent Removal	Reference
Precipitation with Ferric Hydroxide	-	0.6	-	Berezman (1965)
Precipitation with Ferric Hydroxide	362.0	15-20	9-96	Cherkinski (1941)
Ferric Sulfide Filter Bed	0.8	0.05	94	Shen and Chen (1964)
Precipitation with Sulfide	-	0.05	-	Curry (1972)
Precipitation as As_2S_3 (Below pH 4))**	-	0.001	-	Kondo (1980)
Precipitation with Sulfide	132.0	26.4	80	Rosehart and Lee (1972)
Precipitation with Lime, $BaCl_2$*	-	0.01	99+	Clarke, et al. (1980)
Precipitation with Barium*	-	***	-	Chukhlansev (1956)
Precipitation with Lime, $BaCl_2$*	-	***	-	Sherritt Gordon Patents (1980, 1982)
From Cyanide Solution by:				
SO_2-Air in Presence of Iron	-	-	-	Devuyst, et al. (1984)
Precipitation on T_1O_2 Pellets	-	-	-	Sato, et al. (1978)
Precipitation with Titanium Oxide as as Titanium Arsenate	-	-	-	U.S. Patent (1932)
Precipitation as TiO $HASO_4$	-	-	-	Ugorets, et al. (____)
Precipitation as Ti IV-As V	-	1.0	-	Robins (1984)
Precipitation with Mg SO_4 as Mg NH_3 AsO_3 $6H_2O$	-	-	-	Kondo (1980)
Low Solubility Arsenates of Pb, Cu, Cd, Ni, and Zn at pH 4-8	-	-	-	Robins and Tozawa (1982)
Algae as Uptake - Biological	-	-	-	Spisak (1978)

*Note: ROBINS (1985) shows that the solubilities of barium arsenates are much higher than believed, and that the basis for the patent is not well founded.

**Note: ROBINS (1984) found that above pH 4, arsenic converts from As_2S_3 to a soluble form.

***Note: ROBINS (1984, 1985) finds that these Ca arsenates and Ba arsenates are unstable in the presence of dissolved carbon dioxide.

$FeSO_4/Na_2S$ effectively reduces cyanide levels in the tailings which are discharged at a high pH (10-11) after gold cyanidation. The $FeSO_4$ also precipitates arsenic to a sub-ppm level. There are several interesting aspects of this approach to arsenic removal.

Ferrous sulfate rather than ferric sulfate addition offers four advantages according to KUIT (1985):

1. Because there is no vigorous agitation, iron added in ferric form would rapidly convert to ferric hydroxide which would not carry too much arsenic with it under these conditions.

   Ferrous sulfate slowly oxidizes to ferric and provides a better opportunity for the gradually generated ferric hydroxides to absorb arsenic because conditions are more favorable for co-precipitation than if the iron was all immediately precipitated as ferric hydroxide. This, at least, is a logical explanation of the phenomenon that was found to occur during empirical tests.

2. Ferrous sulfide in the presence of sulfide forms FeS which provides a reserve of sulfide ions which pull base metals such as Cu, Ni, etc. from complexes, including cyanide complexes. Ferrous and ferric ions remove cyanide effectively as a precipitate. The base metals co-precipitate with arsenite and/or arsenate as found by ROBINS and TOZAWA (1982).

3. Ferrous sulfate is easier to handle than the extremely corrosive ferric sulfate.

4. Ferrous sulfate is considerably less expensive than ferric sulfate.

ROSEHART and LEE (1972) refer to a gold ore extraction process waste stream at pH 9.5 containing 900 ppm particulate arsenic and only 10.1 mg/l soluble arsenic. The soluble arsenic, constituting only 1% of the total arsenic present, was in the arsenite form. A second stream described at pH 3.1 contained 880 ppm particulate arsenic and 132 mg/l

(13%) soluble arsenic. LARSEN, et al. (1973) described acid mine drainage in the Rocky Mountains containing 6.0-22.0 mg/l soluble arsenic. Arsenic wastes from nonferrous smelting have been reported where the main form appears to be extremely small (1-3 u diameter) particles from which arsenic could profitably be recovered. SWAIN (1939), DEAN, et al. (1972), and STOOF and HAASE (1938). However, most people in the mineral processing industry would be able to find relatively abundant sources of cheap arsenic today without having to filter such fine particles.

ARSENIC IN GOLD AND SILVER MINE AND MILL EFFLUENTS

Arsenic finds its way into minewater when oxidation of underground sulfides occurs which can, if arsenic is contained in the ore, introduce some arsenic into the acid mine drainage. Seepage from tailings ponds can also introduce arsenic into minewater. Later in this discussion, mention is made of an interesting and simple method of treating acid mine drainage containing arsenic.

Arsenic finds its way into tailings decant water and mill effluents in different ways, too, depending on how the arsenic is present and the type of process employed:

- Where concentrates are roasted ahead of cyanidation, some arsenic, if present in the concentrate, will get into solution during water quenching of the calcine prior to leaching.

- Unless arsenic is efficiently removed from the roaster gas stream, it can be distributed to the area surrounding the plant site where it will contaminate surface drainage from precipitation.

- If arsenic dusts and sludges are not disposed of in a stable fashion, these can introduce arsenic into both runoff and seepage water.

- At El Indio, gold copper sulfide concentrates are roasted to reduce arsenic. How the concentrates and roaster gas condensed dusts are handled can affect arsenic levels in effluents from this type of plant.

  Much of the groundwater available near the El Indio mine site was contaminated by nature with metals including arsenic and has been that way since before mining started.

- The new HOMESTAKE McLaughlin project will treat ore by pressure oxidation to make gold amenable to cyanidation. The oxidized ore will be washed before cyanide leaching to remove base metals and arsenic; the arsenic and metals will then be precipitated from the washwater in a separate circuit and discharged in the

precipitate sludge (thickener u/f) to the impermeable (subaerial) tailing impoundment.

HOMESTAKE MINING COMPANY
650 California Street
San Francisco, CA 94108
(415) 981-8150
David Crouch,
Chief, Environmental Department
Rex Guinivere
Vice President, Engineering

- The new Hemlo gold project of NORANDA MINES LTD. and TECK CORP. uses neither roasting nor pressure oxidation, and arsenic is still expected to range between 0.5-2.0 mg/l in the wastewater. It will be reduced to below 0.5 ppm by treatment which will employ SO_2-air for cyanide destruction and $Fe_2(SO_4)_3$/lime addition in agitated tanks for removal of more persistent metals. Both steps would reduce arsenic levels.

  Information on water treatment facilities and processes to be installed at Hemlo can be requested from:

NORANDA MINES LTD.
Post Office Box 45
Commerce Court West
Toronto, Ontario M5L 1B6
(416) 867-7000
Frank Frantisak

NORANDA RESEARCH CENTRE
240 Hymus Boulevard
Point Claire, Quebec
Canada H9R 165
(514) 697-6640
Dr. Ken Wheeland

Arsenic is present in high concentrations in ores that more often than not are classed as "refractory." The ultimate fate and distribution of arsenic in tailings and effluents from the operation depends to a large extent on the process employed to treat the ore. Most recently, the trend in treatment of sulfide ores has been away from roasting and toward hydrometallurgical approaches such as pressure oxidation. WEIR and BEREZOWSKI (1984) describe the Sherritt-Gordon pressure oxidation process for the treatment of sulfide ores. As in the case of HOMESTAKE's McLaughlin project described by KUNTER, et al. (1984) and GUINIVERE (1984), arsenic can be removed to low levels in the presence of iron solubilized during oxidation of the pyrite as well as other metals.

There are five aspects to controlling arsenic in effluents:

- Trace amounts of arsenic may require treatment of the total effluent to meet discharge limits, perhaps in conjunction with cyanide and other metals removal.

- Segregation of smaller, more concentrated flows may make it possible to solve the problem with lower overall capital and operating costs.

- Prevention is better than cure. As noted above, as much arsenic as possible should be prevented from reaching the environment where a more expensive cure may be necessary.

- In roasting plants and calcine cyanidation, it is likely that all effluent streams will contain some arsenic, although the most concentrated stream is likely to be the calcine washwater.

- In treating arsenic-bearing effluents, precipitate sludges are commonly produced. It is necessary to consider the long-term stability of these sludges in the manner in which they are disposed of.

The following summarizes some of the measures adopted to remove arsenic from gold and silver mill effluents. More detailed accounts are included in trip reports for GIANT YELLOWKNIFE, THE CON MINE, and ERGO in Appendix I.

ARSENIC IN SILVER RECOVERY OPERATIONS

Arsenic frequently occurs with silver in sulfosalts which are also likely to contain antimony, copper, iron, and of course sulfur, e.g. tetrahedrite $(Au\ Ag\ Fe)_{12}\ Sb_4\ S_{12}$ and Tennantite $(Au\ Ag\ Fe)_{12}\ As_4\ S_{13}$. In fact, arsenic occurs in many silver minerals and sulfide minerals that are recovered with sulfide concentrates containing silver, e.g.:

Enargite $Cu_3\ As\ S_4$, Billingsleyete $Ag_7\ (As\ S6)S_6$, Esmitite $Ag\ As\ S_2$, Hutchinsonite (PbTl) (Cu Ag) As_5S_{10}, Kutinaite $Au_2\ Ag\ As$, Laffithte $Ag\ Hg\ As\ S_3$, Langenbachite $Pb_{37}\ Ag_7\ Au_6\ As23\ S_{78}$; Marrite P6 $Ag\ As\ S_3$; Novakite $(Au\ Ag)\ As_3$, Perceite (Ag-Cu)16 $As_2\ S_{11}$; Smithite $Ag\ As\ S_2$; Trechmanite $Ag\ As\ S_2$ and Xanthoconite $Ag_3\ As\ S_3$, etc.

Arsenic contained in concentrates shipped to smelters is disposed of at that end of the operation, but inevitably some arsenic remains in the tailings and wasterock.

EQUITY SILVER MINES LTD. is an interesting, although unique, example of ways to deal with arsenic and other contamination.

Silver, gold, and copper occur with sulfide minerals in EQUITY SILVER ores which occurred in two ore zones, the higher grade Southern Tail Zone and the Main Ore Zone. Each of those has led to different arsenic disposal methods. In addition, EQUITY SILVER has developed a simple, yet effective, acid mine drainage treatment which meets the British Columbia Special Wastes Act exemption criteria.

A flotation concentrate with 17% Cu, 7,000 g Ag/t, and 15 g Au/t but with 7% Sb and 4% As was produced from the Southern Tail Zone. In order to meet concentrate sales specs of max. 0.6% Sb and 1.6% As, the concentrate was pressure leached using the EQUITY SILVER process. In the end, this cost C$10 million in research and development and C$46 million in capital to build a plant to treat 2,500 tpm concentrate. This ore type was exhausted in 1984, and the plant was shut down. Nevertheless, the approach to arsenic and antimony removal from the silver-copper concentrate is of interest. It is also an example of how, even with some of the industry's top metallurgical brains to help, developing and installing complex new processes can be more trouble and expense than originally expected.

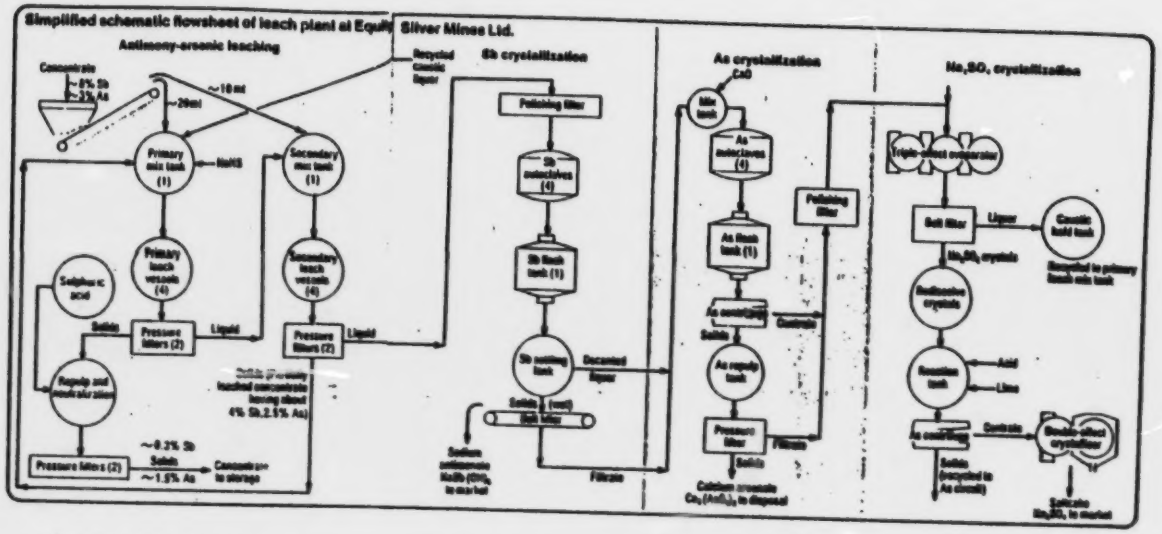
In a two-stage counter current batch caustic leach with fresh NaHS, the antimony and arsenic is removed from the concentrate and separated in solution from the concentrate by pressure filtration.

Leached concentrate was then repulped and rinsed with water prior to pressure filter dewatering and shipment. This step is necessary because the lower pH reduces the pyrophoric nature of the concentrate.

Leach liquor advances from the primary circuit to the secondary leach circuit. Liquor filtered off after the secondary leaching contains As and Sb and is treated sequentially for antimony recovery, arsenic recovery, and sodium sulfate crystallization. Excess sodium sulfate is generated as a reaction product during arsenic and antimony crystallization and must be bled before the leach liquor is recycled.

In contrast to SUNSHINE MINING which uses sulfur and NaOH to make a Na_2S, NaHS, and $Na_2S_2O_3$ lixiviant to remove As and Sb from a copper silver concentrate, EQUITY SILVER used NaHS generated by mixing Na_2S and NaOH. $Na_2S_2O_3$ was avoided because it would have dissolved gold which would be precipitated again with the sodium arsenate in the solution treatment step.

The EQUITY SILVER process is described in the following flowsheet from E/MJ January 1982.



Source: E&MJ January, 1982

SOLUTION TREAMENT

Filter-press filtrate is passed through a polishing filter to remove residual fines before being pumped to the Sb removal section. It contains Sb, As, NaOH, and Na_2S.

The liquor was held at 85°C and then autoclaved in 5/8" carbon steel autoclaves lined 3/16" nickel 200 cladding. Monel piping was used. Three autoclaves were installed in parallel with a fourth as a spare. Once filled, the autoclaves were held at 150°C and 80 psi O_2 for about 1-2 hours; then the contents of the autoclaves were discharged into an 8'Ø x 16' flash tank where premire is lowered. Much water evaporates, and sodium antimonate crystallizes out. The liquor contained around 8% solid Na antimonate with 50-100 g/l NaOH solution which is fed to a belt filter. After washing twice, it is packed for shipment. Liquor advances via a holding tank to the arsenic removal circuit.

Calcium arsenate was precipitated by adding lime to a 10' x 10' tank ahead of autoclaving the liquor. The formation of calcium arsenate requires a very high oxygen pressure and temperature to complete the oxidation of thiosulfate to sulfate.

Arsenic precipitation is accomplished at 190°C and 230 psig O_2, and after 1-2 hours conversion of arsenic to sparingly soluble Ca arsenate, all thromlfate has oxidized to sulfate. Release of the autoclave contents to a flash tank loses 12% volume through water evaporation. Crystals of calcium arsenate are separated from the liquor in a Bird centrifuge. Crystals from the centrifuge discharge contained about 50% moisture and are repulped and pressure filtered. The liquor fraction from the 38 chamber Lasta pressure filter joins the centrate fraction from the centrifuge for treatment in the sodium sulfate removal circuit.

SODIUM SULFATE RECOVERY

Liquor, after arsenic removal, contains small amounts of entrained solids and excess sodium sulfate generated during autoclaving of antimony and arsenic. This liquor has a trace amount of arsenic, and so the sodium sulfate circuit was equipped to remove it.

A polishing filter is used to remove traces of suspended solids from the liquor fed to the sodium sulfide section. Liquor is then stored in holding tanks serving a triple effect evaporator supplied by HPD Corp., Pittsburgh, Pennsylvania. The triple effect evaporator uses steam counter currently. NaOH is added to the holding tanks to salt out the Na_2SO_4 ahead of the triple effect evaporator which concentrates the Na_2SO_4 to the point of crystallization. Na_2SO_4 is separated out on a belt filter allowing the caustic solution to be recycled to the primary concentrate thickener.

The filtered Na_2SO_4 crystals contain entrained arsenic. To strip out the arsenic, the Na_2SO_4 crystals must be redissolved in a pair of steam heated reaction tanks to which lime or sulfuric acid are added to adjust pH. Arsenic is precipitated as calcium arsenate and subsequently removed from the liquor by centrifuge. The liquor 's polished and evaporated in a double-effect crystallizer with chambers at 96°C and 123°C respectively. Na_2SO_4 crystals were dewatered in a hydrocyclone followed by two centrifuges before passing through a 3' x 16' long rotary drier.

The double and triple effect crystallizers for Na_2SO_4 recovery were supplied by:

A. H. LUNDBERG EQUIPMENT LTD.
150-10551 Shellbridge Way
Richmond, B.C. V6X 2W8
(604) 273-5204

Anticipated by-products and waste from treating around 2,500 tpd concentrates was 500 tpm sodium antimonate, 600 tpm calcium arsenate, and 1,200 tpm Na sulfate.

The batch process required many sensors and microprocessors. EQUITY SILVER has installed a microprocessor system supplied by:

MODICON CANADA
2045 West Broadway
Vancouver, B.C. V6J 176
(604) 738-2525
Rod Madison

EQUITY SILVER, in 1982, declined to pass out operating cost data but volunteered that reagent costs are the largest component.

More information is availale in Appendix II of RANDOL's "Innovations in Gold and Silver Recovery" or might be available from:

EQUITY SILVER MINES LTD.
Post Office
Houston, B.C.
(604) 845-7799
Brad Marchant

PLACER DEVELOPMENT CORP.
Post Office Box 49330
Bentall Postal Staton
Vancouver, B.C. V7X 1P1
(604) 682-7082
Douglas A. Knight
General Mill Superintent

Although encouraging attempts were subsequently made to make a marketable copper arsenate by-product (used in chrome asenate manufacture), EQUITY SILVER shipped their calcium arsenate residue to a hazardous waste disposal site in Arlington, Oregon. The

cost of disposing of arsenic in this way was "prohibitive." Sludges were packaged and shipped to:

CHEM. SECURITY SYSTEMS
Arlington, Oregon
(503) 454-2777

Enquiries regarding hazardous waste disposal at this site should be directed to:

CHEM. SECURITY SYSTEMS
Post Office Box 1269
Portland, OR 97207
(503) 223-1912
Bill Van Dyk
Sales Manager

PROCESSING THE MAIN ZONE

The Main Zone can be treated by flotation to recover an acceptable grade of concentrate with As and Sb levels acceptable for shipment.

PROCESSING SOUTHERN ZONE TAILINGS

Flotation of Southern Zone tailings under different conditions allows a pyrite-arsenopyrite concentrate containing gold to be recovered. EQUITY SILVER has reputedly accumulated some 60,000 t of arsenopyrite-pyrite concentrates containing some gold.

Conventional cyanidation recovers only 15% of the gold content from this refractory concentrate. However, by oxidizing 6-10% of the sulfide content, recovery is increased to the 90% range. This 6-10% sulfide corresponds to the arsenopyrite content of the ore, although some pyrite is also oxidized.

EQUITY SILVER is currently building a vat bio-oxidation process to selectively oxidize arsenopyrite without attacking the pyrite to liberate the gold and silver values. This process is to be described by MARCHANT (1985).

In the bioleaching process, arsenic is solubilized with numerous other cations at an operating pH of 0.9. There is a ferric ion concentration of 5-8,000 ppm which oxidizes all arsenic to arsenic (+5) as long as the Fe^{3+}/As ratio is kept above four. The bioleach liquor is recycled in the process to conserve nutrient additions, but a bleed stream is taken off to remove arsenic and other excess impurities. This bleed stream is partially neutralized to pH 3 with soda ash to precipitate arsenic as ferric arsenate. (Once arsenic is completely in the arsenate form, it could be precipitated several ways

including as copper arsenate if desired to make an intermediate product.) Once all the arsenic has precipitated lime is added to pH 9 to precipitate the remaining metals, Fe, Cu, Zn, etc.

The sludge is disposed of as acid mine drainage sludge (as described below) to the tailings pond. EQUITY SILVER has shown that this sludge meets the B.C. disposal criteria when mixed with tailings (the same as the EP acetic acid test) and is currently conducting long-term pond stability tests.

EQUITY SILVER MINES' address was shown above. It is believed that B.C. RESEARCH assisted in developing the bench scale process:

B.C. RESEARCH
3650 Westbrook Mall
Vancouver, B.C. V6S 2L2
(604) 224-4331
Telex: 04-507748
Richard W. Lawrence, Head
Head Division of Intractive Metallurgy

TREATMENT OF ACID MINE DRAINAGE

EQUITY SILVER MINES LTD. has developed and installed a simple, yet effective, acid mine drainage control system that meets British Columbia's very strict environment protection regulations. The AMD sludge, when mixed with tailings solids in a ratio of one sludge to four parts by volume mill tailings slurry at 35% solids, yields a settled tailings residue that meets the criteria for exemption from the B.C. Special Wastes Act. These criteria involve a leachability test similar to the U.S. EPA EP leach test using acetic acid.

Lime is added from an automatic lime slaker directly to a reaction tank. The reacted effluent is allowed to settle out precipitate in a sludge settling pond.

According to EQUITY SILVER staff, when this sludge, which includes precipitated arsenic, is mixed with the tailings slurry, the precipitate remains stable and meets the EP leach test. Although possibly not a suitable criteria for long-term stability testing from a chemistry point of view, the buffering nature of dissolved solids and excess alkalinity in the tailings is said to avoid CO_2 effects found in pure solutions/precipitate by ROBINS and TOZAWA (1982) and ROBINS (1984).

The sludge generated from the bio-leach pilot plant effluent treatment process is found to behave in the same way yielding a stable waste when mixed with tailings. EQUITY SILVER is currently running simulated long-term pond stability tests which take into account thiosulfate effects which seasonally reduce the pH of the tailings decant during the spring runoff.

Based on success at Key Lake in encapsulating arsenic precipitates in sub-aerial tailings which have extremely low permeabilities, EQUITY SILVER is also testing this technique with its tailings. In retrospect, this approach could also potentially have saved costs when disposing of its pressure oxidaton calcium arsenate sludges.

EQUITY SILVER MINES LTD.
ACID MINE DRAINAGE TREATMENT
(mg/l)

	Influent	Treated and Settled Decant to Discharge
Fe	600	LT 0.03
Cu	50	0.01
Zn	35	0.01
Al	--	0.15
Sb	LT 0.1	LT 0.01
As	15	0.002
Cd	--	0.005
$SO_4^{=}$	5,000	2,500
Total Acidity $CaCO_3$)	5,000	--

Information on effluent quality, plant design, etc. is in the public domaine and available from:

WASTE MANAGEMENT BRANCH
Ministry of the Environment
Government of British Columbia
Smithers, B.C.
Terry Roberts
Manager
(604) 847-7260

ARSENIC FROM ACID MINE DRAINAGE

In addition to the results on AMD treatment reported by EQUITY SILVER MINES LTD., the EPA INDUSTRIAL ENVIRONMENTAL RESEARCH LABS in Cincinnati, Ohio, found that lime neutralization, reverse osmosis, and ion exchange removed As, Cu, Hg, Ni, Se, and Zn from acid mine drainage but did not remove B or P. Although reverse osmosis and ion exchange were slightly more effective overall than neutralization, the

chemical requirements and need for subsequent waste treatment offset their advantages.

ARSENIC FROM COPPER AND LEAD SMELTERS

Arsenic removal is necessary from most copper and lead refineries. Arsenic accumulates in roaster flue dusts which are recycled in many cases resulting in further concentration. Gas scrubbing in roaster and smelter gas entrainment systems results in arsenic entering the water system. Also, concentrate and flue dust stockpiles, as well as loading and handling areas, may become contaminated. Areas around older roasters and smelters prior to recent air cleaning requirements may have been contaminated by fallout from stackgasses, possibly over many years' prior operations.

According to PATTERSON (1975), arsenic wastes from nonferrous smelting has been reported in the form of extremely small (1-3 u diameter) particles from which arsenic could profitably be recovered as described by SWAIN (1939).

Where sulfuric acid is produced from such operations, it is possible that some residual arsenic will end up in the acid according to OHSAKO and YONEYAMA (1973). They report cases where acid contained 200-500 mg arsenic. They also describe how this acid was treated.

A literature search yielded the following references to arsenic removal from copper and lead smelters:

DIMITROVA, M.G. (1971-1972) - Selection of cobalt ions in aqueous sulfuric acid medium were recovered selectively by flotation of sediments. Following this, Zn, As, and Pb ions from the clarified water are separated by precipitation as hydroxides by limewater.

REBROVA, et al. (1977) found that the arsenic levels in wastewaters from a Pb-Zn plant varies between 0.1-0.4 g As/l at pH 12-12.5. Tests using: 1) $FeSO_4$; 2) Fe SO_4 and $H2SO_4$; and 3) a two-stage method of applying $FeSO_4$ with subsequent neutralization with a mixture of lime and soda ash at a ratio 2:1 were tried. $FeSO_4$ alone yielded satisfactory results (98-99%) when Fe:As ratios of 7:1 and 9:1 were used at pH 7-7.5. The use of H_2SO_4 to adjust pH to 10-10.5 and $FeSO_4$ addition worked well at a ratio of Fe:As of 5:1, but the two-stage method worked most efficiently.

SCHWITZGEBEL, et al. (1979) studied the path of arsenic through a copper reverberating furnace and is an interesting example of how a material balance for arsenic is computed for a unit operation. Their paper is inserted below, and more information or help in this sort of survey may be requested from:

RADIAN CORPORATION
8500 Shoal Creek Blvd.
Austin, TX 78758
(512) 454-4797
Klaus Schwitzgebel

At Lead Smelter B in eastern Canada, lime settling and flocculated clarification has not achieved perfect arsenic removal in effluents for discharge. BRUNSWICK SMELTING staff were testing the effect of oxidation of the arsenic using Cl_2 and peroxide to improve the process. In the absence of adequate excess ferric ions, the arsenic was not precipitating well.

At this lead smelter, the 170 m^3/d effluent treatment plant has failed to remove arsenic. As a result of the recycling of in-plant generated flue dusts and sludges from the effluent treatment plant as well as the addition of flue dust containing arsenic from other plants to feedstocks and the recirculation of slag granulation water which is integrated with the plant effluent system, average arsenic levels in the effluent system are building up steadily. Arsenic levels vary significantly from day to day, and there is speculation that accumulation of arsenic precipitate in the holding and cooling pond sediment may be responsible for sporadic releases of arsenic back to the effluent.

SHIMOIIZAKA and MATSUOKA (1975) reviewed (in Japanese) the precipitation of metal hydroxides by neutralization with $CaCO_3$ and $Ca(OH)_2$. The effects of coexisting ferrous/ferric ions on the precipitation of Cd^{24}, AsO_4^{3-2}, and the oxidation of ferrous ions with air, bacteria, and oxidants in the presence of a catalyst were reviewed.

BOLIDEN, SKELLEFTHAM, SWEDEN

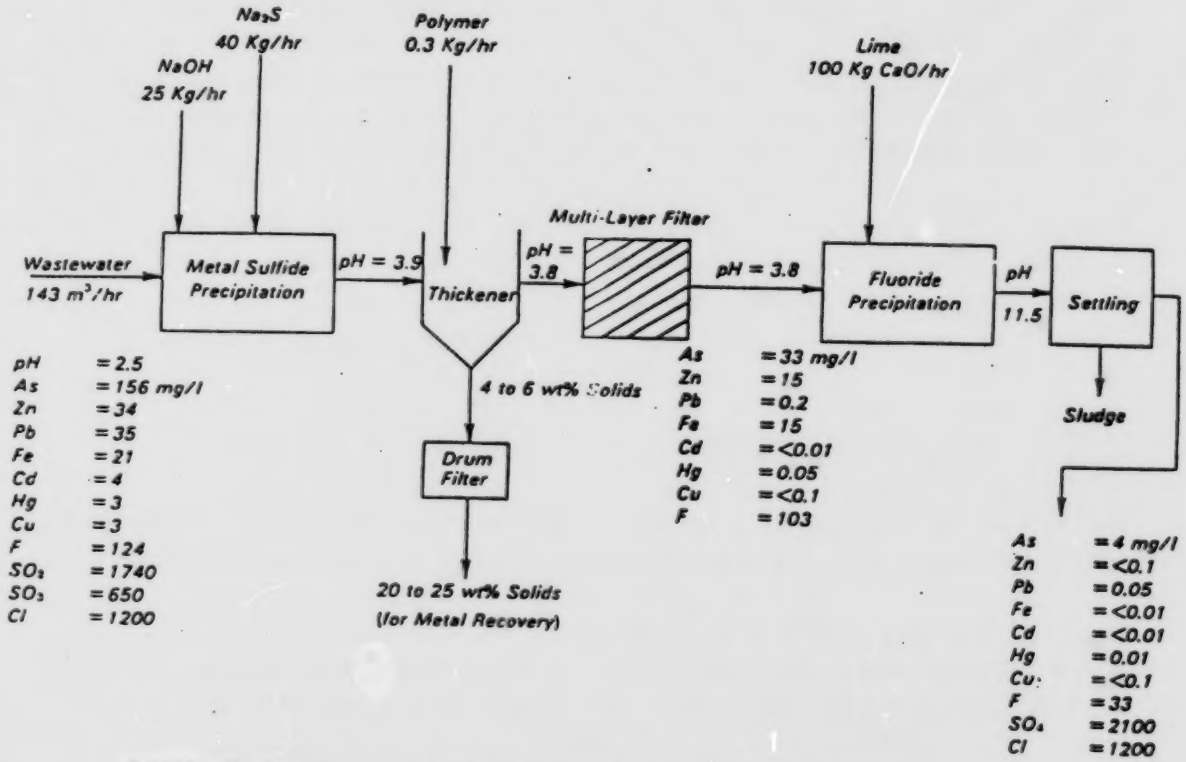
BOLIDEN at its Skeileftham copper smelter and metallurgical plant in Sweden employs sulfide precipitation of metals from metallurgical effluents at several points in their plant.

The U.S. EPA sent a team of investigators to describe the operation and performance of the operation which was documented in a report with Order Number PB81-209272 and EPA Summary Report EPA-600/S2-81-081, August 1981, by BLYTHE, et al. (1981).

The influent solution contains arsenic, other metals, and about 120 ppm F^- as well as 650 ppm SO_3. The use of sulfide precipitation at high pH would fail to remove arsenic effectively and would precipitate CaF_2 which is contaminated with metals and therefore unfit for land disposal. Low pH sulfide precipitation does not precipitate fluoride. Also, the use of sulfide at a low pH in the presence of sulfite results in excess sulfide consumption with generation of sulfur and thiosulfate.

To best meet all these conditions, metal sulfides are precipitated at pH 3.9 which has to be maintained by NaOH addition until all metals are precipitated. Sulfide addition is

controlled using a pH meter which shows a distinct increase when all metals are precipitated during controlled rate addition and multi-media filtration followed by lime addition and settling to remove fluoride, as illustrated schematically by BLYTHE, et al. (1981) below. Arsenic is reduced from 156 mg/l in the influent to 33 mg/l in the low pH sulfide precipitation and finally to 4 mg/l after lime precipitation and settling. It is surprising that arsenic is not removed much lower than this. Removal of other metals, however, appears to be very effective as seen on the diagram. In the case of BOLIDEN, the metal sulfide precipitate is stored in tanks pending development of a hydrometallurgical process to recover the metal values.



Typical residual metal concentrations obtained by full-scale test run (Boliden Metall).

Removal of Metals by Sulfide Precipitation and by Sulfide Precipitation Followed by Lime Precipitation (Full-Scale Process)

Component	% Removal	
	Sulfide Precipitation*	Sulfide + Lime Precipitation**
As	67-87	96-99
Zn	51-75	99
Pb	97-99	97-99
Cd	99	99
Cu	>90	>90
Hg	99	99
Fe	2-26	>99
Fluoride	0	70-78

*Sampling point 7 in Figure 2
**Sampling point 8 in Figure 2

More information would be available from:

BOLIDEN METALL AB
Skellefteå, Sweden
Rolf Sevedberg

D. BHATTACHARYYA
Chemical Engineering Dept.
University of Kentucky
Lexington, KY 40506-0046
(606) 257-2798

According to BHATTACHARYYA (1985, personal communication), one of the problems is excessive cost at low pH due to $SO_3^=$ consumption of sulfide and the efficient removal of metal sulfides by settling and filtration. Especially copper forms very finely divided sulfide precipitate which is difficult to remove. Another problem is the less effective precipitation of weaker sulfide precipitates in the presence of chelating agents such as cyanide.

ARSENIC DISCHARGE FROM A PRIMARY COPPER SMELTER

Klaus Schwitzgebel*, R. V. Collins*, R. T. Coleman*

Proc. International Conference on
Management & Control of Heavy Metals
in the Environment. London Sept. 1979

ABSTRACT

In this study, the path of arsenic through a copper reverberatory furnace was determined. 50% of the arsenic entering the furnace in the concentrate feed exited in the off-gases, 25% left with the slag, and 25% was transported to the converters in the matte.

In addition, arsenic concentrations at the inlet and outlet of the electrostatic precipitator (ESP), the blowdown of the sulfuric acid plant, and concentrate feed are reported. One major arsenic compound in the discharge from the reverberatory furnace ESP was determined by X-ray diffraction to be arsenic trioxide, As_2O_3. Arsenic emission rates from the ESP as a function of time varied between 25 and 140 pounds per hour. These fluctuations were due partly to variations in the concentrate arsenic composition and partly to intermittent recycling to ESP dusts.

INTRODUCTION

The original goal of this study was the evaluation of the electrostatic precipitator performance servicing the reverberatory furnace (ref 1). Cross-checking of the arsenic emission rates by plant personnel broadened the scope considerably.

The smelter studied has a daily production capacity of 200 tons anode copper. The gas flow from the reverberatory furnace to the ESP is 160,000 acfm. The precipitator operated at approximately 600°F which is above the dew point of sulfuric acid. Certain arsenic compounds are volatile at 600°F and escape the ESP uncontrolled.

The article describes the smelting operation, the sampling, the analytical techniques, the arsenic flow rates and arsenic emissions.

SMELTER DESCRIPTION

The major pieces of equipment for the copper smelter studied are: 1) reverberatory furnace; 2) converters; 3) anode furnace; 4) casting wheel; and 5) gas and particulate control equipment.

The reverberatory furnace is green fed. The off-gases are cooled in two waste heat boilers (WHB), cleaned in two electrostatic precipitators (ESP) in parallel, and discharged to the stack. Deposits formed on the WHB tubes were periodically removed using steam sootblowers. Dust collected in both the waste heat boilers and electrostatic precipitators is recycled to the feed preparation area.

The off-gases from the converters are treated in a similar fashion. Heat is recovered in waste heat boilers. Particulate matter settles in the balloon flue and is retained in the electrostatic precipitator (ESP). Dust collected in the WHB is recycled directly to the converters. Balloon flue and ESP dusts are recycled to the reverberatory furnace feed preparation area. The SO_2-rich converter gases are then cleaned in a gas conditioning unit followed by a wet electrostatic precipitator. Sulfur dioxide is finally oxidized catalytically to produce 93% sulfuric acid in a single contact acid plant.

The concentrate is the only significant arsenic-containing feed stream. Arsenic-containing discharge streams are the reverberatory furnace slag, acid plant blowdown, anode copper, and the gases discharged from the electrostatic precipitator to the stack. The arsenic

entering with the fuel and flux material and exiting with the sulfuric acid plant tail gas can be neglected.

SAMPLING

Four approaches were chosen to quantify the arsenic discharge from the reverberatory furnace ESP: 1) a material balance approach around the plant for arsenic; 2) a filter impinger train used at the reverb ESP exit; 3) a wet electrostatic precipitator followed by an impinger train at the ESP exit; and 4) a modified EPA Method 5 train at the ESP exit.

The material balance approach used to arrive at discharge averages for two entire months was based on the As flows (lb/hr) according to the following equation:

ESP Discharge	=	Concentrate Feed	+	Flux & Fuel	-	Reverberatory Furnace Slag	-	Anode Copper

The filter impinger train was used by plant personnel to cross check the results.

The wet electrostatic precipitator (WEP) which preceded an impinger train was 3" in diameter and 2' tall. Ultrapure dilute nitric acid was circulated through a 500 ml round bottom flask and a vertical glass cylinder by a peristaltic pump. The walls of the cylinder were wetted by the falling film of electrolyte. A thin platinum wire was suspended in the center of the glass cylinder. A corona discharge at the center electrode was generated by a 12 to 15 kV DC voltage. The gas flow rate through the WEP was approximately 0.5 ft^3/min. The gas entering the WEP was first scrubbed and cooled in the round bottom flask. Particulates and mist not retained here were electrostatically charged in the glass cylinder, collected in the falling film, and washed into the electrolyte reservoir. This sampling device does not clog like a filter or thimble and no analytical background corrections are necessary as are needed with filters. Contents of the eight impingers following the WEP were 1:1:1 H_2SO_4-HNO_3-H_2O(#1,2), dry impingers (#3,7), 20% KOH (#4,5), H_2O_2 (#6), silica gel (#8).

ANALYSIS

Liquid samples were filtered and the solids digested using nitric and perchloric acids. Insoluble silicates were subjected to an HNO_3/HF digestion. The filtrate and digested solids were combined for analysis.

Samples for arsenic analysis were complexed as the heteropoly acid of molybdenum. Quantitative determinations were made by injecting an aqueous aliquot into the graphite furnace attachment of an atomic absoption spectrophotometer. This method of analysis was developed by Ramakrishna, Robinson, and West (ref 2), and Ediger (ref 3). The complexing step avoids the volatilization of arsenic compounds at low temperatures, thus a charring temperature of 1200°C could be used. Working at this temperature also reduces interferences experienced at lower temperatures.

ARSENIC DISCHARGE DETERMINED BY MATERIAL BALANCE DIFFERENCE

The weight fractions of arsenic in the incoming or outgoing streams (lb As/lb) multiplied by the stream flow rates (lb/hr) give the arsenic flow rate in the corresponding streams in lb As/hr. This material balance approach was used to estimate the amount of arsenic escaping the reverberatory furnace electrostatic precipitator. The following average rates were found during the month of January 1977.

Incoming Streams:			Outgoing Streams:		
Concentrate Feed	102	lb/hr	Reverb Furnace Slag	26	lb/hr
Flux and Fuel	0	lb/hr	Acid Plant Blowdown	27	lb/hr
TOTAL ARSENIC IN	102	lb/hr	Anode Copper	5	lb/hr
			Reverb ESP Discharge	X	lb/hr
			TOTAL ARSENIC OUT	58 + X	lb/hr

Reverb ESP Discharge = 102 - 58 = 44 lb/hr

These data indicate that roughly 50% (44.6 lb/hr) of the incoming arsenic (102 lb/hr) leaves the smelter with the reverberatory furnace flue gas, 25% (26 lb/hr) is discharged with the reverberatory furnace slag, and 25% (27 lb/hr) is transported with the matte to the converters. The same 50-25-25 split was indicated in the reverberatory balance for arsenic based on the samples obtained during the July 1976 sampling effort.

The same balance approach repeated during March 1977 showed the following results:

Incoming Streams:			Outgoing Streams:		
Concentrate Feed	103	lb/hr	Reverb Furnace Slag	31	lb/hr
Flux and Fuel	0	lb/hr	Acid Plant Purge Water	27	lb/hr
TOTAL ARSENIC IN	103	lb/hr	Anode Copper	5	lb/hr
			Reverb ESP Discharge	X	
			TOTAL ARSENIC OUT	63 + X	lb/hr

Bydifference:
Reverb ESP Discharge = 103 - 63 = 40 lb/hr

ARSENIC DISCHARGE DETERMINED BY DIRECT MEASUREMENT

Smelter personnel measured arsenic emissions during March, 1977 using a filter/impinger train. The arsenic emission values obtained at the ESP outlet were: 25 lb/hr (March 1, 1977), 34 lb/hr (March 2, 1977), and 49 lb/hr (March 3, 1977). Of these emissions, 16, 17 and 23 lb/hr respectively were in the form of gaseous arsenic. Difficulties were encountered during these experiments due to the deposit of a yellow-orange material on the walls of the sampling lines which caused the filter to clog.

On July 11, 1976, the authors used the WEP train to make determinations at the ESP inlet and outlet. These determinations showed arsenic flows of 190 lb/hr at the inlet and 140 lb/hr at the outlet duct indicating an ESP efficiency of 26 percent. A second determination on July 13, using the WEP train showed an emission rate of 76 lb/hr at the ESP outlet.

The modified EPA Method 5 train followed by a set of 6 impingers was used by the authors to collect samples at the inlet and outlet of the ESP on July 13 and July 14, 1976. Arsenic flow rates of 59, 73 and 75 lb/hr giving an average of 69 lb/hr were found at the inlet. The corresponding values at the outlet were 54, 45 and 51 lb/hr or an average of 50 lb/hr. This indicates that an average of 72% of the incoming arsenic is discharged to the stack. These values are slightly higher than the flows determined by material balance difference (44 lb/hr in January and 40 lb/hr in March 1977) and the measurements made by smelter personnel using the filter/impinger train described above.

A summary of all the measured arsenic emission rates from the reverb ESP is as follows:

Jan. 1977 - Mat. balance	- 44 lb/hr	July 1976 - WEP-Imp.	- 140 lb/hr
Mar. 1977 - Mat. balance	- 40 lb/hr	July 1976 - WEP-Imp.	- 76 lb/hr
Mar. 1977 - Filter Imp.	- 25 lb/hr	July 1976 - EPA Meth. 5	- 54 lb/hr
Mar. 1977 - Filter Imp.	- 34 lb/hr	July 1976 - EPA Meth. 5	- 45 lb/hr
Mar. 1977 - Filter Imp.	- 49 lb/hr	July 1976 - EPA Meth. 5	- 51 lb/hr

FLUCTUATIONS OF THE ARSENIC CONCENTRATION IN THE REVERBERATORY FURNACE FEED

The reasons for the varying arsenic emissions are different dust recycling rates and changing As concentrations in the Cu ore. Recycle dust for instance contains 5-10% As. Both factors can lead to wide variations in the reverberatory furnace feed as is shown for the A, B, and C shifts of February 28, 1977 through March 4, 1977:

Date	ppm As in feed	Date	ppm As in feed	Date	ppm As in feed
A 2/28/77	= 1400	B 2/28/77	= 1200	C 2/28/77	= 2900
A 3/1/77	= 3100	B 3/1/77	= 7400	C 3/1/77	= 3100
A 3/2/77	= 1400	B 3/2/77	= 2400	C 3/2/77	= 3300
A 3/3/77	= 3100	B 3/3/77	= 2300	C 3/3/77	= 4000
A 3/4/77	= 1800	B 3/4/77	= 780	C 3/4/77	= 3700

The ESP efficiency for arsenic removal was found to be 26 and 28%. The variation in discharge rates are explainable in the light of the above As variations in the feed which range from 7400 ppm As (B 3/1/77) to 780 ppm As (B 3/4/77).

IDENTIFICATION OF MAJOR CRYSTALLINE SPECIES

X-ray diffraction was used to investigate the nature of the major crystalline phases. The goniometer technique using Cu Kα radiation was applied.

Arsenolite (As_2O_3) was positively identified in the hopper dust. Arsenolite was also present in the material collected by the in-stack filter, the out-of-stack filter, and the impingers used at the ESP outlet. These findings indicate that arsenolite leaves the ESP in both a solid and a gaseous phase.

SUMMARY AND CONCLUSIONS

The data obtained from the reverberatory furnace electrostatic precipitator emission tests can be summarized as follows: 1) Approximately 50 percent of the arsenic entering the green fed reverberatory furnace is fumed off and leaves the furnace in the off-gases; approximately 25 percent leaves the smelter with the reverberatory slag; approximately 25 percent is transported with the matte to the converters. A portion of the arsenic sent to the converters is fumed off and exits the smelter in the sulfuric acid plant blowdown; 2) the arsenic emitted from the reverberatory furnace ESP varies from 25 to 140 pounds per hour; 3) the ESP control efficiency for arsenic is between 26 to 28 percent at 600°F; 4) part of the arsenic escaping the reverb ESP is in the gaseous state; 5) arsenolite, As_2O_3, is the major identified arsenic species emitted. The observed preferrential emission of arsenic in the gaseous streams in this study is the same as that observed at the primary copper smelter in Bor, Jugoslavia (ref 4). Based on these results it can be concluded that the hot ESP's servicing green fed reverberatory furnaces do not effectively control arsenic emissions.

REFERENCES

1. Schwitzgebel, K., EPA Contract No. 68-01-4136, 1978.
2. Ramakrishna, T. V. J. W. Robinson, and D. W. West, "Anal. Chem. Acta 45, 43-49, (1969).
3. Ediger, R., Study No. 584, Perkin-Elmer, 1975
4. Research Triangle Institute, EPA Contract No. 68-02-1325, Task 47, 1976.

* Radian Corporation, 8500 Shoal Creek Blvd., Austin, Texas 78758, U.S.A.

ARSENIC IN URANIUM MILL EFFLUENTS

The summarized data reported above from the PEDCO (1983) report on mine-mill wastes in the U.S.A. indicated that arsenic levels in liquid effluents and seepage from uranium mines in the U.S.A. is likely to be low.

ERGO

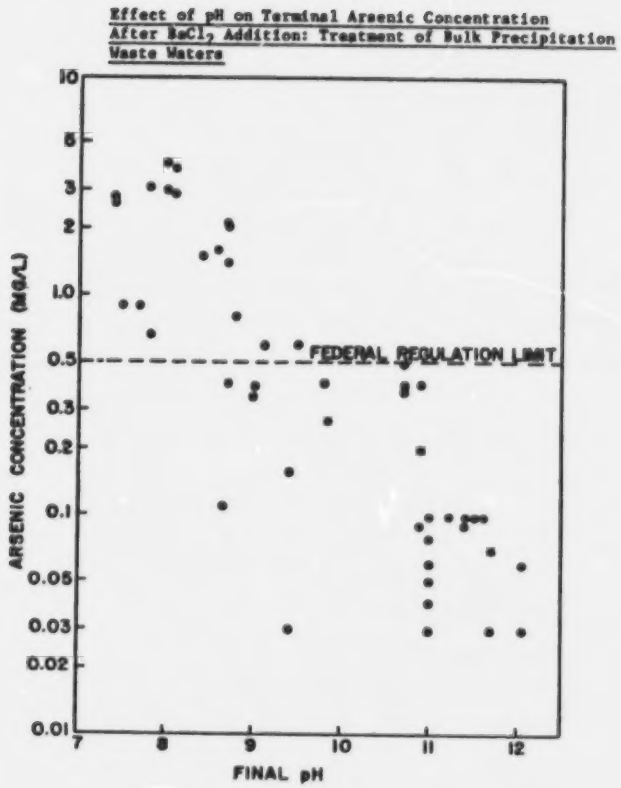
Roasted pyrite concentrates produced on the Witwatersrand yield some arsenic in the calcine washwaters. These are treated for effective arsenic removal by the addition of ferric iron (in raffinate) and vigorous aeration agitation with lime to reduce arsenic in solution to below 0.5 ppm As. One such treatment arrangement is briefly described in the Appendix I trip report. More data may be requested from:

EAST RAND GOLD AND URANIUM
COMPANY LTD.
Post Office Box 980
Brakpan 1540
South Africa
(011) 559050
Ken Henderson
Metallurgical Manager

KEY LAKE

The very rich uranium deposits is Saskatchewan are characterized by high Ni and Co values, often with high arsenic levels. Two arsenic removal methods are described in Appendix I for KEY LAKE MINING LTD. and for RABBIT LAKE.

The process developed for KEY LAKE arsenic removal and described by CLARKE, et al. (1980) is one in which arsenic is removed with other metals in wastewater and excess minewater by staged addition of lime via flash mixers followed by radium removal by $BaCl_2$ and lime addition again using flash mixers. This process reduces effluents to less than 0.1 ppm As. CLARKE, et al. (1980) found that the higher the pH, the lower the arsenic level that can be achieved as shown in the following diagram.



SHERRITT GORDON MINES LIMITED

This arsenic removal process was believed to be due to extremely low solubilities of $BaRaAsO_4$ which led to patents by SHERRITT GORDON MINES (1980). The chemical basis for the patent has been challenged by ROBINS (1985), but the fact remains that arsenic is removed from the system even if the interpretation of the mechanism is not altogether accurate.

KEY LAKE MINING operations as described by CLARKE, et al. (1980), show how subaerial tailings disposal in layers are extremely impermeable and results in an excellent method of encapsulating the arsenic-rich precipitate sludges generated by the water treatment plant. This circumvents any question about the stability of arsenic precipitates in the presence of CO_2.

The arsenic removal testwork and also the subaerial tailings disposal method was deminstrated for KEY LAKE MINING by:

SHERRITT GORDON MINES LTD.
Fort Saskatchewan, Alberta
Canada T8L2P2
(403) 998-6911
Herbert Veltman
Director
D. Robert Weir
Manager Boren Research
Roman M. P. G. Berezowsky
Ian M. Masters

Additional information may be available from:

KEY LAKE MINING CORPORATION
229 Fourth Avenue South
Saskatoon, Saskatchewan S7K 4K3
(306) 665-7000
B. Rosner
Engineering Manager

RABBIT LAKE

At RABBIT LAKE operations, a change in ore type from the RABBIT LAKE ore deposit, which is now exhausted, to the Collins Bay B-Zone ore which has much higher arsenic levels (up to 10% As in the LRC high grade ore), meant that a new process flowsheet had to be installed. Metallurgically, other significant differences were the higher concentrations of nickel, molybdenum, cobalt, as well as arsenic in the Collins Bay B-Zone ore.

Nickel and arsenic solubilize under leaching conditions favorable for uranium, and both of these metals extract in excess of 80%. Major modifications were necessary to the solvent extraction process, to the uranium precipitation process, and to the tailings disposal and effluent treatment processes which are described in the discussion of RABBIT LAKE in Appendix I.

Arsenic is precipitated as ferric arsenate by the addition of ferric sulfate followed by pH controlled addition of slaked lime to an approximate pH of 3.5 and magnesium hydroxide to an approximate pH of 3.8. The solution with precipitate (iron cake) is thickened. The precipitate is leached with pregnant aqueous solution from the leach process for uranium recovery as some uranium is precipitated during the $Mg(OH)_2$ additon step. The ferric arsenate eventually leaves the circuit in the tailing stream from the CCD circuit. Maximum allowable levels of arsenic in the final effluent are 0.5 mg As/l.

Arsenic is precipitated from tailings slurry in the form of ferric arsenate. Barren solution containing the majority of the arsenic is treated separately. The equipment consists of a number of tanks where a 1% mixture of SO_2 from the sulfuric acid plant in air is sparged into the agitated solution to insure that all iron present in the solution is

oxidized to the ferric state. Lime is added to maintain the pH at 1.3. Thereafter, the pH is raised to 4.5 by adding more lime and arsenic precipitates as ferric arsenate. The slurry is thickened to recover solution from where solids are pumped to the first stage in the neutralization circuit. Thickener overflow was planned to be used as CCD wash solution or pumped to the neutralization circuit if its quality is not good enough for CCD washing.

Nickel in the effluent could also be precipitated by further pH adjustment which would further scavenge arsenic from solution.

United States Patent [19]

Weir et al.

[11] **4,366,128**

[45] **Dec. 28, 1982**

[54] **REMOVAL OF ARSENIC FROM AQUEOUS SOLUTIONS**

[75] Inventors: **Donald R. Weir; Ian M. Masters,** both of Fort Saskatchewan, Canada

[73] Assignee: **Sherritt Gordon Mines Limited,** Toronto, Canada

[21] Appl. No.: **192,766**

[22] Filed: **Oct. 1, 1980**

[30] **Foreign Application Priority Data**

Aug. 22, 1980 [CA] Canada 358966

[51] Int. Cl.[3] C01G 28/02

[52] U.S. Cl. 423/87; 423/602; 423/11; 423/18; 423/8

[58] Field of Search 423/602, 87, 11, 18

[56] **References Cited**

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4,244,735	1/1981	Reynolds et al.	423/87

OTHER PUBLICATIONS

Jacobson, "Encyclopedia of Chemical Reactions", vol. 1, Reinhold Publishing Corp., N.Y., 1946, p. 472.

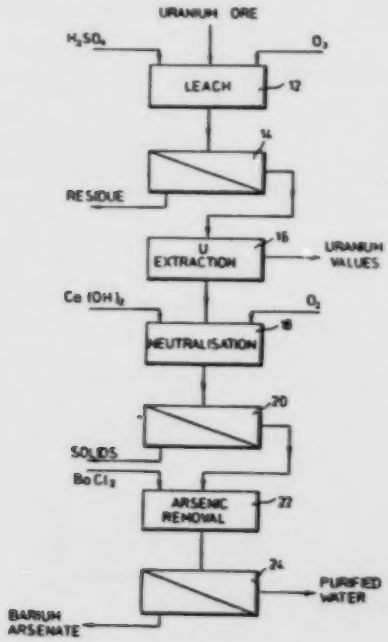
Primary Examiner—Herbert T. Carter

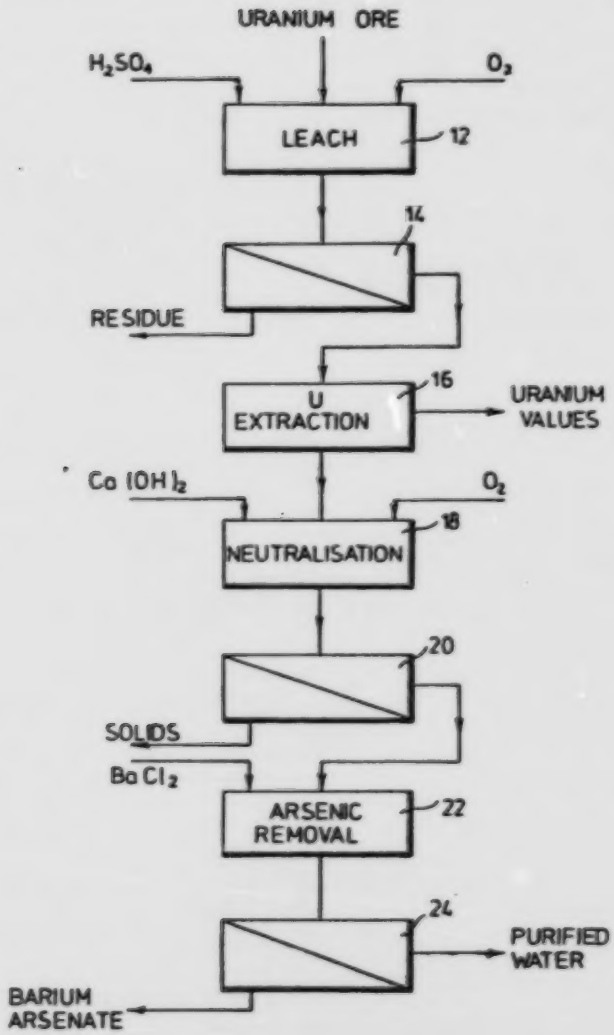
Attorney, Agent, or Firm—Robert F. Delbridge; Arne I. Fors

[57] **ABSTRACT**

A process for removing arsenic from an aqueous solution containing arsenic in the form of a soluble arsenate includes adjusting the pH of the solution if necessary to at least about 10, adding a soluble barium salt to precipitate arsenic as barium arsenate, and removing the precipitated barium arsenate from the solution.

14 Claims, 1 Drawing Figure




URANIUM ORE
H_2SO_4
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LEACH
12
14
RESIDUE
U EXTRACTION
16
URANIUM VALUES
$Ca(OH)_2$
O_2
NEUTRALISATION
18
20
SOLIDS
$BaCl_2$
ARSENIC REMOVAL
22
24
PURIFIED WATER
BARIUM ARSENATE

REMOVAL OF ARSENIC FROM AQUEOUS SOLUTIONS

This invention relates to the removal of traces of dissolved arsenic from aqueous solutions to reduce the dissolved arsenic concentration to very low values for example less than 0.5 mg/L.

There are various industrial processes in which a waste aqueous solution contains arsenic whose concentration must be reduced to an extremely low level before the aqueous solution is considered safe for disposal by discharge to the environment. For example, in hydrometallurgical processes for the recovery of metals from their ores, the ore treated often contains arsenic which is dissolved during the hydrometallurgical operation. Although various methods are known for removing some arsenic from solution, known methods which are commercially acceptable are only able to reduce the concentration of dissolved arsenic to about 1 or 2 mg/L. However, environmental regulations in many places do not permit the discharge to the environment of water containing such concentrations of arsenic, but only permit discharge when the arsenic concentration is much lower, for example below 0.5 mg/L.

It is known to precipitate dissolved arsenic as calcium arsenate and/or ferric arsenate, for example by the addition of lime and/or ferric sulphate, in order to reduce the dissolved arsenic content of an aqueous solution from relatively high concentrations down to about 1 or 2 mg/L. However, the solubilities of calcium arsenate and ferric arsenate are such that it is not possible to reduce the dissolved arsenic concentration still further by this method.

The present invention is based on the discovery that the arsenic concentration in an aqueous solution containing dissolved arsenic in the form of a soluble arsenate, such as calcium arsenate and/or ferric arsenate, can be significantly reduced by adjusting the pH of the solution if necessary to at least 10, preferably to 11 or 12, and adding a soluble barium salt, such as barium chloride, to precipitate dissolved arsenic as barium arsentate. In this way, the dissolved arsenic concentration can be reduced to less than 0.5 mg/L and, at the preferred pH of 11 of 12, probably to less than 0.2 mg/L. The soluble barium salt may be added before, during or after the pH adjustment.

Preferably, any pH adjustment is carried out and any precipitate, formed as a result of the pH adjustment, is removed before addition of the soluble barium salt.

The invention may be used to remove dissolved arsenic from an acidic aqueous solution by raising the pH of the solution to at least about 3, preferably at least about 5 and more preferably at least about 7, and adding ions selected from the group consisting of calcium ions and ferric ions if necessary to precipitate some of the arsenic as at least one of the compounds selected from the group consisting of calcium arsenate and ferric arsenate, separating the precipitate from the remaining solution to provide an aqueous solution containing at least one dissolved arsenate selected from the group consisting of calcium arsenate and ferric arsenate, adjusting the pH of the solution if necessary to at least about 10, adding barium chloride to precipitate arsenic as barium arsenate, and separating the precipitated barium arsenate from the solution.

The invention is especially useful in the recovery of uranium from uranium ores which also contain arsenic and iron.

One embodiment of the invention will now be described, by way of example, with reference to the accompanying drawing which shows a flow diagram of a uranium recovery process.

Referring to the drawing, a uranium-bearing ore of a sulphidic nature which also contains arsenic and iron in addition to other impurities is leached in aqueous sulphuric acid solution under oxidizing conditions in leach step 12. The leached slurry is subjected to a liquid-solids separation step 14 where the undissolved residue is removed for disposal as desired, for example by inclusion in the neutralization step which will be described later. The leach solution proceeds to a uranium extraction step 16 where uranium values are extracted from the leach solution, for example by solvent extraction.

The remaining solution containing dissolved arsenic and other impurities including iron then proceeds to a neutralization step 18 where lime is added to raise the pH of the solution to about 11 or 12 to cause precipitation of most of the dissolved impurities. In particular, most of the arsenic precipitates as calcium arsenate and/or ferric arsenate. Oxygen is bubbled into the solution during this step to oxidize any arsenite ions to arsenate ions. As mentioned above, the residue from the liquid-solids separation step 14 may be fed to this neutralization step. The resultant slurry passes to a further liquid-solids separation step 20, from which the solids may be dealt with as desired.

The aqueous liquid leaving the separation step 20 still contains small amounts of various impurities including arsenic as dissolved calcium arsenate and ferric arsenate, the arsenic concentration being about 1 or 2 mg/L. Since this arsenic concentration is too high to permit discharge of the aqueous liquid to the environment, the liquid is treated in an arsenic removal step 22 in accordance with the invention where barium chloride solution is added to precipitate much of the remaining arsenic as barium arsenate. In the arsenic removal step 22, the pH of the liquid is about 11 or 12 as a result of the lime treatment in the neutralization step 18. In this manner, the arsenic concentration is reduced to less than 0.5 mg/L, and can be reduced to as low as 0.1 mg/L.

The precipitated barium arsenate is removed from the liquid in a subsequent liquid-solids separation step 24, and the separated liquid now qualifies as purified water which can be discharged to the environment. The separated barium arsenate can be dealt with as desired.

An example of the invention will now be described.

EXAMPLE

Solution from a uranium extraction step, from which uranium had been extracted by solvent extraction, was treated with lime in a neutralization step to raise the pH to 11.6 and the resultant precipitate was separated from the remaining solution by settling. The concentrations (in mg/L) of various impurities in the solution before and after the neutralization step are shown in Table 1.

TABLE 1

Impurities	Before Neutralization	After Neutralization
Arsenic	1940	1.2
Nickel	2850	0.2
Iron	2680	<0.1

TABLE 1-continued

Impurities	Before Neutralization	After Neutralization
Aluminum	1250	0.4
Magnesium	1180	0.2
Sulphur	13400	550

The arsenic concentration of 1.2 mg/L after neutralization is too high to permit the solution to be discharged to the environment. Different portions of the solution were treated with barium chloride at different concentrations and temperatures. The resultant barium arsenate precipitate was removed in each case by filtration and the arsenic concentrations in the resultant liquids were determined. The results are shown in Table 2.

TABLE 2

Barium Conc.	Temp (°C.)	Initial pH	Final pH	Arsenic Conc.
100	25	11.6	11.5	0.1
200	25	11.6	11.4	0.1
50	50	11.6	11.6	0.1
100	50	11.6	11.2	0.1
200	50	11.6	11.2	0.1

It will be observed that in all these tests the arsenic concentration was reduced to 0.1 mg/L.

Other embodiments and examples will be readily apparent to a person skilled in the art, the scope of the invention being defined in the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A process for removing arsenic from an aqueous solution containing arsenic in the form of a soluble arsenate selected from the group consisting of calcium arsenate and ferric arsenate, comprising ensuring that the pH of the solution is at least about 10, adding a soluble barium salt to precipitate arsenic as barium arsenate, and removing the precipitated barium arsenate from the solution.

2. A solution according to claim 1 comprising ensuring that the pH of the solution is in the range of from about 11 to about 12.

3. A process according to claim 1 wherein the aqueous solution contains at least 1 mg/L dissolved arsenic, and the addition of barium chloride to precipitate barium arsenate reduces the concentration of dissolved arsenic to less than 0.5 mg/L.

4. A process according to claim 1 wherein the aqueous solution contains at least 0.5 mg/L dissolved arsenic, and addition of barium chloride to precipitate barium arsenate reduces the concentration of dissolved arsenic to less than 0.2 mg/L.

5. A process according to claim 1 wherein the soluble barium salt is barium chloride.

6. A process according to claim 1 wherein the pH of the solution is adjusted to at least about 10 from a lower value and any precipitate formed as a result of pH adjustment is separated from the solution before addition of the soluble barium salt.

7. A process for removing dissolved arsenic from an acidic aqueous solution comprising raising the pH of the solution to at least about 3 and adding ions selected from the group consisting of calcium ions and ferric ions to precipitate some of the arsenic as at least one of the compounds selected from the group consisting of calcium arsenate and ferric arsenate, separating the precipitate from the remaining solution to provide an aqueous solution containing at least one dissolved arsenate selected from the group consisting of calcium arsenate and ferric arsenate, ensuring that the pH of the solution is at least about 10, adding barium chloride to precipitate arsenic as barium arsenate, and separating the precipitated barium arsenate from the solution.

8. A process according to claim 7 comprising ensuring that the solution containing at least one dissolved arsenate is in the range of from about 11 to about 12.

9. A process according to claim 7 wherein the solution containing at least one dissolved arsenate contains at least 1 mg/L dissolved arsenic and the addition of barium chloride to precipitate barium arsenate reduces the concentration of dissolved arsenic to less than 0.5 mg/L.

10. A process according to claim 7 wherein the solution containing at least one dissolved arsenate contains at least 0.5 mg/L dissolved arsenic, and the addition of barium chloride to precipitate barium arsenate reduces the concentration of dissolved arsenic to less than 0.2 mg/L.

11. A process according to claim 7 wherein the pH of the acidic aqueous solution is raised to at least about 5 to precipitate some of the arsenic.

12. A process according to claim 7 wherein the pH of the acidic aqueous solution is raised to at least about 7 to precipitate some of the arsenic.

13. A process according to claim 7 including supplying oxygen to the acidic aqueous solution during the first mentioned arsenate precipitation step to oxidize arsenite ions to arsenate ions.

14. A process according to claim 7 wherein the pH of the solution containing at least one dissolved arsenate is adjusted to at least about 10 from a lower value and any precipitate formed as a result of pH adjustment is separated from the solution before addition of the soluble barium salt.

• • • • •

ARSENIC PRECIPITATE DISPOSAL

Disposal of arsenic precipitate ranges from the most expensive approach of shipping it in a dewatered, packaged form to a hazardous waste disposal site hundreds of miles away to simply decanting water from the precipitate in exposed settling ponds which are used to accumulate the precipitates.

Arsenic precipitate disposal:

CHEM. SECURITY SYSTEMS
Post Office Box 1269
Portland, Oregon
(503) 223-1912
Bill Van Dyk
Sales Manager

ROBINS (1985) and ROBINS and TOZAWA (1982), as mentioned, express concern for the stability of arsenic precipitates in water exposed to the air due to CO_2 destabilization of the precipitate liberating arsenic back to solution with time. However, since numerous other metals are co-precipitated, the stabilities of the precipitate may well be much greater to CO_2 than indicated on the basis of the above laboratory experiments.

EQUITY SILVER MINES (1985) has developed a simple direct lime addition process to precipitate arsenic as ferric arsenate. By blending the precipitate back with the tailings slurry which has excess alkalinity, a waste that meets British Columbia criteria for exemption from the Special Wastes Act is demonstrably achieved.

One of the most innovative and effective arsenic precipitate disposal methods is the encapsulation technique practiced at the KEY LAKE MINING CORPORATION which was developed by:

KNIGHT AND PIEZOLD
409 Granville
Vancouver, B.C. V6C 1T2
(604) 685-0543
R. Bruce Knight
Partner

and elsewhere by the South African affiliates of:

STEFFEN, ROBERTSON & KIRSTEN
#801, 1030 West Georgia
Vancouver, B.C. V6E 2Y3
(604) 681-4196
Telex: 04-352578
Andrew McG. Robertson

WILSON et al. (?) reported an interesting account of how natural freeze-thaw cycling of arsenic precipitate sludges had a marked effect on sludge density increasing it from 5% to 50% solids. Tests on a semi-commercial scale at the Deloro, Ontario, site were described and their performance discussed. Dusting problems remained to be overcome as well as arsenic leaching from the residue.

More information would be available from:

IEC BEAK CONSULTANTS LTD.
Mississauga, Ontario L4V 1P1
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Principal

Arsenic removal from gold processing waste waters: the potential ineffectiveness of lime

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ABSTRACT

The stability of calcium arsenate is discussed in relation to the possible misuse of lime in the treatment of gold processing waste waters. Stability diagrams have been derived and experimental results cited to show that calcium arsenate has a higher solubility in neutral to alkaline solution than has previously been recognized and this solubility is further enhanced by the presence of carbon dioxide, bicarbonate or carbonate.

Introduction

The removal of arsenic from gold mine waste waters has been of interest[1] for more than thirty years, but with the recent emphasis on clean water standards there has been renewed activity in relation to that problem[2,3,4,5]. The processing of gold-bearing sulphides which contain arsenopyrite and other complex arsenic sulphides is well established. Initial roasting to oxidize the sulphides leaves the arsenic in the form of both arsenic (III) and arsenic (V), in which forms it is soluble in the subsequent leaching stage. Further oxidation of the leach liquors is required[5] before the well-established procedure of precipitating calcium arsenate with lime, which is carried out despite an immense lack of knowledge of the calcium-arsenic-water system.

The solubility product and free energy of formation for $Ca_3(AsO_4)_2$, which are to be found in recent and reliable sources of data[6,7], originate from the work of Chukhlansev[8], whose experimental determination of the concentration of calcium from the solubility of calcium arsenate in solutions of various pH yields the results plotted in Figure 1. This is the work which has resulted in a wide acceptance of the "insolubility" of calcium arsenate and the use of lime to stabilize arsenic in that form.

Laguitton[9] attempted to further elucidate the chemistry of the lime addition method for treating arsenical waste waters from gold processing operations. The low solubility product for $Ca_3(AsO_4)_2$ was the basis for his examination of likely chemical equilibria in the system. Laguitton and other workers[10,11] have not considered atmospheric carbon dioxide as an important component in this system.

The Solubility of Calcium Arsenate

Tozawa, Umetsu and Nishimura[12] further investigated the solubility of calcium arsenate over a wide range of pH by measuring both calcium and arsenic concentrations in solution. Their results, which are plotted in Figure 2, show the trend toward a minimum concentration of both calcium and arsenic at about pH 11, but with the arsenic concentration approximately sixteen times (stoichiometric) that for calcium. These results were interpreted by Robins[13] using ther-

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Bob Robins is Associate Professor in Chemical Engineering in the School of Chemical Engineering and Industrial Chemistry at the University of New South Wales, Sydney, Australia. Dr. Robins received his B.Sc. and M.Sc. degrees in chemical engineering in 1953 and 1955 and a Ph.D. degree in metallurgy in 1958 from The University of New South Wales. He carried out post-doctoral work at the U.K. Atomic Energy Research Establishment, Harwell, from 1958 to 1961 and then became a Senior Lecturer in Metallurgy at Wollongong University.

Dr. Robins' research activities over the past 20 years have been related to aqueous process development, particularly associated with hydrometallurgical processes. Recently, he was awarded the 1982 Extractive Metallurgy Science Award by the Metallurgical Society of AIME for his work on the solubility of metal arsenates.

K. Tozawa

Kazuteru Tozawa is Professor of Metallurgy and in charge of the Hydrometallurgy Research Division of the Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai, Japan. Professor Tozawa graduated from the Department of Metallurgical Engineering, Tohoku University, in 1948 and then joined the Akita Mining College as Assistant Professor and worked there for 23 years. He obtained the degree of Doctor of Engineering in 1968 for the thesis entitled "Fundamental Research on Pressure Hydrometallurgical Treatment of Complex Sulphide Ores". In 1972, he transferred from Akita University to his present position.

His current interests include the recovery of values from metallurgical intermediates, zinc hydrometallurgy and the problems associated with arsenic residuals from metal extraction processes.

Keywords: Mineral processing, Gold processing, Waste waters, Arsenic removal, Lime, Calcium arsenate.

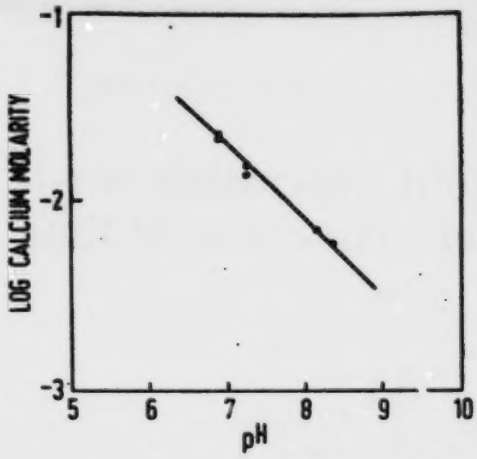

FIGURE 1. Calcium analyses from the determination of calcium arsenate solubility by Chukhlantsev[10].

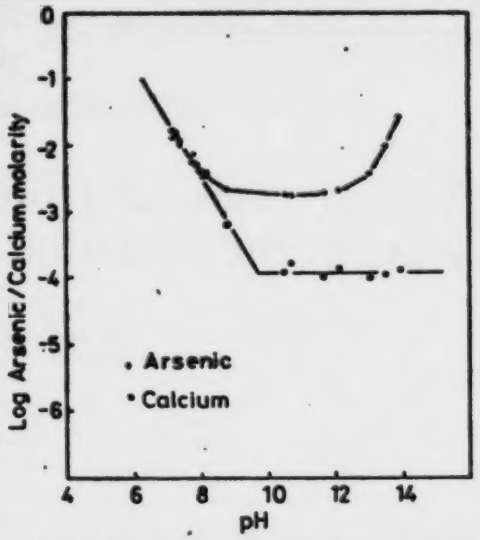

FIGURE 2. Calcium and arsenic analyses from the determination of calcium arsenate solubility by Tozawa, Umetsu and Nishimura[12].

modynamic equilibrium calculations and a presentation in the form of stability diagrams.

Robins suggested that the results of Tozawa, Umetsu and Nishimura were influenced by the presence of carbon dioxide in the atmosphere ($P_{CO_2} = 10^{-3.52}$ ats.), which causes a reduced stability of calcium arsenate and its decomposition into calcium carbonate. This proposition has much greater significance as carbon dioxide pressures or dissolved carbonate concentrations are increased. The stability diagrams which supported this explanation of the work of Tozawa *et al.* are further modified in this paper by considering the formation of the calcium carbonate complexes $CaCO_3^o$ and $CaHCO_3^+$ in aqueous solution, which leads to a closer agreement between experimental and predicted stability.

Stability Diagrams for Calcium Arsenate - Carbonate - Water

The derivation of log activity versus pH diagrams is based on a consideration of all of the known and likely reactions in the particular system in the general form:

$$aA + xH^+ = bB + cH_2O$$

and a calculation of equilibrium from the standard reaction isotherm

$$\Delta G^o = -R\,T \ln K$$

expanded by taking T = 298.15, pH = $-\log a_{H^+}$ and $a_{H_2O} = 1$, to obtain the equation

$$xpH = \frac{-\Delta G^o}{1.364} - \log \frac{a_B^b}{a_A^a}$$

which results in a series of straight lines which delineate the stability regions for the compounds and ions considered on a plot of log activity versus pH.

Stability diagrams for the calcium arsenate - carbonate - water system were calculated using the free energy data (listed in Table 1), taken mostly from NBS Technical Note 270[7]. The equilibria considered are set out as follows:

$H_3AsO_4^- + H^+ = H_3AsO_4$ ..... (1)
$HAsO_4^{2-} + H^+ = H_2AsO_4^-$ ..... (2)
$AsO_4^{3-} + H^+ = HAsO_4^{2-}$ ..... (3)
$CaOH^+ + H^+ = Ca^{2+} + H_2O$ ..... (4)
$Ca(OH)_2^o + H^+ = CaOH^+ + H_2O$ ..... (5)
$Ca(OH)_2 + 2H^+ = Ca^{2} + 2H_2O$ ..... (6)
$Ca(OH)_2 + H^+ = CaOH^+ + H_2O$ ..... (7)
$Ca(OH)_2 = Ca(OH)_2^o$ ..... (8)
$Ca_3(AsO)_2 = 2H_2AsO_4^- + 3Ca^{2+}$ ..... (9)
$Ca_3(AsO_4)_2 + 2H^+ = 2HAsO_4^{2-} + 3Ca^{2+}$ ..... (10)
$Ca_3(AsO_4)_2 = 2AsO_4^{3-} + 3Ca^{2+}$ ..... (11)
$Ca_3(AsO_4)_2 + 3H_2O = 2AsO_4^{3-} + 3CaOH^+ + 3H^+$ .. (12)
$Ca_3(AsO_4)_2 + 6H_2O = 2AsO_4^{3-} + 3Ca(OH)_2 + 6H^+$. (13)
$H_2CO_3 = CO_2 + H_2O$ ..... (14)
$HCO_3^- + H^+ = H_2CO_3$ ..... (15)
$CO_3^= + H^+ = HCO_3^-$ ..... (16)
$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$ ..... (17)
$CaCO_3 + 2H^+ = Ca^{++} + H_2CO_3$ ..... (18)
$CaCO_3 + H^+ = CaHCO_3^+$ ..... (19)
$Ca_3(AsO_4)_2 + 3HCO_3^- = 3CaCO_3 + 2HAsO_4^{2-} + H^+$. (20)
$Ca_3(AsO_4)_2 + 3CO_3^{2-} + 2H^+ = 3CaCO_3 + 2HAsO_4^{2-}$ ..... (21)
$Ca_3(AsO_4)_2 + 3H_2CO_3 = 3CaCO_3 + 2H_2AsO_4^- + 2H^+$. (22)
$Ca(OH)_2 + CO_3^{2-} + 2H^+ = CaCO_3 + 2H_2O$ ..... (23)
$Ca^{++} + HCO_3^- = CaHCO_3^+$ ..... (24)

TABLE 1. Free energy data[7] for the various substances considered

Formula		ΔG^o_f,298.15K kcal
H_2O	(liq)	-56.688
H_3AsO_4	(m = 1)	-183.1
$H_2AsO_4^-$	(m = 1)	-180.04
$HAsO_4^{2-}$	(m = 1)	-170.82
Ca^{2+}	(m = 1)	-132.30
$CaOH^+$	(m = 1)	-171.7
$Ca(OH)_2^o$	(m = 1)	-207.49
$H_2CO_3^o$	(m = 1)	-148.94
HCO_3^-	(m = 1)	-140.26
CO_3^{2-}	(m = 1)	-126.17)
$CaHCO_3^+$	(m = 1)	-273.92*
$CaCO_3^o$	(m = 1)	-262.77*
$Ca(OH)_2$	(c)	-214.76
$Ca_3(AsO_4)_2$	(c)	-732.1
$CaCO_3$, calcite	(c)	-269.80

* calculated from data in Reference 14

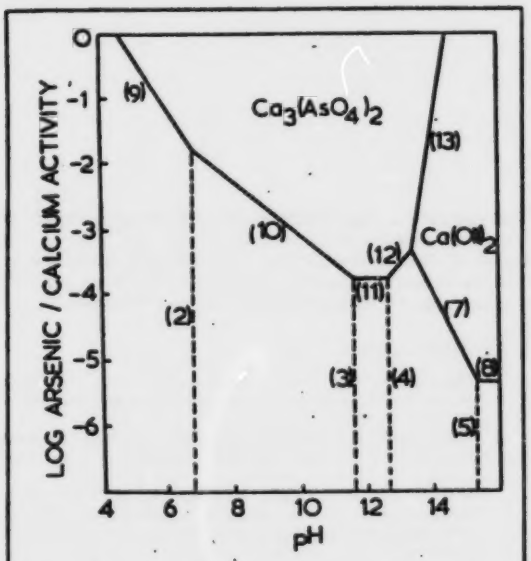

FIGURE 3. The calcium arsenate - water system for equal activities of dissolved calcium and arsenic species in the region of the calcium arsenate/solution interface.

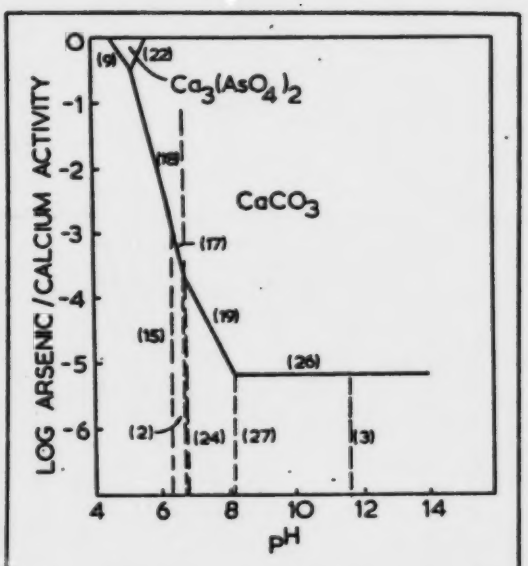

FIGURE 5. The calcium arsenate-carbonate-water system for P_{CO_2} = 1 atmosphere and equal activities of dissolved calcium and arsenic at the calcium arsenate/solution interface.

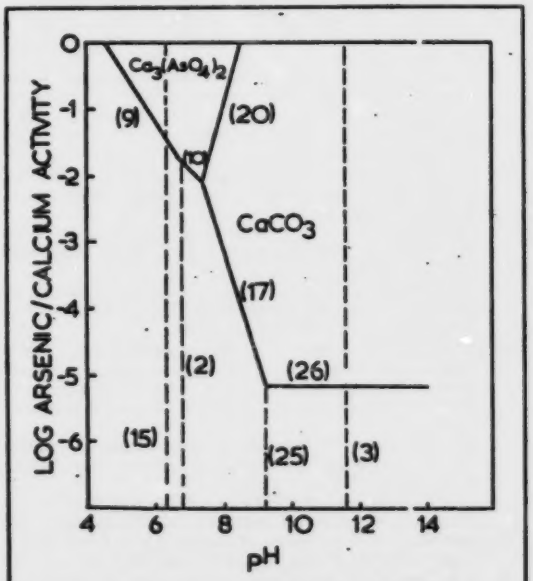

FIGURE 4. The calcium arsenate-cirbonate-water system for P_{CO_2} = $10^{-3.52}$ atmospheres and equal activities of dissolved calcium and arsenic at the calcium arsenate/solution interface.

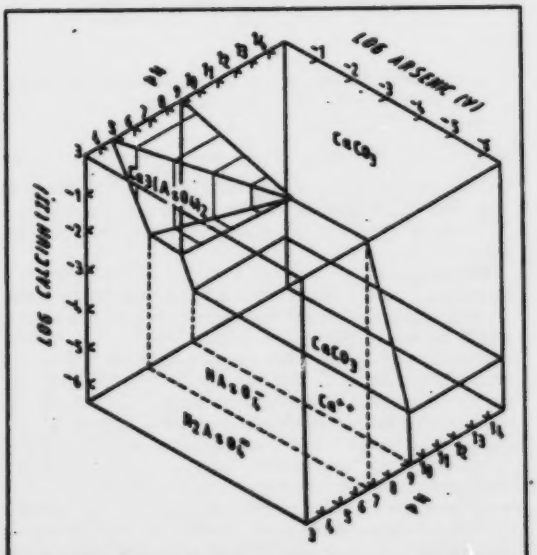

FIGURE 6. The calcium arsenate-carbonate-water system for P_{CO_2} = $10^{-3.52}$ atmospheres.

$Ca^{++} + HCO_3^- = CaCO_3^o + H^+$ ..... (25)

$CaCO_3 = CaCO_3^o$ ..... (26)

$CaHCO_3^+ = CaCO_3^o + H^+$ ..... (27)

The stability diagrams presented here in Figures 3 to 6 show that calcium arsenate is more soluble than is widely accepted, particularly in relation to the treatment of gold processing waste waters. This is substantiated to some extent by experimental solubility determinations[12], but it is obvious that further verification is required. An attempt has been made here to take into account all of the reactions which could influence the solubility of calcium arsenate, and Figures 3-5 are drawn for the case of equal activities of calcium and arsenic. Figure 6 is a three-dimensional diagram showing the effects of calcium and arsenic independently. Only one calcium arsenate, $Ca_3(AsO_4)_2$, is considered in this work, although several other calcium-arsenic (v) compounds have been reported in the literature[13]. It is therefore stressed that the considerations presented here relate to a simple system which in fact may not

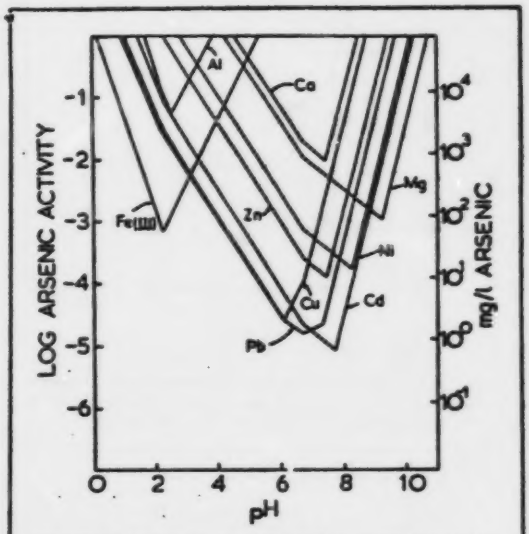

FIGURE 7. Stability regions for metal arsenates in water influenced by carbon dioxide in the atmosphere ($P_{CO_2} = 10^{-3.52}$ ats.).

take into account all of the chemical factors which should be considered in the disposal of arsenic. Also, in the real situation, adsorption and organic complexing are likely to be of importance.

However, if the solubility of a particular metal arsenate is taken as the criterion for stabilization of arsenic residues, then it would appear that certain metal arsenates other than calcium would be more appropriate. Figure 7 shows the stability regions for a number of metal arsenates under the influence of atmospheric carbon dioxide ($p_{CO_2} = 10^{-3.52}$ ats). The comparative insolubility of several arsenates (Pb, Cu, Cd, Ni, Zn) shown here may explain why the disposal of mineral processing arsenical wastes is reasonably effective, and may depend on traces of these metals rather than on calcium. The suggestion[9] that phosphate in the lime system would further help to stabilize arsenic is correct in terms of thermodynamic stability (as well as having experimental support), but there is also the same problem of conversion of phosphate to carbonate under the influence of carbon dioxide in alkaline conditions. There have been other methods proposed by Miyamoto, Suginohara and Yaganase[16,17] for the removal of arsenic from waste waters, but these too would appear to be influenced by the effects of carbon dioxide.

The problem of stabilizing arsenic is one which needs further investigation, initially at the fundamental level of determining experimental solubilities of metal arsenates and as well the possible existence of metal double-salt arsenates. Also, in view of the oxidation stability of arsenic (III), the solubilities of arsenities should be determined. These studies are currently in progress in the laboratories of both of the authors.

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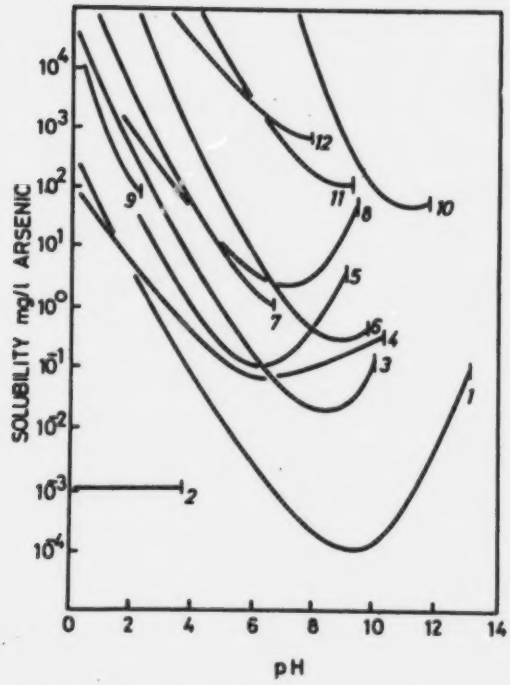

FIGURE 1. THE SOLUBILITY OF VARIOUS ARSENIC COMPOUNDS. The curves indicate the region of pH in which the particular compound is stable.

1. Bn(11)As(V) 2. As_2S_3 3. Fe(11)As(V) 4. Hg(1)As(V)
5. Cr(111)As(V) 6. Ca(11)P(V)/As(V) 7. Pb(11)As(V)
8. Ti(IV)As(V) 9. Fe(111)As(V) 10. $MgNH_4As(V)$
11. Mg(11) As(V) 12. Ca(11)As(V)

Source: ROBINS R.G. (1984)

The Solubility of Barium Arsenate: Sherritt's Barium Arsenate Process

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In August 1980 a paper[1] entitled "The Key Lake Uranium Process" was presented at the 19th Annual Conference of Metallurgists of the Canadian Institute of Mining and Metallurgy at Halifax, Nova Scotia. The pre-printed paper described in detail the extraction of uranium at Key Lake in Northern Saskatchewan and was prepared jointly by authors from Key Lake Mining Corporation and Sherritt Gordon Mines Limited. Part III of the paper covers the area of waste control and by-product recovery and on pages 90-91 is a short section on arsenic removal showing effluent pH and arsenic concentrations after barium chloride addition. It is stated that arsenic is precipitated as barium arsenate according to the equation

$$Ca_3(As\ O_4)_2 + 3\ Ba\ Cl_2 \rightarrow Ba_3(AsO_4)_2 + 3CaCl_2$$

and further that the literature[2] reports barium arsenate as the least soluble arsenate with a solubility product of $8x10^{-51}$ which is significantly lower than those for calcium arsenate (3×10^{-19}) and ferric arsenate (6×10^{-21}). The original source of this data is the work by Chukhlansev[3,4] in 1956, where the solubility of many metal arsenates has been determined.

The Sherritt process for removing arsenic (v) from solution with barium chloride or a soluble barium salt was patented in Canada[5] with a priority date of 22nd August 1980. Similar patents have been granted in other countries including U.S.A.[6], but in Australia, Australian Patent Application No. 73159/81 has not yet been examined.

The Sherritt Patent is obviously based on the solubility data for $Ba_3(As_3O_4)_2$ originating from Chukhlansev's work.

There is other perhaps more readily available data[7] for a range of barium arsenate compounds which originate from Guerin's work[8] published in 1938. The solubility of $BaH\ AsO_4$ reported by Guerin at pH = 7 is five orders of magnitude higher than that which can be obtained by extrapolating Chuklansev's solubility of "$Ba_3(AsO_4)_2$" obtained at pH = 2-3 up to pH = 7. This inconsistency led the author to obtain independent solubility data by mixing solutions of 0.1 M H_3AsO_4 and 0.1 M $Ba(OH)_2$ adjusted to various pH levels with perchloric acid to obtain precipitates of the two arsenates $BaH\ AsO_4$ and $Ba_3(AsO_4)_2$ which were stable over the pH range 5-12. The solutions which remained in contact with the precipitates after several weeks of mixing under an atmosphere of high purity nitrogen (to exclude atmospheric carbon dioxide) were analysed for barium using the barium o-cresolphthalein complexone method and turbidimetric analysis as the sulphate, and arsenic using the silver diethyldithiocarbamate complex in pyridine. The results were consistent with Guerin's data (see Figure 1). All experiments were performed in a laboratory which is controlled at 25°C.

The solubility of the two barium arsenates can be described by the following equations:

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(1) $\underline{Ba\ H\ AsO_4}$

In the pH range 5.0 - 6.76

$Ba\ H\ AsO_4 + H^+ = Ba^{2+} + H_2AsO_4^-$

$pH = 1.22 - \log Ba^{2+} - \log H_2AsO_4^-$

In the pH range 6.76 - 9.3

$Ba\ H\ AsO_4 = Ba^{2+} + H\ As\ O_4^{2-}$

$\log H\ AsO_4^{2-} = -5.54 - \log Ba^{2+}$

(2) $\underline{Ba_3(AsO_4)_2}$

In the pH range 9.3 - 11.6

$Ba_3(As\ O_4)_2 + 2H^+ = 3Ba^{2+} + 2HAsO_4^{2-}$

$pH = 2.60 - \frac{3}{2} \log Ba^{2+} - \log H\ AsO_4^{2-}$

From the above experimental equations the free energies of formation of the two barium arsenate compounds can calculated:

$BaH\ AsO_4$: $\Delta G^o_{f,298.15} = -1307$ kJ

$Ba_3(AsO_4)_2$: $\Delta G^o_{f,298.15} = -2521$ kJ

These compounds are similar to those in the calcium-arsenic (v)- water system which has been studied by Nishimura Tozawa and Robins[9], in which the effect of atmospheric carbon dioxide at pH > 8.1 is to cause decomposition of calcium arsenate to calcium carbonate. This reaction which was predicted by the author[10] has caused some concern about the efficacy of stabilizing arsenical wastes with lime.

In the case of the barium arsenates, it can also be shown theoretically that at pH > 8.3 in the presence of atmospheric carbon dioxide the carbonate will be formed. The author has aerated slurries of $Ba_3(AsO_4)_2$ (pH = 11.6) to prove the reaction

$$Ba_3(AsO_4)_2 + CO_2 + H_2O = BaCO_3 + 2Ba\ H\ AsO_4$$

which drops the pH to 8.3 where the arsenic solubility is about 135 mg/l.

The author has also investigated the magnesium-arsenic (v)-water system and a comparison of the solubilities of calcium, magnesium and barium arsenates is presented in Figure 2. It is obvious from this figure that barium arsenate offers little advantage for removing arsenic as a stable and highly insoluble material.

The Sherritt patent claims the use of barium chloride or a soluble barium salt at a pH of at least 10 but preferably 11 or 12 to precipate arsenic and the removal of the precipitated barium arsenate from solution.

The solubility of barium arsenate, $Ba_3(AsO_4)_2$, in the absence of carbon dioxide is approximately 75 mg/l at pH 10, 40 mg/l at pH 11 and 10 mg/l at pH 12. In the presence of the carbon dioxide in atmospheric air ($p_{CO_2} = 10^{-3.47}$ atmospheres) barium arsenate is unstable above pH 8.3.

It appears that there is no chemical solubility basis for the Sherritt Patent, and that in the Key Lake effluents some other chemical or physical factor apart from the solubility of barium arsenate is responsible for low arsenic levels.

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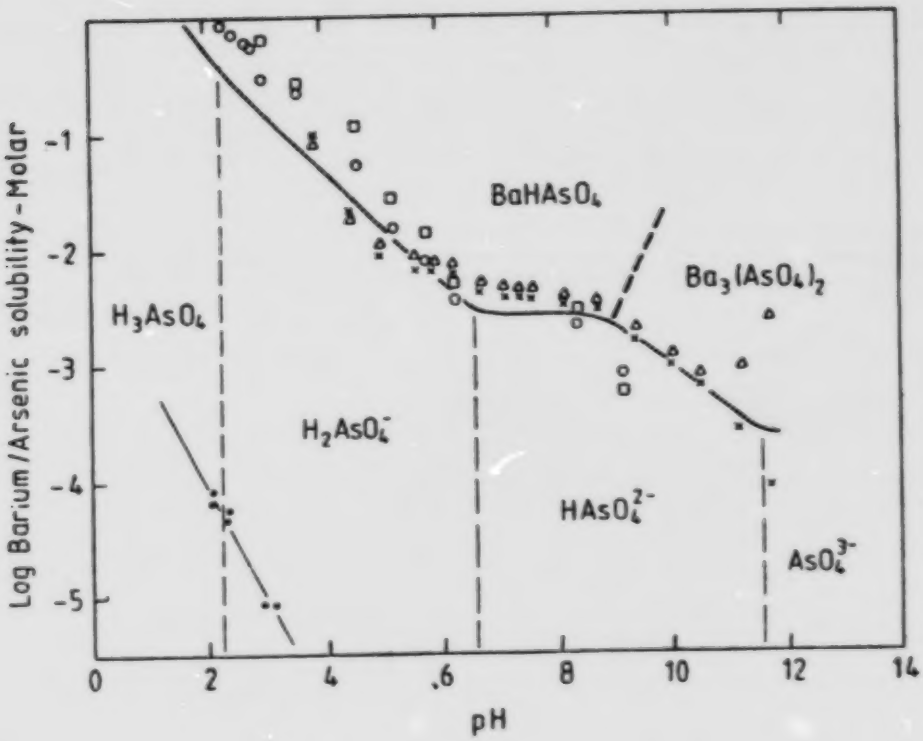

FIGURE 1 THE SOLUBILITY OF BARIUM ARSENATE
(Guerin's results ○ Ba □ As ;
This work △ Ba x As ; Chukhlansev
Ba only determined).

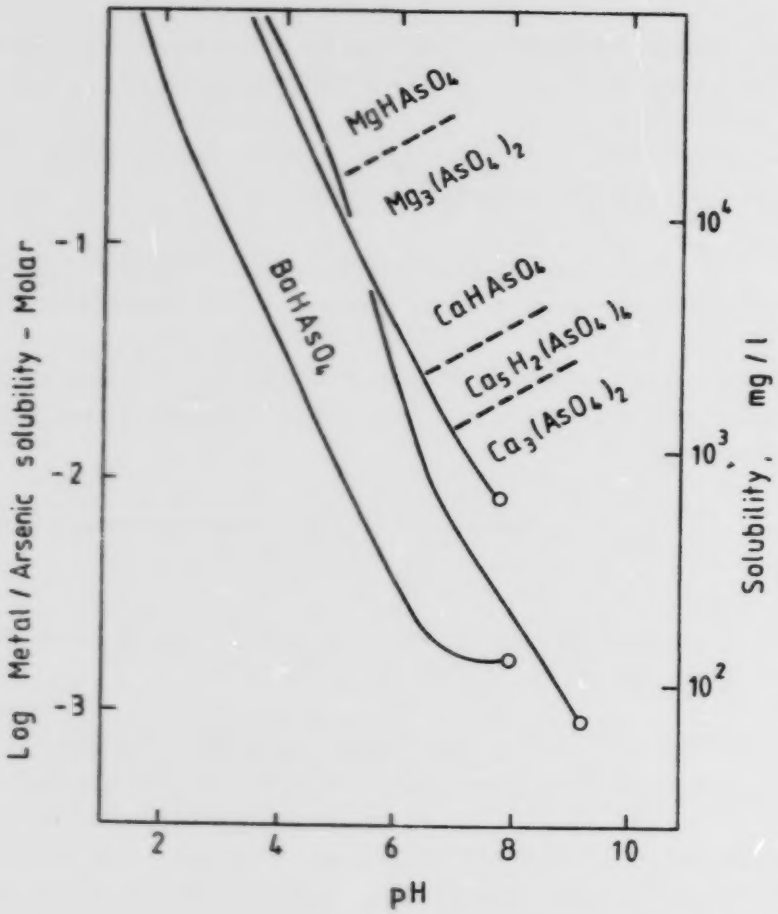

FIGURE 2 A COMPARISON OF THE SOLUBILITIES OF THE CALCIUM, MAGNESIUM AND BARIUM ARSENATES. To the right of the small circle terminating these curves the arsenate is unstable in respect to carbonate which is formed due to carbon dioxide in the atmosphere.

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CHAPTER 30

BARIUM Ba

Barium in solution is acutely toxic to humans and aquatic life.

Fortunately, because barium sulfate has an extremely low solubility in water at all pH's, soluble barium is most unlikely to occur in mine and mill effluents. There is almost always adequate sulfate available in water to quantitatively remove Ba^{+2} from solution to a level of insignificance.

The need to remove Ba from solution was not once encountered. In fact, $BaCl_2$ addition is used as a treatment process for the removal of radium from uranium mine and mill effluents.

CHAPTER 31

BERYLLIUM Be

Beryllium oxide is very toxic to humans when inhaled, and beryl mineral processing plants must use special precautions.

Soluble beryllium is seldom encountered in mine-mill environments and, in this investigation, no cases were encountered where beryllium has to be removed from effluents.

A major source of Be to the aquatic environment is the burning of fossil fuels, especially coal, according to TEPPER (1972).

A source of soluble beryllium would be expected to be effluents from Cu-Be metal alloyers, for example, from beryl processors, or acid mine drainage from beryl quarries in pegmatite belts.

Inadequate information is available on the occurrence of beryllium in water and on its toxicity effects.

Little information was found during this investigation on the technology for beryllium removal from water. The EPA (1981) Treatability Manual reports limited information on Be removal in which sodium carbonate precipitation was able to remove 75% of the Be content of an effluent to between 0.1 and 11 ppb. Combined precipitants were able to remove up to 99% of Be down to the detection limit of Be. Unfortunately, the removal processes are not referenced to be able to find the installation, and no details are provided on how Be was precipitated to make this information more useful than a guide to what process might be tried.

ENVIRONMENT PROTECTION CRITERIA

U.S. EPA (1976) established criteria for total beryllium in fresh water to be 11 ug Be/l for soft water with less than 75 mg/l hardness, and 1,000 ug/l Be for hard water with in excess of 75 mg/l total hardness. Ontario (1978) established the same criteria as EPA (1976).

In marine environments, levels of less than 100 ug/l Be was found to present minimal risk to marine organisms.

Be (ug/L) BERYLLIUM

Summary of North American Water Quality Criteria for Beryllium

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9]	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE				(Recommendations only)							
OBJECTIVE		--	11 (Soft H_2O) 1,110 (hard H_2O)	5.3 (Chronic Effects) 130 (Acute Toxicity)	<11	11 if Hard<75 1,100 if Hard >75	--	--		--	--
MAX. PERMISSIBLE LIMIT		--	--		11*	--	--	--		--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<100 .01 (96-hr LC50)	--	--	<1500	--	--	--		--	--
MAX. PERMISSIBLE LIMIT		1500	--	--	--	--	--	--		--	--
PUBLIC WATER SUPPLY		--	--	0	--	--	--	--		--	--
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	-- No recommendation, only notes	--	--	--	--	--	--		--	--
	IRRIGATION	100	100-all soils 500-alkaline soils	--	100*	100	--	--		--	100

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Environmental Protection Agency Ambient Water Quality Criteria not available for Beryllium, EPA-440/5-80-024.
4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada 1979. Guidelines for Surface Water Quality. Vol.1. Inorganic Chemical Substances, Preamble.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Gouin, B. et Malo, B. 1977. Rapport Technique No. II. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9. British Columbia - Receiving water quality objectives not available.
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

Beryllium has been found to be acutely toxic to aquatic life at concentrations as low as 5.3 ug/l for D. magna. According to the EPA Treatability Manual, Be is chronically and acutely toxic to freshwater aquatic life at 130 and 5.3 ug/l respectively, and some species are expected to be even more sensitive. Hardness has a big effect on toxicity.

For maximum protection of human health from the carcinogenic effects of beryllium in water and contaminated aquatic organisms, the ambient water concentration should be zero based on the non-threshold assumption for Be. Since zero level is not attainable, a criteria in the parts per trillion range has been suggested.

VOGEL (1961) discusses some basic chemistry methods for separating beryllium from solutions on a laboratory scale. It may be precipitated with aqueous ammonia solution in the presence of ammonium chloride or nitrate. The precipitate is gelatinous and has a tendency to adsorb onto glass and may adsorb other species. It may be precipitated together with aluminum hydroxide which it resembles in many respects. Beryllium may also be precipitated as beryllium ammonium phosphate.

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ONTARIO (1978), Ontario Ministry of the Environment, Water Management, November 1978.

TEPPER, L.B., Beryllium in D.H.K., Lee, Ed. (1972). Metallic Contaminants and Human Health, Academic Press.

U.S. EPA (1976) Quality Criteria for Water, Pp21-23.

U.S. EPA (1981) Treatability Manual, September 1981, Volume I.

CHAPTER 33

BORON B

Boron does not appear to be a common problem in mine-mill effluents, and no information was gathered about regulatory criteria for this element or borate BO_3^- ions which is its most common form in nature.

Borates do occur in some western waters and have been observed precipitating from geothermal water springs located just north of Lake Beryessa, California.

HOMESTAKE's NPDES permit for the McLaughlin project states that any discharges shall not cause a statistically significant, incremental increase of more than 10% over upstream levels of the receiving waters for mercury, chromium, cadmium, boron, copper, and nickel. Their permit allows discharge of water from sedimentation ponds installed to remove sediments from collected drainage water from the site. Discharge of process effluent is not permitted for this zero discharge operation.

Information on industrial waste levels of boron and on treatment processes for its removal is scarce. Boron levels up to 5.5 mg/l have been reported in raw sewage by WAGGOTT (1969).

A major source of boron in this wastewater is sodium perborate which is used as a bleach in washing powders.

Fluoborate solutions are also used in plating cadmium, copper, lead, nickel, tin, and zinc according to LOWE (1970) up to 125,000-265,000 mg/l.

REMOVAL OF BORATES AND BORON FROM WATER

PATTERSON (1975) found few techniques for the removal of boron from aqueous solutions. A patented process (DOELDNER, 1970) using VCE does not appear to be very effective in that water recovered from a waste containing 20,000 ppm boron still contained around 50 mg/l B. After passing the water through a 6-foot reflux column, the boron level dropped to 2 ppm.

WAGGOTT (1969) reported the failure of several common water treatment processes to remove boron. The conventional biological waste treatment process has no effect on boron levels in domestic sewage. Lime, aluminum, and ferric sulfate coagulants up to dosages of 400, 100, and 100 mg/l are also ineffective. In one reverse osmosis test reported by PATTERSON (1975) only 10% of the total boron was removed from the wastewater.

WILMOTH, et al. (1979) tested lime neutralization reverse osmosis and ion exchange for their effectiveness in removing ten trace elements from acid mine drainage. Lime neutralization was ineffective in removing boron. Two bed (strong acid-weak base) ion exchange systems were ineffective in removing P and B, but apparently reverse osmosis removed an unspecified amount of Boron.

CRUVER (1973) found that reverse osmosis using a cellulose acetate membrane at pH 5 can remove 38-65% of boron in feedwater. R.O. treatment of brackish groundwater with 0.35 ppm B achieved a level of 0.14 mg/l B in permeate and 0.4 mg/l in the concentrate which works out at 60% rejection rate by the cellulose acetate membrane.

FLETCHER (1971) has described a commercially available solvent extraction reagent from the DOW CHEMICAL CO. which is used for boron extraction from brines, but SX usually would not be economical down to ppm levels in effluent treatment.

MAVIS (1984, personal communication) is aware of only two plants in the world where boron is selectively removed from water by ion exchange. A Rohm and Haas resin is used, and the process is reputedly very expensive. More information may probably be available from:

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James D. Mavis, Jr.

ROHM AND HAAS COMPANY
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Philadelphia, PA 19105
(215) 592-2376
Carl A. Panza
Market Development Manager

PATTERSON (1975) and KUNIN, R., (1973) refer to a Rohm and Haas ion-exchange resin, IRA-943, which is highly selective for the removal of boron as borate and boric acid which is not interfered with by the presence of other inorganic salts. For solutions containing ten mg/l boron, levels down to one mg/l were achieved. Removal efficiency is dependent on the flow rate through the column.

According to CALMON (1974), the 1974 costs of removing boron by ion exchange was $0.12-$0.30/1000 gallons.

MAVIS (1984, personal communication) referred to the increased efficiency of ion exchange removal of boron in the presence of F^- ions, apparently in the form of BF_4.

HOLM AND SIMPSON (1984) describe an acid mine drainage treatment demonstration using the Wannamaker continuous concentrator which is a simplified version of a cross-flow

micro filter in which the solids fraction are recirculated through a porous fire-hose type textile allowing the filtrate to pass through. Although in the treatment of the Argo tunnel and mine drainage described, boron removal is not considered a factor, the developers of the equipment claim that the Wannamaker Continuous Concentrator can be used for the removal of boron from municipal and other water. The people involved decline to divulge details of the equipment but are prepared to act as consultants:

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Camden, SC 29020
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George M. Morris

Similar equipment is marketed by:

NEPTUNE MICROFLOC
Post Office Box 612
1965 Airport Road
Corvallis, OR 97339
(503) 754-7654
Stephen Uban
Director, Research and Technology

MEMTEK CORP.
42 Cummings Park
Woburn, MA 01801
(617) 935-7756
Telex: 949329

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CALMON, C. (1974) Trace Heavy Metal Removal by Ion Exchange In Traces of Heavy Metals in Water-Removal Processes and Monitoring. U.S. EPA - EPA-902/9-74-001.

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CHAPTER 32

BISMUTH Bi

Bismuth is rarely found in minewater or metallurgical solutions. No case was encountered where bismuth is included in the list of metals to be analyzed for and reported in mine-mill effluents; but an exhaustive search was not made.

No data was found on the health effects of bismuth on humans or aquatic species, although the use of Pepto Bismol containing bismuth as a medicine is noted.

No effluent criteria for Bi in fresh or marine effluents were found.

MENNE (1984, personal communication) noted one case where the presence of Bi in a gold ore interfered with carbon absorption of gold from a cyanided pulp. At RIO TINTO's Renco operation in Zimbabwe described by RANDOL (1981). After CIP recovery of gold, a flotation concentrate is recovered containing .26% Cu and 1,000 g Bi/t. Bi absorbed on the carbon surface and depressed the gold absorption characteristics. Nonetheless, the Renco CIP plant has operated very satisfactorily despite the bismuth occurrence.

In RANDOL (1981), a description of the Athens mine of LONRHO in Zimbabwe revealed that they, too, experience a problem with gold absorption from the cyanided leach pulp with gold recoveries of only 60-85% and barrens solution of around 1 ppm in tailings pulp. It is noted that bismuth occurs in the ore which is dissolved, absorbed on carbon, desorbed, and also partially removed from the steel wool cathodes by washing. The cathode acid solution contained 1,000 ppm Bi. It is surmized that bismuth may be the cause of the carbon absorption problem experienced by LONRHO at Athens.

It is concluded that not enough information is available on health and environmental effects or on the metallurgical effects of bismuth when it occurs in metallurgical solutions.

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RANDOL (1981) MULTI-CLIENT STUDY, "Innovations in Gold & Silver Recovery," RANDOL INTERNATIONAL LTD., Golden, Colorado.

CHAPTER 34

CADMIUM Cd

Introduction of Cadmium to the Environment 2040

- List of Sites Where Cd Was Produced in the U.S.A. 2041
- PEDCo Survey: Summary of Cd in Mine-Mill Effluents (U.S.A.) 2043

Regulatory Effluent Limits - Cadmium 2045

Process for Removal of Cadmium 2049

- Cadmium in Mineral Processing Effluents - Summary Table 2050
- Theoretical Solubilities: Hydroxide 2054
  - Carbonate 2054
  - Sulfide 2054
- Effect of Carbonate on Cd Solubility 2056
- PERMUTIT Sulfex Process 2057
- INCO Metals, Sudbury, Lime Precipitation 2057
- Starch Xanthate Cd Removal 2057
- Chelation Cd Recovery, Devoe-Holbein 2059
- Magnesium Oxide Precipitation 2060
- Ion Exchange 2060
- Magnesium Carbonate Process 2061
- Natural Biological Systems 2065

Case Studies: 2065

- AMAX - Mount Emmons 2065
- ARCO Tunnel AMD 2066
- BOLIDEN Metall, Skellefteå, Sweden 2067
- Canadian Lead Smelter B 2069
- Eastern Canada Cu-Pb-Zn Mine B 2070
- COTTER CORPORATION, Schwartzwalder Mine 2071
- EXXON MINERALS, Crandon Project, Wisconsin 2072
- RAND MINES ERPM, South Africa 2072

- References 2073

Cadmium is one of the greater nuisances environmentally for mine-mill operators. It is toxic to humans and to aquatic life at very low levels and is mobile. Regulatory criteria in the U.S.A. and Canada for fresh water discharge at no more than 0.2 ug/l Cd are both difficult to attain and difficult to determine analytically. The environmental justification for such a low-level limit for Cd is controversial. An important observation is that effective filtration is a necessary polishing step to achieve 1 ppb Cd levels.

INTRODUCTION OF CADMIUM TO THE ENVIRONMENT

Potential sources of Cd in wastewaters include metallurgical alloying, ceramics manufacture, electroplating, inorganic pigments, textile printing, and mine drainage according to McKEE and WOLF (1963), SANTIANELLO (1971), and PATTERSON (1975). Reported instances of high concentrations of cadmium in plating wastes and mine drainage were levels of 1,000 ug Cd/l were found by McKEE and WOLF (1963) and of 440-100 ug Cd/l by LARSEN, et al. (1973).

FULKERSON and GOELLER, Eds., (1973) prepared a massive document under a National Science Foundation RANN program grant as part of the Oak Ridge National Laboratory - NSF Environmental Program titled "Cadmium - The Dissipated Element" which provides copious data on cadmium and its environmental effects including a map of the U.S.A. showing zinc-cadmium producing facilities.

There are no known mines which produce Cd as the primary product. Cadmium frequently occurs with zinc, lead, and copper ore deposits as a minor constituent and is concentrated with these metals in the sulfide flotation process. In the treatment of these concentrates, cadmium is volatilized in the roasting and sintering steps and is further concentrated in fluedusts, particularly if these are recycled in the process. Prior to the need to clean stack gases, cadmium would be widely distributed around smelter and refinery sites as a result of fallout from stack gases from such facilities. Seepage from accumulated piles of pyrometallurgical plant residues to the inevitable nearby stream presents(ed) one pathway for cadmium to enter receiving waters.

In modern base metal smelters and refineries, the main pathway appears to be through liquid effluents from the process and plant runoff after appropriate treatment, and the introduction of Cd to aqueous environment from this source has been greatly reduced. Recycling of water, however, can result in increased Cd levels in effluent bleeds.

In the U.S.A., several abandoned or no longer operating zinc mine and refinery sites have been designated superfund sites because of metal (including Cd) leakages to nearby streams.

CHAPTER 33

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Stephen Uban
Director, Research and Technology

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(617) 935-7756
Telex: 949329

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List of Sites Where Cd Was Produced in the U.S.A.

(1968 Data: How Things Have Changed Since Then)

Table IV-22. Summary of U.S. Zinc and Cadmium Producers (refs. 20,30)

Rank in primary zinc output	Company	Type plant (see map)	Location	Map designation	Primary cadmium producer
1	St. Joseph Lead Co.*	ET	Josephtown, Pa.	1	X
		SF	Herculaneum, Mo.	17	
2	New Jersey Zinc Co.*	VR	Palmerton, Pa.	2	X
		VR	Depue, Ill.	3	X
3	American Smelting & Refining Co.	HR	Amarillo, Tex.	4	
		E	Corpus Christi, Tex.	5	X
		SF	Selby, Calif	18	
		SF	El Paso, Tex.	19	
		CD	Denver, Colo.	22	X
		SS	Bockemeyer, Ill.	(1)	
		SS	Sand Springs, Okla.	(2)	
		SS	Trenton, N.J.	(3)	
4	The Anaconda Co.	E	Anaconda, Mont.	6	
		E	Great Falls, Mont.	7	X
		SF	E. Helena, Mont.	20	
5	American Zinc Co. of Illinois*	E	E. St. Louis, Ill.	8	X
		HR	Dumas, Tex.	9	
		SS	Hillsboro, Ill.	(4)	
6	The Bunker Hill Co.	E	Kellog, Ida.	10	X
7	Blackwell Zinc Co.	HR	Blackwell, Okla.	11	X
8	The Eagle Pitcher Company*	HR	Henryetta, Okla.	12	
		CD	Galena, Kansas	23	X
9	National Zinc Co.	HR	Bartlesville, Okla.	13	X
10	Matthiessen & Hegler Zinc Co.	VR	Meadowbrook, W. Va.	15	X
	Sherwin Williams Co.	CD	Coffeyville, Kan.	24	X
	Apex Smelting Co.	SS	Chicago, Ill.	(5)	
	Acro Die Cast Metals Co.	SS	Detroit, Mich.	(6)	
	W. J. Bullock, Inc.	SS	Fairfield, Ala.	(7)	
	General Smelting Co.	SS	Bristol, Pa.	(8)	
	Gulf Reduction Co.	SS	Houston, Tex	(9)	
	H. Kramer Co.	SS	El Segundo, Calif.	(10)	
	Pacific Smelting Co.	SS	Torrance, Calif.	(11)	
	Sandoval Zinc Co.	SS	Sandoval, Ill.	(12)	
	Superior Zinc Co.	SS	Bristol, Pa.	(13)	
	Wheeling Steel Corp.	SS	Martins Ferry, Ohio	(14)	
	Arkansas Metals Co.	CS	Jonesboro, Ark.	(15)	
	United Refining & Smelting Co.	CS	Chicago, Ill.	(16)	

*These companies also produce major quantities of zinc pigments and compounds directly from ore at eight plants.

Table IV-21. Major Zinc Producing Mines and Their Affiliated Companies (refs. 20, 30)

Company	Mine	Rank in zinc prod.	Location (county, state)	Type ore
St. Joseph Lead Co.	Balmat	1	St. Lawrence, N.Y.	Zn
	Edwards	10	St. Lawrence, N.Y.	Zn
	Fletcher	24	Reynolds, Mo.	Pb
The New Jersey Zinc Co.	Friedensville	2	Lehigh, Pa.	Zn
	Sterling Hill	3	Sussex, N.J.	Zn
	Eagle	5	Eagle, Colo.	Zn, Ag
	Austinville	8	Wythe, Va.	Zn
	Jefferson City	11	Jefferson, Tenn.	Zn
	Flat Gap	16	Hancock, Tenn.	Zn
	Elmo No. 1	23	Grant, Wisconsin	Zn
American Smelting & Refining Co.	Page	22	Shoshone, Idaho	Pb, Zn
American Zinc Co.	Young	4	Jefferson, Tenn.	Zn
	Mascot No. 2	15	Knox, Tenn.	Zn
	Calhoun	19	Stevens, Wash.	Zn
	Immel	21	Knox, Tenn.	Zn
The Bunker Hill Co.	Bunker Hill	6	Shoshone, Ida.	Pb-Zn, Zn
The Eagle Pitcher Co.	Shullsburg	17	Lafayette, Wisc.	Zn
United States Steel Corp.	Zinc Mine Works	7	Jefferson, Tenn.	Zn
New Market Zinc Co.	New Market	9	Jefferson, Tenn.	Zn
Hecla Mining Co.	Star-Morning	12	Shoshone, Idaho	Pb-Zn
Idarado Mining Co.	Idarado	13	Ouray and San Miguel, Colorado	Cu-Pb-Zn
U.S. Smelting, Refining & Mining Co.	U.S. and Lark	14	Salt Lake, Utah	Pb-Zn
Kennecott Copper Co.	Burgin	18	Utah, Utah	Pb-Zn
Tennessee Copper Co.	Copper Hill	20	Polk, Tenn.	Cu-Zn
Ozark-Mahoning Co.	Deardorff	25	Hardin and Pope, Ill.	F-Zn

ORNL DWG 71-13240

Fig. IV-5. Location of U.S. Deposits of Lead, Lead-Zinc and Zinc-Lead Ore.

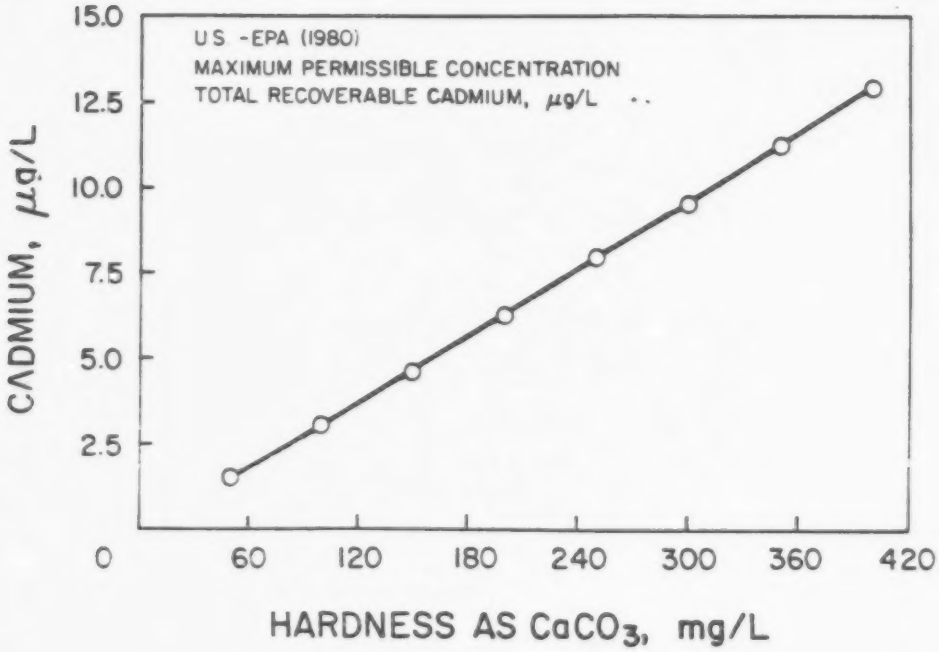
PEDCO (1983) CADMIUM DATA (ug/g or mg/l)

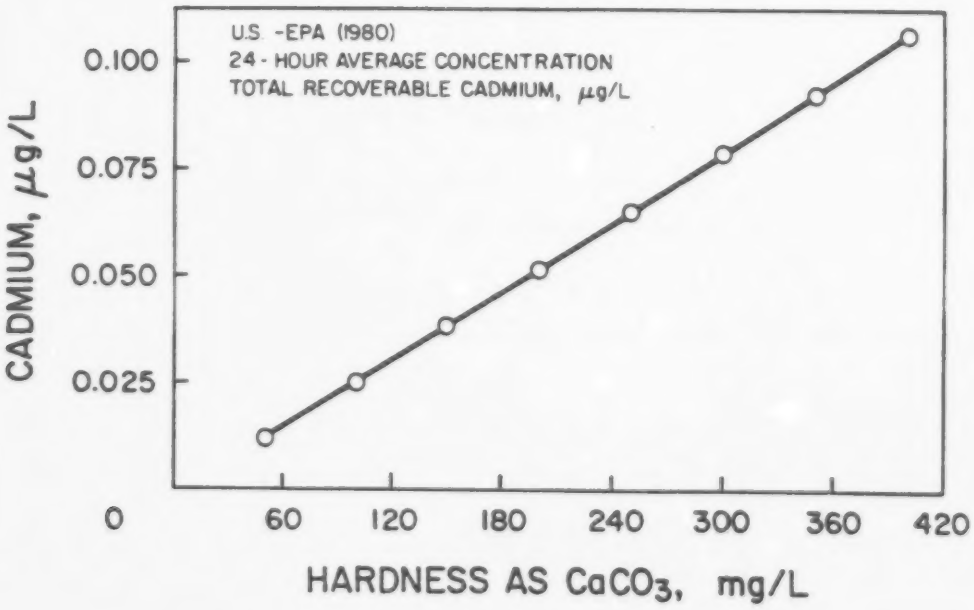
	Untreated Minewater	Mine-water Pond Liquid	Minewater Pond Solids: Pond Solids	Minewater Pond Solids: EP Leachite	Tailings Pond Liquid	Low Grade Ore: Solids	Low Grade Ore: EP Leachite	Waste Rock: Solids	Waste Rock: EP Leach	Tailings Pond Solids: Solids	Tailings Pond Solids: EP Leach	Pregnant Heap Leach Liquor
Uranium, New Mexico												
Mine No. 12		LT0.010	LT10.03	LT0.01		LT10.030	LT0.01					
Mine No. 14		LT0.010	LT10.03	LT0.01		LT10.030	LT0.01					
Mine No. 15	LT0.008	LT0.010	LT10.03	LT0.008				LT10.030	LT0.01			
Uranium, Other												
Mine No. 20	LT0.0840	LT0.008	LT10.03	LT0.040								
Phosphate, Florida												
Mine No. 1			LT10.03	0.010	LT0.040			LT10.03	LT0.01			
Mine No. 2	LT0.008				0.0660			LT10.03	LT0.01	LT10.030	LT0.008	
Phosphate, Idaho												
Mine No. 5					LT0.0080			LT10.03	LT0.0015	65.390	0.430	
Mine No. 6					0.0480			13.590	0.170			
Copper, Southwest USA												
Mine No. 28					LT0.0100	LT10.030	LT0.008	LT10.030	0.011	LT10.030	LT0.008	
Mine No. 29					0.032			LT10.030	LT0.008			
Mine No. 30											LT0.008	
Mine No. 31					0.190			LT10.03	LT0.008	LT10.030	LT0.010	1.715
Lead-Zinc-West												
Mine No. 34	0.190				LT0.008			LT10.03	LT0.008	LT10.03	LT0.008	
Mine No. 35						LT10.030	LT.008	LT10.03	0.088	LT10.03	LT0.010	
Mine No. 37		0.240			4.100			LT250.66	0.40	LT10.03	0.031	
Mine No. 38		LT0.040			LT0.040					LT10.03	.0390	
Mine No. 39		0.170			0.014							

PEDCO (1983) CADMIUM DATA (ug/g or mg/l)

	Untreated Minewater	Mine-water Pond Liquid	Minewater Pond Solids: Pond Solids	Minewater Pond Solids: EP Leachite	Tailings Pond Liquid	Low Grade Ore: Solids	Low Grade Ore: EP Leachite	Waste Rock: Solids	Waste Rock: EP Leach	Tailings Pond Solids: Solids	Tailings Pond Solids: EP Leach	Pregnant Heap Leach Liquor
Lead-Zinc-East												
Mine No. 40		LT0.010	LT0.030	LT10.040	LT0.010					LT10.03	LT0.040	
Mine No. 41	LT0.010				LT0.008					LT10.03	0.0120	
Mine No. 42	LT0.010									10.490	0.0240	
Mine No. 43	LT0.010	LT0.008	LT250.66	0.013	LT0.010			LT250.66	0.090	LT10.03	LT0.008	
Lead-Zinc-Missouri												
Mine No. 45		LT0.008			LT0.008					LT10.03	LT0.040	
Mine No. 46			17.890	0.023	LT0.008			25.110	0.058	LT10.03	0.012	
Molybdenum												
Mine No. 49	0.430				LT0.008	LT10.030	LT0.008			LT10.03	LT0.008	
Mine No. 50	LT0.008	LT0.008	LT10.030	LT0.008	LT0.008					LT10.03	LT0.008	
Nevada Gold/Silver												
Mine No. 52					0.045	LT10.030	LT0.010	LT10.03	LT0.008	LT10.03	0.008	
Mine No. 54						LT10.030	LT0.010	LT10.03	LT0.010	LT10.03	LT0.0265	
Gold-Silver, Other												
Mine No. 55		LT0.008			LT0.008			LT10.030	LT0.040	LT250.660	LT0.008	
Mine No. 56		LT0.073				LT250.66	0.087	13.280	0.098	LT10.030	0.190	
Mine No. 57					LT0.003	LT10.030	LT0.008	LT10.030	LT0.008	LT250.660	0.360	

CADMIUM


U.S. -EPA (1980)
MAXIMUM PERMISSIBLE CONCENTRATION
TOTAL RECOVERABLE CADMIUM, µg/L
CADMIUM, µg/L
15.0
12.5
10.0
7.5
5.0
2.5
0
60
120
180
240
300
360
420
HARDNESS AS CaCO3, mg/L


U.S. -EPA (1980)
24 - HOUR AVERAGE CONCENTRATION
TOTAL RECOVERABLE CADMIUM, µg/L
CADMIUM, µg/L
0.100
0.075
0.050
0.025
0
60
120
180
240
300
360
420
HARDNESS AS CaCO3, mg/L

Compiled by NORANDA

Cd (ug/L) CADMIUM

Summary of North American Water Quality Criteria for Cadmium

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	--	24-hr mean (1.05 (ln (hard))-8.53)	0.2	<0.2	N.D. - .4	--	10 - 100	--	--
MAX. PERMISSIBLE LIMIT		30 hard>100 mg/L 4 hard<100 mg/L	.4-4 if hard 0-75 1.2-12 if hard 150-300	(1.05 (ln (hard))-3.73)	--	0.2	.2 - 30	10	--	10	10 (hard >100) 4 (hard <100)
PROTECTION OF MARINE LIFE											
OBJECTIVE		<.2 or .01 (96-hr LC50)	5.0	24-hr mean 4.5	<5.0*	--	--	--	10 - 100	--	--
MAX. PERMISSIBLE LIMIT		<10	--	59.0	5.0*	--	--	--	--	--	--
PUBLIC WATER SUPPLY		10	10	10	10	10	N.D. (obj) 10 (limit)	(10)	--	10	10
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	50	(10)	--	20	50	--	(10)	--	--	50
	IRRIGATION	10	(10)	--	10	10	--	(10)	--	--	10

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Cadmium, EPA 440/5-80-025.
4. Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada. 1979. Guidelines for Surface Water Quality. Vol. I. Inorganic Chemical Substances, Cadmium.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Couin, D. et Melo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'Etude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9. British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries.
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

CADMIUM

Acid mine drainage from numerous abandoned base metal mines and tailings impoundments represents a source of uncontrolled Cd loss to the environment.

During this investigation, it was found that some base metal mines, mills, and refineries "do not have" Cd associated with their effluents. Others clearly do, yet have the cadmium situation under such tight control that it does not appear on their list of elements analyzed in their effluent monitoring program. The following table shows a summary of Cd in effluents before and after treatment as encountered in this investigation (see trip reports in Appendix I) and reported in the literature. A second table is provided which summarizes the PEDCO (1984) data on analyses in mine and mill waste materials in the U.S.A.

An interesting aspect of the PEDCo report is that very few of the mine and mill tailings and solutions had cadmium in excess of detection limits of the analysis methods used. The acetic acid EP leach test leaches very little cadmium from mineral wastes that contain cadmium as can be noted in the table summary.

Tailings pond liquid ranged from 4.1 mg/l and 0.190 mg/l Cd for a lead zinc mine (No. 37) and copper mine (No. 31) to less than 0.008 mg/l which was the level often found. In only one case did tailings pond liquid exceed 1 ppm, and in only two cases did it exceed 0.10 ppm. Similarly, untreated minewater was all less than 0.010 mg/l except one molybdenum mine effluent at 0.43 ppm Cd and one lead zinc mine at 0.19 ppm.

Surprisingly, one Idaho phosphate mine (No. 5) had 65.390 ppm Cd in the tailings settled solids which yielded the highest EP leach test result of 0.43 ppm--all the other EP leach tests of settled tailings solids were less than 0.040 ug/g.

Based on the PEDCo data, it would be concluded that cadmium rarely occurs in significant quantities in mine-mill operations and is likely to be located around smelters and roasting plants if at all. The locations of major lead, zinc-lead, and lead-zinc ores as at 1972, i.e., shown in the diagram, bearing in mind that many of these operations have shut down since then due to contraction of the U.S. base metal mining and refining industry. It is around these locations, however, that cadmium may possibly occur in effluents.

REGULATORY EFFLUENT LIMITS - CADMIUM

Regulatory limits for Cd in effluents vary considerably and are controversial in that proposed levels and objectives are very much lower than what is actually enforced in permits of operating mines.

The U.S. EPA (1980) objective and maximum permissible limit for Cd are considerably more lenient for hard water than for soft water as shown in the graph below from the

U.S. EPA (1980). In fact, the EPA 1980 criteria and maximum allowable is a logarithmic function of hardness. In 1984, New York state was proposing to enforce a standard of cadmium on similar lines which involves more than simple mathematics to determine.

Cd Max. = Exp (1.16 [ln hardness ppm] - 6.14)

This works out at follows:

Hardness	50	100	200 mg/l
Maximum Cd Allowed	0.2	0.45	20 mg/l

Persuant to Section 304(a) (1) of the Federal Clean Water Act, the U.S. EPA developed water quality criteria for Cd. For freshwater aquatic life, the total recoverable cadmium criterion is given by e(1.05[ln(hardness)]-8.53) as a 24-hour average with a maximum at any time of e(1.05[ln hardness]-3.73).

This works out as follows in mg Cd/l in ppb (ug/l):

Hardness As $CaCO_3$ mg/l	Total Recoverable 24-Hours	Total Recoverable Grab
50	0.12	1.5
100	0.025	3.0
200	0.051	6.3

In seawater, the criterion developed by the EPA to protect saltwater aquatic life is 4.5 ug/l as the 24-hour average, and 59 ug/l not to be exceeded at any time.

The existing drinking water standard for Cd is 10 ug/l (0.010 ppm Cd) according to 45 Federal Register No. 231 (1980).

South African law makes no provision for cadmium removal from effluents to be discharged as specified in the South African Government Gazette (1962).

According to PRODUCTS FINISHING (1983), the 1984 requirement for electroplating effluents is 1.2 mg/l Cd as a daily maximum. This is clearly markedly less strict that proposed for mining and metallurgical effluents under RCRA.

	Daily Max. (mg/l)	30d Ave. (mg/l)
HOMESTAKE McLaughlin Project NPDES Permit 9/83	0.02	0.01
Waite-Amulet Reclaimed Tailings, Quebec Order No. 19	0.50	0.50

	CADMIUM	
	Daily Max. (mg/l)	30d Ave. (mg/l)
Brunswick Mining, New Brunswick	0.05	0.05
Brunswick Smelting, New Brunswick	0.05	0.05
COTTER CORP. Schwarzwalder, Colo. NPDS	0.0004	0.0004
ARCO Tunnel AMD, Colorado, Colo. Proposed	0.002	0.002

PROCESSES FOR REMOVAL OF CADMIUM

Cadmium removal from effluents is achieved in much the same way as other base metals such as copper, lead, zinc, nickel, etc., i.e. by precipitation processes. Since cadmium is most unlikely to occur on its own in mining and mineral processing effluents, it will usually be removed in the same process as other related metals and end up in the same sludge.

There are two aspects of cadmium removal to be borne in mind. First, the levels likely to be required in dischargable effluents are much lower than for the other metals. For cadmium, levels of around 1-2 ppb and even into the parts per trillion range are talked about as being required to avoid environmental damage. This requirement is controversial, and although hopefully the ultimate needs will prove to be more reasonable, nonetheless the lowest possible levels in this range are being called for at this time.

Secondly, when cadmium is precipitated as a hydroxide, the precipitate is fluffy and somewhat more difficult to settle than most metal hydroxides.

Theoretical solubilities of hydroxides and sulfides of selected metals as presented in the EPA Treatability Manual (1982) are shown below. According to this table, cadmium is the least soluble of the metal hydroxides. As opposed to lead and zinc, the hydroxide is less soluble than the carbonate as well. Cadmium sulfide is very much less soluble than the hydroxide at 6×10^{-10}.

The wellknown curve of metal concentration versus pH shows that cadmium only starts to precipitate above pH 8 reaching a level of less than 0.1 ppm Cd only around pH 10.8 and above. To achieve minimum cadmium levels, the pH must increase to a level at which zinc will have started to increase again.

According to the EPA Treatability Manual which reviews contaminant removal from non-mining effluents, cadmium can be reduced by lime precipitation followed by settling to 0.05-0.10 ppm, and to 0.01-0.10 by sulfide precipitation followed by filtration. The EPA Treatability Manual (1982) also states that organic ligands of biological origin may affect the solubility and adsorption of cadmium.

CADMIUM IN MINERAL PROCESSING EFFLUENTS

Operation	Ref.	Type of Operation	Effluent Flow Rate (m^3/d)	Cd in Effluent: Before Treatment (ppm)	Cd in Effluent: After Treatment (ppm)	Regulatory Discharge Limit (ppm Max.)	Treatment Process	Treatment Plant Sludge Cd (% Solids, % Cd)	Disposal of Sludge	Comment
1. SMELTING	RANDOL (1985)	Lead Smelter								
Surface Drainage				1.0						
Sewage				0.5						
Recycled Process Water Bleed				100.0		0.05 (1)		1-5% Solids	To Sinter Plant	Some Cd escapes in suspended solids in thickener o/f.
Combined Wastewater			170 m^3/h	0.5-50	0.06-4.0	0.50 (2)	Lime, Settle	2-3% Cd		
2.	RANDOL (1985)	Cn-Pb-Zn Mine & Mill								
N Mine Water Treatment Plant Effluent (1983)				2.30	0.04		Lime, Settle in Pond		Settle in Pond	Lamella Thickener failed due to scaling.
Tailings Pond Influent				0.21						
Railings Pond Reclaim					0.04					
Sludge Pond Overflow					0.08					
Final Effluent					0.06	0.05 (1)				
River Water (Receiving)					0.01-0.03	0.50 (2)				
3. COTTER CORPORATION Schwarzwalder Mine	PALMER et al. (1984)	U-Minewater	500 U.S. gpm	0.002	0.0004	0.004	Downflow IX		High Uranium Eluate to Mill	Unique new CIX system.

(1) Environment Canada: Metal Mining Liquid Effluent Regulations.
(2) Environment : Max. Permissable for Water with Hardness Less than 250 mg/l (as $CaCO_3$).

Operation	Ref.	Type of Operation	Effluent Flow Rate (m^3/d)	Cd in Effluent: Before Treatment (ppm)	Cd in Effluent: After Treatment (ppm)	Regulatory Discharge Limit (ppm Max.)	Treatment Process	Treatment Plant Sludge Cd (% Solids, % Cd)	Disposal of Sludge	Comment
4. BOLIDEN AB Sweden	BLYTHE et al. (1981)	Cu-Pb Smelter		3/16	0.02-0.06	N/A	$S^{=}$ Precipitation	N/A	N/A	Sulfite-Sulfide reaction noted; consumes sulfide to generate S^{0} & Thiosulfate.
5. AMAX, Mt. Emmons, Colorado	RANDOL (1985)	Zinc Mine Tailings Seepage & AMD	200-2,000 U.S. gpm	0.40-0.70	0.001	Not Stated	Lime Precipitation Lectro-flotation	N/A	Beltpress Dewatering & Cement Stabilization	Dissolved air flotation may be more economical.
6. ARGO Tunnel Test Colorado	HOLM & SIMPSON (1981)	AMD	Demo	0.29	0.005	0.002 Proposed	NaOH Precip. & Filtration	N/A	N/A	Potentially low capital cost process--the Wannamaker Continuous Concentrator.
7. GILMAN MINE Colorado	RANDOL (1985)	AMD	90-300 gpm	0.15	LT0.003	0.002 Proposed	Lime Settle	N/A	Underground Workings & Tailings Pond	
8. NORANDA, WAITE AMULET	RANDOL (1985)	AMD	800 Igpm	0.034	LT0.005	0.50	Lime HDS	N/A	Dewater to Stable Sludge	Eventually discard on tailings area.
9. SUPERIOR MINING STIBNITE Idaho	STOTIS (1985)	Cyanide Neutralization Pond	Pond		0.016	N/A	Cyanide Fill by U_2	None	None	Solution used to add Cl_2 to heaps & is discharged at end of season.
10. LEAD MINE U.S.A.		Tailings Decant	N/A	0.008	0.002	0.002	Natural Marsh Polishing	None Recovered	Stays in Marsh	Natural system.

Operation	Ref.	Type of Operation	Effluent Flow Rate (m^3/d)	Cd in Effluent: Before Treatment (ppm)	Cd in Effluent: After Treatment (ppm)	Regulatory Discharge Limit (ppm Max.)	Treatment Process	Treatment Plant Sludge Cd (% Solids, % Cd)	Disposal of Sludge	Comment
11. ST. JOE MINERALS Monaca, PA	RANDOL (1985)	Zn Plant Effluent	1200 gpm	2.40	0.19	0.40	Lime Settle Filter	10% Zn 1% Cd	Recycle to Plant	New regulations will severely cut allowed Cd discharge.
12. RAND MINES ERPM Brakpan	RANDOL (1985)	AMD	5 m^3/d Pilot	0.02	0.005	N/A	Slurry Seeded Reverse Osmosis Desalination	0.06 ppm Cd Mainly Gypsum	N/A	Aim of Desalination is removal of TDS. Cd reduction is incidental.

Data shown in the EPA Treatability Manual (1982) refers to the SORG, et al. (1977) report that cadmium can be much more effectively removed by adding ferric sulfate as a coagulant achieving almost total removal from an 0.3 ppm solution at pH 9.0.

Cadmium forms complexes with numerous ligands, and the formation constants for these complexes is shown below as extracted from FULKERSON and GOELLER (1973).

Although the hydroxide solubility shows a cadmium concentration decreasing with pH up to pH 11.5 or so, the following graph from FULKERSON and GOELLER (1973) shows that if carbonate ions are present, then cadmium has a minimum solubility at pH 9.5 of 10^{-3} mg/l.

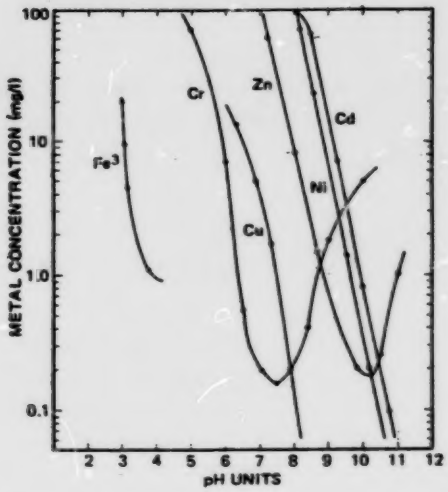
The presence of complexing agents clearly will have a marked effect on the degree to which cadmium can be removed by straightforward hydroxide precipitation. Ammonia, if present as in the effluent from ST JOE's zinc refinary at Monaca, will inhibit the precipitation of cadmium.

Cadmium sulfide, on the other hand, has such a low solubility at 10^{-10} that undoubtably this precipitate would be more stable than cyanide complexes, and precipitation to lower levels would be achievable.

PATTERSON (1975) also mentions that cadmium removal methods in use in industry are typically hydroxide or sulfide precipitation and ion exchange. He points out that cadmium is valuable enough that where waste streams are concentrated enough, electrolysis and evaporation may be viable. PATTERSON shows the results of cadmium removal by various processes which were able to reduce Cd down to 1.0 ppm to 0.70 ppb. Sulfide precipitation in the one reported case dropped Cd to 0.008 mg/l from an effluent containing 440-1000 ppm. Most interesting is the reported removal of Cd to 0.0007 ppm by hydroxide precipitation at pH 11 by CULP and CULP (1974) which is remarkable. the CULPS are principals in one of the most highly respected water treatment consulting engineering firms in the U.S.A. It was pointed out that changing the pH from 8 to 11 makes all the difference in cadmium precipitation, dropping the Cd in solution from 1 ppm to 0.00075 ppm. (This may have been a misprint, however.)

CULP and CULP (1974) also point out that co-precipitation with alum also effectively reduces the residual Cd, Zn, and Ni in solution when hydroxide precipitation is used.

MARUYAMA, et al. (1972) reported that cadmium is reasonably effectively co-precipitated with iron at pH 6. Results were obtained as follows:



Precipitation of metal salts versus pH

TABLE 3.1.3-1. THEORETICAL SOLUBILITIES OF HYDROXIDES AND SULFIDES OF SELECTED METALS IN PURE WATER [3-12]

Metal	Solubility of metal ion, mg/L: As hydroxide	As carbonate	As sulfide
Cadmium (Cd^{++})	2.3×10^{-5}	1.0×10^{-4}	6.7×10^{-18}
Chromium (Cr^{+++})	8.4×10^{-4}		No precipitate
Cobalt (Co^{++})	2.2×10^{-1}		1.0×10^{-8}
Copper (Cu^{++})	2.2×10^{-2}		5.8×10^{-18}
Iron (Fe^{++})	8.9×10^{-1}		3.4×10^{-5}
Lead (Pb^{++})	2.1	7.0×10^{-3}	3.8×10^{-9}
Manganese (Mn^{++})	1.2		2.1×10^{-3}
Mercury (Hg^{++})	3.9×10^{-4}	3.9×10^{-2}	9.0×10^{-28}
Nickel (Ni^{++})	6.9×10^{-3}	1.9×10^{-1}	6.9×10^{-8}
Silver (Ag^{+})	13.3	2.1×10^{-1}	7.4×10^{-12}
Tin (Sn^{++})	1.1×10^{-4}		3.8×10^{-8}
Zinc (Zn^{++})	1.1	7.0×10^{-4}	2.3×10^{-7}

TABLE 3.1.3-2. ESTIMATED ACHIEVABLE MAXIMUM 30-DAY AVERAGES FOR THE APPLIED TECHNOLOGIES [3-4]

	FINAL CONCENTRATIONS (mg/L)					
	Lime ppt. followed by filtration	Lime ppt. followed by filtration	Sulfide ppt. followed by filtration	Ferrite coprecipitation followed by filtration	Soda ash addition followed by sedimentation	Soda ash addition followed by filtration
Antimony, Sb	0.8-1.5	0.4-0.8				
Arsenic, As	0.5-1.0	0.5-1.0	0.05-0.1			
Beryllium, Be	0.1-0.5	0.01-0.1				
Cadmium, Cd	0.1-0.5	0.05-0.1	0.01-0.1	<0.05		
Copper, Cu	0.05-1.0	0.4-0.7	0.05-0.5	<0.05		
Chromium, Cr(+3)	0.8-0.5	0.05-0.5		0.01		
Lead, Pb	0.3-1.6	0.05-0.6	0.05-0.4	- 0.20	0.4-0.8	0.1-0.6
Mercury, Hg(+2)			0.01-0.05	<0.01		
Nickel, Ni	0.2-1.5	0.1-0.5	0.05-0.5			
Silver, Ag	0.4-0.8	0.2-0.4	0.05-0.2			
Selenium, Se	0.2-1.0	0.1-0.5				
Thallium, Tl	0.2-1.0	0.1-0.5				
Zinc, Zn	0.5-1.5	0.4-1.2	0.02-1.2	0.02-0.5		

Table III-4. Stepwise Formation Constants of Various Cadmium Complexes[a]

Ligand L	$\frac{[CdL]}{[Cd^{2+}][L]}$	$\frac{[CdL_2]}{[CdL][L]}$	$\frac{[CdL_3]}{[CdL_2][L]}$	$\frac{[CdL_4]}{[CdL_3][L]}$
Cyanide, CN^-	300,000	140,000	36,000	4000
Pyrophosphate, $P_2O_7^{4-}$	10,000	200		
Hydroxide, OH^-	8,500	(1000)	(180)	22
Ammonia, NH_3	550	150	30	10
Sulfate, SO_4^{2-}	130			
Iodide, I^-	120	5.9	140	30
Nitrite, NO_2^-	63	16	6	
Bromide, Br^-	57	4	10	2
Chloride, Cl^-	35	5	1	
Fluoride, F^-	3			

[a]All values are from Ref. 9 and, except for the case of sulfate, were determined in 2 to 3 molar salt solutions. The sulfate value refers to very dilute solutions, and as a result is somewhat higher than it otherwise would be. Electric charges are omitted in the formulae shown for the complexes.

Of the ligands shown above, the most important are cyanide (CN^-), hydroxide (OH^-), ammonia (NH_3), and chloride (Cl^-). Cyanide, ammonia and hydroxide complexes are relatively stable and form in a number of industrial or natural aqueous systems. Chloride complexes, while relatively much less stable, are important because chloride concentrations can be high in many aqueous systems. The distribution of the various complexes of Cd^{2+} formed by these ligands is shown as a function of the free ligand concentration in Fig. III-4.

The hydroxyl complexes are especially important because OH^- ion is always present in water, and its concentration can vary over a wide range as a result of the water dissociation equilibrium

$$H_2O \rightleftarrows H^+ + OH^-$$

$$K_w = [H^+][OH^-] = 10^{-14} \text{ moles}^2/\text{liter}^2 .$$

Hydroxyl complexes are formed by most metal cations in the periodic table. However, in many cases their identity and stability have been difficult to establish for two reasons: (1) the extent of their formation in solution is usually limited by the precipitation of the metal hydroxide, and (2) in addition to complexes containing only one metal ion, of the sort considered thus far, polymeric species, $M_x(OH)_y$, are often formed, the presence of which greatly complicates the interpretation of the experimental measurements.

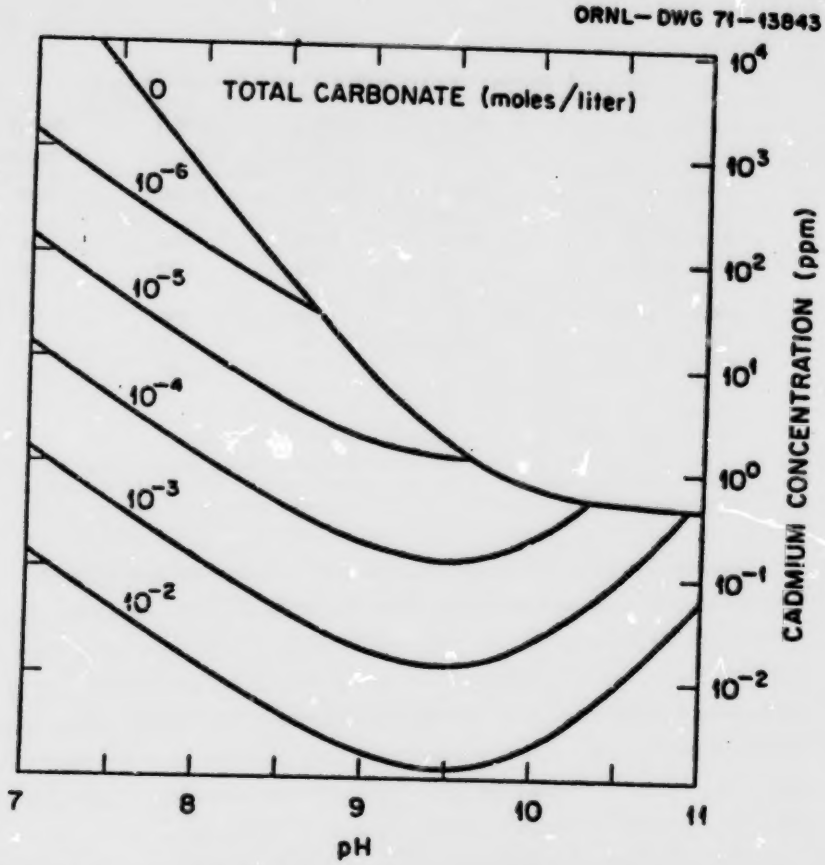


Fig. III-6. The Solubility of Cadmium vs pH and vs Total Carbonate Concentration. For zero carbonate, the solid is cadmium hydroxide [$Cd(OH)_2$]. For the other curves it is cadmium carbonate ($CdCO_3$).

Source: FULKERSON and COELLER (1973)

Precipitation Chemical Addition	Effluent*
45 mg/l Fe as $FeSO_4$ at pH 6	0.05 mg/l Cd
20 mg/l Fe as $FeSO_4$ plus 260 mg/l lime, pH 10.0	0.044 mg/l Cd
0 mg/l Fe plus 600 mg/l lime, pH 11.5	0.014 mg/l Cd

* After flocculation, settling, mixed media separation, and activated carbon columns.

It was reported in ENVIRON SCI. TECHNOLOGY (1971) that DuPont's patented Kastone process for oxidation-precipitation of metals from cyanide solution by peroxide addition precipitates cadmium as oxide while decomposing cyanide. It was claimed that the Cd oxide precipitate is easier to remove than cadmium hydroxide.

PATTERSON (1975) refers to two applications of sulfide precipitation of cadmium including one in acid mine drainage (LARSEN, et al., 1973).

SHIMOIIZAKA (1972) describes one method of removing cadmium using xanthate and describes a method to recover xanthate from cadmium xanthate.

The PERMUTIT COMPANY in their promotional literature describes the Sulfex process which employs freshly prepared iron sulfide in a sludge blanket contactor. More information on this patented process is available from:

PERMUTIT COMPANY,INC.
Post Office Box 355
Paramus, NJ 07652
(201) 564-6000
Telex: 134-488
Robert V. Nagiel
Product Manager

The PERMUTIT COMPANY was contacted, and it appears that their experience in the application of the Sulfex process is limited to relatively small streams such as plating wastes. PERMUTIT has developed a sludge blanket clarifier device to optimize the Sulfex process and avoid the possibility of excess sulfide ion concentrations in solution.

SHIMOIIZAKA and MATSUOKA (1975) reviewed the precipitation of cadmium and arsenic with $CaCO_3$ and $Ca(OH)_3$. The effects of coexisting ferrous/ferric ions on the precipitation of Cd^{2+}, AsO_3^{3-}, and $As_2O_3^{3-}$ and the oxidation of ferrous ions with air, bacteria, and oxidants in the presence of a catalyst were reviewed.

INCO METALS, INC., according to Butler (1984, personal communication) on applying lime precipitation and settling, achieves an effluent from their Copper Cliff water treatment plant at Sudbury of less than 0.002 ppm Cd which is remarkable for a process that does not employ filtration or one of the more exotic precipitation chemistries. Confirmation and more information could be requested from:

INCO METALS LTD.
Ontario Division
Copper Cliff, Ontario POMINO
(705) 682-8341
Bob Butler
Environmenal Control Manager

STARCH XANTHATE REMOVAL OF Cd

WING, et al. (1974) showed that starch xanthate could remove Cd from a 56.2 mg/l solution at pH 3.1 down to 0.008 mg/l as compared with precipitation by addition of

hydroxides to 29,600 and 4,500 ppb at pH 7 and 9 respectively. WING, et al. (1974) showed that at the optimum pH of 6.7, the Ksp for metal ethyl xanthate was 2.6×10^{-14}.

Later in their paper, WING, et al. (1974) showed that cadmium in a solution containing 10 ppb Cd could be reduced to 2 ppb using starch xanthate PVBTMAC. A second solution was dropped from 29 ppb to 11 ppb. PVBTMAC is added at 1 ml to 50 ml of sample solution and starch xanthate with 0.23 degree of substitution to obtain maximum flocculation. PVBTMAC (poly-vinyl benzyltrimethyl ammonium chloride) is a cationic co-precipitant. Robert Wing is employed at:

CEREAL PRODUCTS LABORATORY
Northern Regional Reseach Lab
Agricultural Research Service
U.S. Dept. of Agriculture
Peoria, Illinois

WING, et al. (1974) describe the principles of using starch xanthate for effluent treatment in which the SH^- and $S^=$ groups are attached to insoluble starch molecules. They indicate that this method of heavy metal ion removal for polishing has several advantages:

- Recovery of the adsorbant is simple. Treating the polyelectrolyte complex with mild acid releases the metal and regenerates the starch xanthate.
- The volume of sludge is small compared with that from lime treatment.
- The physical nature of the sludge is not gelatinous as is usual with basic precipitation, and the floc settles faster and can be removed more easily by filtration, centrifuging, or settling.
- In some effluents, suspended solids have to be removed before treatment; this is not necessary with the xanthate method.
- Careful control of pH is necessary when heavy metals are precipitated with a base because some metallic hydroxides will redissolve if the pH is too high. The starch xanthate method is claimed to be effective over the pH range 3 to 11.
- Several chemical treatments require a large excess of reagent to get the heavy metal levels down. In the xanthate method, only a slight excess of reagent is necessary.
- A single treatment will remove most metals to very low levels equivalent to sulfide precipitation.

The cationic polymer PVBTMAC is, or was, available from DOW CHEMICAL COMPANY, Midland, Michigan, as Product No. Experimental Resin ZX-2611.F. Insoluble starch xanthate is also produced and marketed by:

POLLUTION TECHNOLOGY SYSTEMS, INC.
3015 Benton Street
Garland, TX 75042
(214) 272-4010
Mile Coward
Manager-Systems Engineering

POLLUTION TECHNOLOGY SYSTEMS' insoluble starch xanthate ISX/5-CM is applied at a ratio 12.0:1 ISX to Cd by weight.

No data on any particular applications of this product was obtained, nor on the cost of the material or process.

CHELATION RECOVERY

POLLUTION TECHNOLOGY SYSTEMS, INC. offers a product known as DX-2000 which is a buffered organic material that effectively precipitates complexed or chelated cationic heavy metals of 10 mg/l or greater from difficult-to-treat industrial process waters effective over a pH range of 3-11. 155 grams of Cd^{+2} can be removed per liter DX-2000. No case histories were available on its use, however. More information is available from POLLUTION TECHNOLOGY SYSTEMS, INC., Garland, Texas; contact: Mike Coward.

Another company that has devoted an enormous effort to removal of low levels of metals from solution is DEVOE-HOLBEIN, INC. A paper by HOLBEIN, et al. (____) was included in Chapter 25 on Removal of Contaminants, and more information is available from:

DEVOE-HOLBEIN (CANADA), INC.
175 Bouchard Blvd.
Dorval, Quebec H95 1A9
Canada
(514) 636-6042
Dr. Bruce E. Holbein
Dr. L. G. Neirink

One DEVOE-HOLBEIN formulation, DH-516, was able to remove Cd from an inflow concentration of less than 1 ppb which is a truly remarkable achievement even though the nature of the test or the test solution was not described.

Although the cost of the formulation in laboratory scale quantities is very high, the developers envisage that should a large market develop, the cost of mass-produced material would be reasonable--how reasonable is anybody's guess. Some of the compositions are extremely selective, too. Another demonstrated advantage is the ability

to regenerate the composition in may cases quantitatively in only one bed volume of 2NHCl.

In a full scale test using a 140 l-composition column operating on influent with 2500 ppm Cd effluent ran 0.01 ppm. About 80% of the composition-bound Cd would be displaced in 0.15-bed volumes of regenerant and 100% in two-bed volumes.

Although little is as yet known about the economics and applicability of the DEVOE-HOLBEIN processes and compositions, this frontier technology quite clearly has some very special aspects and is of considerable importance in future metals removal.

MAGNESIUM OXIDE PRECIPITATION

BLACK, et al. (1974) describe the tests of a process in which about 40 mg/l of magnesium precipitated as a carbonate in water containing 0.36 ppm Cd could be reduced by 99% to 0.01 ppm Cd in solution. On filtration, the cadmium concentration was dropped to 0.005 ppm or less.

The tests were carried out at the Montgomery Water and Sanitary Sewer Board, Post Office Box 1631, Montgomery, Alabama, and the report is available from NTIS as PB-241 884, EPA-660/2-75-006. Magnesium carbonate and CO_2 are recycled.

The development and demonstration of the recyclable magnesium carbonate water treatment process was carried out by:

BLACK, CROW AND EIDSNESS, INC.
777 South Lawrence Street
Mongomery, Alabama
A. P. Black
C. G. Thompson

This process has been employed on a commercial scale at Montgomery, Alabama, and in Ohio for municipal water treatment, but none has been found on mining or mineral processing effluents.

ION EXCHANGE

Ion exchange resins are available that are metal specific, but such processes and systems for large flows are invariably expensive and require a fair degree of expertise to operate and maintain.

In the case of Cd, except where there is enough Cd for profitable recovery as a product, selective removal of Cd is unlikely to be needed; more likely, removal of all toxic metals

PLANT SCALE STUDIES OF THE MAGNESIUM CARBONATE WATER TREATMENT PROCESS

A. P. Black, et al

Black, Crow and Eidsness, Incorporated

TABLE 11. USE OF CHLORINE TO REDUCE ORGANIC COLOR

Chlorine (mg/l)	Original Color (Pt-Co)	Residual Color (after 60 minutes)	% Removal
50	647	202	69
100	616	103	83
150	591	63	90
200	566	55	91
250	544	53	91

CADMIUM STUDY

The effectiveness of this new process in the removal of heavy metals was studied in both jar tests and in the pilot plant. Cadmium was chosen because of its easy and accurate determination by atomic adsorption as well as for the fact that it would likely be solubilized at a pH of 7.0, the pH of sludge carbonation. The results of jar tests are shown in Tables 12, 13 and 14.

TABLE 12. EFFECTIVENESS OF ALUM IN REMOVING CADMIUM

Alum Dosage (ppm)	Cadmium Residual (mg/l)
5	1.04
7	1.09
9	1.09
11	1.10
13	1.07

Initial cadmium level - 1.1 mg/l
Comments - Good floc formed in all jars

TABLE 13. EFFECTIVENESS OF LIME IN REMOVING CADMIUM FROM WATER IN JAR TESTS[a]

Lime Dosage (ppm)	pH	Cadmium Residual (mg/l)
40	10.65	0.73
50	10.70	0.81
60	10.95	0.72
80	11.10	0.71
100	11.25	0.60
120	11.30	0.60

[a]1.0 mg/l cadmium present in raw water.

TABLE 14. EFFECTIVENESS OF MAGNESIUM HYDROXIDE IN REMOVING CADMIUM FROM WATER IN JAR TESTS

Magnesium Precipitated (mg/l)	Cadmium Residual (mg/l)	% Removal
2.9	.36	58
7.5	.15	82
13.4	.05	94
21.4	.02	98
31.4	.01	99
42.2	.01	99

Reagent grade cadmium chloride was used as a source of cadmium in all studies. Samples taken after settling were filtered through Whatman #40 paper prior to analysis. Unfiltered samples taken during the study reported in Table 15 showed similar removals.

During pilot plant studies cadmium chloride was added continously to the raw water for a period of ten days. The magnesium and lime dosage was 40 and 100 mg/l respectively. The raw water cadmium level ranged from 0.75 to 1.0 mg/l. The settled water ranged from 0.003 to 0.007 mg/l and the filtered water ranged from 0.000 to 0.005 mg/l of cadmium. Table 14 summarizes the analytical results.

Cadmium was not released in any appreciable amounts on carbonation regardless of the pH to which carbonation was carried. A pH range of 6.0 to 7.7 generally resulted in a cadmium concentration of 0.1 mg/l or less in the recycled magnesium bicarbonate solution.

FILTRATION STUDIES

Two identical 1.5 square foot pilot filters with continuous turbidity monitoring equipment were made available to the project by the Taulman Company, Atlanta, Georgia. Combinations of sand and various sized anthracite media were evaluated as to water quality produced and operating characteristics. Initial studies compared the filterability of the alum treated water, piped from the full scale plant, with the stabilized magnesium treated water. Later studies were made using the proper stabilization pH, type media, and depths of sand anthracite required.

These studies allowed the following conclusions:

1) Filtration efficiency is directly related to

TABLE 15. PILOT PLANT RESULTS - CADMIUM STUDY
(Cadmium concentration - ppm mg/l)

Date/ Time	Raw Water	Carbonate Sludge	Clarified Water	Filtered Water
7/20:				
1400	0.92	--	--	--
1600	0.75	--	--	--
7/21:				
0930	0.94	--	0.005	0.005
1300	1.00	--	0.007	0.00[illegible]
1510	0.78	--	0.003	0.00[illegible]
7/25:				
1300	0.80	--	0.030	0.00
1500	0.81	--	0.030	0.00
1610	0.82	--	--	0.00
7/26:				
0830	0.55	0.12	0.030	0.00
1320	0.60	--	0.060	0.003
1530	--	0.12	--	0.005
7/27:				
0930	0.87	0.14	0.060	--
1415	--	0.16	0.050	--
1540	0.90	0.10	0.030	--
7/28	--	0.05	--	--

coagulation and clarification efficiency for both the alum and magnesium process. When proper pretreatment has not been accomplished, filtration will not provide adequate treatment.

2) The carryover of calcium carbonate will not shorten filter runs or reduce the quality of the filtered water.

3) In Montgomery, filtration of waters which had not been stabilized below pH 9.0 resulted in calcium carbonate precipitation on the anthracite and sand media. Precipitation occurred more rapidly and extensively on the sand. Extremely short filter runs were obtained under these conditions and the calcium carbonate formed could not be washed from the filter. These "balls" gradually worked their way into the gravel underdrain, eventually requiring acidification treatment of the filter. These studies provided a severe warning as to the necessity of adequately maintaining the proper stabilization pH in full scale operation.

4) Maximum filter runs were obtained with four inches of 1.2 mm anthracite media over twenty-four inches of standard filter sand. Increase in anthracite media depth did not increase filter performance either in length of filter run or water quality produced.

5) In general, two filter rates were studied, 2 and 3.5 gal./sq.ft./min. The higher rate on the average produced a slightly better water quality. It appeared that backwash requirements were essentially the same, based on percentage of the water produced during the run.

6) The geometry of the pilot filters was such that backwashing was not equivalent to the full scale filters. Side wall friction was considerably higher, resulting in an unusual backwash pattern. Considerable care was required to prevent backwashing of media from the system. Backwash rates of 15 gal./sq.ft./min were not possible, so that some of the calcium found on the media could possibly have been removed at higher backwash rates.

7) Finished water stabilization appears to enhance filtration efficiency. Clarifier turbidity carryover serves as a nucleus for calcium carbonate precipitation, enlarging the particle size and changing the chemical-physical properties, increasing the opportunity for removal by filtration.

8) Calcium carbonate carryover to the filters does not shorten filter runs and can be easily removed on backwash. Calcium carbonate precipitation on the filter media drastically shortens filter runs and cannot be removed efficiently by backwashing.

MONTGOMERY FULL SCALE STUDIES

From November 1972 until June 1973 full scale evaluation of the Magnesium Process was conducted in Montgomery. The Magnesium Process was found to compare favorably with the alum process in both overall operation and water quality produced.

During the study voluminous data were collected at many points of the process. Figure 16 illustrates a summary of process control points and a brief discussion as to

at a low cost is needed and if possible, without the need to change the pH of the water being treated more than necessary.

NATURAL BIOLOGICAL SYSTEMS

WIXSON describes a successful biological system in a meander arrangement built into an effluent stream at AMAX-HOMESTAKE's Buick Mine-Mill in the New Lead Belt of Missouri. Heavy metals are very effectively removed from the effluent in this polishing step as well as organic flotation reagents. In this case, algae grow prolifically in the meandor system. More details are provided in Chapter 25.

ST. JOE MINERALS at Edwards, New York, also finds that an effluent decanted from their Edwards tailing pond is polished on passing through a natural marsh area to below 1 ppb Cd as discussed in chapters 24 and 25.

Individuals with a particular interest and achievement in this field include:

PROFESSOR BOBBY G. WIXSON
Director and Professor of Environmental Health
Center for International Programs and Studies
University of Missouri - Rolla
Rolla, MO 65401
(314) 341-4208/4483

ST. JOE MINERALS CORP.
Balmat, New York 13609
(315) 287-2500
J. G. Reilly

Randol International Ltd. believes that passive, natural biological polishing eco-systems, as well as the field of bacterial metal removal systems, are important avenues for future development work.

When sulfite is present in water, sulfide consumption can be excessive at low pH before metals will precipitate. This may be one way that natural biological polishing can be inhibited, i.e., if the effluent contains thiosulfates or sulfite and where biological reduction of sulfate to sulfide is part of the polishing process. However, it appears that very low Cd levels can be achieved through effective removal of very small hydroxide particles by filtration, which would occur in a marsh with dense vegetation.

AMAX MOLYBDENUM DIVISION, MOUNT EMMONS, COLORADO

AMAX stabilized the site of the old Keystone Zinc Mine and mill outside Crested Butte, Colorado. This entailed a $1.9 million program to stabilize and recontour old tailings dams and a further $10.9 million for a state of the art (1981) water treatment plant with a

capacity of 2,000 U.S. gpm to treat collected seepage and acid mine drainage containing, Fe, Zn, Mn, Ca, Cd, and Pb.

The plant is located at 11,000 feet, and one of the parameters is low water temperature, close to 0°C for many months of the year, which makes coagulation of precipitates more difficult.

The plant employs electrocoagulation and Swift (now Dravo) Lectroclear flotation for recovery of the precipitate followed by filtration of the effluent and beltpress dewatering of the precipitate sludge to 12% solids and cement stabilization as described in Appendix I.

Cadmium levels are reduced from 0.42-0.70 ppm to 0.001 ppm in the polished effluent. This clearly demonstrates the effectiveness of sand-filtration in reducing suspended Cd hydroxide as a polishing step.

Based on pilot scale tests by AMAX, dissolved air flotation was found to work as well as Lectroclear flotation and would be less costly to install and operate for a new installation.

There are undoubtably less costly ways of treating AMD in flows comparable to Mt. Emmons. Lectroclear flotation was selected here before AMD treatment processes had all been tested and at the time, this process was the only one that had been demonstrated in comparable conditions when a decision had to be made.

ARGO TUNNEL ACID MINE DRAINAGE

Acid mine drainage from the Argo Tunnel, Idaho Springs, Colorado, contains iron, copper, lead, maganese, nickel, zinc, and cadmium in excess of proposed water quality standards. Cadmium levels range between 0.23-0.29 ppm, and the proposed water standard is shown by HOLM and SIMPSON (1981) as 0.002 ppm.

HOLM and SIMPSON (1981) whose paper is included in the chapter on Acid Mine Drainage Treatment, describe a test installation of the Wannamaker continuous concentrator which incorporates the principles of sludge recycling, NaOH precipitation, and crossflow filtration to yield a dense slurry.

When adjusted to pH 9.2, cadmium was dropped to .04 mg/l from feed at 0.29 mg/l. This does not meet the proposed water standard of 0.002 ppm but is very low nonetheless. Most other metals were reduced to below the proposed water quality standard.

The Wannamaker Continuous Concentrator has not been used on a commercial scale, but since a unit capable of treating 80 gpm would cost around $5,000, it would appear that

for $100,000, a system capable of treating 1,600 gpm could be installed. The units are, however, not commercially available although other larger capacity cross-flow micro filtration units are available from other suppliers.

More information on the ARGO tunnel test is available in HOLM and SIMPSON (1981) and from:

J. DAVID HOLM
Colorado Bureau of Natural Resources
Bureau of Land Reclamation
1313 Sherman, #423
Denver, CO 80203
(303) 866-3567

W. W. (BILL) WANNAMAKER
Post Office Box 1121
Camden, SC 29020
(800) 845-2202

Information on a commercial scale crossflow filtration device that could possibly be used in the place of the Wannamaker Continuous Concentrator could be designed around a system offered by:

NEPTUNE MICROFLOC
Post Office Box 612
1965 Airport Road
Corvallis, OR 97339
(503) 754-7654

In order to reduce the Cd level further to below 0.002 ppm, RANDOL INTERNATIONAL LTD. proposes that the following be tested:

1. Add freshly prepared FeS to the recirculating slurry in the cross flow filtration unit with pH adjustment as before.

2. Set up the cross flow filtration system in a sludge recycle HDS mode with lime addition as opposed to NaOH and some FeS for polishing. This would require an additional tank for sludge/lime premixing.

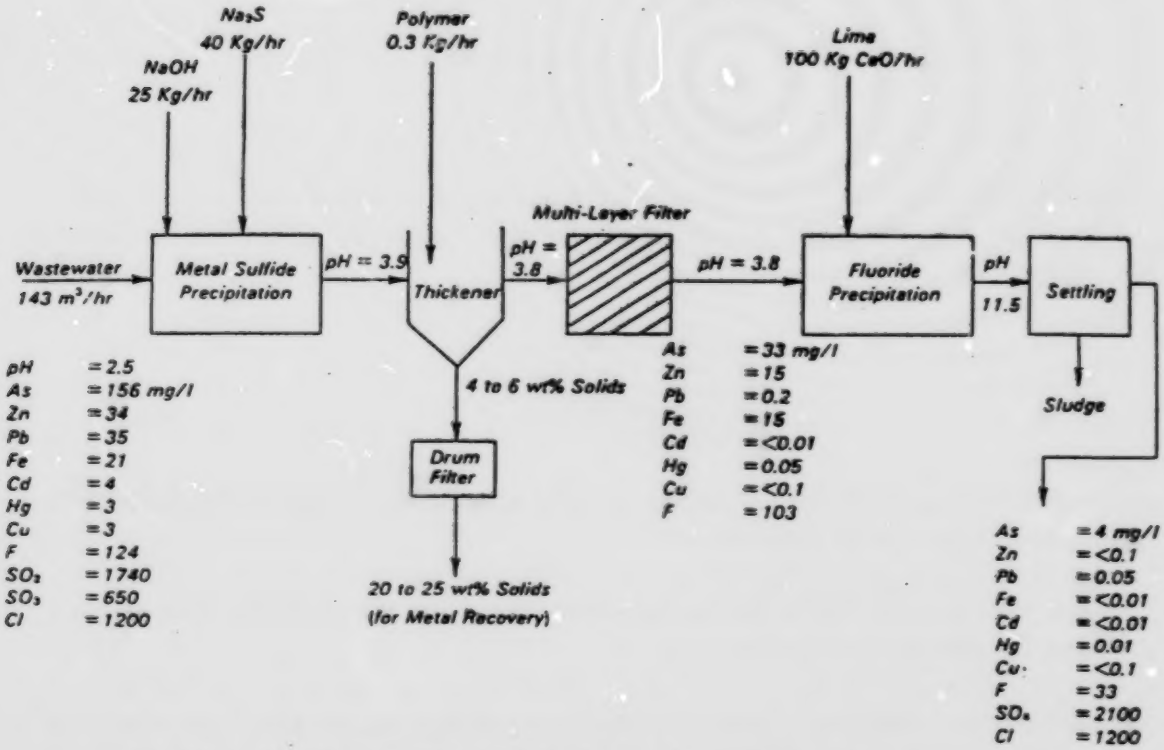
No known tests of the above have ever been carried out.

BOLIDEN AB, SKELLEFTHAM

Boliden AB, at its copper smelter and metallurgical complex, Skellefteå, applies sulfide precipitation at several points in the plant for metal removal. One effluent treated has the following composition:

These metals are effectively removed by adding Na_2S. Because arsenic sulfide As_2S_3 is insoluble only at low pH, around 3, they have to use a six-step process.

1. Precipitaton of As_2S_3 and other metals, pH 3.9.
2. Anionic polymer addition.
3. Sedimentation.
4. Multimedia filtration at pH 3.8.
5. Lime addition to pH 11.5.
6. CaF_2 sedimentation and decant.



Typical residual metal concentrations obtained by full-scale test run (Boliden Metall).

Because of the presence of arsenic and the need to operate at a low pH, sulfide reacts with SO_2 or $SO_3^{=}$ present in solution. This consumes excess $S^{=}$ which is expensive. (At higher pH, the reaction is minimal so operating at high pH 6-8 is preferable when arsenic is not present.)

At BOLIDEN, solutions contain $SO_3^{=}$, so considerable amounts of S^{o} and $S_2O_3^{=}$ are generated. Sulfur is collected with the metal sulfide precipitates. According to BLYTHE, et al. (1981), treated solutions with 0.02-0.06 ppm Cd are achieved.

BOLIDEN was stockpiling the recovered sulfide sludges with a view to possible future metal value recovery by hydrometallurgy.

According to BHATTACHARYYA (1985, personal communication), the generation of H_2S that could be expected has not been a problem at this plant.

More information can be obtained in the more detailed EPA Report PB81-209-272 by SCHWITZGEBEL, et al. (1981) and from:

BHATTACHARYYA, D.
Dept. of Chemical Engineering
University of Kentucky
773 Anderson Hall
Lexington, KY 40506-0046
(606) 257-2794

BOLIDEN METALL AB
Skellefteham,
Sweden
Rolf Sevedberg

BOLIDEN built a commercial scale plant to treat 800,000 gpd 3600 m^3/d process effluent and collected runoff. Runoff contains arsenic in this case. From a metals removal point of view, the process works well. BOLIDEN uses a pH meter to control sulfide addition. There is an abrupt pH change as soon as $S^=$ is in excess.

LEAD SMELTER B, EASTERN CANADA

Cadmium contamination of seawater in a harbour on the Atlantic seaboard was recognized as a result of earlier discharges from a lead smelter and refinery in Canada, as described by BEWERS, et al. (1984) and DUGDALE and HUMMEL (1977), which manifested itself in lobsters with elevated Cd content.

This contamination was greatly reduced by segregating effluents which contain Cd from those that do not and by diverting unaffected runoff waters from the plantsite. Recycling of slag granulation water reduced the volume of water affected, and dry disposal of slag at a remote site prevented leachate from the slag from reaching the ocean. At 140 m^3/h (design), the effluent treatment plant was installed employing lime neutralization and settling to treat all effluents before discharge to the ocean as described in Appendix I.

The Cd and As levels in recycled water have risen steadily since the program was instituted, and the effluent treatment plant discharge runs between 0.06-40 ppm Cd which sometimes exceeds the 0.5 ppm design, mainly due to underdesign of the clarifier and lack of a polishing filter shown to be essential above in achieving the very low levels required.

Sludges containing 2-3% Cd, up to 13% As, 5-10% Zn, and 1% pb at 1-5% solids are recycled to the sinter plant in the hope that these metals will ultimately end up in a stabilized form in the lead smelter slag or in a Cd fluedust which is sold to a cadmium producer. It is possible that generating a high density sludge, which could be removed from the system and stabilized for disposal or would have a much higher Cd content for shipment, might possibly be considered for similar applications.

Design capital and operating cost for the water management and treatment program instituted in 1980/81 was C$427,000 and C$245/day respectively.

However, the above information was obtained from reliable sources and is an important illustration of what is required to achieve low Cd levels as well as results when no polishing filter is installed. The identity of the operation is, after all, of secondary importance. Please bear in mind that this report is submitted to you on a confidential basis.

Cu-Pb-Zn Mine-Mill B

A large mine-mill-concentrator complex shown in Appendix I as Mine-Mill B is located in eastern Canada. Treated minewater and tailings decant in excess of that which can be recycled to the process are discharged to streams that are part of an important salmon fishery.

Cd levels in the AMD and tailings decant are not very high at 0.21-2.30 ppm Cd and drop to around 0.04-0.06 ppm in the final effluent which, after dilution, results in a Cd level of 0.01-0.03 mg/l Cd in the riverwater.

The operation uses straightforward lime neutralization for treatment of their minewater and tailings pond decant solutions. Lime adjusted effluents were previously clarified in a lamella thickener which had to be abandoned in 1984 due to severe scaling problems. Settling in an aging pond has been applied. However, until the wall of the aging pond could be raised to provide the additional capacity needed, decanted effluent overflowing from this pond ran 0.23 ppm Cd which is in excess of effluent limit of 0.05 ppm Cd.

It is believed that this operation has simpliflied its flotation circuit arrangement which reputedly will allow the use of close to 100% water recycle, which will allow them to reduce the volume of effluent to be discharged. However, at the time of the visit, this was still in the development stages and premature for discussion. Of interest in the Appendix I report is the high cost of effluent treatment at this operation where lime precipitation and settling costs between C$0.60-C$1.83/m^3.

COTTER CORPORATION - SCHWARZWALDER MINE

This uranium mine is located in the front range of the Rockies at Golden, Colorado, some 125 miles away from the mill that processes the ore. Mine drainage, although neutral pH, contains uranium and radium which must be removed from solution before the excess water can be discarded to a stream. It also contains 0.002 mg/l Cd. In the unique continuous fixed bed ion exchange system employed to remove uranium and described by PALMER, et al. (1984), cadmium levels are reduced from 0.002 to 0.0004 mg/l indicating an effective cadmium polishing step--albeit from an already very low level but still not quite achieving the EPA criteria considered safe for aqueous organisms. In this case, the eluate contains concentrated uranium values which are shipped to the mill for precipitation. The minute quantities of cadmium in the eluate ultimately ends up in the Cotter Mill process water sand tailings.

EXXON MINERALS COMPANY, CRANDON, WISCONSIN, PROJECT

EXXON is evaluating and designing a mine-mill-tailings system for a complex sulfide orebody at Crandon, Wisconsin.

Because the deposit is located in an area with net precipitaton, zero discharge will not be possible. Some effluent will have to be discharged.

EXXON has undertaken a massive and detailed study of all possible ways of treating the effluent to meet regulatory requirements. Since the state of Wisconsin was initially not very experienced in dealing with mine and mill development, a clearcut regulation on mine-mill effluents did not exist, and the company had first to help the state formulate their mining waste control policy.

Many of the developments are sub-judice, so not too much detail is available although, undoubtably, a copy of the Environmental Impact Statement will eventually be available in Madison, Wisconsin.

It is rumored that initially the state of Wisconsin specified 0.2 ppb Cd as the maximum level for Cd in effluents. Subsequently this is believed to have been "relaxed" to 1 ppb. As of January, 1985, the effluent discharge limits for the Crandon project have still not been established by the state.

EXXON has examined just about every possible method of removing heavy metals from their proposed effluent including lime precipitaton, sulfide precipitation, and starch xanthate precipitation. In due course, details of this work will hopefully be published.

Much of the water management and water treatment investigation was carried out by Dr. John Shafer who has now been transferred to a different division of EXXON in Houston. The following people would be able to direct inquiries:

EXXON MINERALS COMPANY
Post Office Box 4508
Houston, TX 77210-4508
(713) 895-1110
Roger Kust

EXXON MINERALS COMPANY
Crandon Project
Post Office Box 813
Rinelander, WI 54501
Carlton C. Schroeder
(715) 369-2800

STATE OF WISCONSIN
Dept. of Natural Resources
Bureau of Solid Waste Management
101 South Webster Street GEF11
Box 7921
Madison, WI 53707
(603) 266-2178
Robert P. Grefe
Environmental Engineer

CH2M HILL
2929 North Mayfair Road
Milwaukee, WI 53222
(414) 272-2426
Michael R. Harris

RAND MINES ERPM, WITWATERSRAND, SOUTH AFRICA

A demonstration pilot plant to reduce TDS, particularly $SO_4^=$, from neutralized acid mine drainage pumped from underground at the Hercules Shaft, EAST RAND PROPRIETORY MINES LTD. as described in the Appendix I trip report, was installed in 1984 with about 5 m^3/d capacity.

The process employs seeded slurry recycling and achieves 95% plus water recovery from a feedwater which is nearly saturated with gypsum.

The process is operated at a controlled slightly acidic pH; in other words, with acid addition to maintain the pH in the operating range for the tubular cellulose acetate membrane R.O. modules.

Interestingly enough, the cadmium level is reduced from 0.02 ppm to 0.005 ppm. The Cd level is very low to start with, and it would be interesting to determine what the removal efficiency would be like using this process on a solution with higher cadmium levels.

At 0.005 ppm in the effluent, Cd is removed by the R.O. membrane to a level much lower than its solubility at the same pH which would be in the tens of mg/l.

Cadmium removal was not one of the objectives of this seeded slurry R.O. demonstration plant, yet the results show that R.O. may conceivably be used to effectively reduce Cd levels at a low pH.

Operating costs of tubular R.O. membrane units are currently estimated at around Rands 0.50/m^3 (U.S. \$0.22/m^3 or about U.S. \$1.00/1,000 U.S. gallons).

More information on seeded slurry reverse osmosis can be obtained from:

RESOURCE CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350 160
Reams R. Goodloe
Product Application
Thomas Wolfe
Research and Development

REFERENCES

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CHAPTER 35

CALCIUM Ca AND MAGNESIUM Mg

Calcium and magnesium are common constituents of water of virtually all kinds from seawater to wellwater and including most mine and mill effluents. Ca and Mg are not toxic, and no water quality criteria or regulatory limits were encountered for calcium and magnesium for mine and mill effluents.

Calcium and magnesium enter the water supply in many different ways. In nature, acidic water in contact with soil and rocks containing calcium carbonate (limestone, marble, and calcite) will dissolve calcium, and magnesium is dissolved from dolomite. Dissolved CO_2 from the air can drop the pH enough that calcium goes into solution. The more recently recognized phenomenon of acid rain also dissolves Ca and Mg from natural soils and rocks. Dissolution of calcium into groundwater is discussed by HEM (1970).

Lime is, of course, very commonly used to adjust pH of solutions as well as municipal drinking water. It is used in very large quantities to neutralize acid mine drainage and all kinds of gas scrubbing effluents, particularly from coal-burning power plants.

Gypsum, $CaSO_4$, has a solubility of around 2000 mg/l and consequently, as long as it is present below this level, all the $CaSO_4$ will be in solution. $CaSO_4$ waters readily supersaturate, however.

Calcium carbonate at neutral and high pH is much less soluble than calcium sulfate. A curve showing the solubility of calcium as $CaCO_3$ versus carbonate content in mg/l $CaCO_3$ is shown below indicating the steep decrease in calcium solubility in water as $CO_3^{=}$ is added.

Acidity-alkalinity relationships in water in relation to the solubility of minerals such as calcium carbonate and magnesium hydroxide is more complicated to predict than the solubility product suggests. Even for the simplest case of calcium precipitating from water as calcium carbonate, numerous interrelated equilibrium reactions occur at the same time and affect the interpretation of simple chemical data. For that reason, the NALCO Water Handbook states that water chemists usually rely on data based on empirical data.

Figure 4.7 shows data generally used for predicting calcium carbonate solubility which is useful in precipitation of calcium used in the lime-softening operation. The difference in results between the hot process at around 100°C and the cold process is considerably beyond what would be predicted on purely solubility data which show a decrease of only about 2 mg/l solubility at the higher temperature. The empirical temperature effect is believed to be caused by factors such as rate of reaction (which halves for each 10°C

temperature drop), the nature of the crystalline or amorphous precipitate, and the possible effect of coagulating organic materials at higher temperatures.

Another example of organic coagulant effects is in cold lime-softening of municipal sewage in which the residual calcium carbonate level is invariably higher than when the same process is used in the treatment of fresh water as shown in figure 4-8 from the Nalco Water Handbook. If, however, the sewage is heated above approximately 160°F (71°C), then results approach those achieved in cold water

It has also been found that if magnesium is present in solution, then the residual calcium in solution may be increased. Other impurities such as strontium have the same effect of increasing the solubility of $CaCO_3$. There is no substitute for an actual bench test to determine the response of a given water to lime treatment.

When water is softened with lime in the pH range 9.5-10.5, magnesium precipitates as the hydroxide, and the precipitate is positively charged. In the same pH range, $CaCO_3$ precipitate is negatively charged. Silica in the system is usually present as a strong negatively charged colloid, or may be present as sodium aluminate which is a strong anionic complex. All of this accounts for the co-precipitation of magnesium with calcium and the strong adsorption of silica on $Mg(OH)_2$, as well as the low residual magnesium often achieved by the treatment of water with sodium aluminate as well as lime.

In conventional softening operations, it is usual to show that lime treatment of fresh water produces a $CaCO_3$ solubility of about 35 mg/l cold and 35 mg/l hot and a residual magnesium hydroxide solubility of around 35 mg/l cold and 2-3 mg/l hot.

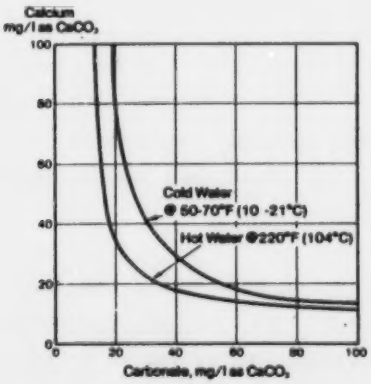


Figure 4.7 $CaCO_3$ solubility in hot and cold systems—empirical data based on 60–90 minutes reaction time and settling time.

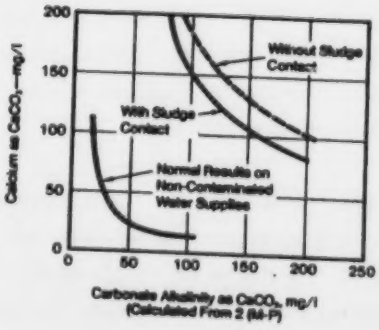


Figure 4.8 Cold lime softening of sewage (upper two curves) compared to noncontaminated water.

Source: NALCO (1979)

CALCIUM AND MAGNESIUM

Calcium carbonate and magnesium hydroxide are precipitated in the lime softening operation. However, these can also precipitate from unstable water--that is, water containing these materials in a supersaturated condition--if anything else is done to the system to upset the equilibrium. This can be an increase in temperature, a decrease in pressure, turbulence, or contact with surfaces which seed the chemical precipitation. The most common product of instability of fresh water is $CaCO_3$; in seawater, the usual precipitate is $Mg(OH)_2$ or one of its complex carbonate hydroxide salts.

Consequently, although it is not likely that calcium will need to be removed from water to meet effluent discharge limitations, calcium and magnesium do play a critical role in scale formation when reclaimed waters are recycled to a metallurgical process. In acidic systems, the formation of gypsum scale is particularly a problem.

In mineral processing operations, these phenomena may, on occasion, completely rule out the use of lamella plate pack clarification, for example. Elsewhere, high calcium levels could lead to severe fouling in the pores of in-situ leach wellfields or in the ion exchange metal recovery units treating the solution. Special provisions may be required in deep-bed sand filtration.

In acid mine drainage desalination to remove high TDS as is being tested in South Africa, desalination of water containing nearly saturated gypsum concentrations would be expected to cause membrane fouling problems as TDS levels increase in the concentrate. Sequestering agents can allow gypsum in the concentrate to increase up to three or four times saturation before gypsum crystallizes out to foul the system.

In heap leaching operations, calcium salts can precipitate out as $CaCO_3$ or $CaSO_4$ or as some Ca, Mg carbonate-hydroxy scale and cause problems with the heap porosity.

In flotation mills, lime is often used as a pH modifying reagent, and it can be introduced into minewater as a result of using cement in backfill. High Ca and Mg process waters are believed to interfere with the efficiency of some flotation recoveries or their selectivity. However, they may also be an indication of plant feed contamination by cement containing dispersants.

When treating gold ores by the carbon in pulp process, it has been found that magnesium species in the pulp have a positive zeta potential. MENNE (1984, personal communication) advises that the presence or absence of magnesium in cyanided pulps fed to a CIP circuit has a marked impact on compatability of the pulp and the activated charcoal used. This effect can alter the performance ranking of carbons for gold recovery from such pulps depending on the presence or absence of magnesium which undoubtably will be in the hydroxide form in such pulps, usually at pH 9-10.5.

HOFFMAN (1984) reported on the Schullsberg Mine of EAGLE PICHER INDUSTRIES in Wisconsin where, when mining stopped and the water table was allowed to rise, sulfate ion concentrations increased dramatically as magnesium and calcium sulfate dissolved from dolomitic rocks as a result of acid mine drainage.

In this case, the calcium and sulfate ion concentrations exceeded the calcium sulfate solubility product by many times due to the presence of magnesium to the extent that at 3,500 ppm SO_4 levels, the groundwater became no longer suitable for human consumption or stock watering.

The relationship of calcium carbonate solubility and the bicarbonate-carbonate equilibrium shift with pH is of particular importance in metallurgical circuits, especially those in which process solutions and/or tailings reclaim solutions are recycled.

Because as pH is increased (most often through addition of lime, but also Na_2CO_3, or NaOH), the following equilibrium shifts to the right.

$$HCO_3^- + OH^- = CO_3^=$$

Consequently, solubility of calcium in solution or added in the pH adjustment step is greatly reduced as pH is increased and as the HCO_3^- concentration in the feedwater is increased. In the graph from HEM (1970) shown below, if bicarbonate is present at 100 ppm at pH 6.5, then 700 mg/l Ca can be in solution without being saturated. If, however, the pH is increased to 8 and 9, the solubility of Ca drops to 15 and 1.5 ppm respectively. Consequently, the effect of pH increases on $CaCO_3$ solubility is pronounced and has a big impact on scaling wherever waters are mined or pH adjusted such as in gold cyanidation circuits, for example, and flotation circuits, even if NaOH is used for pH adjustment, and particularly if Na_2CO_3 is used.

When using carbonate and hydroxide to precipitate calcium from solutions, it is found that calcium carbonate precipitates at pH 9-11.2. Above pH 11.8, calcium forms a soluble complex with hydroxide which competes with $CaCO_3$ precipitation, and the calcium concentration in solution is not as low as at pH 11.2.

$$\begin{aligned} Ca\,(HCO_3)_2 &= Ca^{2+} + 2HCO_3^- \\ 2HCO_3^- + 20H^- &= 2CO_3^= + 2H_20 \\ Ca^{2+} + CO_3^= &= \underline{CaCO_3} \\ \hline Ca(HCO_3)_2 + 20H^- &= \underline{CaCO_3} + 2H_20 + CO_3^= \end{aligned}$$

When lime water is used as the base:

$$Ca(HCO_3)_2 + Ca(OH)_2 = \underline{2CaCO_3} = 2H_20$$

At a high pH above pH 11.8:

$$CaCO_3 + 4OH^- = [Ca(OH)_4]^= + CO_3^=$$

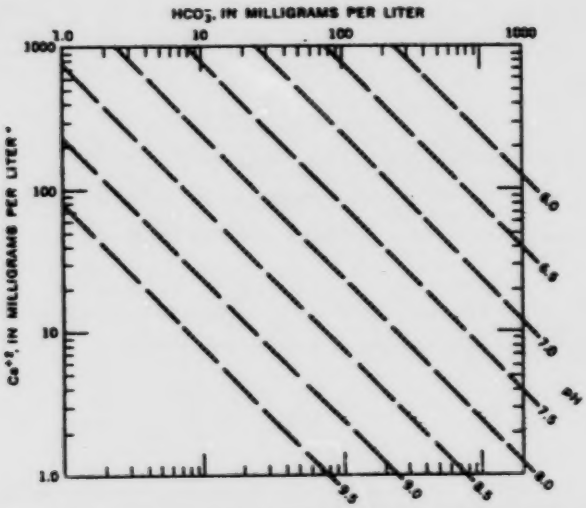


FIGURE 17.—Equilibrium pH in relation to calcium and bicarbonate activities in solutions in contact with calcite. Total pressure 1 atmosphere; temperature 30°C.

Source: HEM (1970)

SCALE IN CIP AND HEAP LEACHING

The effect of calcium sulfate and calcium carbonate scaling on carbon fouling on heap leaching and in CIP gold recovery plants is clearly important. CALGON CORP. and NALCO have both studied these phenomena, and major breakthroughs have been made in scale inhibition through addition of reagents. More information is available from:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Ben Boffardi

NALCO CHEMICAL COMPANY
1801 Duhl Road
Naperville, IL 60540
(312) 961-9500
William J. Roe, Group Leader
Mining and Mineral Processing
Research Dept.

RANDOL INTERNATIONAL LTD. believes that some simple water management practices can also help reduce the scaling problem with or without the use of additives.

One highly innovative way of controlling the sealing phenomenon was observed during a visit to PINSON MINING COMPANY, Nevada. It is believed that this simple innovation was suggested and first implemented by Roger Leonard, Plant Metallurgist at PINSON at that time. It was observed that scale formation and calcium carbonate precipitates form at the point where water from different sources are mixed, e.g., tailings dam return water mixed with fresh water. To overcome problems of scaling and carbon fouling, PINSON MINING adds fresh water to the circuit at the tailings pond and allows the solutions to equilibrate and precipitate to decant further in the dam before recycling solution to the plant. Taking this effect further, it would be possible to inject fresh water into the tailings line allowing the tailings solids in the slurry to nucleate precipitates and bring the water mixture to equilibrium before it is decanted and returned to the mill. In this way, most of the scale should precipitate in the tailings pond rather than in the plant or on the activated carbon.

More information can be obtained from:

PINSON MINING COMPANY
Post Office Box 192
Winnemucca, NV 89445
(702) 623-5036
R. Bruce Thorndycraft
Mill Superintendent

To avoid $CaCO_3$ precipitation, it is possible to reduce calcium levels, carbonate levels, or both. It is also possible to equilibrate the solution at a higher pH, but not beyond pH 11.8, and then to adjust this slightly downwards so that the solubility of $CaCO_3$ is increased.

BETHLEHEM STEEL CORP. at their Panther Valley Mines in Pennsylvania, an anthacite coal producer, uses vigorous aeration at low pH to blow off CO_2. It is found that by doing this, the pH increases, and the amount of lime consumed is reduced more than enough to pay for the decarbonization, and the smaller amount of precipitate puts less load on the thickener. The economics of this step are not known in detail, but BETHLEHEM STEEL finds it cost effective at this location where lime costs are low.

[Ca] reduction is possible by lime or lime-soda softening processes. Eight examples of acid mine drainage neutralization by various processes show that in most cases where lime is added, [Ca] will be increased. In only two of these, where reverse osmosis and ion exchange are applied, were Ca values dropped.

Magnesium concentrations in AMD were reduced to relatively low levels, however, by ion exchange, reverse osmosis, alumina lime-soda treatment, and lime-soda treatment at

hardness less than 100 ppm. In the remaining processes, magnesium levels were only marginally reduced.

The lime softening and lime-soda softening processes are discussed in greater detail in The NALCO Water Handbook.

During this investigaton, very few mines and mills were found to be employing water softening Ca removal processes for use of the water as process water. Several do use softening as a precursor to ion exchange demineralization for boiler feedwater, however.

Calcium fouling of activated charcoal is a common phenomenon in gold recovery CIP operations. The use of air agitation which introduces CO_2 into the pulp solution undoubtably enhances the effect, especially when high concentrations of free cyanide are employed. It has been pointed out that $CaCO_3$ fouling of carbon can be reduced by operating at a lower pH or through the use of additives.

In some heap leaching operations in cold climates, the solutions are heated to extend the operating season. Submerged exhaust gas heaters were initially popular for this purpose; however, the CO_2 in these gases could be expected to precipitate calcium from the solutions which could cause problems on the heaps and in the carbon adsorption tanks.

A very interesting case where $CaCO_3$ solubility in solutions is manipulated was described by YAN (1983):

In in-situ leaching of uranium using a carbonate lixiviant, CO_2 may be added to the leach solution under pressure. When the pregnant solution is pumped back to the surface, uranium is recovered by ion exchange. Open ion exchange vessels are preferred to closed pressurized IX systems. When the pregnant solution reaches the surface at ambient pressure, excess CO_2 boils off. When this occurs, $\underline{CaCO_3}$ precipitates. While CO_2 is under high pressure, Ca is kept in solution as a bicarbonate complex. When the excess CO_2 boils off on lowering the pressure, $\underline{CaCO_3}$ exceeds its solubility.

The solution at first remains supersaturated and then, when in contact with the large surface area of ion exchange resin, severe $CaCO_3$ fouling was found to occur.

T. Y. YAN and coworkers developed an application for the SPIRACTOR cone (believed to be supplied by ENVIREX) to recirculate a slurry of calcite crystals to seed the supersaturated $CaCO_3$ solution ahead of the IX contactors. In this way, $CaCO_3$ is precipated from solution onto the calcite slurry in the SPIRACTOR and can be recovered in a cyclone from which a solids bleed removes $CaCO_3$ from the system.

The alternative of adding a $CaCO_3$ scale inhibitor to the solution is not favored because these chemicals might also inhibit U_3O_8 dissolution. Another alternative of using

pressurized IX systems is not favored because of the greater expense and reduced convenience.

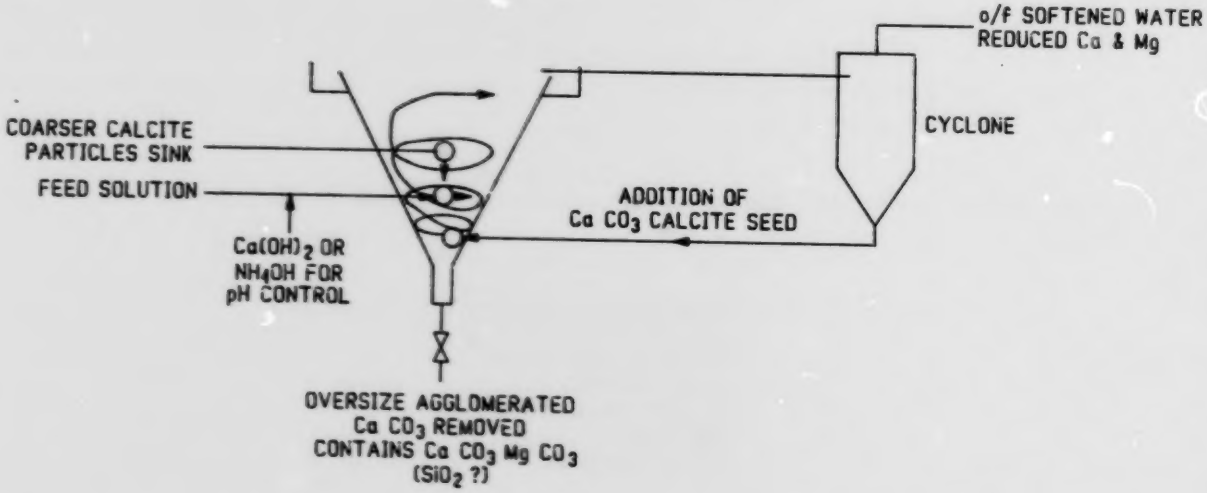
The process requirements for the in situ leach facility are:

- Avoid additives.
- Must treat a large volume of water and yield a small volume of effluent.
- Must result in a minimal loss of $CO_3^{=}$.
- Must remove as much Ca^{2+} as possible.

The SPIRACTOR cone is designed for tangential feedwater and chemical inlets, and the water spirals upward to overflow as softened water at the top. A bed of seed crystals is charged periodically, and larger agglomerated particles are removed from the bottom. pH control and the technique whereby chemicals are added are critical for a successful operation.

When using milk of lime for pH adjustment, it has been found that 95% of the calcium and 75% of the magnesium are removed from solution. If, however, NH_3 is used, 95% of the Ca is removed but much less Mg.

Ca & Mg REMOVAL



The SPIRACTOR was tested at an in situ leach site by MOBIL OIL COMPANY. The system described by YAN (1983) was found to perform well.

More information can be obtained from:

T.Y.YAN
W. (Will) Espenscheid
Mobil R&D Corp.
Princeton, NJ

Wayne C. Henderson
Kennecott Copper Company
1515 Mineral Square
Box 11248
Salt Lake City, UT 84147
(801) 534-8000

REVERSE OSMOSIS

Normally, when relatively high levels of soluble $CaSO_4$ are present in water, reverse osmosis or electrodialysis processes cannot be used to achieve a high water recovery without running the risk of fouling the membranes.

RESOURCES CONSERVATION CO. of Bellevue, Washington, has developed a seeded slurry application of tubular reverse osmosis which achieves a 95% recovery from virtually $CaSO_4$ saturated feedwater. Be recirculating a gypsum slurry to the system, $CaSO_4$ precipitates onto the seed crystals rather than the membrane.

Acid mine water containing 400-450 ppm Ca and a total hardness of 1300 ppm $CaCO_3$ with 1600 ppm $SO_4^{=}$ was fed to a test unit which achieved over 95% recovery. Permeate contained only 10 ppm Ca; ie., there was a 97.5% removal of Ca^{++}. Ca in the concentrate solution remained at around 450 ppm, but the solids in the seed slurry ran 25% Ca, 55% $SO_4^{=}$, 0.23% Fe, and 0.6% Al.

More information on the seeded slurry process is available in chapters 14 and 24 and from:

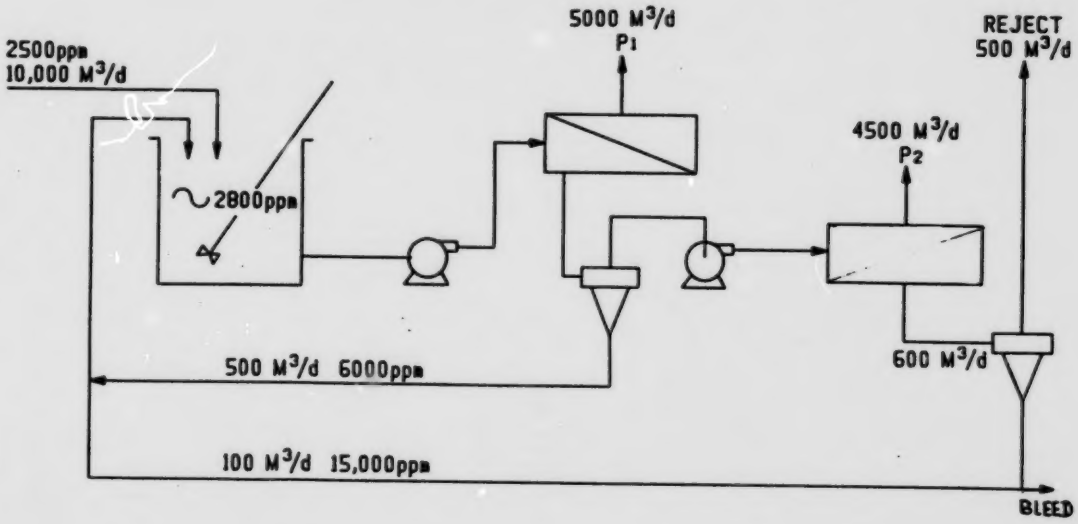
RESOURCE CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 824-2499
Russell Vandenberg
Tom Wolf
Reams Goodloe

Data on the innovative low-cost tubular R.O. system is available from:

BINTECH PTY LTD.
Post Office Box 344
Paarl CP
South Africa
(02211) 23031
D. B. Smit

Approximate cost of this process for desalination of brackish water works out to RO.50/m³ or $0.25/m³. The seeded slurry process is patented by RESOURCES CONSERVATION COMPANY.

CONCEPTUAL SEEDED SLURRY
REVERSE OSMOSIS ARRANGEMENT



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MENNE, DAVID (1984) Personal Communication, Edward L. Bateman Pty Ltd., Post Office Box 7023, Perth, WA, 6000, (09) 322-4740.

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CHAPTER 36

CHLORIDE Cl^- AND CHLORINE CL_2

Chlorides are present in virtually all water, being derived from natural origin (e.g., halite in rocks), from seawater contamination of ground water supplies, from salts spread on fields for agricultural purposes, from human or animal sewage, from industrial effluents including food processing, galvanizing plants, and oil wells and petroleum refineries. Chloride also gets into the water supply through water softening plants that use ion exchange. Disinfection of municipal drinking water using chlorine also adds chloride to water.

In the mining and metallurgical industry, chlorides can be introduced in water softening for boiler feedwater, in any metallurgical process employing chlorine or sodium chlorate, in zinc plants employing ammionium chloride fluxes or consuming flue dusts, and drosses and ash from galvanizing plants. Some ion exchange metal recovery plants use NaCl to regenerate resins. Hydrochloric acid can be used in some precious metals refining operations. Aquifers in many desert regions where mines are located often contain brackish saline water which is very high in chloride.

Chloride levels in fresh water supplies typically range from 10 to 100 mg/l. Seawater contains over 30,000 mg/l as NaCl, and some underground brine wells may be saturated at around 25% NaCl. Many geological formations were lain down as sedimentary rocks in the sea so it is not surprising that they contain chlorides that continuously leach into fresh water supplies. Typical sewage chloride content is 20-50 mg/l above the municipal water supply which accounts in part for the increase in salinity of rivers as they proceed to the oceans.

Many wastewater treatment plants are required to maintain a minimum residual chlorine concentration of 0.5-2.0 mg/l. Most plant operators control chlorination using the orthotolidene method of determining Cl_2 which has been shown to be biased on the low side resulting in much higher concentrations than necessary for adquate disinfection adding to toxicity problems in receiving waters according to the ONTARIO MOE (1979).

Total residual chlorine (TRC) concentration in 20 Illinois municipal sewage plant effluents ranged from 0.98-5.17 mg TRC/l according to SNOEYINK and MARKUS (1974). A similar survey of 22 plants in southern Wisconcsin found TRC values of 0.18-10.3 mg/l according to McKERSIE (1974).

Although chlorine and chloride levels are not frequently high in metallurgical effluents, the use and contemplated use of alkaline chlorination for cyanide removal makes the toxicity of chlorine of importance. It would be ludicrous to require chlorination to

detoxify cyanide in effluents if the chlorine levels in the treated effluent are themselves toxic. In this case, the treatment plant effluent may itself require further treatment to render the final effluent non-toxic.

Also, where great trouble and expense is devoted to making a mine-mill effluent non-toxic, it would be just as absurd to discard the effluents into a receiving stream before or after discharge of sewage plant effluents that contain residual chlorine levels that make the stream toxic to fish.

At the Beisa Mine in the Orange Free State, the minewater contains high chlorides and TDS values at 2,000 and 4,000 mg/l respectively. Much to the metallurgist's surprise, it was found that when this water is used in leach pulps, the filtration rate is about 20% faster than when Orange Free State Water Board water is used.

At the RUSTENBURG platinum refinery in the South African Bushveld igneous complex, it was found that during the recent drought, the chloride level in intake water increased at times to 150-200 ppm. Since this water is recycled within the plant, chloride levels were increased still further in the process solution with the result that pitting corrosion damaged the acid pressure leaching autoclaves which are fabricated from 316L stainless steel that cannot tolerate high Cl^- levels at elevated temperature and pressure. In the process, a two-fold increase in concentration of salt load occurs in the process water.

For this reason it is very important for this operation that high chloride levels in feedwater to the plant be avoided. If this is not possible, then a desalination plant will have to be considered to treat the water before it gets to the plant.

ENVIRONMENTAL AND HEALTH EFFECTS OF CHLORINE

Chloride as NaCl is an essential life supporting constituent, and no criteria exist for human toxicity. Excessive chlorides in water render it unsuitable for use in irrigation. Different crops have a wide range in tolerance to salinity.

The recommended upper limit for chloride in drinking water is 250 mg/l based entirely on taste, not on any known physiological hazards.

Chlorine, usually measured as total residual chlorine (TRC) includes Cl_2, hypochlorite (OCl^-), and hypochlorous acid (HOCl) which is toxic to fish and other aquatic species at sub ppm levels. Chlorine is used to disinfect water; in other words, it is highly toxic to microbiota (bacteria).

An ONTARIO MINISTRY OF THE ENVIRONMENT (1979) document provides numerous references to discussion on toxicity of chlorine in water.

The MICHIGAN DEPT. OF NATURAL RESOURCES (1971) reported effects on caged fish in several receiving streams below wastewater discharges. 96-hour LC_{50} for trout were found to be between 0.014-0.029 mg/l TRC. The same discharges were studied when chlorination was temporarily interrupted, and no mortality was observed. The toxicity effects of Cl_2 was observed for a distance of 1.3 km below the outfall. In addition, dechlorination with sodium thiosulfate eliminated toxicity in four-day tests with undiluted effluent.

ARTHUR, et al. (1975) studied the effect of chlorinated secondary wastewater treatment plant effluent containing only domestic sewage effluent. Daphnia magna was the most sensitive invertebrate species and died at a TRC concentration of 0.014 mg/l. Acceptable reproduction occured at 0.003 mg/l and below.

MARTENS and SERVIZI (1974) observed mortality of salmon in receiving streams at TRC concentrations as low as 0.02 mg/l. Lethal concentrations persisted in undiluted effluent for at least 50 hours.

REGULATORY LIMITS AND CRITERIA

Several reviewers of chlorine toxicity have recommended objectives for concentrations of TRC that would not adversely affect aquatic environments. BASCH AND TRUCHAN (1974) recommended maximum concentrations of 0.02 and 0.005 mg/l for warmwater and coldwater fish, respectively. The EUROPEAN INLAND FISHERIES ADVISORY COMMISSION (1973) has suggested objectives dependent on pH and temperature with an acceptable upper limit of 0.0004 mg/l TRC at pH 6.0 and 5°C to 0.121 mg/l at pH 9.0 and 25°C.

BRUNGS (1973) recommended objectives of 0.01 mg/l for warmwater fish and 0.002 mg/l for coldwater species and the most sensitive food organisms. Since then, however, several authors have refuted the distinction between cold and warmwater fish tolerance to chlorine. BRUNGS (1976) supports the objective for a total residual chlorine level of 0.002 mg/l for all species.

Chlorine generally does not appear on the list of contaminants to be controlled in mine-mill effluents. Surprisingly, chloride levels must be sampled and analyzed daily in effluent from each runoff water sedimentation pond on the property at HOMESTAKE MINING COMPANY's NPDES permit for their new McLaughlin operation in California.

The only case encountered during the course of this investigation where chlorine levels in effluents are regulated was in South Africa (1962) where TRC levels as Cl_2 are regulated in their general standard at 0.1 mg/l Cl_2 max. and in the special standard applicable to water discharged to trout supporting streams of Nil mg/l Cl_2 max.

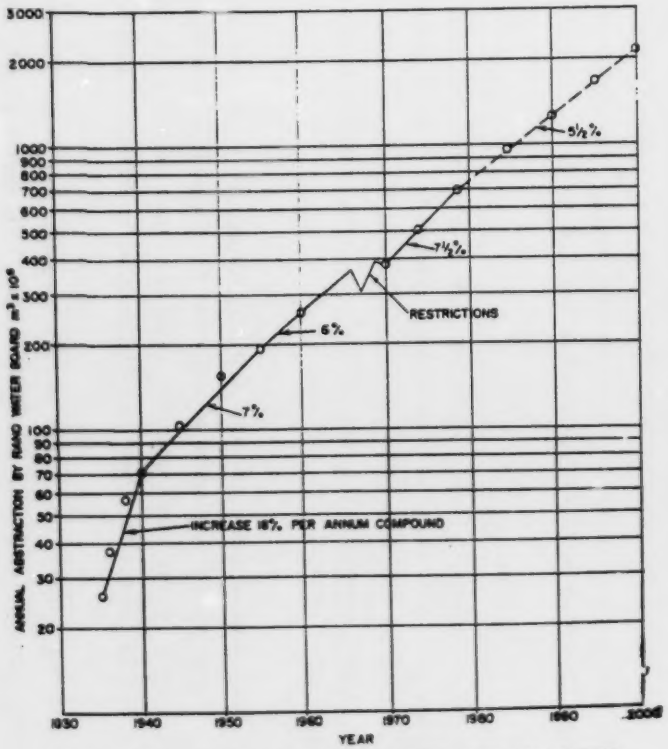
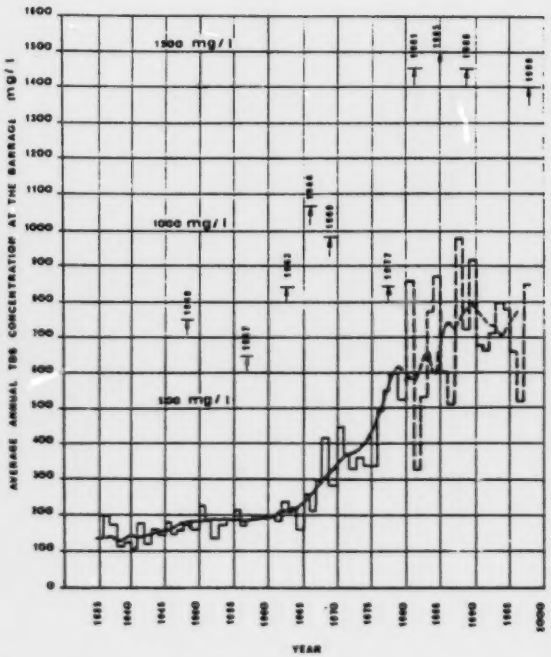


FIG. 2. ANNUAL RAND WATER BOARD ABSTRACTION FROM VAAL SYSTEM 1935 TO 1979 AND PROJECTED ABSTRACTION 1980 TO 2000.

J.J.C. HEYSIKE and S.F. MCCULLOCH

Impact of mineral pollution in the water supply

PAST AND PROJECTED AVERAGE ANNUAL TDS CONCENTRATION AT THE RAND WATER BOARDS VEREENIGING INTAKE



LEGEND

PAST AND PROJECTED TDS CONCENTRATION

TREND OF INCREASE 5 YEAR MOVING AVERAGE

REPRESENT PEAK OR PROJECTED PEAK IN THE YEAR INDICATED

In South Africa, the TDS, including Cl^- in water from the Vaal Dam, has been rising steadily over the years to the extent that it is causing concern due to increased cost of corrosion. It is likely that new regulations will be introduced to restrict the TDS levels in effluents to around 250 milliSiemens/m which equates to about 2,000 ppm tds.

ANALYSIS FOR CHLORINE

A disposable rapid method for Cl_2 level analysis is available from:

PARK DAVIS AND CO.
11471 Vanowen Street
Post Office Box 9338
North Hollywood, CA 91609
(213) 765-7830

The test is known as the Water-Chex Color Comparison Test for chlorine at 0-11 ppm. It is an aseptic-thermo indicator which changes color proportionately to the Cl_2 level in the test solution.

The Water-Chex chlorine test kit is available in Canada from:

MILLER WILLIAMS HYDRONICS LTD.
4060 Fiarview Street, Unit 12
Burlington, Ontario L7L 4Y8
(Catalogue No. 00200)

This test is good down to 1 ppm which is still too high for meaningful effluent management.

Normally chlorine can be measured down to 0.1 ppm using a Hach kit available from:

HACH COMPANY
Post Office Box 389
Loveland, CO 80539
(303) 669-3050
Telex: 910-930-9038

REMOVAL AND DISPOSAL OF CHLORIDES

Two of the most frequently employed methods (according to PATTERSON, 1975) of controlling high chloride wastes involve techniques that more closely achieve ultimate disposal than chloride reduction per se. These methods are deep well injection and holding basins including solar evaporating ponds.

Methods for removing chloride ions from a waste stream include anion exchange, reverse osmosis, electrodialysis, and evaporation which are discussed in the chapters on desalination.

ION EXCHANGE

Chloride can be removed from water by strong base (type I and type II) resins. Usually high concentrations of chemicals are required for the elution and regeneration of the resin. A very interesting development employing hot water to elute resins loaded with Na and Cl ions has been reported by BOLTO (1975) and BALTO, et al. (1982). The CSIRO Sirotherm desalinating ion exchange process uses a mixture of magnetic polymers containing basic and acidic groups for removal of Na and Cl ions. The adsorption equilibrium is temperature sensitive based on the fact that water ionization is greatly enhanced from 25°C to 85°C. After years of research and development work and pilot testing, the second commercial scale Sirotherm plant is being installed at Leaderville, East Perth for startup in February, 1985. The Sirotherm process is designed specifically for removal of NaCl from water, and the results of the new installation will be most interesting. More information on the new installation can be obtained from AMDEL or from ICI, the manufacturers of the resin.

CSIRO
Division of Chemical and Wood Technology
Bayview Avenue
Private Bag 10
Clayton, Victoria
Australia 3168
(03) 542-2244
Telex: AA 35675
Brian A. Bolto

AMDEL
The Australian Mineral Developement
Laboratories
182 Wittenoon Street
East Perth, WA 6000
(06) 325-7311
Neville Blesing
Manager

ICI AUSTRALIAN OPERATIONS PTY LTD.
Central Research Laboratories
Newson Street
Ascotvale, Victoria
Australia 3032
(03) 377-2288
Bernie Reichert
Polymer Materials Research Manager

SIROTHERM

Technology for desalting brackish waters (after softening for removal of hardness, e.g., Ca, Mg, and $SO_4^=$ has been developed and demonstrated in Australia and described by BALTO (1975) and BALTO, et al. (1982). The first paper reports on how the problems of synthesizing polymers with adequate thermally regenerable capacity and rates of salt

uptake were overcome. Pilot plant trials were claimed to have confirmed a technically feasible and economically viable process.

A major CSIRO contribution to ion exchange technology has been the invention of resin systems which can be regenerated by washing them with hot water. Sirotherm resins are polymers of the weak electrolyte type which must always be employed as a mixture of polymers containing basic and acid groups. The sites for absorption of ions are formed from the uncharged groups by transfer of protons from the acidic to the basic species.

$$R'CO_2H + R''NR_2 + Na^+ + Cl^- \underset{\leftarrow \text{Hot}}{\overset{\text{Cold} \rightarrow}{=}} R'CO_2^-Na^+ + R''NH_2H^+Cl^-.$$

The overall equilibrium is temperature sensitive with the uncharged forms of the resins being favored at higher temperatures. The driving force behind the equilibrium is the large increase in the ionization of water that occurs on heating, about 30-fold from 25°C to 85°C. The additional protons and hydroxyl ions suppress the ionization of the weak electrolyte resins; the hot water can be looked upon as providing the acidic and basic regenerants which have to be separately added in the more conventional ion-exchange systems.

The main advantages of thermal regeneration are the low energy requirement (when low-grade waste heat is available) and the avoidance of chemicals for regeneration. The concentrated effluent contains only the salt removed from the resins, whereas in conventional IX processes, two to three times the stoichiometric amount of acid and alkali must be used to regenerate strong electrolyte resins.

BOLTO (1975) described the operation in its simplest mode where water containing, for example, 1,000 mg/l TDS is passed through a bed of Sirotherm resin until the average salt content of product is reduced to say 500 mg/l. Feedwater heated to 80-90°C is used as a regenerant. About 85% of the water passed through the column is obtainable as product, the remainder being disposed of as waste averaging 3,800 mg/l. Conceptually, the process is applicable to low salinity waters with up to 3,000 mg/l TDS where the contained salts consist mainly of NaCl, and a convenient disposal site for the concentrate exists.

BALTO (1975) describes various aspects of resin design as well as several early fixed-bed plants using the Sirotherm process, the largest being a 600 m^3/d unit at an ICI ammonia/soda ash plant at Osborne, near Adelaide, South Australia, as a primary step for boiler feedwater desalination.

It was concluded that Sirotherm was unlikely to compete with R.O. and EDR unless it could be operated as a continuous system.

Progress in the development of the Sirotherm process was described by BOLTO, et al. (1982), the latest developments being the development of thermally regenerable desalting resins in the form of magnetic microbeads and a continuous contacting system for desalination of feed water and resin regeneration. A prototype plant with a throughput of 1,000 m^3/d has been installed near Perth at Leederville to treat a sub-artesian municipal supply of water.

Advantages of Continuous Systems

- Reduced heat costs because of the smaller volume of regenerant.
- Greater yield of product water because of improved heat and mass transfer.
- Lower heat costs because both adsorber and regenerator are maintained at a constant temperature instead of cycling through hot and cold regimes.
- Simpler method of controling pH to optimize for buffering conditions.
- Simpler method of excluding or destroying oxygen dissolved in the water.

Magnetic Resins

Magnetic microbead resins were developed by CSIRO to obtain a simpler moving-bed system which exploits the more rapid reaction rates of much smaller resin particles. When magnetized microbeads with particle diameters as low as 100 microns (compared with normal beads of 300-1,200 microns) clump together, they form flocs containing 50 or more beads. These flocs settle considerably faster than individual beads and yet, in normal agitated condition, have kinetic properties that are little different from individual beads.

Magnetic resin beads are prepared in their simplist form by incorporating 10-15% by volume of magnetic oxidized ferrites into the reaction mixture. The kinetic and hydrodynamic properties were optimized, particularly in relation to their effect on engineering costs for a large scale counter current plant.

Adsorption Kinetics

GLUECKHAUF (1955) and others showed that reaction rates may be particle diffuson kinetics controlled in proportion to the distance to be traversed, i.e., particle radius divided by the volume or $r/r^3 = r^{-2}$. However, if the rate is controlled by film diffusion kinetics, then the rate is proportional to the surface area divided by the volume, i.e. $r^2/r^3 = R^{-1}$, and is profoundly affected by the degree of turbulence in the liquid phase. The rate of reaction can vary from one mode to the other in practice depending on the type of resin, size of bead, degree of agitation, and concentration of the solution. Where particle diffusion is dominant, the immediate past history of the bead can also be significant.

BOLTO, et al. (1982) go into some detail in showing the influence of particle size, turbulence, and hydrodynamics showing that for small magnetic beads, kinetics is more likely to be film diffusion kinetics controlled and that the rate of absorption can be greatly enhanced when a stirrer is added into the adsorption stages. Also, magnetized beads exhibited a faster settling rate than unmagnetized beads and as such, when magnetized, allowed a much greater upflow velocity through the adsorption contactor.

Magnetic filters are necessary to retrieve stray beads, and reference is made to high-gradient magnetic filters which use sharp-edged elements in a strong magnetic field which, however, allow non-magnetic particles to pass through the filter. This allows magnetic resin fluidized bed contactors to handle dirty waters and even dilute slurries.

The following diagrams from BOLTO, et al. (1982) illustrate the Sirotherm pilot plant arrangement incorporating a continuous flow and also a McCabe-Thiele diagram defining the Sirotherm pilot plant operation.

The pilot plant absorption unit consisted of 11 stirred stages in a vertical column, and the regenerator unit consisted of 17 perforated plate stages of which the first five stages served to preheat resin, and the center six stages were for regeneration followed by five stages for resin cooling.

LEADERVILLE (PERTH) DEMONSTRATION PLANT

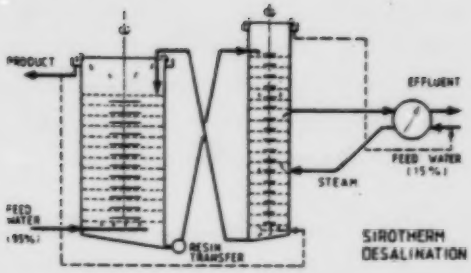
The demonstration plant is installed outside Perth to desalinate wellwater with the following composition:

Raw Water

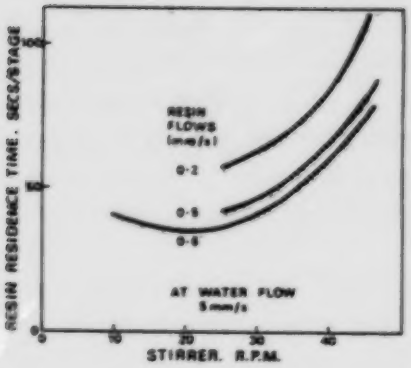
TDS	1,340 mg/l
Total Hardness (ppm $CaCo_3$)	119
Total Alkalinity (as $CaCO_3$)	153
pH	7.8
Temp °C	37
Na^+	444 mg/l
Cl^-	643 mg/l
HCO_3^-	187 mg/l

Product Water - Sirotherm

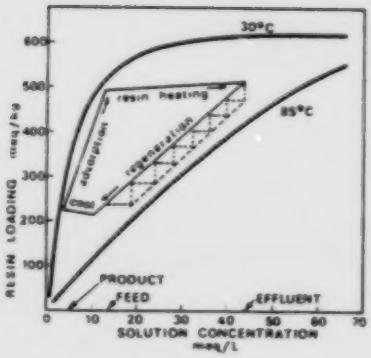
TDS	290 mg/l



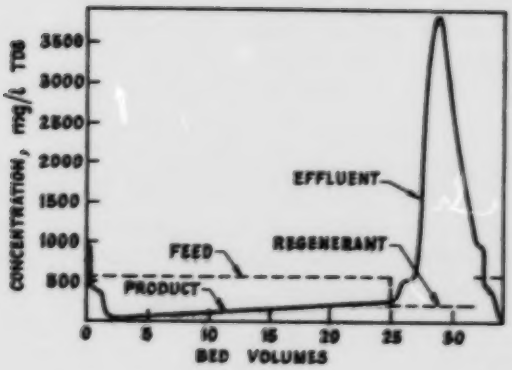
Diagrammatic flowsheet of continuous "Sirotherm" process



Effect of stirrer speed on resin residence time



"Sirotherm" pilot plant McCabe-Thiele diagram



Concentration profile for treatment of a water simulating the Osborne application.

The demonstration plant has a diameter of 1.5m for 1,000 m^3/d throughout. The Sirotherm process requires softened feedwater which is achieved with a primary fixed bed ion exchange system. Major items in the plant are the softener columns, the Sirotherm adsorber, and the regenerator. Raw water, after softening and pH adjustment, passes up through the adsorber, overflows at the top, and passes through a strainer and a magnetic filter to trap stray resin beads.

A side stream of about 20% of the raw water passes through a heat-exchanger which recovers sensible heat from the effluent, then through an oil-fired heater to bring its temperature up to around 100°C' and then to the regenerator.

Hot effluent leaves via the heat exchanger which recoups heat to the incoming regenerant stream. A small flow of water is used to cool the resin after regeneration, and the same volume of hot effluent is allowed to pass upwards through the top section of the regenerator to heat the resin.

Both adsorber and regenerator are open topped and are virtually the same height. The resin transfer system has to operate over a head of only a fraction of a metre. To reduce attrition, a gas lift is used initially with a recirculating stream of nitrogen since air is inadmissible because of resin oxidation.

Resin transfer from the base of the regenerator to the adsorber is by gravity with small side streams of water recycling around these two loops to assist resin flow.

Provision has been made for sulfite dosing of the raw water to counteract any small quantities of oxygen that might leak into the system.

Pretreatment requirements for 'Sirotherm'

Although the concept of regeneration with hot water is enticingly simple, the ionic equilibria involved are quite complex, especially when there are many types of ions present in the feedwater and particularly if they are capable of buffering action. Recent understanding of the physical chemistry involved has revealed that it is not necessary to remove competing buffers as a pretreatment step as had been initially thought in the case of bicarbonate--a simple pH adjustment of the hot and cold feedwater being all that is necessary.

One aspect of the resin equilibria which is not readily controllable is the high selectivity of the weak base functionality in the form of carboxylate groups for divalent and higher charged cations. Because of this, it is difficult to achieve effluent removal of both Ca^{2+} and Na^{+} salts in the same column.

The most economic use of the Sirotherm resin is to remove hardness cations separately by means of a brine-regenerated strong acid ion-exchange resin so that the desalting step is carried out on a fully softened water. However, BOLTO, et al. (1982) do claim that suitably tailored resins can be applied successfully to predominantly hard waters in a hot-water regenerated softening process. This has two advantages over conventional ion exchange softening: an equivalent amount of anions are removed as well as hardness cations (in the normal process calcium is replaced by sodium, and there is no reduction of TDS); and there is no heavy excess of salt in the effluent.

For surface waters containing oxygen, it is necessary to remove dissolved oxygen to prevent irreversible degradation of the amino groups which are the weak base active sites on the resin. These would be slowly oxidized by oxygen at the hot regeneration temperature. Chemical dosing with sulfite is the preferred method for oxygen removal since experience with vacuum de-aeration has shown this method to be less reliable.

Sirotherm resins are fairly resistant to organic fouling by dissolved color bodies. Small molecules are absorbed and desorbed again by hot water. Very large molecules do not enter the resin structure. Medium sized color molecules must be removed using a resin trap.

In contrast with most other desalination processes, preclarification of the feedwater is not needed for a magnetic resin system. In almost all cases, resin can be regenerated even if it has become contaminated by organic or color fouling. However, oxygen oxidation of the amine groups is irreversible.

CONCLUSIONS ON "SIROTHERM' PROCESS FOR AMD TREATMENT

1. Sirotherm as described by BOLTO (1975) and BOLTO, et al. (1982) does not appear applicable to TDS removal from AMD as it is necessary to remove "hardness" ions from feedwater to Sirotherm, i.e., Ca, Mg, SO_4.

2. Sirotherm appears applicable for NaCl removal from soft wellwaters in the range 1,000-3,000 mg/l TDS.

CONVENTIONAL IX NaCl REMOVAL

Ion Exchange demineralization is routinely used in treatment of boiler feed waters, and the results of several ion exchange desalination installations treating municipal waste plant effluents are reported by CULP, et al. (1978).

Typical chloride removal of efficiency in ion exchange processes appears to be in the 90-95% range at the levels encountered in wastewaters.

It should be remembered that in most ion exchange processes, concentrated eluants are used, often concentrated brine or acid which require special disposal measures such as ponding or deep well disposal. More often than not, however, the ion exchange regenerating solutions are discarded to the sewer or, in the case of mine-mill complexes, to the tailings pond. Usually this does not present a problem.

Chloride removal from waste waters has been discussed by HIGGINS (1969) who developed the Chemseps loop continuous plugflow ion exchange system. HIGGINS points out that the removal of strong acid and acidic ions such as chloride, fluoride, and phosphate anions requires a weak base type anion exchange resin. Strong-base anion exchange resins are more selective for common ions such as hydroxide and bicarbonate than for chloride and thus are less selective for chloride removal.

When resins are exhausted in a chloride removal plant, salt exchange capacity can be regenerated with weak alkali-ammonia solution according to HIGGINS (1969), but this introduces the question of what to do with the regenerant waste containing ammonium. Cost data reported by HIGGINS (1969) and others in CULP, et al. (1975) would by now be largely obsolete. In 1970, the capital cost for a 100,000 gallon/day anion exchange plant treating a 1,500 mg/l Cl^- waste was estimated at $169,000, and operating costs of U.S. $0.27/1000 gal. have been projected by the U.S. EPA (1971).

Several HIGGINS loops have been installed for boiler feed water dimineralization including one at SIMPLOT CHEMICAL COMPANY LTD., Brandon, Manitoba, in 1967. TDS in brackish feedwater was claimed to have been reduced from 1,800 ppm to less than 3 ppm. More information can be obtained about the HIGGINS loop from:

CHEMICAL SEPARATIONS CORPORATION
795 Oak Ridge Turnpike
Oak Ridge, TN 37830
(615) 483-7424
Irwin R. Higgins
Vice President

As always, it is advisable to check on the performance of processing units from past users as well as the vendor.

Numerous other water treatment companies offer ion exchange desalination plants as standard equipment. Wellknown ones are:

PERMUTIT COMPANY, INC.
Post Office Box 355
E 49 Midland Avenue
Paramus, NJ 07652
(201) 967-6000
Telex: 134-488

PATERSON CANDY UK LTD.

PORTALS WATER TREATMENT S.A. PTY LTD.
Post Office Box 61188
Marshalltown 2107
South Africa
(011) 21-0401
W. Monday

HIMSLEY ENGINEERING CO.
250 Merton Street
Toronto, Ontario M4S 1B1
(011) 485-4441
Alec Himsley

EDWARD L. BATEMENT LTD.
Post Office Box 565
Boksburg 1460
South Africa
(011) 899-9111
Licensies of Crane Cochrane
DIVISION, U.S.A.

ELECTRODIALYSIS/ELECTRODIALYSIS REVERSAL/REVERSE OSMOSIS

Electrodialysis and reverse osmosis have and are used for chloride removal from water. A notable application is for recovery of potable water from seawater, and numerous huge reverse osmosis plants have been installed for the purpose in the Middle Eastern oil states, in parts of Florida, on Malta, and elsewhere. This application falls under potable water rather than the subject at hand, however.

It is not considered likely that reverse osmosis or electrodialysis would be found economically attractive for removal of chloride from minewater or metallurgical effluents except in very special cases. No such installations were identified during this investigation. R.O. and EDR desalination are discussed in the chapters on Desalination.

EDR has been employed to treat 6,000 m^3/day feedwater for rougher demineralization of feedwater from 300 ppm to 40 ppm TDS ahead of ion exchange at the Kriel power plant of ESCOM outside Johannesburg, South Africa. This unit is an IONICS EDR plant installed by:

PROCESS SYSTEMS PTY LTD.
Post Office Box 10142
Johannesburg 2000
(011) 802-4230
Ralph A. Jones
Managing Director

IONICS INCORPORATED
65 Grove Street
Watertown, MA 02172
(617) 926-2500
W. E. Katz

The capital cost for a plant of this size including building would be around R3.0 million and operating costs about R0.35/m^3 ($0.17/$m^3$).

GARLING (?) of UNC TETON EXPLORATION DRILLING, INC., Casper, Wyoming, described an evaluation of electrodialysis for process water treatment for in situ mining of uranium. A 30,000 gpd (114 m^3/d) IONICS test unit was tested at the Teton-Nedco Leuenberger Research and Development plant in Wyoming. The dual-state unit was expected to yield 665 mg/l TDS water from feed of 2,650 mg/l with a water recovery of around 80%.

Chloride in the feedwater of 432 ppm was reduced to 61 ppm giving a rejection of 85.9% with rejection of gypsum in excess of 92%, although chloride removal was not the primary objective of the test.

PATTERSON (1975) describes several electrodialysis plants for chloride removal with saline and brack water in municipal water supply. In one plant (SMITH AND EISENMANN, 1964), chlorides were reduced from 115 to 80.5 mg/l which is not exactly impressive. KATZ (1968) reported chloride reduction from 122 to 58 mg/l. Capital costs for EDR installations are proportional to plant size from 1.0 mm gpd through 10 mm gpd.

PATTERSON (1973) showed some now ten-year-old data for R.O. removal of chlorides from various types of water as reported by SHIELDS (1972), NUSBAUM, et al. (1972), and CRUVER and NUSBAUM (1974). Additional cost data are provided in the chapters on desalination.

A company with recent experience in water desalination of all kinds that would be able to provide guidance on chloride removal is:

RESOURCE CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 828-2400
Russ Vandenberg
Tom Wolfe
Reams Goodloe

Table 16. Reverse Osmosis Treatment for Chloride and TDS.

Source	Volume (gpd)	Chloride (mg/l) Initial	Chloride (mg/l) Final	TDS (mg/l) Initial	TDS (mg/l) Final	Ref.
Brackish ground water	24,000	96	59	1800	155	19
Brackish ground water	150,000	351	32	2100	170	19
Brackish ground water	50,000	2020	170	4580	310	18
Sewage treatment plant effluent	10,000	280	15	756	24	20
Sewage treatment plant effluent	—	209–378	14–44	757–1170	49–92	21

Source: PATTERSON (1975)

Based on evidence so far, RANDOL INTERNATIONAL LTD. would favor the RCC seeded slurry reverse osmosis process wherever water is scaling in character or high in $CaSO_4$ content. The seeded slurry R.O. process is still to be demonstrated on a commercial scale, however.

SEALED CELL ELECTRODIALYSIS

A most innovative new electrodialysis desalination device which uses pulverized carbon electrodes as an electron pump was demonstrated at the World Desalination Conference in May, 1983, in Venice, Italy.

Electro-osmotic ion transfer through the membranes is used. Desalination of NaCl solutions was demonstrated as follows:

C_f Feed mg/l	C_p Product mg/l	Output $m^3/m^2/d$	DC Energy kWh/m^3	Brine mg/l	Volts/ Cell Pair Volts
2,500	500	1.81	1.04	86,000	0.7
1,000	430	4.2	0.29		0.7
500	10	1.05	0.63	47,000	1.0
485	50	2.36	0.34		1.0
1,000	50	1.40	0.20	26,000	1.5
100	10	2.08	0.12	23,000	1.0

r = Recovery
V_b = Brine Volume
V_o = Feed Volume

$$r = 1 - \frac{V_b}{V_o} \cdot \frac{V_b}{V_o} = \frac{C_f - C_p}{C_b - C_p} - \frac{C_f - C_p}{C_b}$$

In porous carbon electrodes, high charging currents were reported; the double layer capacity on an internal area of 500 m^3/g-800 m^3/g leads to electrosorption of Na^+ on the cathode and Cl^- on the anode up to 0.6 meq/g. In the new system, effective periodic charge reversal of c electrodes is achieved by circulating a suspension of carbon black or activated charcoal between anode and cathode compartments, and continuous current is maintained by circulating carbon between the electrode compartments.

The interesting aspect of the sealed cell electrodialysis process is the extremely high concentration of brine achieved and the low energy consumption indicated in the results above.

More details could be requested from:

DEPT. OF MEMBRANE RESEARCH
The Weizmann Institute of Science
76100 Rohovot
Israel
Telex: 361 900
Dr. Ora Kedem

DISPOSAL OF BRINES

Concentrated chloride wastes, for example, ion exchange eluates, or reverse osmosis concentrate have been disposed of in holding ponds, evaporation basins or deep well disposal.

PATTERSON (1975) mentions deep well disposal for a chemical industry wastewater containing 10-15% NaCl at volumes of 500-600 gpm. This system was described by HENKEL, H.O. (1966). THE INTERSTATE OIL COMPACT COMMISSION (1968) also reviewed the Subsurface Disposal of Industrial Wastes. Since then deep well disposal has become a relatively commonplace occurrence and injection pressures of 200-5000 psi have been recorded for chloride wastes by GLOYNA and FORD (1970).

Most states and the petroleum industry employ experts in deep well disposal of oil industry wastes. There remain many questions as to the environmental safety of deep

well disposal and THE INTERSTATE OIL COMPACT COMMISSION (1968) concluded then that it could create pollution problems far more severe than those being corrected.

During the course of this investigation, deep well injection technology as a means of disposal was not investigated although it was often mentioned as one possible answer to the concentrated waste disposal problem. One person specializing in this aspect and interested in groundwater contamination problems is:

EDICIA M. RODRIQUEZ
State of Nebraska
Oil and Gas Conservation Commission
Box 399
Sidney, NE 69162

Edicia Rodriquez may be able to steer engineers to more senior sources of expertise and information on deep well disposal of wastes. Based on data provided by PATTERSON (1975), the cost of deep well disposal is not very exorbitant, ranging from $75,000/year to $100,000/year to dispose of one million gpd at 0 to 1,400 psi with capital costs varying in 1975 from $225,000 to $270,000.

It is known that DuPONT de NEMOURS AND COMPANY uses deep well injection for disposal of a ferric chloride effluent stream generated at a large new titanium oxide pigment plant in the southern U.S.A.

PONDS AND BASINS

Holding ponds are used to store wastewater in times of low-receiving stream flow with gradual wastewater release to the stream in high-flow periods at rates necessary to maintain acceptable stream quality standards.

Solar evaporating ponds use solar evaporation to avoid the release of wastewater to receiving streams. Disposal by evaporation is limited by geographical location, climate, and land availability as discussed by U.S. DEPT. OF THE INTERIOR (1967).

JONES (1961) reported the use of a holding pond and controlled discharge of a chloride waste. The holding basin to contain an effluent containing 9% Cl^- with a capacity of 150,000 ft^3 cost about $1 million in 1958, including land.

BENTEL and JAMES (1983) described the design of evaporation ponds for the disposal of high chloride minewater from gold mines in the Orange Free State Goldfields of South Africa. These ponds are not lined.

They concluded that evaporation ponds are by far the least expensive way of disposing of brack water and are much more economical than the desalination alternative. More information was requested (but not provided) from:

STEFFEN, ROBERTSON AND KIRSTEN
Post Office Box 8856
Johannesburg 2000
South Africa
B. M. James
D. L. Bentel

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CHAPTER 37

CHROMIUM Cr

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OCCURRENCE OF CHROMIUM IN THE ENVIRONMENT

Chromium is a relatively common element geologically, but the chromate and dichromate forms are very seldom found except in polluted water. The median value for public water supplies studied by DURFOR and BECKER (1964) was 0.43 mg/l as Cr, and, for North American rivers, the median reported by DURUM and HAFFTY (1963) was 5.8 mg/l.

Chromium has several possible oxidation states. Thermodynamic data by LATIMER (1952) show that Cr^{3+} and Cr^{6+} species are stable in water, and that solubility of chromium is less than 0.5 mg/l Cr only between pH 8.0 and pH 9.5 and in solutions having a slightly lower eH than imparted by saturation with atmospheric oxygen.

The anionic species dichromate $Cr_2O_7^{=}$ and chromate $CrO_4^{=}$ are relatively stable in groundwater environments. In strongly reducing environments below pH 8.0, the predominant form is the complex cation $CrOH^{2+}$ according to HEM (1970).

Chromium as Cr(VI) can enter aquatic systems from the production and use of explosives, paper, dyes, paints, plated materials, and tanning. As Cr(III), chromium is present in glass, ceramics, photography processes, and textile dying mordants.

Plating wastes have been the most common source of chromium contamination to municipal and receiving waters in the U.S.A. and may still be so in some countries. This industry uses chromium as dichromate (the more enviromentally undesirable form) and at relatively high concentrations.

Another common use of chromate has been in corrosion control for cooling towers and boiler tubes in steam boiler plants for power plants and also for mining and metallurgical operations. This use, as well as more recent trends to limit its use or to reduce the dosages of chromium used, is reviewed in the NALCO WATER HANDBOOK (1979). Chromate is an exceptionally reliable corrosion inhibitor and formerly was applied in concentrations of 200-300 mg/l as $CrO_4^{=}$ at pH 60-7.

This treatment was also found effective as a scale inhibitor. ONTARIO MOE (1979) and SHEPHERD & JONES (1971) mention cases where up to 1700 mg/l of chromium as dichromate is used in this way. Subsequently, chromate at 20-30 mg/l $CrO_4^{=}$ was combined with other inhibitors such as zinc and polyphosphonate, also at pH 6-7, with even better results. Environmental pressures have resulted in the development of anti-corrosion treatments using only 10 mg/l $CrO_4^{=}$ in a recirculating system, but these require more careful pH control, and the addition of biocides to prevent uncontrolled microbial activity.

Environmental pressure has resulted in the development of more advanced corrosion prevention additives such as organo-zinc combinations and or organo-phospherus additives. Experts in this highly specialized field include:

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Dr. Frank Daniher
Dr. Ben Boffardi

Chrome or processing plants - e.g., the small number of chrome chemical producers and possibly chromium ferro alloy producers are possible industrial sources of chromium contamination of water, i.e., locations where treatment technology may be found. However, these were not investigated in this survey.

A discussion of chromium introduction to the environment is provided by ONTARIO MOE (1979).

CHROMIUM IN THE MINE-MILL ENVIRONMENT

The mineral processing industries use dichromate for galena depression from lead-copper sulfide mineral separation in flotation plants although its use for this purpose has, to a large extent, been reduced in recent times. Flotation tailing effluents formerly could be discarded without concern for the environment. More recently, the emphasis has been placed on recycling as much of this water as possible to reduce the volume of effluent requiring treatment. If water containing dichromate ions is returned to the front end of the process, there is the danger of depressing mineral values in the primary flotation step which would be undesirable. Consequently, alternative flotation circuit arrangements have been sought where possible. In 1985, the Newmont Mining Corp. was served with three law suits totalling $150 million in connection with hexavalent chromium contamination of water at their Idarado Mine in Colorado which shut down six years ago.

GROVE, et al. (1979) of the USGS, Denver, reported data on 38 groundwater and 25 near surface water samples analyzed for hexavalent chromium. These were taken within the city limits of Telluride during October, 1978. Twenty-four groundwater samples and six surface water samples contained more than 50 ug/l hexavalent chromium. Hexavalent chromium in groundwaters ranged from 0-2,700 ug per l and, in surface waters, from 0-160 ug/l. More information may be available from:

U.S. GEOLOGICAL SURVEY WRD
Post Office Box 25046, MS 413
Denver Federal Center
Denver, CO 80225
(303) 236-4997
David B. Grove

LEVINS (1979) reported 10-50 mg/l Cr in the decanted acid tailings/raffinate effluents from leached Jabiluka uranium ore in Northern Territory, Australia, where Alligator Rivers-type ores contain some chromium.

Another potential source of chromium in water could be expected to be the chromite mining and processing industry although this was not investigated. Water in and around the Bushveld Igueous complex of the Transvaal would be a good place to examine this possibility although high chrome content soils and resources in California and Montana

could also be included in this category. The Bushveld complex contains about 80% of the world's chromite reserves.

The PEDCO (1983) Report which surveyed the composition of water at various points in many mines and mills covering a very broad cross section of the industry as well as acetic acid leachates of solid materials encountered in mines, mills, and tailings, presented data in a comprehensive report. The data for chromium indicated that, although chromium is present in the solids at many of these mines in tailings, ore, or sediments, there are few cases where the level exceeds 0.100 mg/l in the effluent or leachate. Typical concentrations range between 0.010 and 0.90 mg/l Cr (total) in effluents and leachates.

The table on the following page lists all cases where Cr (total) in an effluent, water, or acetic and leachate exceeded 0.10 mg/l.

The PEDCO (1983) data indicates that Cr very seldom exceeds 1.0 mg/l in water and leachates from mine/mill tailings material. In all the hundreds of samples analyzed, Cr exceeded 1.0 mg/l only twice and exceeded 0.100 mg/l only about thirty times.

It is concluded that if a limit of 100 ppb Cr were to be set, most mines and mills would be able to comply without installing a water treatment plant. Tailings pond liquid from ten operations exceeded 0.100 mg/l and minewater from five. It is also concluded that if 0.05 ppm Cr average is set as a limit for effluents, then about half the operations involve liquids that exceed this limit. Setting a limit of 0.24 ug/l, which is the EPA water quality objective for hexavalent chromium in freshwater, would be extremely difficult to meet for any mine or mill using hexavalent chromium.

Unless the U.S. chromium standard objectives are relaxed, many mining operations may, in the future, have to treat effluents for chromium removal to meet anticipated effluent discharge regulations.

Mine No.	Type	Untreated Mine Water	Mine Water Pond Liquid	Tailings Pond Liquid	Tailings Pond Solids Leachate	Surface Mine Wasterock	u/g Mine Wasterock	Spent Oxide Liquor Residue Leachate	HL Material Leachate	Pregnant HL Liquor	Coarse Tailings Dike	Wastewater Treatment Sludge
14	New Mexico U_3O_8		0.980									
26	Uranium Other	0.100	0.100									
No. 1	Florida Phosphate			0.490		0.150						
No. 2	Florida Phosphate			0.390								
No. 4	Florida Phosphate			0.980								
No. 5	Idaho Phosphate			0.110	0.430							
No. 7	Idaho Phosphate			0.110	0.180							
No. 9	Phosphate Other				0.160							
No. 10	Phosphate Other					0.160						
No. 11	Phosphate Other			0.280								
No. 28	Copper S.W.	0.170										
No. 29	Copper S.W.							1.200				
No. 31	Copper S.W.								0.150			
No. 33	Copper S.W,									0.450	0.110	
No. 34	Copper Other	0.120										
No. 36	Copper Other							1.400				
No. 41	Pb-Zn West						0.180					
No. 42	Pb-Zn West			0.110	0.106							
No. 45	Pb-Zn East				0.140							
No. 46	Pb-Zn East			0.340								
No. 49	Pb-Zn Missouri											0.210
No. 50	Pb-Zn Missouri				0.120							
No. 51	Pb-Zn Missouri	0.110		0.180								
No. 53	Pb-Zn Missouri			1.49								
No. 55	Gold-Silver Other						0.140					
No. 61	Taconite Iron	0.200										

THE USE OF DICHROMATE IN FLOTATION PLANTS

A common arrangement in flotation plants treating complex sulfide copper-lead-zinc ores is to float a copper-lead rougher concentrate which is then separated by depressing galena and floating a copper sulfide concentrate, with or without a regrind of the rougher concentrate. Addition of dichromate ions has been a popular way of depressing galena in this process; for example, as referred to in the trip report on HEATHE STEEL in Appendix I, which adds 130 mg dichromate per ton of ore treated. A sometimes used alternative is to depress copper sulfides with cyanide and to float the galena.

Typical chromium levels encountered in flotation plants have been reported in a proprietory report by a major engineering company at 0.001-0.1 mg/l. Virtually no other data on Cr levels in flotation plant effluents were encountered during this survey. Many operations visited do not use flowsheets that require dischromate use. Most often the nature of the ore determines the appropriate flotation plant flowsheet and whether or not dichromate use is metallurgically advantageous. The Newmont Mining Company employed dichromate as a flotation reagent at their Idarado Mine outside Telluride, Colorado, for a brief period some years ago. Details of actual damage caused by this chromium use, if any, have yet to emerge, however.

It is believed that EXXON MINERALS COMPANY has considered the use dichomate as a galena depressant for their CRANDON operation in Wisconsin. In this case, as much water as possible will be reclaimed from the tailings pond and recycled. Dichromate has not been an item of major concern as it was anticipated that it would quantitatively be converted to trivalent chromium in the tailings pond. In view of 1985 litigation against the Newmont Mining Company, it can be expected that the use of dichromate at Crandon may be reconsidered.

It has been pointed out that in operations where thiosulfate is present in tailings ponds and in reclaimed water and where the pH is allowed to drop to pH 3-4, any excess dichromate ions should quantitatively be reduced to trivalent chromium. Often, when thiosulfate is present, pH will automatically drop to these levels as thiosulfate oxidizes to $SO_4^{=}$, particularly in warm seasons.

Detailed work by CANMET and NORANDA RESEARCH found that in winter about 60-70% of the thiosulfate in water is oxidized. In summer, about 95% of the thiosulfate can be oxidized in a holding pond. According to CANMET, NORANDA, and others, thiosulfate is generated when ores containing reactive sulfide minerals, particularly certain types of pyrrhotite, are ground at a high pH in mills to which lime or soda ash have been added. There is a wide range in the degree of thiosulfate generation from one mine-mill complex to the next. For example, BRUNSWICK MINING in New Brunswick generates very high levels of thiosulfate, but NORANDA MINES, MATTABI, does not. Thiosulfate generation

and removal or inhibition is the subject of a major study by CANMET and NORANDA, and preliminary data indicates that the understanding of this phenomenon is far from simple.

BRUNSWICK MINING is reputedly working on a new simplified flotation arrangement that reduces the use of SO_2 and allows for much greater use of recycle water and a smaller volume of effluent.

WASSERLAUF and DUTRIZAC (1982, 1983) reviewed CANMET's project on the chemistry, generation, and treatment of thiosalts in milling effluents. Much more information is however available in CANMET files, and an excellent picture of the phenomena can be obtained through consultation with those who have been devoting years to this investigation:

CANMET
Energy, Mines and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1
(613) 995-4823
Telex: 053-3117
John E. Dutrizac

NORANDA RESEARCH CENTRE
240 Hymus Blvd.
Point Claire, Quebec
Canada H9R 1G5
(514) 697-6640
Ken Wheeland

GIONET, MELLOR AND LIEBICH ASSOCIATES
2125 Boul Industrial
Chambly, Quebec J3L 4C5
(514) 658-4366
Mark Wasserlauf

Dichromate addition for galena depression is or has been used by, amongst others, the NEWMONT MINING COMPANY, BOLIDEN MINERAL AB, HEATHE STEEL, and at the Missouri Lead Belt. NEWMONT indicates that in their experience one cannot rely on thiosulfates in the tailings pond to convert hexavalent chromium to the trivalent form adequately to avoid metallurgical problems when the water is recycled. BOLIDEN pointed out that the thiosulfate reaction with Cr(IV) may be the reason for some otherwise unexplained Cr(VI) to thiosulfate ratios found in their tailings pond water. Copies of letters from NEWMONT and BOLIDEN MINERAL AB provide further interesting comments and the names and addresses of contacts in these companies through whom this point could be followed up further if needed.

It is concluded during this RANDOL investigation that very limited detailed knowledge is available on the behavior and control of hexavalent chromium in metallurgical circuits.

NEWMONT MINING CORPORATION
200 PARK AVENUE
NEW YORK, N. Y. 10166

LEONARD HARRIS
VICE PRESIDENT
METALLURGICAL OPERATIONS

June 15, 1984

Mr. Hans von Michaelis
Randol International Limited
21578 Mountsfield Drive
Golden, Colorado 80401

Dear Hans:

Many thanks for your letter of April 20, 1984 and the copy of Randol's report "CIX-RIP For Uranium Recovery".

With respect to hexavalent chromium in flotation, I note the following: You are probably right that thiosulfate ions are formed during the grinding of sulfide ores in an alkaline pulp. The problem is that sodium dicromate is not added to this circuit. It is added to the copper/lead separation circuit where little or no thiosulfate is present. Based on our experience, I think that it is dangerous to rely on the reduction of hexavalent chromium to trivalent chromium by means of thiosulfate in the tailings dam. It most certainly did not happen in our case.

When I checked into this matter about a year ago, I talked with Norman Holme, Chief Metallurgist, Cyanamid who noted that in the Missouri lead belt where dichromate is used for copper/lead separation, the water is always kept separate except at the Magmont mill where only 25 percent water is recycled. Deleterious results were experienced in the early days of operations in the Missouri lead belt.

Dichromate is a potent depressant even in very small quantities so that apart from the toxicity problem, one can expect problems in the flotation plant. In our opinion, the copper/lead separation circuit should be clearly isolated from the rest of the circuit to prevent these problems.

Best personal regards.

Sincerely

Leonard Harris

LH:emd
Enclosure

P.S. I note your reference to enhanced decomposition of thiosulfate at higher temperatures. Our problem was in the cold mountain climate of Colorado.

boliden mineral

Date
June 4, 1984

Reference

Yours dated

Your reference

Attending to this matter
Mineral Processing Development
Per G. Broman/eb

Mr Hans von Michaelis
Randol International Ltd.
21578 Mountsfield Drive
GOLDEN, Colorado 80401
USA

Dear Mr von Michaelis,

Thank you for your note on Cr (VI) reduction by thiosulphate ions. This has not been studied or even observed by us. We know however that thiosulphate could reduce Cu (II) to the monovalent or even elemental state. This is in fact what we think happens in the SO_2-promoted flotation processes.

Your idea actually made us consider this phenomenon being behind some so far unexplained Cr (VI) to $S_2O_3^{2-}$ ratios being observed in our effluent streams.

Thank you once more. We look forward to seeing your final report.

Yours sincerely,

BOLIDEN MINERAL AB
Research and Development

Per G. Broman

[illegible], know how.
[illegible] • Boliden Bergsöe • Boliden Kemi • Supra • Boliden Intertrade • WP-System • Boliden France
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Banken

Levels of chromium (VI) at which it interferes with bulk or semi-bulk flotation efficiency when present in recycled water has not yet been clearly determined or reported in the literature although the levels will be low.

ENVIRONMENTAL IMPACT OF CHROMIUM

Chromium at low concentrations may be a nutrient for plants and animals. Although not proven to be essential for plants, low concentrations in soil and water appear to stimulate growth of terrestrial and aquatic species (ONTARIO MOE, 1979). A United States National Research Council panel on chromium concluded that chromium must be considered an essential element for mammalian health (NRCUS, 1974).

Toxicity of chromium to aquatic biota is quite variable and depends on the species tested. Daphnia magna reproduction and activity were inhibited by 330 ug/l chromium.

A series of unpublished studies by BENOIT and PICKERING reported in Water Quality Criteria, 1972 (NAS/NAE, 1973) demonstrated "safe" concentrations based on reproduction of 300,600 and 1,000 ug/l hexavalent chromium for rainbow trout (Salmo gardineri), brook trout (Salveliorus fontiralis), and fathead minnow respectively.

ONTARIO MOE (1979) cites references showing that the acute toxicity levels of Cr(III) is higher than that of Cr(VI).

Chromium levels in dressed samples of fish tissue were found by UTHE and BLIGH (1971) to range from less than 0.017 ug/g to 0.034 ug/g wet weight indicating that chromium may be lower in flesh than in the whole fish which was found to be in the range 0.9-16 ug/g by LUCAS and EDINGTON (1970). There was no variation in chromium concentrations in the flesh of fish taken from Lake Erie and those from a lake in Manitoba which was not affected by industry.

Experimental exposures indicate that Cr(VI) was taken up from water at concentrations as low as 1 ug/l. At 2,500 ug/l, uptake was via the gills, and metal occurred in the spleen, posterior gut, and other organs in preference to the muscle tissue. It is concluded that chromium uptake in fish is not a potential problem for species that eat fish according to ONTARIO MOE (1979).

The ONTARIO MOE (1979) review found that no objective for chromium concentrations in fish are needed. Based on algal growth response to chromium and the mortality of chinook salmon, a concentration of 100 ug/l should protect aquatic life. This figure in unfiltered water is also used by ONTARIO MOE (1978) as an objective.

The U.S. EPA (1980), on the other hand, set criteria for hexavalent chromium in freshwater at 0.29 ug/l as a 24-hour average concentration and 21.0 ug/l as maximum permissable concentration.

The U.S. EPA (1980) also set a maximum permissable concentration for Cr(III) as a function of hardness where the maximum permissable concentration (MPC) is computed as follows:

$$MPC = e^{(1.08[\text{in hardness}] = 3.48)}$$

This computes out as illustrated in the graph on the following page.

Elsewhere, CANADA (1979) and QUEBEC (1977) set a recommended objective of 40 ug/l total Cr.

The U.S. EPA set a marine water criteria of 18 ug/l for hexavalent Cr for 24-hour samples and a MPC of 1260 ug/l.

It can be concluded from available data that:

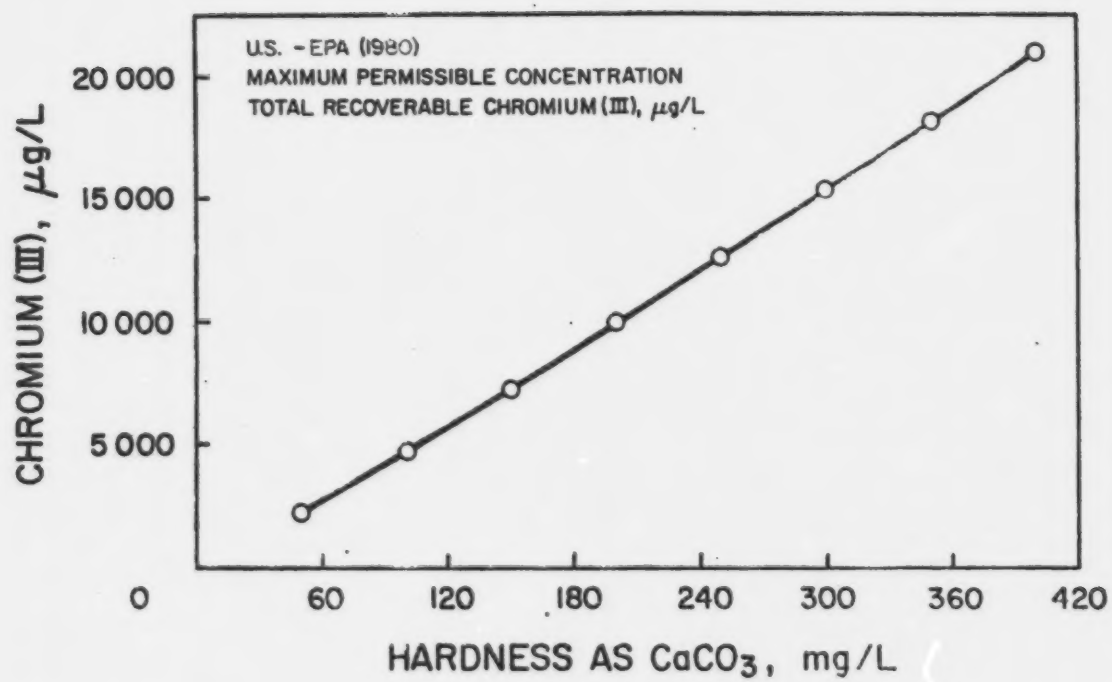
- The U.S. EPA (1980) criteria for 24-hour average concentration for hexavalent chromium in fresh water of 0.24 ug/l appears to be stricter than called for by the data.

- Toxicity of chromium compounds in the marine environment occurs at much higher concentrations than in fresh water.

- Chromium in aquatic environments is less toxic than many other metals, and the toxicity of trivalent chromium appears to be affected by hardness of the water which does not change the toxicity of hexavalent chromium.

SAMPLE PRESERVATION FOR Cr(VI) ANALYSIS

STOLLENWERK and GROVES (1985) report the potential loss of hexavalent chromium under common sample-preservation techniques. The standard preservation technique for water samples analyzed for Cr(VI) consists of filtration through a 0.45 u membrane, acidification to below pH 2, and storage in plastic bottles. Batch experiments were conducted to evaluate the effect of hydrogen ion (H^+) concentration and temperature on the reduction of Cr(VI) to Cr(III). Results showed that significant reduction of Cr(VI) to Cr(III) can occur at pH below 2 and that the rate of reduction increases with decreasing pH and increasing temperature. Reduction of Cr(VI) is inhibited by storing the sample at 4°C'. The authors indicate that water samples collected for the determination of Cr(VI) need to


U.S. - EPA (1980)
MAXIMUM PERMISSIBLE CONCENTRATION
TOTAL RECOVERABLE CHROMIUM (III), µg/L
CHROMIUM (III), µg/L
20 000
15 000
10 000
5 000
0
60
120
180
240
300
360
420
HARDNESS AS CaCO3, mg/L

Cr (ug/L) CHROMIUM

Summary of North American Water Quality Criteria for Chromium

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9]** 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	100	Cr^{+6} 0.29 / 21.0	40	<100	--	--	50-300	--	--
MAX. PERMISSIBLE LIMIT		50	--	Cr^{+6} e(1.08 (ln (hard))+3.48	--	100	50	50	--	50	100
PROTECTION OF MARINE LIFE											
OBJECTIVE		<50	--	18 (24-hr mean)	<0.1*	--	--	--	50-300	--	--
MAX. PERMISSIBLE LIMIT		100	--	1250	0.1*	--	--	--	--	--	--
PUBLIC WATER SUPPLY		50	50	(Cr^{+3}+Cr^{+6}) 50	100	50	50 (limit)	(50)	--	50	50
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	1,000	(50)	--	1,000	1,000	--	(50)	--	--	1,000
	IRRIGATION	100	(50)	--	100	100	--	(50)	--	--	50

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Chromium, EPA 440/5-80-035.
4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada. 1980. Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances, Chromium.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Gouin, D. et Kalo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9.** British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries. (Receiving water objectives not available)
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

TABLE

CHROMIUM

be filtered (0.45 u membrane), acidified (pH 2.0-2.5), and refrigerated until analyzed. Measurement of total Cr in addition to Cr(VI) would indicate if reduction of Cr(VI) had occurred, provided that no Cr(III) existed in the sample initially. More information or a copy of this paper are available from:

U.S. GEOLOGICAL SURVEY
Box 25046 MS413
Federal Center
Denver, CO 80225
(303) 236-4994
Kenneth G. Stollenwerk
David B. Grove

EFFLUENT REGULATIONS - CHROMIUM

In very few of the mining and milling operation permits reviewed was chromium even listed. The only two cases identified are for HOMESTAKE MINING COMPANY operations at Lead, South Dakota, and the new McLAUGHLIN project in California. The latter is permitted for zero-discharge except for runoff waters collected on the site.

HOMESTAKE MINING COMPANY

	Lead, SD NPDES	McLaughlin NPDES Permit 30d Ave.	Daily Max.
Cr Total	0.85 mg/l	0.05 mg/l	0.10 mg/l

Surprisingly, no examples of permits for flotation plants recovering copper, lead, and zinc ores were encountered which stipulated limits for chromium.

Chromium is considered by the Environmental Protection Agency to be a hazardous substance according to BAKER AND BHAPPU (?). They listed a New Mexico Water Quality Control Commission regulation promulgated on August 27, 1971, forbidding discharge of an effluent containing in excess of 0.01 mg/l total chromium.

On February 7, 1984, EPA (1984) published a revised Ambient Water Quality Criteria document for chromium in which they proposed several changes in the criteria to better reflect real world situations. These changes concern the analytical species to be controlled and the time period over which the parameter average concentration is to be measured. The analysis is restricted to "active" trivalent chromium and dissolved hexavalent chromium, and it was proposed to calculate the criteria average on a 30-day basis rather than the previous 24-hour time frame. The American Mining Congress is working on further clarification and modification of the EPA (1984) proposed new water quality control criteria for Cr. New terms such as family mean acute values (FMAV) and species mean acute values (SMAV) have been introduced into the regulatory language. In

industrial waste disposal, the present EP Leach test limit for trivalent chromium is 5 ppm. It is reputed that the EPA is now getting ready to lower these limits significantly. This could be important when final regulations for mine/mill waste disposal are formalized.

Public water supply criteria for chromium in the U.S.A. are as follows:

	Cr (Total)	Cr(VI)
U.S. EPA (1972)	50 ug/l	
U.S. EPA (1976)	50 ug/l	
U.S. EPA (1980)		50 ug/l
CANADA (1979)	100 ug/l	
CANADA (1980)	100 ug/l	
ONTARO (1978)	50 ug/l	
QUEBEC (1977)	50 ug/l	
ALBERTA (1977)	50 ug/l	
SASKATCHEWAN (1975)	50 ug/l	
MANITOBA (1979)	50 ug/l	
NEW MEXICO (1971)	10 ug/l	

Regulation changes concerning chromite levels in effluents are of interest to manufacturers of chrome chemicals whose market may be affected, and some update on regulatory trends may be available from:

DIAMOND SHAMROCK CHEMICALS
Post Office Box 191
Painesville, OH 44077
(216) 357-3800
Ralph Temple

DIAMOND SHAMROCK CHEMICALS
Los Colinas, TX
(214) 659-7120

Chromium producers in the U.S.A. and Europe are represented on an environmental subcommittee of the Industrial Health Foundation, Pittsburgh, to review regulatory and environmental problems associated with chromium.

INDUSTRIAL HEALTH FOUNDATION, INC.
34 Penn Circle West
Pittsburgh, PA 15206
(412) 363-6600

On problem with chromium and the EP Leach Toxicity test is that under the conditions of the test (namely a leach by acetic acid at pH 5, both chrome (III) and Cr(VI) are soluble. Cr(III) is almost insoluble at pH 7-10, but Cr(VI) is soluble throughout the whole pH range.

The EP Toxicity Leach test can be overcome if excess alkali is added to the waste to prevent a pH drop when acetic acid is added.

In South Africa (1983), a proposed standard of 0.5 ppm total chromium and 0.05 ppm hexavalent chromium has been proposed for effluents discharged in the Witwaterstrand area.

Inquiries to the Colorado Dept. of Health regarding chromium regulations in the state and how they are enforced were referred to Carol Russell, who was unable to discuss details of the state's approach to enforcement of regulations regarding chromite contamination in view of the pending CERCLA (Superfund) litigation which she is directly involved in.

COLORADO DEPT. OF HEALTH
4210 East 11th Avenue
Denver, CO 80220
(303) 320-8333, Ext. 3902
Bob Shukle
Unit Chief, Industrial Permits
and Enforcement, Water Quality
Control Division
Carol Russell

METHODS FOR REMOVING CHROMIUM FROM EFFLUENTS

Several methods are in use for removal or reduction of chromium from solutions. Selection of a suitable process undoubtably depends on the level of chromium in the effluent to be treated and the level that must be achieved before the effluent can legally be discharged. Another aspect of recent interest is how to remove chromium (VI) from groundwater once contamination has occurred.

No case was encountered where mine and mill tailings water is treated specifically to remove chromium as Cr(III), Cr(VI), or total chromium although LEVINS (1978) showed that by adding lime to adjust the pH of Jabiluka uranium mill effluent (tailings decant/raffinate mixture), chromium was dropped from 10-50 mg/l to 0.3 mg/l. Several other metal contaminants and gypsum were also reduced in this way.

In other industries, chromium removal is practised, and some of these processes are reviewed here. Also, in the literature, several examples of newer processes were encountered which claim to be able to remove chromium either very specifically or at an economical cost.

PATTERSON (1975) points out that reduction of hexavalent chromium from a valence of +6 to +3 and subsequent hydroxide precipitation of the trivalent chromium ions is the most common method of hexavalent chromium removal. He points out that ion exchange is also being used to treat chromate and chromic acid wastes in the metal finishing industry.

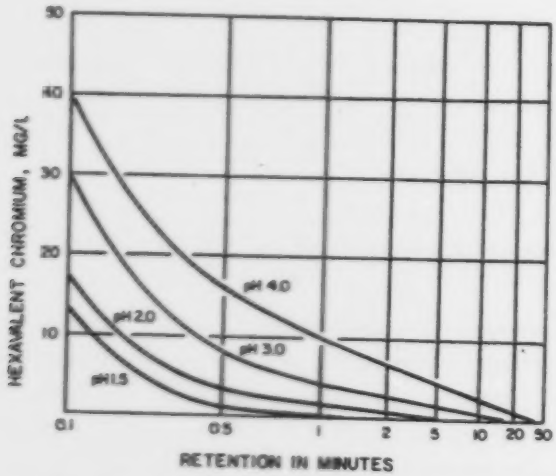
REDUCTION

The standard reduction treatment is to reduce the waste stream to pH 3.0 or below with sulfuric acid and to convert hexavalent chromium to trivalent chromium with a chemical reducing agent such as sulfur dioxide, sodium bisulfite, metabisulfite, hydrosulfite, or ferrous sulfate. Trivalent chromium is then removed, usually by precipitation with lime, according to MACDOUGALL (1954) and BESSELIEVRE (1969).

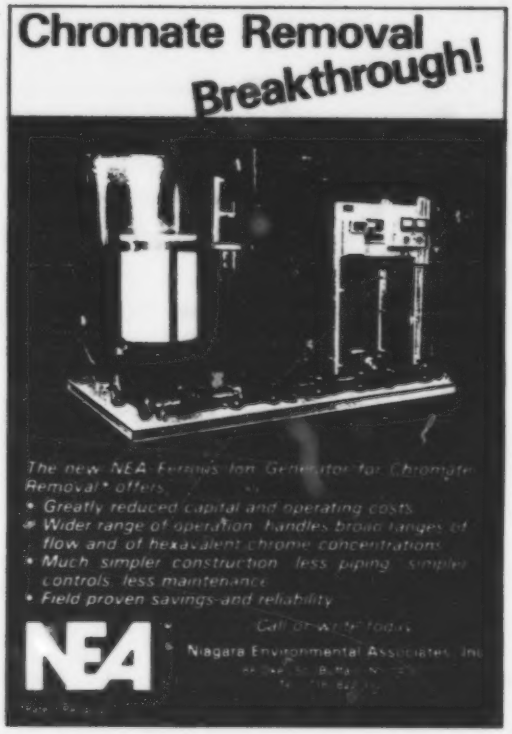
ROUSE (1985, personal communication) suggests that the best way to remove Cr(VI) from groundwater is to precipitate it in situ by adding pyrosulfate ions to reduce it to a form that can be geochemically immobilized.

ENVIROLOGIC SERVICES INTERNATIONAL
Division of J. H. Kleinfelder and Associates
2425 South Colorado Blvd.
Denver, CO 80222
(303) 759-2611
Jim V. Rouse

The reduction of hexavalent to trivalent chromium is not 100% effective, and the amount of unreduced hexavalent chromium depends on the time allowed for the reaction, pH and concentration, and the type of reducing agent employed. The interdependence of variables is shown in the following diagram:



Effect of treatment pH and reaction time on conversion of hexavalent to trivalent chromium. [From Beevers (15), courtesy of Metal Finishing Journal.]



Sulfur dioxide is the most popular reducing agent used in the treatment of chromium in industrial wastes because it is relatively cheap according to PATTERSON (1975) and STONE (1972). SO_2 for Cr(VI) reduction at low pH has been in use at a BOEING plant, according to HALSE, et al. (1960).

In this process, a waste was reduced to pH 2.5 with sulfuric acid before reduction.

SO_2 used to treat chromic acid plating bath wastes at an average waste flow of 40 gpm for 20-30 minutes yielded a residual hexavalent chromium level of less than 1.0 ppm according to SHINK (1968). Although this and several other references describe Cr(VI) reduction, the question arises whether chromium can be reduced to the much lower levels demanded for mine-mill-tailings effluents and at the much larger flowrates typical of these systems.

CURRY (1972) pointed out that hexavalent chromium levels of 0.01 mg/l can be achieved by reduction at pH 2.5-4.0.

LAVIN and LAVIN (1972) described a fully automated continuous flow chromate waste treatment system for reducing hexavalent chromium to below 0.05 mg/l. The cost of the

system, including a chromium hydroxide precipitation step, was quoted at $12-15,000 indicating that this must be a small scale operation.

TEER and RUSSELL (1972) described an SO_2 chromate reduction process used to treat wood preserving wastewater in which effluents with 0.23-1.5 mg/l hexavalent chromium were reduced to 0.1 mg/l.

At one plant described by FISCO (1970) to treat hexavalent chromium in plating waste, sulfur dioxide is washed out of the powerhouse stack gas and used for hexavalent chromium reduction. The plant has been in operation since 1959, and when additional reduction is necessary, sodium bisulfite is employed as a supplement.

PATTERSON (1975) points out that the use of SO_2 results in an oxygen demand in the product water unless the effluent is oxygenated by aeration. Required SO_2 dosages of 2.0 lbs. per pound hexavalent Cr has been reported in small industrial applications by the U.S. EPA (1971) and BEEVERS (1972).

AVRUTSKII (1969) described the removal of 140 mg/l Cr(VI) from a plating waste reduced at pH 2.5-2.8 with sodium bisulfite to 0.7-1.0 mg/l Cr(VI). There have been reports of replacing sodium bisulfite with SO_2 because of odors and corrosion hazards experienced with sodium bisulfite. The use of sodium bisulfite to treat a chrome plating waste was reported to yield an effluent hexavalent chromium level of 0.05-0.1 mg/l by METAL FINISH. J. (1971).

The above examples almost all refer to industrial effluents at small flowrates. One treatment plant reduced their initial chrome level from 31.4 mg/l in a cooling tower blowdown of 3600 U.S. gpm to below 0.5 mg/l as reported by LANDY (1971) at pH 2.0. This required the addition of 4.2 pounds of metabisulfite per pound of chromium representing 75% excess over the theoretical dosage required. Elsewhere, PATTERSON (1975) refers to reductive chromate removal from a similar blowdown waste achieving hexavalent chromium levels of 0.025-0.05 ppm.

Three cases, in steel mills where pickle liquor was available for use in the reduction process, were found in which ferrous sulfate reduced hexavalent chromium. These were described by DONOVAN (1970), HEINIKE and VON REICHE (1969), and STONER (1971).

According to GERMAIN, et al. (1968) ferrous sulfate reduction of hexavalent chromium has the advantage of being independent of pH, although BENNETT (1972) found that ferrous sulfate reduction at pH 2-3 proceeds within 30 minutes to a residual Cr(VI) level of 1 mg/l but requires one hour at pH 4-10. The use of ferrous sulfate also yields much larger quantities of sludge than are produced through the use of SO_2 although this is unlikely to be an important factor at the hexavalent chromium levels usually encountered in mineral processing plants.

In 1972, the cost of hexavalent chromium removal from 120 mg/l solution at 100 gpm, including precipitation of $Cr(OH)_3$, came to $1.80/lb. Cr removed.

REMOVAL OF CHROMIUM BY PRECIPITATION

$Fe_2(SO_4)_3$ addition at pH 3.5-4.5 followed by electrocoagulation and Lectroclear flotation has been demonstrated for removal of molybdenum from mine and tailings decant effluents by RAMIREZ (1980) and is the subject of a patent by RAMIREZ and RAMADORAI. According to RAMIREZ (1980), the same process demonstrated, on a laboratory scale, its ability to remove Cr as well. No further details were provided in the chemical abstract CA95(8):67356a.

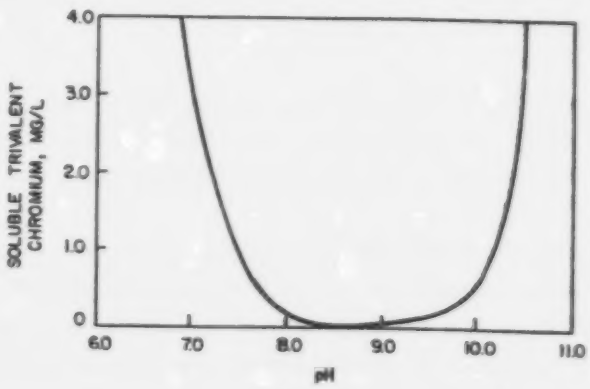
Co-precipitaton with ferric sulfate when the precipitatable solids load is very small could mean that the cost of clarification of the solution after precipitating the chromium is expensive--ie., clarfier size is determined by liquid flowrate, not the solids loading. In such a case, dissolved air flotation could be considered as a less expensive route than clarification by either Lectroclear flotation or conventional clarification.

No operation was identified that uses these processes for chromate removal from recycle solutions or effluents from mines or mills.

REMOVAL OF CHROMIUM (III) BY PRECIPITATION

Trivalent chromium may be removed by precipitation as the hydroxide by the addition of lime or caustic soda yielding a precipitate which is considered safe for landfill disposal according to PATTERSON (1975).

Treatment Technology for Trivalent Chromium



Effect of pH on solubility of trivalent chromium. [From Parsons courtesy of National Lime Association.]

Precipitation is most effective at pH 8.5-9.5 due to the low solubility of chromic hydroxide in that range, although best removal has been reported in one case by WANG, et al. (1973) at pH 12.2. Because metal-bearing effluents include other metal ions as well as chromium to be removed by precipitation and because the optimum pH for precipitation of different metal hydroxides varies, an average waste stream pH of about 8 is often used in waste treatment from metal finishers according to ZIEVERS, et al. (1968).

Lime is the most commonly used reagent for chromium (III) precipitation although soda ash has also been used. In waste treatment at an IBM plant, hexavalent chromium at 1300 mg/l in one waste stream was converted to trivalent chromium and precipitated with lime to achieve an effluent containing no hexavalent chromium and 0.06 mg/l trivalent chromium according to HANSEN and ZABBEN (1955). A coagulant aid was employed to improve the precipitation-sedimentation removal of chromic hydroxide which had a lot to do with the performance in that 99-99.5% of the suspended solids were removed though the use of the coagulant.

Filtration of precipitated and decanted effluents has significantly improved the quality of a treated effluent from a British metal alloy plant. Precipitation reduced chromium to 1.3-4.6 ppm whereas subsequent filtration reduced it further to 0.3-1.3 mg/l according to PATTERSON (1975). On the other hand, TEER and RUSSELL (1972) described lime precipitation of a dilute wood preserving wastewater containing trivalent chromium up to 2.2 mg/l which yielded an average effluent of 0.02 mg/l in which solids separation was by settling.

In precipitation of metal hydroxides from industrial wastes, large quantities of sludge are produced. Typically, these sludges settle rapidly but do not compact very well and contain only 2-3% solids.

In one case where vacuum filtration was not necessary, sludge from the sedimentation basin was stored for short periods in sludge storage tanks allowing it to compact to 10-12% solids equivalent to that obtainable by vacuum filtration according to HANSEN and ZABBEN (1959).

ANDERSON, et al. (1971) listed several ways of concentrating and disposing of precipitate sludges. Lagooning requires large areas of land and may contaminate ground water unless the lagoon is properly lined. Vacuum and pressure filtration is costly and probably is more applicable to industrial effluent treatment sludges.

REMOVAL OF CR(VI) AND CR(III) BY HDS

BETHLEHEM STEEL COMPANY generates effluents containing chromium in their steelmaking process which must be treated. According to S. T. Herman (1984 Randol

Workshop), the high density sludge (HDS) process has been tested and shown able to remove both Cr(VI) and Cr(III). This process entails recirculating underflow sludges almost quantitatively for mixing with the lime used for pH adjustment ahead of its addition to the effluent stream. More details can be requested from:

BETHLEHEM INTERNATIONAL ENGINEERING CO.
Bethlehem, PA 18016
(215) 694-2424
James Forand
Vice President
Stewart T. Herman

This is a relatively new development, and it was not determined to what levels chromate and chromium ions can be removed using this process, nor where it is applicable. HDS process sludges are often amenable to mixing with pozzolonic materials (e.g., cement, flyash, etc.) to make a stable solid waste disposable in municipal sanitary landfills as it generally passes the EPA toxicity leach test. HDS also has the ability to reduce metal concentrations often to below their theoretical solubilities.

PRECIPITATION - MgO

SCHILLER and KHALAFALLA (1981) applied for a patent for a process which is claimed to be more efficient for the removal of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from wastewaters. Disadvantages of the prior art processes are largely overcome by the use of a substantial excess of essentially dry powdered reactive MgO as a precipitant in the place of conventional precipitants. The resulting precipitate settles rapidly to a small volume and is not readily redispersed or redissolved. The purified water is claimed to be easily clarified avoiding the need for filtration. The U.S. patent application U.S. 325269 AO dated March 18, 1983, is available from NTIS, Springfield, Virginia, NTIS Order No. PAT-APPL-6-325-269, but it contains almost no useful information. The process belongs to the U.S. Dept. of the Interior and is available under license. Application forms for licensing of the process are available from the NTIS.

HYDROGEN PEROXIDE AND LIME FOR CHROMIUM REMOVAL

BARNES, et al. (date unknown) reported treatment of an industrial effluent containing chromium and phenolic compounds with hydrogen peroxide and lime. Chromium was reduced from 100 mg/l to less than 0.1 mg/l. Chromium originally present as chromate is reduced via a peroxychromium intermediate and precipitates out with the lime sludge. Following this treatment, the effluent is suitable for discharge into biological wastewater treatment plants.

The purpose of peroxide addition is to remove phenol. The process employs a 3:1 peroxide to phenol ratio with 10 mg/l iron and two hours aeration to oxidize the phenol at pH around 4 followed by addition of 6 mg/l lime reduced chromium and phenol concentration in the supernatant. This raised the pH to around 12 during which the chromium was precipitated in the lime sludge.

At the low pH of the oxidaton step of the treatment process, chromium (VI) oxidizes hydrogen peroxide and is thereby reduced to chromium (III). There is evidence that the reaction proceeds via a number of unstable peroxychromium complexes such as $CrO(O_2)_2$, but the mechanism of the process has not been established. Chromium (III) is probably produced by an internal oxidation reduction reaction occurring on decomposition of these complexes.

It is important that any residual peroxide remaining from the initial reaction step is removed prior to the addition of lime since under alkaline conditions hydrogen peroxide will oxidize chromium (III).

$$2Cr^{+++} + 3H_2C_2 + 10\ OH^- = 2CrO_4^{=} + 8H_2O$$

This can be done quite simply by adding 500 mg/l ferrous sulfate which also aids in the following lime treatment process when the pH is increased.

The above process may not be an economical way to treat mine-mill effluents but is reported to provide further understanding of the chemistry of chromium under different conditions.

David Barnes is employed at the School of Civil Engineering, University of New South Wales, Sydney, Australia.

SULFEX PRECIPITATION OF CHROMIUM

Hydroxide precipitation of chromium (III) yields a minimum solubility of about 0.2 mg/l Cr at around pH 7, and the increase in solubility at higher and lower pH values are steep as illustrated graphically below. For example, at pH 10, where zinc has its minimum solubility, the solubility of Cr(III) is around 6 mg/l.

SCOTT (?) showed that with the sulfide precipitation process, it is possible to achieve Cr(III) levels of below 0.05 ppm even though the chromium is, in fact, not precipitated as a sulfide.

Hexavalent chromium is reduced and removed in a single step in the insoluble sulfide precipitation process, the chemistry of which is illustrated by the equation:

$$Na_2CrO_4 + FeS + 4H_2O = \underline{Cr(OH)_3} + \underline{Fe(OH)_3} + NaOH + \underline{S} + 2H_2O$$

In the soluble sulfide process, the sulfide ion is capable of reducing hexavalent chromium as follows:

$$2H_2CrO_4 + 3NaHS + XH_2O = \underline{2Cr(OH)_3} + 3\underline{S} + 3NaOH$$

A U.S. EPA (1980) Summary report claims that a pilot study carried out for the U.S. Navy concluded that the reduction of chromate by a soluble sulfide reagent would be accomplished in the presence of ferrous ions (or some other suitable secondary metal). The ferrous ion acts principally as a calatyst for chromium reduction. Less than stoichiometric doses of iron are required to reduce most of the chromium. Nearly stoichiometric dosages are needed to achieve levels typical of other reduction processes, and no operating systems currently employ this one-step process.

More details of the SULFEX insoluble sulfide process are provided in U.S. EPA (1980), which is available from NTIS, Springfield, Virginia. Results of several sulfide precipitation tests are shown in the table below indicating that hexavalent chromium levels of less than 1 ppb are attainable using sulfide addition in some cases.

Another document describing the sulfide precipitation of heavy metals is EPA-600/2-80-139, 1980.

Although thus far employed only for plating and metal finishing waste effluents, the PERMUTIT-patented Sulfex process and the PERMUTIT sulfide sludge blanket clarifier appear potentially adaptable for large volume throughput applications. The Sulfex process is described in Chapter 25, and more information on the SULFEX process and the licensing arrangements can be requested from:

THE PERMUTIT COMPANY, INC.
Post Office Box 355
E49 Midland Avenue
Paramus, NJ 07652
(201) 967-6000

It is believed that the GE RESEARCH AND DEVELOPMENT LABORATORES have patented a calcium sulfide process for metal precipitation from effluents:

GE RESEARCH AND DEVELOPMENT CENTER
Post Office Box 8
Schenectady, NY 12301
(518) 385-8247.

So far, no sulfide effluent treatment plant has been identified for chromium removal from mine or mill effluents in the mineral processing industries.

ION EXCHANGE

ROSS (1968) claimed that ion exchange is an economical way to recover chromium for reuse from plating operations. Cation exchange can be applied to remove trivalent Cr(III) and anion exchange for chromate and dechromate, ie., Cr(VI).

When anion exchange resin is exhausted, it is regenerated with sodium hydroxide to yield sodium chromate in the eluate. The chromate can either be recovered as chromic and/or reduced to trivalent chromium and precipitated with lime.

In the ion exchange removal of chromium, pH is critical. Below pH 4, the oxidizing power of chromic begins to attack the resin. Above pH 6, the ratio of $CrO_4^{=}/Cr_2O_7^{=}$ in solution increases and, since most anion resins are less selective for dichromate, chromium leakage occurs sooner in this case according to ANDERSON (1974).

Highly basic anion exchange resins preferentially remove chromate at pH 4.5-5 before phosphate or sulfate according to CALMON (1974) who reports an exchange capacity of 1.9 lb. $CrO_4^{=}$ per ft^3 resin.

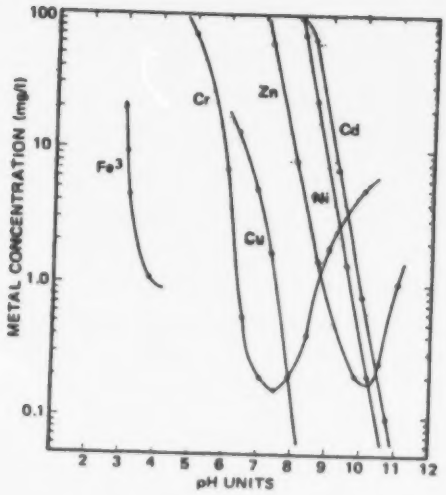
According to ANDERSON (1974) and CALMON (1974), chromate in recirculating cooling waters can be removed at pH 4.5-5 even in the presence of several hundred or thousand ppm sulfate and chloride. CALMON (1974) claimed that at above 100 mg/l chromate, the recovery of chromate by ion exchange can pay for itself.

One ion exchange treatment process was able to meet a chromate effluent standard of 0.05 mg/l for a metal finishing waste as reported by ROTHSTEIN (1958) which is equivalent to a Cr(VI) concentration of 0.023 mg/l.

RICHARDSON, et al. (1968) reported 0.0-0.90 mg/l effluent chromium levels depending on the period of operation, between exchange resin regenerations. On regeneration, the chromate-rich elute solution was returned to the cooling system with makeup water.

A small plating shop which employs ion exchange was reported in IND. WATER (1973) to have reduced chromate levels to 0.025 mg/l. The concentrated eluate is treated with sodium metabisulfite to reduce chromate followed by neutralization and chromic hydroxide precipitaton.

RICHARD, et al. (1968) describe the use of a NALCO patented ion exchange process for <u>selective</u> removal of Cr(VI) from recirculating cooling water at a UNION CARBIDE-



Precipitation of metal salts versus pH

Chemical Analysis of Raw and Treated Wastewater Used in Pilot Tests

Contaminant (µg/l)	Raw feed before treatment	Wastewater after treatment[a]				
		LO-C	LO-CF	LWS-C	LWS-CF	LSPF
Pilot Test 1						
Cadmium	45	15	8	11	7	20
Total chromium	183,000	3,680	250	1,680	68	159
Copper	4,700	135	33	82	18	3
Nickel	185	30	38	33	31	18
Zinc	2,800	44	10	26	2	11
Lead	119	119	88	104	59	120
Pilot Test 2						
Cadmium	58	7	12	<5	<5	<5
Total chromium	6,300	4	2	5	7	3
Hexavalent chromium	<5	<1	<1	<1	<1	<1
Copper	1,100	860	848	13	13	132
Nickel	160	30	34	33	23	34
Zinc	650,000	2,800	2,300	104	19	242
Mercury	<1	NA	NA	NA	NA	NA
Silver	16	NA	NA	NA	NA	NA
Pilot Test 3						
Cadmium	34	21	21	1	1	1
Total chromium	3	NA	NA	NA	NA	NA
Copper	20	7	8	2	1	4
Nickel	64	29	29	72	34	31
Zinc	440,000	37,000	29,000	730	600	2,000
Mercury	<10	NA	NA	NA	NA	NA
Lead	45	13	14	9	11	13
Silver	61	4	4	1	3	4
Tin	200	<10	<10	<10	<10	<10
Ammonium	([b])	NA	NA	NA	NA	NA
Pilot Test 4						
Cadmium	58,000	1,130	923	26	<10	<10
Total chromium	5,000	138	103	49	50	37
Copper	2,000	909	943	60	160	929
Nickel	3,000	2,200	2,300	1,800	1,900	2,600
Zinc	290,000	1,200	510	216	38	12
Iron	740,000	2,000	334	563	229	305
Mercury	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Silver	14	14	10	7	7	8
Tin	5,000	129	81	71	71	71
Pilot Test 5						
Cadmium	<40	<1	<1	<1	<1	<1
Total chromium	1,700	109	39	187	17	20
Copper	21,000	1,300	367	2,250	169	11
Nickel	119,000	12,000	9,400	11,000	3,500	5,300
Zinc	13,000	625	10	122	8	5
Iron	NA	2	<2	5	<2	<2
Lead	13	7	5	4	3	3
Silver	6	NA	NA	NA	NA	NA

[a]LO-C = lime only, clarified; LO-CF = lime only, clarified, filtered; LWS-C = lime with sulfide, clarified; LWS-CF = lime with sulfide, clarified, filtered; LSPF = lime, sulfide polished, filtered; NA = not applicable.

[b]Qualitative tests indicated the presence of significant amounts of ammonium.

Note.—Wastewater by pilot test: 1—high-chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high-zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

SOURCE: *Sulfide Precipitation of Heavy Metals*, EPA Grant 5806413, in preparation.

operated Atomic Energy Commission plant at Paducah, Kentucky. Hexavalent chromium as chromate was removed from 20 mg/l to 0-2 mg/l using sand filtration and ion exchange. Details of the equipment are provided in their paper.

Although cost data presented in 1968 would no longer be valid, the comparison of parameters required for removal of hexavalent chromium by ion exchange and by reduction and precipitation is of interest and probably remains valid. More information can be requested from NALCO or from UNION CARBIDE CORP.:

NALCO CHEMICAL COMPANY
2901 Butterfield Road
Oak Brook, IL 60521
(312) 887-7500
Robert E. Finch

UNION CARBIDE CORPORATION
Nuclear Division
Paducah, KY 42001
(1968 address)
E. W. Richardson
E. D. Stobbe

WASTE CHROMATE DISPOSAL
CHEMICAL CONSUMPTION COMPARISON

Recovery and Reuse (Ion Exchange)

Item	Chemical Usage lb/lb CrO_4
Sulfuric Acid	1.2
Sodium Hydroxide	0.9
Sodium Chloride	1.7
Ion Exchange Resin Replacement	Over 50% of Total

Destruction by Reduction and Precipitation

Sulfuric Acid	0.65
Ferrous Sulfate	10.40
Calcium Hydroxide	3.1

WILMOTH, et al. (1979) found that a dual bed (strong acid-weak base resin combination) ion exchange system was very effective for removal of trace elements including Cr from acid mine drainage.

CHEM-SEPS CHROMIX PROCESS

Chem-Seps Chromix process provides a unique system for recovery of Chrome VI, Chrome III, and Zinc from cooling tower blowdown.

The use of the recovery system allows the preferred corrosion inhibitor chromates to be used and eliminates the pollution problems. The destruct system which is another alternative does not necessarily eliminate pollution. Chrome VI is reduced to Chrome III and precipitated. But today's EPA and other regulatory agencies requirement of 0.05 ppm total chrome are not achievable with the destruct system. Further the destruct systems are expensive to operate. A comparison of chemical consumptions between recovery and destruct is shown below.

	Recovery System	Destruct System
Sulfur Dioxide	None	2 lbs SO_2/lb Cr^{+6} or 1 lb SO_2/lb CrO_4
Sodium Hydroxide	0.75 lbs/lb CrO_4	2.5 lbs/lb Cr^{+6}
Sulfuric Acid	1.00 lbs/lb CrO_4	24.5 lb/lb Cro_4 *

*This consumption is based on 20 ppm of CrO_4 and reduction of pH from 6.0 – 6.5 to 2. The reaction of reduction is best carried out at pH 2.

Typical System

A Chromix system to treat one million gallons per day (700 GPM) of blowdown with a Chromate concentration of 20 ppm would require one Chem-Seps Continuous Unit Model No. 5412 as shown in the flowsheet.

The cooling tower blowdown is pumped to the treatment section of the chromix system where the Chrome VI, Chrome III and Zinc are picked up on Chem-Seps special blend of ion exchange resins. The water leaving this section is essentially chromate-free and may be discharged. After the resin is loaded with the valuable corrosion inhibitors it is moved to the regeneration section. In the regeneration section Sulfuric Acid and Sodium Hydroxide are used to remove the Chrome VI, Chrome III, and Zinc from the resins. The sodium Chromate dichromate and Zinc Sulfate leaving this section may then be recycled to the cooling tower instead of going to sludge as in the destruct system.

OPERATING COST ECONOMIC ANALYSIS

Basis – Chromix System to treat one million gallons per day of cooling tower blowdown containing 20 ppm chromate. Unit model No. 5412 recovers 165 pounds of CrO_4 per day or 4,950 pounds per month. Capital Cost $200,000.

	Cost Per Month
Resin Replacement at $80 per Cu.Ft.	$ 350
Replacement Parts 3 percent of equipment cost	500
Chromate Make Up Cost 1 percent (50 pounds) at $1.75 per pound CrO_4	90
Chemicals and Utilities	
Sulfuric Acid	110
Caustic	180
Power	153
Estimated Labor Cost	
Operation at 1500 per month	1,000
Maintenance at 500 per month	500
TOTAL MONTHLY OPERATING COST	$2,883

Summary

Estimated value of chromate recycled equals $8,662.50 per month.

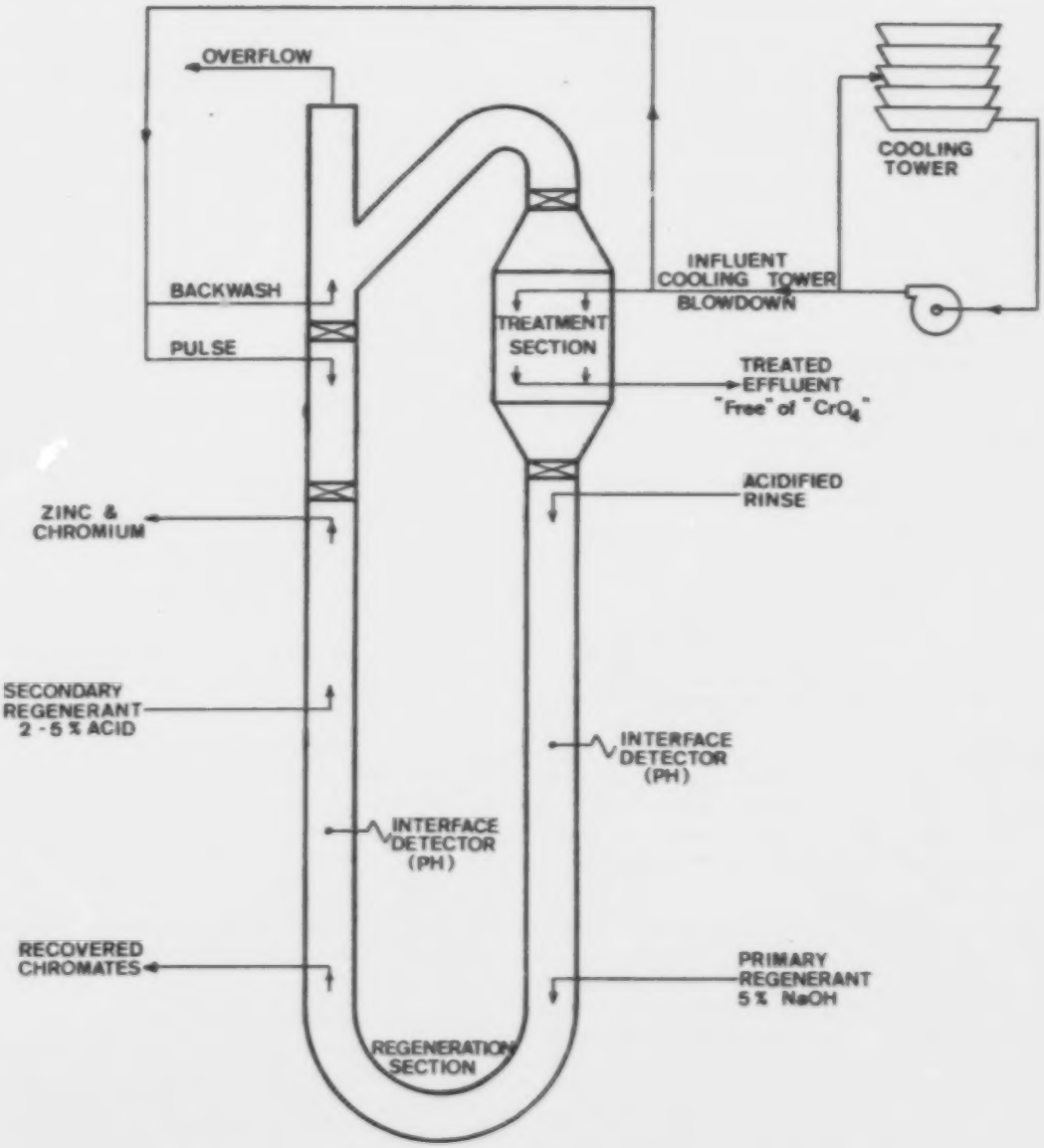
Payback on capital cost is estimated to be 2.9 years, plus installation cost.

Standard Continuous Units Fully Assembled

A full line of standardized continuous countercurrent ion exchange units have been designed to recycle chromates from 100 gpm up to 2000 gpm in a single unit. Each of these units are shipped fully assembled. A unit arrives on your site ready for feed and service piping connections plus power tie-in to the control panel. Installation and Start-Up cost are low.

Equipment Specifications Available

If you now operate a cooling tower and treat with chromates as corrosion inhibitors or if you do not presently use chromates but would prefer to use them, please contact Chem-Seps. Let us know blowdown rate and chromate level. You will receive a prompt reply including equipment specifications, operating data and an economic analysis that fits your specific cooling tower operation. It could be the start of improved, more economical, pollution-free cooling tower operation for you.



CHEM SEPS CHROMIX SYSTEM

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ION EXCHANGE - LIQUID FILLED MEMBRANES

BEND RESEARCH, Oregon, has developed a process for the removal and recovery of hexavalent chromium from plating and metal finishing wastes. They have developed a patented hollow fiber with an inside diameter of around 0.025 inch. The walls of the membrane are "filled" or impregnated with an ion exchanging liquid reagent. Feed solution flows through the filaments and is absorbed into the walls of the filaments and continuously eluted at the outside of the filaments which are submerged in an eluant solution contained in the flow through module. The filaments are packed into modules about 4-6"Ø and three feet long. It was pointed out that these devices are designed to recover usable Cr from plating waste solutions containing approximately 300 mg/l Cr(VI) yielding an effluent with, say, 30 mg/l. The process does not yet appear suitable for removal of Cr(VI) to very low levels needed to meet effluent discharge limits. More information can be requested from:

BEND RESEARCH
64550 Research Road
Bend, OR 97701
(503) 382-4100
Harold K. Lonsdale
President
Dave Kamperman
Manager of Metal Separations

No ion exchange plants recovering or removing chromate from flotation plant effluents were identified during the course of this study. It appears that ion exchange can reach levels below 0.05 mg/l total chromium, but large scale IX plants are expensive and, in the case of this application, could be subject to scaling problems depending on the quality of the effluent or recycled water stream to be treated.

ELECTROCHEMICAL REDUCTION

Reduction of hexavalent chromium to trivalent chromium by cementation with metallic iron or ferrous iron to yield trivalent chromium has been described by PATTERSON (1975).

$$Cr_2O_7^{=} + 3Fe^{o} + 14H^{+} = 2Cr^{3+} + 3Fe^{+2} + 7H_2O$$

$$Cr_2O_7^{=} + 6Fe^{2+} + 14H^{+} = 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The reaction requires acidic conditions and is pH dependent. Complete reduction of 100 mg/l Cr^{+6} solution has been reported within eight minutes at pH 2.0 by CHASE (1974).

In one full scale application, hexavalent chromium at 2.5-52.0 mg/l was reduced to 0.01-1.40 mg/l by the cementation process, and average effluent was 0.09 mg/l for an

average chromate reduction of 99.4% according to JOSTER and TAYLOR (1963). The process used scrap iron suspended in a perforated rotating drum through which the wastewater flows at pH 2-3. A similar electrochemical process, but employing an electrical potential and consumable elctrodes, has been reported to achieve chromate reduction to below 0.05 mg/l in cooling tower blowdown by DUFFEY (1974).

EVAPORATIVE RECOVERY

This is not applicable to the very low levels encountered in mine water and metallurgical processing effluents.

ACTIVATED CARBON

Several successes have been reported of chromate removal by activated carbon. In one case, hexavalent chromium levels of 0.09-0.19 mg/l were reduced to 0.04 mg/l Cr(VI) from municipal effluent according to ARGO and CULP (1972). Initial hexavalent chromium levels of 5 mg/l were reduced to 0.006-0.087 mg/l following carbon adsorption according to MARUYAMA, et al. (1972). According to PATTERSON (1975), activated carbon may not be equally effective at higher chromate levels where chromium (VI) reduction efficiencies of 50-99% were experienced.

FAULKNER (undated) described a process whereby activated carbon will rapidly reduce ferric to ferrous iron when a stoichiometric amount of SO_2 is added to a solution and the solution is then passed through a column of activated carbon. A retention time of only a few minutes is needed, and the ferric iron and SO_2 in the effluent are quantitatively reacted. The SO_2 requirement is 0.57 lb. per lb. Fe^{3+}.

FAULKNER (1983) indicates that hexavalent chromium can be reduced in a similar fashion by SO_2 in contact with granular activated carbon. More information can be obtained from:

CALCON CARBON CORPORATION
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
W. D. Faulkner

SAITO (1979) described bench scale tests in which Cr(VI) was removed from wastewater. He found that removal of Cr(VI) depends on the type of carbon, on pH, and on temperature. The higher the temperature, the lower the residual Cr(VI). The best removal of Cr(VI) was in the pH range 4-6.

Aqueous KOH and sulfuric acid solutions were used to elute chromium from the activated carbon test samples. Residual Cr(VI) showed a tendency to decrease with an increase in the surface area of the carbon used. The data indicates a pH dependence of Cr(VI) adsorption onto carbon but is unclear and does not show evidence of a suitable process for removal of chromium down to very low levels using activated charcoal.

HUANG and BOWERS (1978) investigated the kinetics of Cr(VI) removal by activated carbon. Some of the Cr(VI) is removed by adsorption while the rest (76%) is removed by reduction to Cr(III) which adsorbs less readily onto carbon. By adding 524 mg/l sodium hypochlorite to raise the redox potential or oxidize the carbon surface with 10 normal HNO_3 prior to contact with the solution, the adsorption of hexavalent chromium resulted in 83%-90% total chromium removal after five hours contact time.

There are numerous additional papers on the subject of chromium removal from solutions using activated carbon. Several are listed in HUANG and BOWERS's (1978) paper. These are not listed here because the data and testwork relates more to the levels encountered in plating wastes rather than the very low levels of 0.001-0.100 mg/l that could be expected in flotation plant tailings recycle water and effluents.

DEVOE-HOLBEIN CHROMIUM REMOVAL

DEVOE-HOLBEIN (CANADA), INC. claims to be able to remove metals using a new process which can be tailored to be highly specific, and which they claim reduces metal concentrations to extremely low levels.

DEVOE-HOLBEIN (CANADA), INC. has developed several material "compositions" onto which metals are precipitated. The loaded composition is then recovered and regenerated for reuse in a similar manner to ion exchange resins.

The technology is still in the development stages, and the composition is available in experimental quantities. No cost data is available. However, the company points out that commercial scale operations would be relatively inexpensive once enough of the composition is in use to justify mass production.

More information and details are available from:

DEVOE-HOLBEIN (Canada), INC.
175 Bouchard Blvd.
Dorval, Quebec
Canada H9S-1A9
(514) 636-6042
Dr. Bruce E. Holbein
Dr. L. G. Neirinck

A detailed paper by HOLBEIN, et al. (undated) is included in Chapter 25 on "Removal of Contaminants."

A schematic diagram of the DEVOE-HOLBEIN process is shown overleaf. In addition, the table of data shows that a DEVOE-HOLBEIN composition was able to achieve in excess of 99% chromium removal from two solutions yielding a treated effluent of less than 300 ppb Cr.

HOLBEIN, et al. (undated) showed another example where their composition DH-524 reduced chromium from 694 ppm to less than 0.01 ppm, or a removal efficiency in excess of 99.99%.

DEVOE-HOLBEIN showed three examples of hexavalent chromium containing effluents including one containing calcium and magnesium which would interfere with cation exchange resin removal of Cr(VI). They claim that reduction and precipitation processes for Cr(VI) removal are not quantitative and generate large volumes of sludges that must be disposed of.

The three demonstration solutions were treated using DH-524 composition which reduced Cr(VI) levels to below the detection limit. Capacity of the DH-524 composition for chromium (VI) was claimed to be 20 g Cr(VI) per Kg of composition, and the material was 100% regeneratable resulting in small volumes of concentrated chromium waste which can either be reused in the plating solution at the plant from which it came or sold to the ceramic industry. Spent D-H compositions, after serving their useful lifetime, can also be used as a raw material in the ceramic industry according to the inventors.

DEVOE-HOLBEIN (CANADA), INC. is a research and development company. In order to make their process practical and suitable for use in industry, they have joined forces with the JOHN BROWN COMPANY, an engineering and construction firm, to offer the process to industry. Information is available from:

JOHN BROWN
Engineers and Constructors, Inc.
Post Office Box 1432
Stamford, CT 06904
(203) 327-1450
Telex: 965900

STARCH XANTHATE REMOVAL OF CHROMIUM

WING, et al. (1974) showed that a starch xanthate with a cationic flocculant PVBTMAC (Polyvinylbenzyltrimethylammoniumchloride) could reduce chromium (III) from 2600 mg/l to 21 mg/l. Two other solutions containing 58 mg/l and 8,250 mg/l Cr were reduced to 1 mg/l and 94 mg/l respectively.

& METAL CONCENTRATION

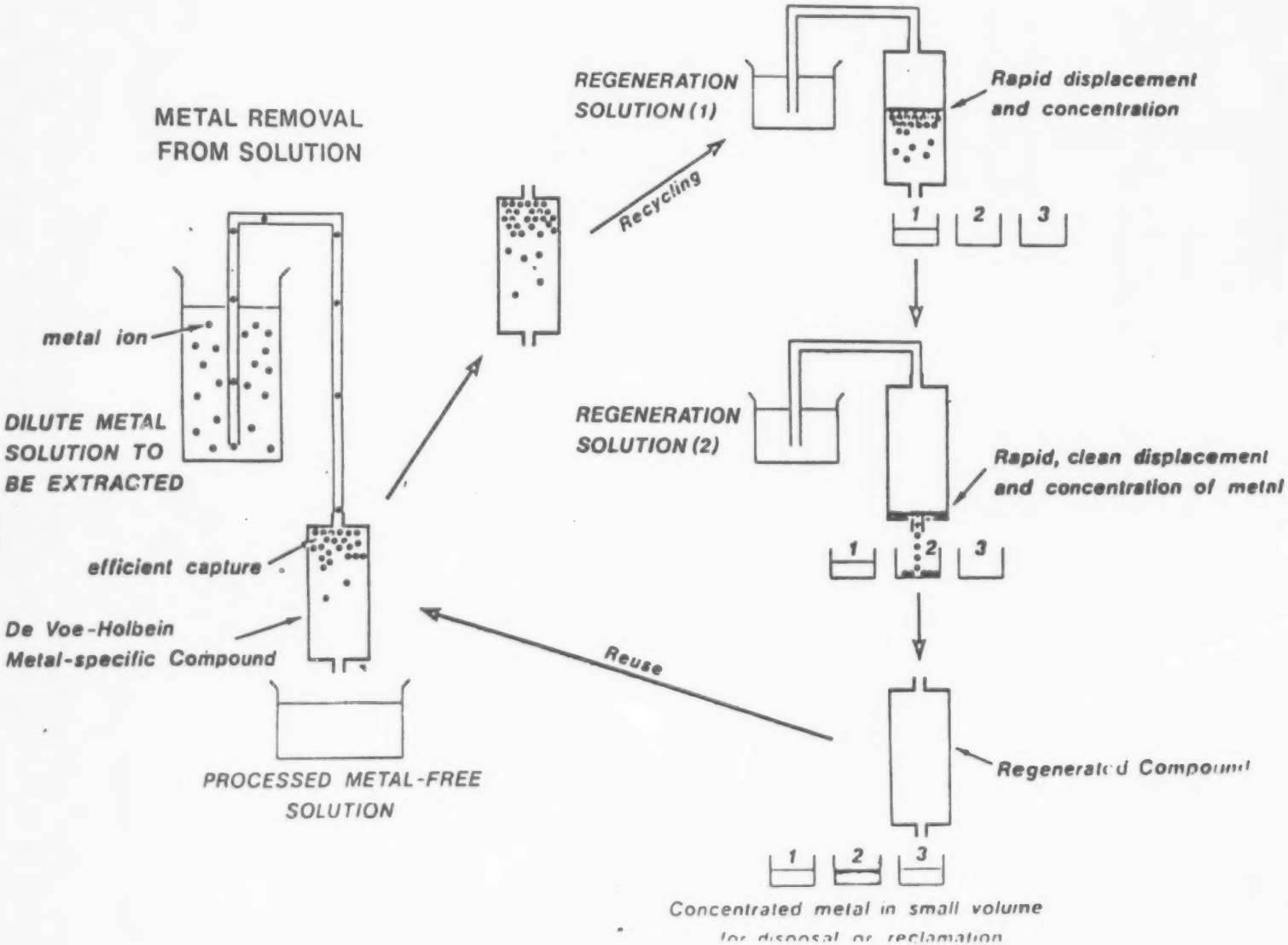

TABLE 1

TYPICAL EXAMPLES OF METAL CAPTURE FROM SOLUTIONS BY REPRESENTATIVE DEVOE-HOLBEIN COMPOSITIONS

Metal	Composi-tion (A)	Starting (B) concentration	Capture effic. (%)	Residual concentr.
Cadmium	B-1 N-2	10 ppm (Dw) 672 ppm (Tw)	99.99 99.99	0.1 ppb < 67 ppb
Cobalt	B-2 A-1	1.2 ppm (Tw) 364 ppm (Dw)	99.99 99.92	< 20 ppt 292 ppb
Cesium	W-3 P-1	7.97 ppm (Dw) 797 ppm (Dw)	99.99 99.97	< 20 ppt < 250 ppb
Chromium	S-2 W-1	31.2 ppm (Dw) 312 ppm (Dw)	99.04 99.9	< 300 ppb < 300 ppb
Copper	W-3 A-1	38.1 ppm (Dw) 381 ppm (Tw)	99.99 99.99	< 1 ppt 3.8 ppt
Gadolinium	A-1 R-1	31 ppb (Dw) 943 ppm (Dw)	99.9 99.9	< 20 ppt 0.7 ppb
Iron	F-1 F-2	58 ppb (Dw) 34 ppm (Sw)	99.99 99	58 ppt 34 ppb
Lead	A-2 P-1	42 ppm (Dw) 1243 ppm (Dw)	99.99 99.92	42 ppb < 940 ppb
Mercury	W-1 Y-2	12.0 ppm (Dw) 120 ppm (Dw)	99.96 > 99.9	4.8 ppb 1.2 ppb
Nickel	G-1 P-1	88 ppb (Tw) 352 ppm (Dw)	99.99 99.94	1.3 ppt < 200 ppb
Silver	W-3 Z-1	10.8 ppm (Dw) 847 ppm (Dw)	99.99 99.87	900 ppt < 870 ppb
Thorium	B-1	139 ppm (Tw)	99.99	139 ppt
Uranium	B-1 F-1	24 ppb (Tw) 24 ppb (Sw)	99.99 99.98	24 ppt 1.7 ppb
Zinc	H-3 W-3	6.8 ppm (Dw) 943 ppm (Dw)	> 99.3 > 99.9	< 20 ppt 0.7 ppb

Low concentrations were measured by counting using radioactive metal tracers.

A. Measured with 4 gms. column of composition: capacities vary with composition but range typically between 3 mg. to 25 mg. metal per gram of compound.

B. Test metal contained in demineralized water (DM), sea water (SW), Montreal tap water, St. Lawrence Seaway (TW) or photographic fix-bleach (PF).

C. Concentrations given as parts metal by weight per parts water by volume (eg. 1 ppt = 1 microgram/litre).

TABLE 7

Recovery of Cr from Various Waste Waters With DH-524

Type of Waste Water	Influent Cr VI ppm	Treated Effluent Cr VI ppm [a]	Cr Removal Efficiency %	Capacity mg CrVI per kilogram Composition	Regeneration Efficiency [c]
1. Boiler Blow Down	694.3	N.D. [b]	>99.99	≈20,000	100%
2. Plating Waste precipitator effluent	3.8	N.D.	>99.99	≈20,000	100%
3. Cooling Tower Bleed	7.6	N.D.	>99.99	≈20,000	100%

[a] Flow rate of 20 bed volumes per hour in a fixed bed of DH 524

[b] N.D. not detectable by atomic absorption spectrophotometry

[c] 100% of bound Cr displaced in approximately 3 bed volumes of regenerant. Fully regenerable over 15 cycles of use so far tested.

	Influent Cr(III) mg/l	Effluent Cr(III) mg/l
Solution A	2600	21
Solution B	58	1
Solution C	8250	94

The above work demonstrating regenerable insoluble starch xanthate was carried out by the U.S. Dept. of Agriculture. An experimental resin containing starch xanthate was prepared by Dow Chemical Co., Midland, Michigan, in 1974. The work was performed by:

CEREAL PRODUCTS LABORATORY
Northern Regional Research Laboratory
Agricultural Research Service
U.S. Department of Agriculture
Peoria, IL
Robert E. Wing

Although demonstrated on a laboratory scale in, 1974 RANDOL INTERNATIONAL LTD. did not encounter any commercial scale applications of this technology--neither in the mining and mineral processing industry nor in industrial effluent treatment. This is not a poor reflection on its performance, however, but rather a reflection on the receptiveness of industry to try new technology. Perhaps chromium adsorbs as $Cr(OH)_3$.

It is interesting that chromium, which does not form an insoluble sulfide precipitate, can still be removed to very low levels using an insoluble starch xanthate which has active groups containing sulfide.

Advantages of the processes claimed by WING, et al. (1974) are:

1) The composition is easily regenerated using a mild acid which elutes the metal.

2) The volume of sludge generated is small compared with lime treatment.

3) The non-gelatinous sludge settles rapidly and more quantitatively than most metal precipitates.

4) Suspended solids need not be removed before treatment with insoluble starch xanthates.

5) The starch xanthate method is effective over a pH range 3-11.

6) Only very slight reagent excess is needed to achieve minimum levels of metal in solution.

Very recent development work along the same lines was identified in 1984-85. Insoluble starch xanthate and carbamate materials as well as the knowhow and equipment in which to use them are available from:

POLLUTION TECHNOLOGY SYSTEMS, INC.
2922 Benton Street
Garland, TX 75042
(214) 272-4010
Mike Coward
Manager Systems Engineering

REVERSE OSMOSIS

R.O. has been reported to have application in hexavalent chromium removal although experience with the process is limited. Improved efficiency seems possible when the solution is first neutralized.

At pH 2.6, a high selectivity cellulose acetate membrane yielded 92.6% with 98.6% rejection at pH 7.6 according to CRUVER (1973).

It is not for one minute proposed that a relatively expensive R.O. plant be installed for hexavalent chromium removal, but if such a plant is installed in any case for any one of several other reasons, then it is interesting to note that it may be possible to benefit from its Cr(VI) removal ability as an added advantage.

In this respect, it is of interest to note that at the pilot plant installed at the RAND MINES ERPM Hercules Shaft on the Witwatersrand, to demonstrate seeded slurry reverse osmosis, total chromium was reduced from 0.08 mg/l to less than the 0.02 mg/l Cr detection limit.

WILMOTH, et al. (1979) found that reverse osmosis was effective in removing mg/l levels of trace elements from acid mine drainage including Cr. It was not determined what type of reverse osmosis system was used for the test except that this work predates seeded slurry developments in R.O. applications.

BIOLOGICAL POLISHING OF EFFLUENTS

Natural marshes may conceivably be developed for effective use in polishing mine and mill tailings effluents for metal removal to very low levels. Biological polishing of effluents occurs in the New Missouri lead belt and at ST. JOE MINERALS operations at Edwards, New York. However, data is not available for chromium removal. Marshes offer the potential for synergistic metal removing processes involving aqueous plants, algae, and bacteria, including generation of sulfides in the anaerobic zone. It is not known what

effect the biological system would have on chromium levels or the effect of accumulated chromium precipitates on the marsh itself. Conceivably, if marsh ecologies remove hexavalent chromium, water reclaimed for recycle could be treated in the bog prior to recycle to the plant to avoid metallurgical interferences by residual Cr(VI).

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Diamond Shamrock
Chemicals Company

April 17, 1985

Mr. Hans Von Michaelis
Metallurgical Consultant
Randol International Limited
21578 Mountsfield Drive
Golden, CO 80401

Dear Mr. Von Michaelis,

Attached is the Diamond Shamrock Technical Bulletin reviewing treatment systems for chromium bearing wastes. I hope this helps your understanding of what is required for treatment of water containing low levels of chromium.

If you should have any further questions, feel free to call.

Sincerely,

DIAMOND SHAMROCK CHEMICALS COMPANY

Roy Yelverton

Roy A. Yelverton
Marketing Manager
Chrome Chemicals

Attachment

RAY:skh

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Technical Bulletin

Introduction

Users of chromium chemicals are, or will be in the near future, required to perform some degree of treatment of chromium bearing effluents before they are discharged. Because of the reported toxic nature of chromium chemicals, specifically chromic acid, chromates, and dichromates (hexavalent compounds), it is essential that these materials do not enter receiving bodies indiscriminately.

Fortunately the technology of treating chromium wastes has been proven and used successfully for several years. So many treatment systems for chromium are commercially available that the problem is choice of a particular system. This bulletin presents some fundamental information relating to commercially available systems.

Toxicity

The toxicity of chromium chemicals has not been well defined and reports on human toxicity are limited. The U.S. Dispensatory, for example characterizes potassium dichromate as a violent irritative and corrosive poison, which can be fatal.[1] On the other hand, consumption of hexavalent chromium in water up to 25 ppm (25 mg/1) has been reported without harmful effects.[2]

McKee and Wolf[3] have concluded that water containing as much as 5 ppm (5 mg/1) of hexavalent chromium could be consumed without deleterious physiological effects. Hexavalent salts will impart a yellow color to water at a very low concentration, 1.5 ppm, and is easily detected in water solutions. This same concentration is near the taste threshold. For domestic water supplies the U.S. Public Health Service set a mandatory limit, in 1946, of 0.05 ppm hexavalent chromium. The World Health Organization (WHO) International Drinking Water Standards prescribed the 0.05 ppm limit. The .05 ppm limit was the lower limit of detectability at that time.

Generally salts of trivalent chromium are not considered to be physiologically harmful.[4] Administered orally, the chromium salts are not retained by the body, but are rapidly and completely eliminated.[5] There is no evidence that trivalent chromium compounds have any toxic effects.[6] In fact, Mertz[7] has concluded that chromium, as Cr^{+3}, appears to be an essential trace metal in mammalian metabolism. The less toxic nature of trivalent chromium was reflected in the 1962 Drinking Water Standards set by the U.S. Department of health, Education, and Welfare which placed a limit of 1.0 ppm trivalent chromium. The 0.05 limit was retained on hexavalent chromium.

Restrictions

Specific restrictions for discharge of chromium bearing wastes vary substantially according to the point of discharge and the nature of the industrial process which generates the waste chromium. The regulatory agency for any particular plant may be a Federal, a State, or local agency, or perhaps a combination of the three.

The United States Environmental Protection Agency (EPA) has been charged with the responsibility of developing effluent limitation guidelines for several industrial operations, as well as setting up a permit system. An initial task has been to survey specific industries to determine, in the case of heavy metals (chromium included), the best practicable control technology currently available to remove all, but small amounts, of heavy metals from the effluent of existing point sources.[8,9] The EPA has concluded that chemical treatment is an acceptable method and has prescribed the quantities or pounds of chromium (hexavalent, trivalent and total) per day which may be discharged. The number is based upon some unit of production and therefore is different depending upon the process. The initial guidelines are for those sources which discharge into navigable waters; however, additional guidelines for new point sources will differ from existing point sources to reflect new technology. The EPA also prescribes guidelines for new point sources discharging into municipal sewage treatment plants, as well as navigable waters.

Discharge of chromium wastes into municipal sewage treatment plants is a different problem as some plants have a capacity to assimilate chromium wastes and others do not. The ability of a municipal plant to receive chromium wastes dependds upon the treatment plant type, the treatment plant capacity and loading, the dilution, the other types of industries discharging into the plant, etc. In some large metropolitan areas chromium has been accepted without treatment, while in other areas some degree of treatment is required. The local regulatory agency generally prescribes the limitation; however, EPA has prepared preliminary pre treatment standards which may influence the treatment requirements.[10]

Information concerning specific requirements should be obtained from State and/or Local Offices, of the EPA. A listing of EPA Regional Offices is located in Appendix I.

Sources of Chromium Pollution

Chromium chemicals have applications in a number of industrial operations including plating and metal finishing, pigments, leather tanning, corrosion control agents, textile dyeing and mordants, wood preservation, photography, catalysts, etc. All of these industrial applications present a potential source of waste material which may require treatment. The extent of treatment required depends upon the specific industrial process used and the particular chromium chemical which is to be treated (hexavalent or trivalent chromium)

Treatment systems for chromium bearing wastes have been commercially developed and include both destructive and recovery systems. Although the systems have been developed primarily for the metal finishing industry, the application is essentially the same for any source of chromium waste. Most processing applications employing hexavalent chromium require rather concentrated chromium solutions. After processing, some sort of a rinising or washing operation is performed whereby a dilute chromium waste is generated. The optimum or most efficient system of rinsing is that which employs counter-current or cascading rinse operations. Use of counter-current rinse operations will reduce water usage, treatment costs and equipment size.

Application

In order to determine the application of a particular waste treatment system for chromium, it is essential to understand some basic chromium chemistry. Specifically, it is necessary to distinguish between hexavalent chromium and trivalent chromium since differences in the chemical properties of the two form the basis of design of destructive and recovery systems.

Hexavalent chromium (Cr^{+6}) is the highest oxidation state of chromium. The common chromium chemicals which are composed of hexavalent chromium are chromic acid (or chromium trioxide) CrO_3; the bichromates, $Cr_2O_7^{=}$ and chromates, $CrO_4^{=}$. The basic building block of all hexavalent chromium chemicals is sodium bichromate dihydrate, $Na_2Cr_2O_7 \cdot 2H_2O$, or technically sodium dichromate, dihydrate. All other common hexavalent chromium chemicals; chromic acid, sodium chromate, and potassium bichromate, are derived from sodium bichromate. Solutions of chromic acid, sodium bichromate, potassium bichromate and sodium chromate, contain hexavalent chromium, which, in dilute solution, is essentially the same regardless of the source. Chemical differences are more pronouned in concentrated solution; for example, concentrated chromic acid solutions have a low pH (2.0 or less) and are very strong oxidizing agents. Sodium bichromate solutions nominally have a pH of 4.0 and are not as strong oxidizers as chromic acid unless the pH is lowered with some mineral acid. Sodium chromate solutions have a nominal pH of 8.6 and show the least oxidizing characteristics. All of the common commercial hexavalent salts are quite soluble at any pH, consequently the chromium cannot be precipitated out of solution as the hydroxide without conversion to trivalent chromium. The process is described later.

Trivalent chromium (Cr^{+3}) is a lower oxidation state of chromium. Trivalent compounds do not exhibit the strong oxidizing characteristics of hexavalent and are soluble only at low or very high pH levels. At a pH of 8.6 trivalent chromium is essentially insoluble.

Trivalent chromium chemicals such as chromic chloride, chromic acetate, and chrome alums are trivalent salts. These salts are soluble since water solutions are acidic. Treatment of waste from these sources is a precipitation of the chromium salts by a simple pH adjustment. Chromic oxide, or chrome green, is obtained by reduction of sodium bichromate and precipitation of the hydroxide $Cr(OH)_3$. Upon dyring Cr_2O_3, chromic oxide, is obtained. This material is highly insoluble and can reaidly be treated by mechanical separation.

Most commercial systems available for treatment of hexavalent chromium wastes are designed to handle rather dilute solutions. Disposal of more concentrated solutions, particularly contaminated processing solutions, will present problems. In these instances, the concentrated material must be slowly introduced. from storage, into the rinse water stream for dilution before treatment.

Process Selection

Process selection and design can be very complex for a number of reasons. Since every operation is different, a good engineering study should be made. This can often be accomplished "in house"; however, employing reputable consulting engineers, or relying upon reputable equipment vendors is highly recommended.

Basically a decision must be made between a destructive system and a recovery system. In order to make such a choice, as well as design the equipment, a number of variables must be considered. Some of these are: The volume (flow rates) and concentration to be treated; chemical costs; energy costs; labor and equipment costs; operating and maintenance costs; the amount and value of the chromium which could be recovered; regulations on effluent quality, etc.

Generally, justification of a recovery system requires that large quantities of hexavalent chromium can be recovered in a usable form, as well as recovery and reuse of water. The capital expenditure for recovery systems is substantially higher than destructive systems. Recovery systems using evaporative methods sometimes require expensive corrosion resistant equipment. Additionally some provision, usually ion exchange, is required to purify the chromium processing solution since impurities concentrate as well as the chemical being recovered. Only certain types of ion exchange resins are useful for purification since the organic resins tend to be oxidized by the hexavalent chromium; however, suitable resins are commercially available. The practical life of these will depend upon the specific application.

Chemical Treatment

The chemical treatment of hexavalent chromium wastes is a two-step process. The first treatment insures the reduction of the hexavalent chromium to trivalent chromium. The second step brings about the removal of the trivalent chromium from solution by precipitation of highly insoluble chromic hydroxide.

Reduction

The most common reducing agents used in the first step are sulfur dioxide, or its salts - sodium meta bisulfite, sodium bisulfite, or sodium sulfite. Ferrous ion, either the chloride or sulfate is an exceptionally good reducing agent which may be used in place of SO_2 or the sulfites. The distinct advantages of ferrous salts are: They are inexpensive, and readily available; there is no need for ventilation of the treatment tank; and the pH or the reaction is not as critical as it is with the sulfite or sulfur dioxide reducing agents.

Sulfur dioxide, SO_2, is the most commonly used reducing agent for hexavalent chromium. The material is supplied as a liquid in various size pressurized cylinders. Application is brought about using a sulfonator (the preferred method), a gas diffuser, or as a water solution.

Addition of SO_2 to water results in the formation of sulfurous acid, H_2SO_3, which is the active reducing agent. Usually the sulfur dioxide is not efficiently converted to sulfurous acid and some of the SO_2 escapes the solution. Because of the toxic and corrosive nature of the SO_2, it is necessary to provide exhaust facilities over the treatment tank.

The alkaline salts of sulfur dioxide-sodium bisulfite, $NaHSO_3$; its anhydride sodium metabisulfite, $Na_2S_2O_5$; or sodium sulfite, Na_2SO_3; find use as reducing agents for hexavalent chromium. These materials are supplied in a dry crystalline form and offer some advantage over SO_2 in ease of handling. Their action as a reducing agent is identical to that of SO_2. These salts, in an acidic solution, generate SO_2 which combines with water to form sulfurous acid. With these salts it is also necessary to provide ventilation since excess SO_2 may be released from solution.

The net result in the reduction reaction is the same as SO_2 at any given pH once the sulfurous acid is generated. The quantities of reducing agent, sulfuric acid, and alkali for precipitation are tabulated in Table 1 for each of the reducing agents.

The quantities tabulated are the exact stoichiometric quantities based on the equations written for chromic acid in water (H_2CrO_4) below. The requirement for sulfuric acid will vary somewhat if the material being treated is a dichromate or a chromate, or there is some alkalinity in the waste water.

(1) Sulphur Dioxide - SO_2
$3\,SO_2 + 2H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 2H_2O$

(2) Sodium Bisulfite
$6NaHSO_3 + 4H_2CrO_4 + 3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 10H_2O$

(3) Metabisulfite - $Na_2S_2O_5$
$3Na_2S_2O_5 + 4H_2CrO_4 + 3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 7H_2O$

(4) Sodium Sulfite - Na_2SO_3
$3Na_2SO_3 + 2H_2CrO_4 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Na_2SO_4 + 5H_2O$

Liquid SO_2 is the most economical of the sulfite reducing agents. The next most economical sulfite salt is sodium metabisulfite which is often referred to as anhydrous sodium bisulfite. The anhydrous material is the normal commercial bisulfite salt as it is less hydroscopic and more stable than sodium bisulfite. On an SO_2 basis sodium metabisulfite is slightly less expensive than sodium sulfite.

From the equations it will be noted that only sulfur dioxide, because of the formation of H_2SO_3, generates sufficient acid to lower the pH of the solution to be treated to approximately 5. With stoichiometric quantities, SO_2 will reduce hexavalent chromium under pH conditions as high as 5.5; however, from Figure 1, which shows the effect of the reaction pH on the rate, a lower pH is required to achieve the optimum rate and minimize the retention time. A pH range of 2 to 3 will permit complete reaction without a large excess of SO_2 and excessive retention time. Although not shown in the table, acid, usually sulfuric, is required to carry out an efficient reduction reaction.

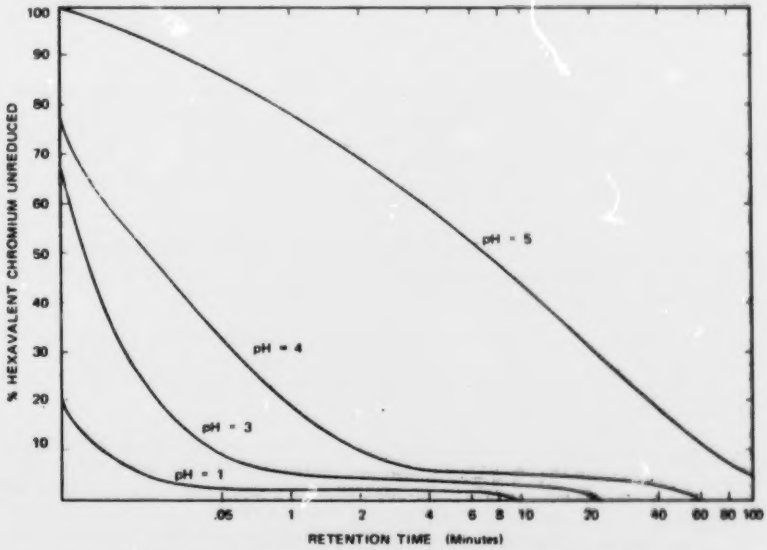

Figure 1 REDUCTION RATE OF HEXAVALENT CHROMIUM WITH SO_2 AT VARIOUS pH LEVELS

A good alternative to sulphur compounds for the reduction process is divalent iron, either ferrous sulfate, $FeSO_4 \cdot 7H_2O$; or ferrous chloride, $FeCl_2$. Ferrous sulfate (copperas) is readily available as a dry crystalline material at a relatively low cost. In some locations spent pickle liquor (hydrochloric or sulfuric acid which has been used to descale or remove rust from steel) is available as a waste material and may be obtained readily at a lower cost than the commercial salts. Spent pickle liquor also contains some free acid thereby reducing the acid requirement when ferrous salts are used.

The reaction which normally is written to illustrate the reduction of chromium with ferrous sulfate is:

$$6\ FeSO_4 \cdot 7H_2O + 2H_2CrO_4\ 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 5OH_2O$$

Thus, the stoichiometry indicates that 16 pounds of ferrous sulfate are required to reduce each pound of chromium, on a Cr basis.

Although the equation shows a requirement for acid, it is not necessary to carry out the reduction since the reduction reaction will proceed in neutral solutions according to the equation:

$$H_2CrO_4 + 8H_2O + 3FeSO_4 \rightarrow Cr(OH)_3 \downarrow + Fe(OH)_3 \downarrow + 3H_2SO_4$$

Table 1: CHEMICAL REQUIREMENTS FOR CHROMIUM TREATMENT

Reducing Agents

	Sulfur Dioxide 100% SO_2	Sodium Bisulfite 97.5% $NaHSO_3$	Sodium Metabisulfite 97.5% $Na_2S_2O_5$	Sodium Sulfite 97.5% Na_2SO_3	Ferrous Sulfate 100% $FeSO_4 \cdot 7H_2O$	Ferrous Chloride 100% $FeCl_2$
Pounds of Reducing Agent Required[1]	1.85	3.10	2.82	3.64	16.0	7.28
Acid 66° Be H_2SO_4 (93%)	0.0[2]	1.61	1.56	3.12	0.0	0.0
Alkali -						
NaOH (100%)	2.31	3.53	3.49	4.67	Variable[3]	Variable[3]
Na_2CO_3 (100%)	3.06	4.68	4.63	6.20		
$Ca(OH)_2$ (100%)	2.14	3.27	3.23	4.33		
Sludge Generated	1.98	1.98	1.98	1.98	8.12	8.12

[1] All table values are the pounds required per pound of chromium as Cr; to convert to pounds required per pound of CrO_3 multiply the table values by 0.52; and to convert to pounds required per pound of $Na_2Cr_2O_7 \cdot 2H_2O$ multiply the table values by 0.349.

[2] In practice sulfuric acid is required to efficiently reduce the chromium.

[3] Alkali requirements depend upon the pH of the chromium solution to be treated.

Similar equations may be written for ferrous chloride. This reaction is only slightly less faborable thermodynamically than the reaction which takes place under acidic conditions; consequently, the acid requirements are of no importance. The ferrous salts are excellent reducing agents in both acid and neutral solutions.[11]

In practice most chromium bearing solutions will be acidic, except for the chromate solutions. Additionally ferrous sulfate, when hydrolized, will provide hydrogen ions which will lower the pH of the solution being treated. Under these conditions the only alkali required would be amount necessary to precipitate the reduced chromium and the iron. Under some conditions it is possible that no alkali is required after a ferrous reduction. This would require that the solution to be treated is alkaline initially and that the resultant pH of the solution after the addition of the ferrous salt is neutral. Usually one would expect the treated solution to be somewhat acidic requiring a small amount of alkali to precipitate the reduced chromium and the iron.

The obvious disadvantage to the ferrous salts is the formation of sludge from the precipitation of ferric oxide. Where separation by settling is employed, the use of ferrous salts may not be a disadvantage since the ferric hydroxide which is formed is an excellent flocculating agent which will hasten the settling of the precipitated chromic hydroxide.[12]

Neutralization and Precipitation

The completely reduced chromium is prepared for separation from the effluent stream by precipitation with alkali. Lime, soda ash, or caustic soda are suitable alkalies for precipitation. Care must be exercised in maintaining the proper pH range for precipitation since trivalent chromium is amphoteric (soluble at both low and high pH levels). Fortunately the optimum pH range for quantitative precipitation, namely 7.5 to 9.0, is essentially within the pH range of acceptance for discharge into most receiving bodies, which generally is 6.0 to 8.5. Figure 2 shows the relationship between the solubility of chromic hydroxide and pH.

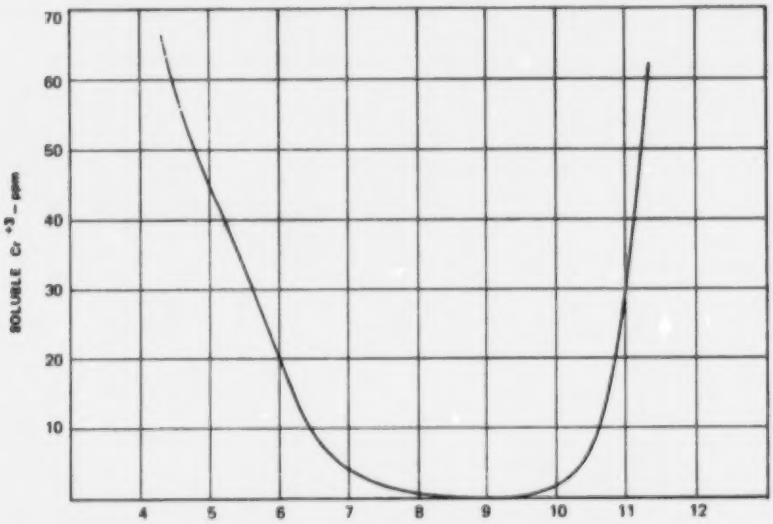

Figure 2: Relationship between the Solubility of $Cr(OH)_3$ and pH

The neutralization reactions are described below:

Alkali	
Caustic Soda NaOH	$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 + 3Na_2SO_4$
Soda Ash Na_2CO_3	$Cr_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O \rightarrow 2Cr(OH)_3 + 3Na_2SO_4 + 3CO_2$
Hydrated Lime	$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4$

From these reactions the stoichiometry is determined and summarized in Table I.

Sludge Removal

The nature and the amount of sludge formed during the treatment are determined by the reducing agent and the alkali used to precipitate the reduced chromium. Table I gives a comparison of the quantities of sludge resulting for the various reducing agents.

Substantially more sludge is generated using ferrous salts as a reducing agent since ferric hydroxide is precipitated from the solution with the chromic hydroxide. If lime is used to precipitate the metals another potential source of sludge is the calcium sulfate by-product from the neutralization reaction. The concentration of calcium sulfate must exceed 3 grams per liter before it will precipitate.

Once the pH has been properly adjusted, the chromium is quantitatively precipitated and may be removed from the effluent stream. The precipitated trivalent chromium is one of the least soluble of the

hydroxides of heavy metals having a solubility product of 6.7×10^{-31}, and is considered insoluble, and inert. The reduced chromium is not, under ordinary conditions, readily reoxidized.

Separation

Since precipitated chromic hydroxide is a gelatinous material, removal and dewatering is not always simple. The surest method of separation is pressure leaf filtration using a filter aid.

Clarifiers, or settling basins (if land is available), are suitable methods of separation. A plain settling clarifier may be unsuitable because the settling rate of the precipitated chromium is slow. This problem may be overcome by:

(1) Using special flocculating agents, or polyelectrolytes.

(2) Using a slant tube clarifier.

(3) Using lime, $Ca(OH)_2$, for neutralization permits slightly faster settling.

(4) Using a ferrous salt for the reduction reaction, which upon neutralization, precipitates ferric hydroxide, a flocculating agent.

With clarifiers or settling basins it is difficult to dewater the sludge. Normally the solids concentration of the sludge from these operations runs between 2% to 15%. Using pre-coat vacuum filtration of the underflow from a clarifier may permit dewatering to a solids concentration of over 20%. The same may be achieved with pre-coat pressure leaf filtration. The advantage of dewatering to this extent is to reduce the volume of the sludge and the handling problems.

In some locations very low limitations on suspended solids concentration may be imposed. In such instances, filtration of the clarifier overflow may be required. This normally is accomplished by means of a sand filter.

One of the most straightforward methods of separation is centrifuging. Centrifuges are available which will continuously discharge partially dewatered sludge from chromium treatment systems. These may be used either to separate the sludge from the underflow of a clarifier, or to separate the sludge from the underflow of a simple settling tank which concentrates the sludge.

The options for separation systems are many since numerous variables enter into design. The choice will be dictated largely by the quality of effluent required. Once this is determined the choice of system can be developed.

Commercial Systems of Chemical Treatment

Equipment for waste treatment systems is readily available commercially. Systems which are sold commercially are both batch treatment and continuous flow-through systems. The equipment is supplied either as separate units for each step in a building block system, or as fully instrumented, automatic, pre-packaged units.

Batch Systems

Batch systems have the distinct advantage over continuous systems since there is complete assurance that the hexavalent chromium is completely treated and removed. This can be determined by an extremely sensitive simple spot test. A simple analytical method is described in Appendix II.

A typical batch system, shown in Figure 3, consists of an agitated treatment tank followed by another tank used as a holding tank while treatment takes place in the first tank. Although the system shown in Figure 3 is somewhat automated with pH probes, metering pumps, and an ORP (oxidation reduction potential) meter, a manual system using simple checks for pH and completeness of reduction as well as a manual addition of chemicals is entirely suitable.

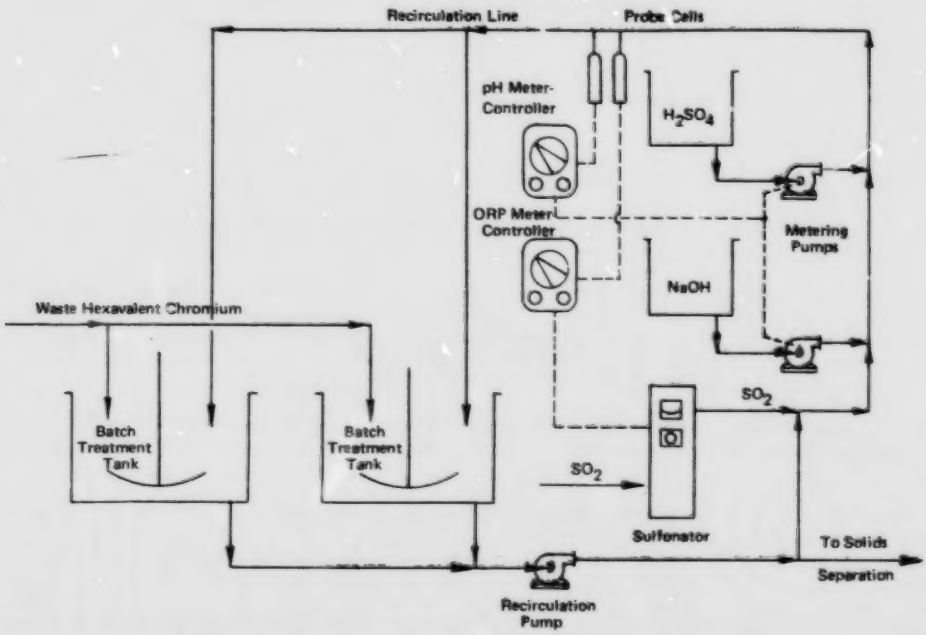

Figure 3 **AUTOMATED BATCH CHROMIUM TREATMENT SYSTEM**

Continuous Systems

A typical continuous flow-through system is shown schematically in Figure 4.

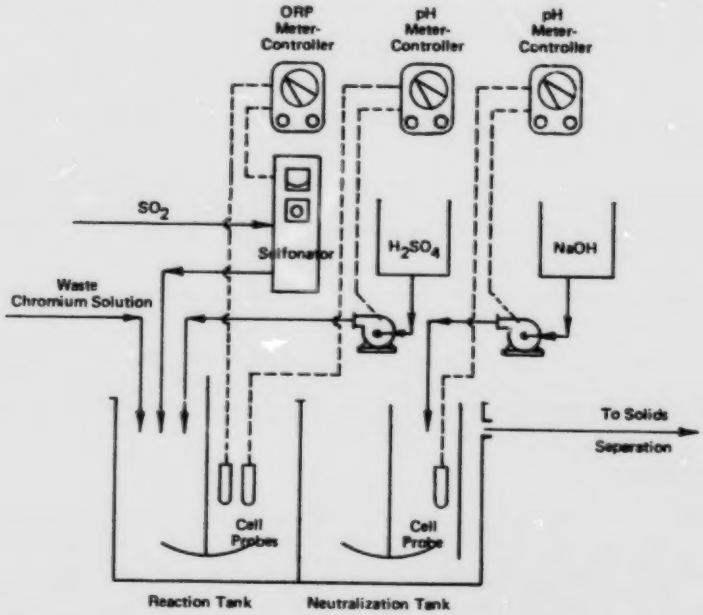

Figure 4 **CONTINUOUS FLOW THROUGH TREATMENT SYSTEM**

The advantage of an automated system is that the reduction-oxidation control is related directly to the concentration of hexavalent chromium. Thus, the reducing agent controller feeds the proper amount of chemical regardless of the concentration of hexavalent chromium. The system cannot adjust for large, rapid changes in concentration, consequently a holding, or equalization tank may be required. A properly sized reaction tank would eliminate problems resulting from rapid fluctuations in concentration.

Savings in chemical costs should be realized by elimination of excessive chemical use and perhaps some labor costs may be realized as opposed to a manual batch operation.

The Integrated System

A unique approach to the destructive chromium system is the integrated waste treatment method.[13] The system was developed specifically for metal finishing wastes, but could possibly be applied to any source of dilute chromium waste rinse. The system uses the final rinse tank, in a series of rinses, as a reduction tank. A solution of the reducing agent is the final rinsing material. The reducing solution is continuously recirculated to the final rinse tank from a reservoir tank.

One advantage of the system is that the concentration of reducing agent in the rinse is much greater than the chromium being treated. This asures complete reduction of the hexavalent chromium and accelerates the reaction without requiring acid. The reduced chromium is returned to the reducing reservoir tank which is sized to provide retention time for settling and separation of the precipitated chromium. Additional chemicals are added, at the rate of their consumption, to the clarified overflow which is recirculated. Other apparent advantages are: (1) Reduction chemicals are not wasted since excess chemicals are recycled; (2) rinse water is recycled continuously therby reducing the amount of water usage; and (3) the need for close chemical control is eliminated.

Electrolytic

A rather unique development which has found commercial application for reduction of chromium is an electrolytic process.[14]

In this cell, a dilute solution of hexavalent chromium is reduced electrolytically at the cathode. The cell contains a bed of semi-conductive particles between the electrodes which permit the passage of direct current at a rather low voltage (1-15 volts) and provides an infinite number of cathode sites where the reduction occurs.

The system reportedly operates with a high efficiency and results in a low power cost; lower than the chemical costs for the chemical destruction process.

Dilute chromium containing wastes are collected in an equalization tank. The pH is lowered and the solution is pumped to the cell through a filter to remove suspended solids. The solution of reduced chromium discharges from the cell. Subsequently, the pH is adjusted to precipitate the reduced chromium which is removed by settling, centrifuging or filtering.

Evaporative Recovery

For recovery of chromium for reuse, evaporative methods have proven successful and are used commercially. The evaporative process can be as simple as heating coils in a tank to evaporate water, or as complex as vacuum systems. The evaporator functions to both concentrate the chromium solution and return high quality water for rinsing operations. The use of an evaporator requires conservation of water for rinsing operations. The use of an evaporator requires conservation of water to justify the operational costs; thus, counter-current rinsing operations are required. Several schemes of operation are possible:

(1) **Closed Loop** - The closed loop system is described in Figure 5.

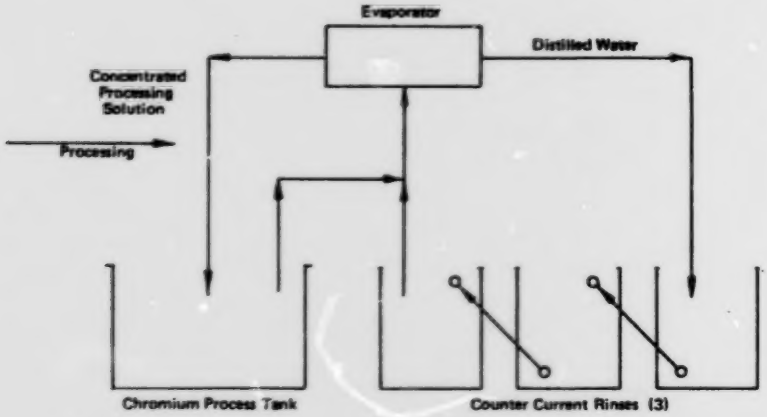

Figure 5 **CLOSED LOOP EVAPORATIVE RECOVERY**

In this system the flow from the first counter-current rinse operation is directed to the evaporator, usually from a holding tank. The concentrate from the evaporator is returned to a holding tank which replenishes the chromium in the processing tank. The condensate (distilled water) is returned to the final rinse tank. It is obvious that no external rinse water is added, except for that lost by atmospheric evaporation; nor are any of the process chemicals lost other than those consumed. All of the chemicals normally lost by drag-out are recovered. To achieve this balance the evaporative capacity must be designed so as to equal the flow of water required for effective rinsing. This usually is not the case therefore, the ideal situation may only be closely approximated. Additionally, all salts added to, or generated by, the processing and rinsing operations are concentrated in the evaporator. These materials may be objectionable in the chromium processing solution. This may be overcome by consideration of the optimized system described in (3) on page 13.

(2) **Open Loop** - This arrangement, shown in Figure 6, is a variation of the closed loop which provides partial recovery.

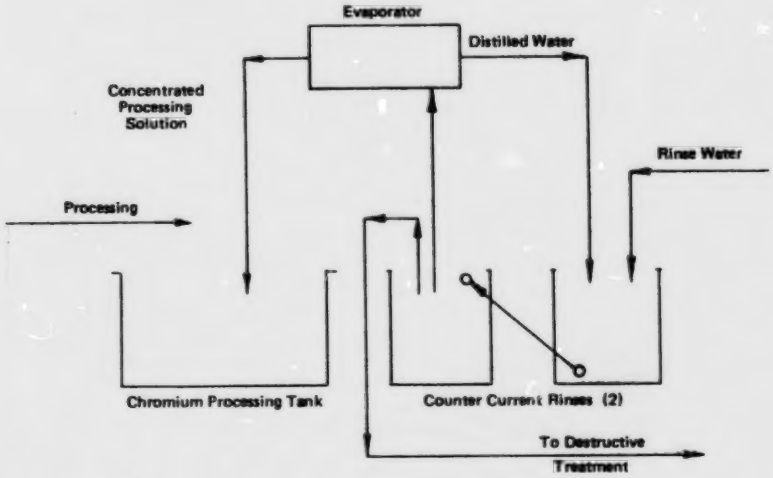

Figure 6 **OPEN LOOP EVAPORATIVE RECOVERY**

The open loop system becomes a necessity if it is not possible to install a sufficient number of counter-current rinse tanks. For this system a portion of the solution from the final rinse operation is not recirculated through the evaporator. This portion is collected and treated by chemical means. With two counter-current rinse tanks after the process solution approximately 96% to 99% recovery may be possible. Provision must be made for treatment of the excess waste.

(3) **Optimized Closed Loop** - The optimized system makes provision to remove impurities which concentrate in the system. Figure 7 is a schematic of the process.

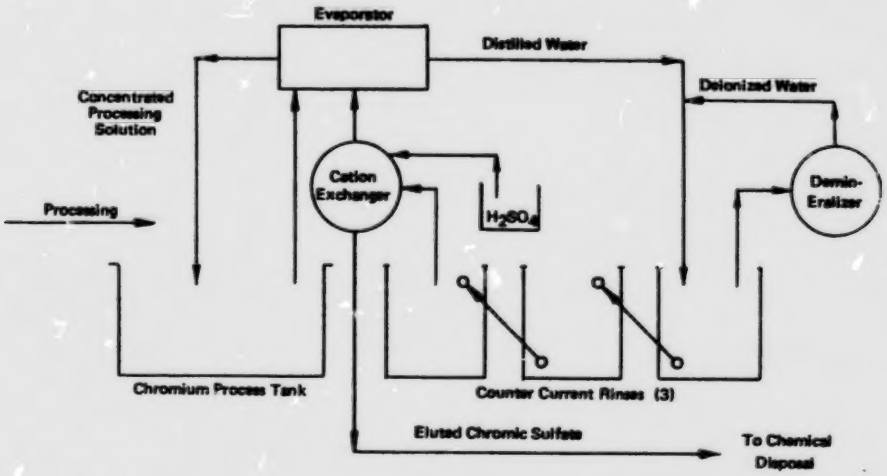

Figure 7 **OPTIMIZED EVAPORATIVE RECOVERY**

The diagram shows a closed loop system to which has been added purification equipment. For hexavalent chromium processing solutions, a cation exchanger is placed in the process between the first rinse station and the evaporator. This exchanger's function is to remove the cationic materials, usually metal contamination such as iron, copper, nickel, etc. Trivalent chromium is also removed selectively from the hexavalent chromium.

A demineralizer is added to the overflow from the final rinse tank. Any mineral contamination is removed by this bed and deionized water is recirculated to the third rinse tank with distilled water from the evaporator.

Provision may also be made to recirculate the process solution, if it is operated at an elevated temperature, through the evaporator. Thus, the process solution may be heated to a specific temperature and maintained at that temperature by the evaporator. Evaporation costs are reduced by not overconcentrating the rinse water. The evaporator will also provide level control for the process solution.

Provison must be made to treat the wastes regenerated from the ion exchanger.

Ion Exchange

Ion exchange is another commercial process which is used for concentration of chromium wastes. In some cases it is possible to recover the hexavalent chromium solution. The flow diagram in Figure 8 describes a typical system.

Dilute chromium waste, from the first rinse in a series of counter flow rinses or from some other source, is pumped through a cation exchanger to remove metals and then through an anion resin. Specific anion resins have the ability to exchange chromates, thus concentrating them on the resin. When the maximum amount of hexavalent chromium has been exchanged, the resin is regenerated with a fairly concentrated solution of sodium hydroxide. A solution of sodium chromate is recovered which may or may not be usable. If it cannot be used as the chromate, the chromium is readily treatable using the conventional destructive system. Savings are realized by the recovery and reuse of water.

An alternative to destroying the eluted sodium chromate is to pass the eluted sodium chromate through a different cation exchanger resin. Concentrated chromic acid is eluted from the bed with sulfuric acid. The chromic acid may be recovered in concentrations up to 6%. If used at a higher concentration evaporation would be required.

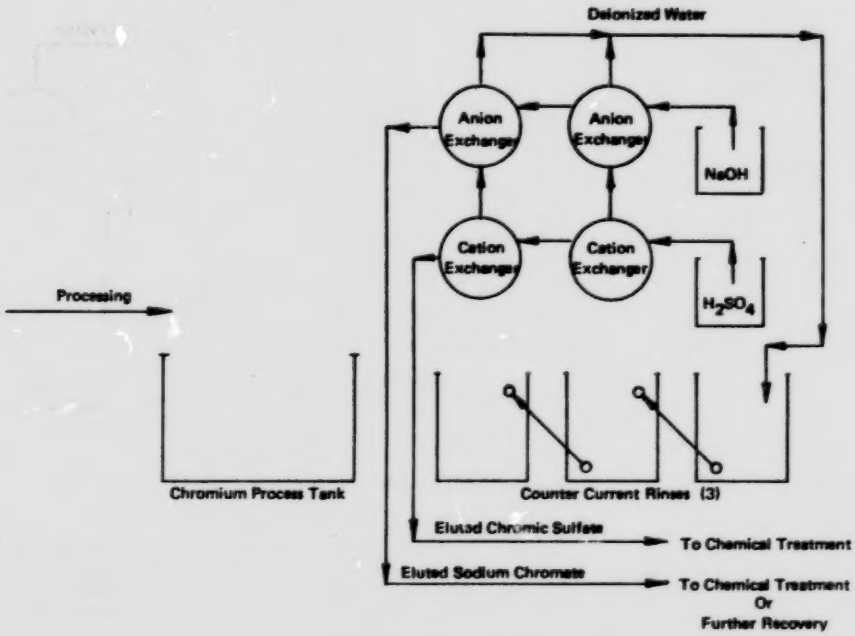

Figure 8 **ION EXCHANGE TREATMENT**

Other Methods

A number of methods have been demonstrated as effective, at least on a laboratory or pilot scale, for chromium waste treatment. Two such processes, namely reverse osmosis and carbon absorption, have the distinct possibility of commercial application.

Reverse Osmosis

This process has been the object of intense development. Basically the process allows separation of a salt from water by applying pressure or energy difference between two solutions of different concentrations separated by a suitable membrane. Thus, the permeate, or the material forced through the membrane, is purified water and the concentrated chromium solution, the concentrate, remains on the high pressure side of the membrane. The reverse osmosis unit may be used in place of either the evaporator or the ion exchange unit in a recovery system. Chromium, in the concentrate, may be recovered and reused, and the purified water, the permeate, may be recycled.

The most commonly used membrane for the process is a cellulose acetate. The membrane cell is operated at high pressure (400-800 psig), below 100°F, and over a pH range of 2.5 to 7.0.

Problems which may arise are fouling of the membrane, by compaction or attack of the membrane by the chromium solution. New developments in membrane materials may solve these problems.

Carbon Adsorption

As a result of a study sponsored by the Metal Finishers' Foundation, a pilot plant operation, based on carbon adsorption, has proved rather successful and could find commercial application.[15] The system is able to remove chromium from dilute rinse solution and is used in both open and closed loop schemes.

Problems with the system are: Relatively few regenerations of the carbon are possible before replacement is necessary; and the chromium which is stripped from the carbon (either with sulfuric acid or sodium hydroxide) is not always in a usable form. It would seem possible that the system is workable for concentrating the chromium for disposal by the conventional chemical destructive system.

Other Methods

A number of schemes have been proposed such as foam flotation, electrodialysis, solvent extraction, freezing, etc. None of these processes have found commercial application for the treatment of chromium wastes; however, as technology develops, these systems may have merit.

Summary

The standard method of treatment of chromium bearing wastes remains the chemical destructive system which has been used successfully for a number of years to control waste chromium in effluents. The EPA has concluded that "the best available demonstrated control technology has been determined to be the extensive use of in-plant controls and process modifications to minimize water use in combination with a well-designed and well-operated chemical treatment system to minimize the discharge of pollutants".[9] Additionally EPA advises that in process controls such as evaporative recovery, ion exchange, reverse osmosis, etc., can reduce costs by chemical conservation and water reuse, but some degree of chemical treatment may still be required.

It is anticipated, particularly for new point sources which would have engineering design capability, that process stream segregation would permit the use of various combinations of treatment techniques to achieve no discharge of process waste water pollutants.

Chemical treatment systems have been designed which can handle up to 100,000 gallons per day; however, for flow rates in excess of 25,000 gallons per day continuous flow-through systems should be considered to minimize equipment.

Recovery systems can show favorable economics if large quantities of valuable chemicals can be recovered and where water and sewer charges can be minimized.

Choosing the proper system which will comply with specific effluent regulations most economically will require a complete in-plant study by a competent engineer.

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Appendix I

U.S. Environmental Protection Agency Offices

U.S. Environmental Protection Agency
Waterside Mall Building
45h & M Streets, S.W.
Washington, D.C. 20460

National Environmental Research Centers

1) P.O. Box 12055
   Research Triangle Park, North Carolina 27711

2) 200 S.W. 35th Street
   Corvallis, Oregon 97330

3) 5555 Ridge Avenue
   Cincinnati, Ohio 54268

4) P.O. Box 15027
   Las Vegas, Nevada 89114

EPA Regional Offices

Region I
Room 2303
J.F.K. Federal Office Building
Boston, Massachusetts 02703

Region II
Room 908
26 Federal Plaza
New York, New York 10007

Region III
Curtis Building
6th & Walnut Streets
Philadelphia, Pennsylvania 19106

Region IV
Suite 300
1421 Peachtree Street, N.E.
Atlanta, Georgia 30309

Region V
200 South Dearborn
Chicago, Illinois

Region VI
Suite 100
1600 Patterson Street
Dallas, Texas 75201

Region VII
1735 Baltimore Avenue
Kansas City, Missouri 64180

Region VIII
Room 900, Lincoln Tower Building
1860 Lincoln Street
Denver, Colorado 80205

Region IX
100 California Street
San Francisco, California 94111

Region X
1200 Sixth Avenue
Seattle, Washington 98101

Appendix II

Analytical Methods

Hexavalent Chrome Trace Amounts

Diphenylcarbazide Method
Application:

For determination of trace amounts of hexavalent chromium, using a colorimeter. The method is recommended for analysis of rinse waters for effluents containingg trace amounts of Cr .

Technical Bulletin

Reagents and Equipment:

Sulfuric Acid -- 6N

Diphenylcarbazide Reagent -- 0.2 g. diphenylcarbazide dissolved in 100 ml ethanol and diluted to volume in a 500 ml volumetric flask with 1:9 H_2SO_4.

Colorimeter with light source in the range of 525 to 540 mμ. The Fisher Electrophotometer with a 525 mμ filter is adequate for this use.)

Procedure:

Place a sample containing 10-50 micrograms Cr^{+6} in a 100 ml Nessler tube (or 100 ml grad ate calibrated "to contain"). Dilute to 50 ml. Add 4 ml of 6 N H_2SO_4 and 3 ml of diphenylcarbazide solution. Dilute to 100 ml and mix thoroughly. Read % transmission at 540 mμ or using 525 mμ filter if Fisher Electrophotometer is used. Reading may be taken immediately if no vanadium is present. If vanadium is present, wait 10 min. before taking reading. Read micrograms of hexavalent chrome from calibration curve previously plotted with known quantities of potassium dichromate.

Calculations:

$$\text{ppm } Cr^{+6} = \frac{\mu\ +6}{\text{ml of Sample}}$$

$$\%\ Cr^{+6} = \frac{(\text{gms } Cr^{+6})\ (100)}{\text{wt. of Sample in gms}} \quad \text{Or} \quad \frac{\mu\ Cr^{+6}}{(10{,}000)\ \text{Sample Wt. in Grams}}$$

μ = micrograms

Calibration Curve:

Accurately weigh out 0.2830 g of $K_2Cr_2O_7$ and dissolve and dilute to one liter in volumetric flask to make a working solution. Pipette a 10 ml sample of working solution into a 1 liter volumetric flask and dilute to volume to make up standard solution. This standard solution contains 1 microgram Cr^{+6} in each ml of solution.

Using 5 -- 100 ml Nessler tubes (or 100 ml graduated cylinders calibrated "to contain"), pipette the following quantities of standard solution into each tube:

Tube No.	ml Standard Solution	$\mu\ Cr^{+6}$
1	10 ml	10
2	20 ml	20
3	30 ml	30
4	40 ml	40
5	50 ml	50

Dilute contents of each tube to 50 ml, add 4 ml of 6N H_2SO_4 and 3 ml of diphenycarbazide solution to each tube. Dilute to 100 ml and mix thoroughly. Read the % transmittance at 540 mμ for each of these solutions and draw a calibration curve showing % transmittance vs. μ Cr^{+6}

Technical Bulletin

Appendix II

Trivalent Chromium

Determination of trivalent chromium in the presence of hexavalent chromium in effluent streams. Trivalent chrome is separated and then oxidized to hexavalent state using perchloric acid. WARNING: An explosive reaction can occur if organics are present in sufficient amounts in persence of perchloric acid. Be sure all organic material is destroyed before adding perchloric acid. This can be determined by the absence of brown fumes during evaporation to dense fumes of sulfuric acid in this method. This procedure should be carried out in a hood as oxides of nitrogen are expelled.

Reagents:

Sodium Hydroxide, 10% solution
Nitric Acid, Concentrated
Perchloric Acid, Concentrated
Sulfuric Acid, Concentrated
Reagents from Trace Amounts Hexavalent Chromium

Preparation of Sample:

Pipette a sample containing 10-50 micrograms of Cr^{+3} into a 250 ml beaker and dilute to 100 ml. Neutralize the solution to a pH of 10 using alkacid test ribbon as the indicator.

Boil for 10 minutes, allow precipitate to settle and filter through a No. 40 Whatman paper. Police the beaker and wash the precipitate with distilled water until free of all hexavalent chromium.

Transfer the paper and precipitate to a 250 ml Erlenmeyer flask. Add 2 or 3 glass beads, 20 ml HNO_3, and 15 ml H_2SO_4. Fit flask with a vapor trap or a short stemmed funnel, and evaporate the dense fumes of sulfuric acid to destroy any organics present. Add 20 more ml of HNO_3 and 25 ml of $HCLO_4$ and evaporate to dense fumes of perchloric acid and fume for 2 minutes after the solution has turned orange. Cool rapidly, wash down sides of flask, and dilute to about 85 ml. Boil for 1 or 2 minutes to drive out chlorine fumes. Cool to room temperature and transfer to a 100 ml Nessler tube and determine the Cr^{+6} concentration using the diphenylcarbazide method.

Total Chromium

The total chromium concentration is simply the sum of the concentrations of Cr^{+6} and Cr^{+3}.

Additionally atomic absorption (AA) spectroscopy may be used to determine the total concentration of soluble chromium. With AA methods special wet techniques of separation must be made to determine trace quantities of Cr^{+6} and Cr^{+3}.

CHAPTER 38

COBALT Co AND NICKEL Ni

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Summary of North American Water Quality Criterial for Nickel	2178
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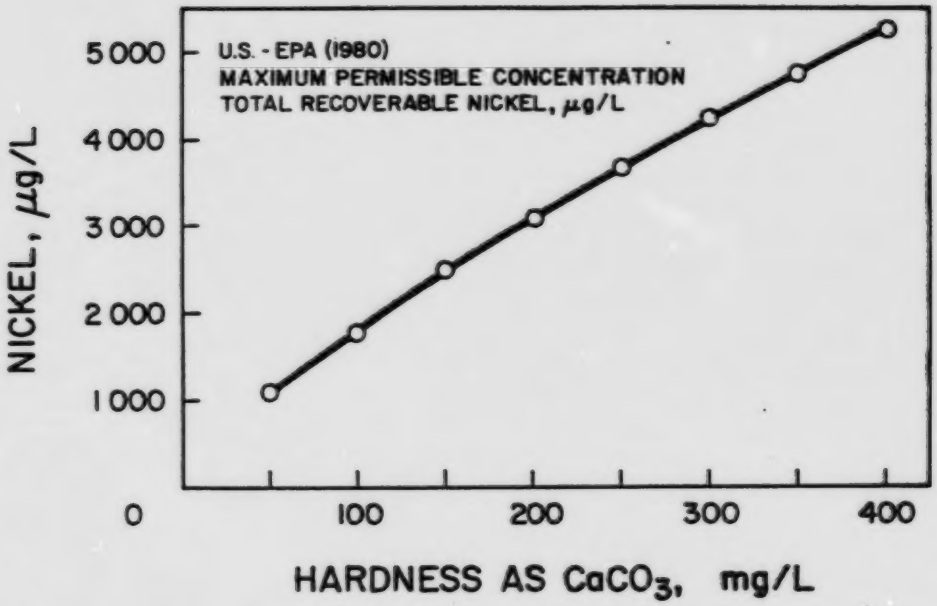
OCCURRENCE

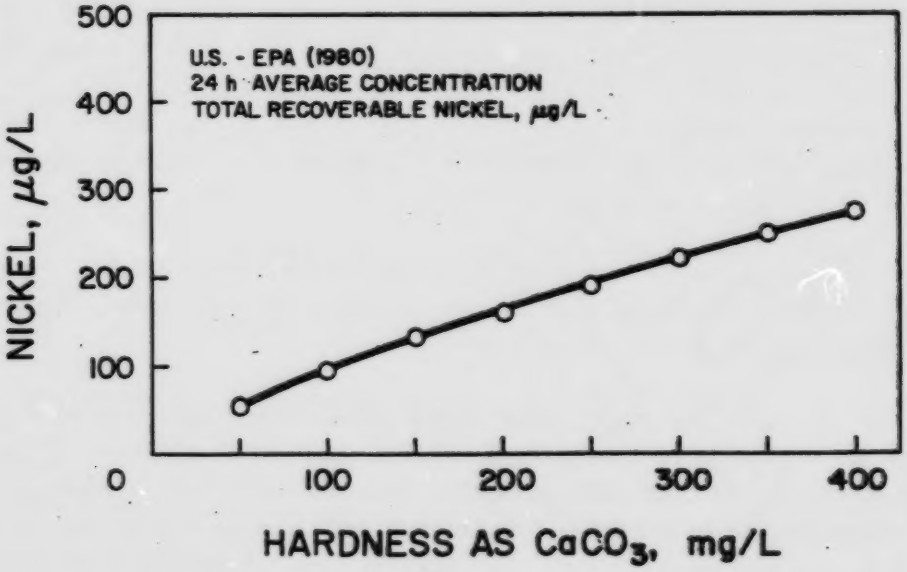
Nickel and cobalt occur in the mining environment primarily around mining centers where they are produced such as Sudbury and Falconbridge, Ontario, and the huge Bushveld Igneous Complex in the Transvaal where both metals are produced as a by-product of platinum recovery operations. Nickel may be produced by smelting ore, by hydrometallurgical processes, or a combination of both, so it can be distributed through plant effluents or smelter gas fallout.

Several deposits are known or have been worked in the past where cobalt is the product of primary economic importance such as the Blackbird Mine in Idaho, a deposit in Missouri, and one in the Ontario cobalt district.

Small amounts of nickel and cobalt occur in the Witwatersrand gold-uranium ore. The quantity is not enough to be considered a valuable resource, except when cobalt prices rise to very high levels, but high enough to be a nuisance when it forms a cobaltic cyanide complex during gold leaching only to foul ion exchange resins used to recover uranium after the subsequent sulfuric acid leaching step. Surprisingly, a mine water samples from Witwatersrand Mines was recently analyzed to contain 8 mg/l Ni and 2 mg/l Co.

Nickel is also produced in New Caledonia where serious damage to the seabed ecology has been reported due to contamination by mine-mill tailings and the toxicity of nickel at very low levels to marine organisms. Jacques Cousteau has documented the effects of submarine tailings disposal at this site.


U.S. - EPA (1980)
MAXIMUM PERMISSIBLE CONCENTRATION
TOTAL RECOVERABLE NICKEL, µg/L
NICKEL, µg/L
5 000
4 000
3 000
2 000
1 000
0
100
200
300
400
HARDNESS AS CaCO3, mg/L


U.S. - EPA (1980)
24 h AVERAGE CONCENTRATION
TOTAL RECOVERABLE NICKEL, µg/L
NICKEL, µg/L
500
400
300
200
100
0
100
200
300
400
HARDNESS AS CaCO3, mg/L

(ug/L) NICKEL

Summary of North American Water Qu. Criteria for Nickel

WATER USAGE	EPA[1]. 1972	EPA[2]. 1976	EPA[3]. 1980	CANADA[4,5]. 1979	ONTARIO[6]. 1978	QUEBEC[7].	ALBERTA[8]. 1977	B.C.[9].	SASK.[10]. 1975	MANITOBA[11]. 1979
PROTECTION OF FRESHWATER AQUATIC LIFE										
OBJECTIVE	.02 (96-hr LC50)	.01 (96-hr LC50)	24-hr mean (0.76 (ln (hard))+1.06	25 (soft water) 250 (Hard>150 mg/L)	<25	N.D.	--		--	--
MAX. PERMISSIBLE LIMIT	--	--	(0.76 (ln (hard))+4.02	--	25	25	--		--	25.0
PROTECTION OF MARINE LIFE										
OBJECTIVE	.02 (96-hr LC50) or 2.0	.01 (96-hr LC50)	24-hr mean 7.1	<100 *	--	--	--		--	--
MAX. PERMISSIBLE LIMIT	100	--	140	--	--	--	--		--	--
PUBLIC WATER SUPPLY	--	--	13.4	250	--	--	--		--	--
AGRICULTURAL WATER SUPPLY — LIVESTOCK WATERING	--	--	--	5,000	1,000	--	--		--	--
AGRICULTURAL WATER SUPPLY — IRRIGATION	200	-- (<100) (2)	--	200	200	--	--		--	200

Compiled by NORANDA

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Cobalt and nickel are discussed together because of the common geochemical association of these two metals. Their chemistries are also similar.

Cobalt and particularly nickel are common contaminants in effluents from plating operations and nickel-silver recycling operations.

Modal concentrations of nickel in the upper Great Lakes are less than 5 ug/l but are often not detected in water intakes. There is some evidence of nickel contamination of Georgian Bay.

ENVIRONMENTAL SENSITIVITY TO NICKEL AND COBALT

Based on available information, freshwater toxicity of cobalt and nickel are lower than most other heavy metals such as zinc and mercury but more toxic than lead.

The toxicity of nickel is related to water hardness in fresh water with a relatively steep gradient as reflected in the U.S. EPA (1980) water quality criteria for this metal.

The ONTARIO MOE (1979) criterion for nickel in Ontario waters is set at 25 ug/l based on observed toxicity to Daphia magna.

Nickel in large doses causes dermatitis to man and lung cancer after chronic inhalation. Oral toxicity of nickel is extremely low.

Nickel is classed as very toxic to plants with toxicity observed at concentrations below 1 mg/l in a nutrient solution. Some fungi and plants adapt to grow in high Ni concentrations, however, and some algal populations have shown tolerance to nickel. This can be observed in the prolificmarsh area that forms part of the water management scheme at Falconbridge, Ontario, where algae thrive in the lime-treated recycle water with nickel levels close to 1 ppm.

Chronic three-week nickel exposures to Daphia magna caused 50% mortality at 130 ug/l and 50% and 16% reproductive impairment at 95 and 30 ug/l according to ONTARIO MOE (1979), which is the basis of Ontario's water quality criteria of 25 ug/l.

Acute toxicity of nickel to fish is less than that of copper or zinc and is in the 4-40 mg Ni/l range depending on the hardness of the water. The 48-hour LC_{50} for rainbow trout is 32,000 ug/l while those for copper and zinc were 750 and 4,000 ug/l respectively (BROWN and DALTON, 1970).

The only marine water criteria for nickel are those of the U.S. EPA (1980) which were developed on the basis of toxicity.

The 140 ug/l maximum permissible level of Ni in marine water has been considered acceptable, but the 7.1 ug/l 24-hour average criterion may be too strict since the lowest level of nickel ever documented to have a chronically toxic effect on marine organisms was greater than 61 ug/l. Most toxicity data for marine organisms indicate no toxic effects at concentrations below 1 mg/l. Shellfish bioaccumulate nickel.

No fresh or marine water criteria for cobalt have been formulated by the regulatory bodies of the main mining countries of the world.

REGULATORY EFFLUENT LIMITS - Ni AND Co

No effluent limits were identified for cobalt.

Effluent limits for nickel were identified as follows:

REGULATED EFFLUENT LIMITS - NICKEL (mg/l)

	Daily Maximum	30d Average	
Falconbridge Onaping, Ontario	1.0	1.0	Ni-Cu Mill
Key Lake Uranium Saskatchewan	1.0	0.50	Uranium Mill
Homestake Mining Lead SD NPDES	1.25	1.25	Gold Mill
Denison Mines Elliot Lake, Ontario	1.0		Uranium Mill
Cominco Ltd., Con Mine Yellowknife NWT	1.00	0.50	Gold Mill
Giant Yellowknife Mines Yellowknife, NWT	1.00	0.50	Gold Mill
New Mexico Water Quality Control Commission	0.10	0.10	General
South Africa	No Standard for Ni.		
Singapore	0.10	0.10	
Singapore to Sewers	10.00	10.00	
Rio de Janeiro State, Brazil	1.0		
Minas Gerais State, Brazil	1.0		
Sao Paulo State, Brazil	2.0		

NICKEL CONTAMINATION ABATEMENT

Good housekeeping and preventing nickel from getting into solution in the first place is the most important means of reducing the need and cost of nickel removal from the mine-mill environment.

When many of today's nickel mine-mill complexes were originally installed, the industry was not aware of many of the housekeeping factors that can influence nickel (and other metal contaminant) levels in effluents. An excellent case in point is the FALCONBRIDGE nickel mining, milling, and smelting operations at Onaping, Ontario, and at Falconbridge, Ontario.

It has been found that drainage from oxidizing wasterock used to build a half mile stretch of road alongside the present day final effluent stream results in an increase in the nickel level in the effluent of 0.1 mg/l. This illustrates the need for great care when using wasterock for construction of road and railbeds as well as service yards, etc.

Also at Falconbridge, Onaping, acid mine drainage containing relatively high levels of nickel is used as process water in the Strathcona mill-concentrator. In this way nickel is precipitated at the high process pH avoiding the need for an expensive treatment plant.

Another aspect of nickel housekeeping is how nickel and copper concentrates are stored and loaded. Windblown spillages of concentrates along railtracks and concentrate that works its way into the ground around loading and storage points both contribute to contamination of runoff water as well as groundwater and seepage. Such areas have been identified and reclaimed in some cases by processing the top several inches of soil through the mill.

A whole host of innovative water, tailings, and wasterock management items have been implemented at FALCONBRIDGE. A most significant improvement in factors that influence water quality has been the extensive gas cleaning steps ahead of the smelter stack which has greatly reduced the amount of metal-bearing particulates as well as acid forming SO_2 that would otherwise escape to the environment around the complex.

TREATMENT FOR COBALT AND NICKEL

Cobalt and nickel are complexed by cyanide to form extremely stable soluble complexes which interfere with both cyanide and nickel treatment.

Treatment for both nickel and cobalt can be destructive, such as precipitation and sludge disposal, or nickel values can be recovered.

PRECIPITATION OF NICKEL

Precipitation of nickel hydroxide is generally the basis for destructive treatment of nickel-bearing wastes. Precipitation with carbonate is most commonly associated with recovery systems in industrial operations where nickel is used.

Nickel forms insoluble nickel hydroxide on addition of lime. $Ni(OH)_2$ has a theoretical minimum solubility of 0.01 mg/l at pH 10 according to JENKINS, et al. (1964).

According to PATTERSON (1975), precipitation of nickel is most effective at a high pH, although little efficiency is gained by increasing pH above about pH 10.

PATTERSON (1975) reported limited application of sulfide precipitation for nickel wastewaters (LARSEN, et al., 1973; ROSEHART and LEE, 1972). In one case, gold ore extraction wastewater at 6.5 mg/l Ni was reduced to 2.1 mg/l Ni after treatment with sodium sulfide at pH 7. Use of alum at pH 7-8 on the same waste reduced nickel to 0.5 mg/l, and the use of lime or caustic at pH over 10 reduced nickel to below detectable limits.

Process	[Ni] in Treated Water
Untreated	6.5 mg/l Ni
Na_2S at pH 7	2.1 mg/l Ni
Na_2S + Alum pH 7-8	0.5 mg/l Ni
Lime or NaOH, pH 10+	LTDL

LTDL = Less than detection limit.

LARSEN, et al. (1973) added lime to pH 5.5-6.5 which reduced nickel levels of 0.19-0.51 mg/l to 0.13-0.29 mg/l. Subsequent pH increase and Na_2S addition reduced Ni levels much lower than this as described by LARSEN, et al. (1976).

Therefore, close pH control is not essential other than from considerations of chemical costs associated with pH adjustment. The following table from PATTERSON (1975) summarizes results of commercial scale effluent treatment plants installed in the metal finishing industry. Effluent nickel values of in excess of 1 mg/l appear to result from improper pH control according to NEMEROW (1963) and TUPPS (1961).

Summary of Effluent Nickel Concentrations after Precipitation Treatment.

Source	Nickel Concentration mg/l Initial	Final	Comments	Reference
Tableware Plating	21	0.09-1.9	$FeCl_3$ + Sand filtration	3
Appliance Manufacturing	35	0.4	—	4
Office Machine Manufacturing	39	0.17	Polyelectrolyte, 1-2 mg/l	19
Nonferrous Metal Works	—	0.05-0.13	6-hr settling	20
	—	0.05-0.13	pH = 8.5-9.0	21
	—	15	pH = 8.1	22
Plating	46	0.8	6-hr detention in circular clarifier	12
Record Changer Manufacturing	—	0.1-0.2	—	23

References:

3 NEMEROW (1963)
4 ANDERSON and IOBST (1968)
19 HANSEN and ZABBAN (1959)
20 STONE (1967)
21 STONE (1972)
22 TUPPS (1961)
12 CHALMERS (1970)
23 METAL FINISHING JOURNAL (1971)

CHEN and TAY (1979) tested a metal finishing waste containing 80 mg/l nickel in the laboratory and found that nickel removal by lime precipitation was increased from 63% to 81% by addition of 2-6 mg/l alum, while a dose of alum in excess of 6 mg/l resulted in a decreased Ni removal due to the decrease in pH. $FeCl_3$ dosage removed only 40% of the nickel at an optimal dosage of 2 mg/l, but this could be improved to 67% by addition of 0.1 mg/l polymer.

By adding 2.5 mg/l lime, 93% Ni removal was achieved, and at 15 mg/l lime dosage, nickel removal was 99%.

BaS dosage at 1 g/l removed 100% of the nickel from solution at pH 2. BaS addition also increased the pH of the solution. The NiS precipitate formed a dense and easily separatable floc.

At FALCONBRIDGE's Sudbury operations, nickel is reduced to 0.1 mg/l in solution after lime precipitation, and nickel levels increase in the marsh area after decantation due to pickup of nickel values from the area that was previously contaminated by smelter stackgas fallout.

RIVETT and OKO described limestone neutralization of waste water at FALCONBRIDGE's Onaping mines. Demonstrating the effects of retention time and neutralizaton from pH 3.5 to pH 7.2 with limestone, the nickel level was reported at 0.6 ppm in the tailings dam water, 0.3 ppm at the inlet to the neutralization dam, and 0.3 ppm Ni after neutralization. This shows that neutralization with ground limestone does not reduce nickel levels in the effluent as a high enough pH is not reached. In 1984, the same operation was visited, only this time nickel levels were around 0.8-0.9 ppm by the time the solution reached the outlet from lower Moose Lake. A further 0.1 ppm Ni was added between the lower Moose Lake overflow point and discharge to the receiving waters due to seepage from the roadbed. It is believed that some as yet unidentified biological nickel removal process occurs in Upper Moose Lake.

Also, at FALCONBRIDGE's Onaping mine, NaOH solution was used for final pH adjustment to precipitate nickel from a small stream of mine water. After addition of the NaOH, the neutralized solution flows to a settling pond with a baffle. Two points of interest arose. First, NaOH was selected for pH adjustment because, due to use of cement in backfill, the mine water was pumped to the surface at an already high pH, and very little reagent was needed and only sometimes. However, when the mine operation was interrupted and no backfill was pumped underground, the mine water pH dropped, and the NaOH consuption needed to precipitate nickel became much more expensive.

Secondly, mine sewage was dumped into the same decant pond. The result was that due to bacterial action, gas bubbles formed from the sewage in the pond sediment. These attached themselves to $Ni(OH)_2$ sediment from the bottom of the dam with the result that 5% Ni precipitate was being transported from the pond via its overflow.

SCHILLER and KHALAFALLA (1983) describe a new patented process for removal of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from wastewater. Specific areas of application include treatment of mine drainage and metal finishing and metallurgy wastewaters. Disadvantages of the prior art are largely overcome by the use of a substantial excess of essentially dry, powdered, reactive MgO as a precipitatant in place of conventional precipitants. The resulting precipitate settles rapidly to a small volume and is not readily redispersed or redissolved. The purified water may be removed by decantation, thus avoiding the necessity of filtration. The technology is available for licensing from the U.S. Dept. of the Interior. The patent application contains very limited information on the process performance.

S. T. Herman of BETHLEHEM INTERNATIONAL ENGINEERING COMPANY (Bethlehem Steel) showed that lime precipitation using the HDS process can reduce dilute effluent solutions of Cu, Cd, Ni, Pb, and Zn to less than 0.1 ppm at a single pH level which would not be possible with conventional neutralization. Also, a settled sludge density of over 20% is achieved compared with the usual 1% solids achieved by conventional neutralization. In addition, BETHLEHEM STEEL has developed an innovative way of

stabilizing HDS sludges using pozzolonic reactions which render the sludge suitable for disposal in a sanitary landfill. More information is available from:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18106
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MIKHNEV, et al. (1978) describe the use of a sulfide solution in $Ca(OH)_2$ to precipitate heavy metals from metallurgical plant effluent. The Cu, Ni, and Fe were precipitated at pH 5.2, 7, and 7-9 respectively. The degree of removal depended on pH and the composition and dosage of the added $Ca(OH)_2$-$S^=$ solution, and to a very limited extent, on temperature (20-80°C). The treatment at final pH 7.5-8 decreased the metal concentrations as follows:

	Inflow	Outflow
Cu (mg/l)	70	0.1
Ni (mg/l)	80	0.01
Fe (mg/l)	10	0.01

The precipitate contained about 12% Cu, 12% Ni, and 20% CaC as CuS, NiS, and $CaSO_4$.

Importantly, the use of $Ca(OH)_2$-$S^=$ solution increased the clarification rate by 50-100%.

ION EXCHANGE

Recovery of nickel by ion exchange has been used for some time in the metal finishing industry although not in the mine-mill effluent treatment. It is unlikely that ion exchange will be competitive with lime precipitation for nickel removal from solutions encountered in mines and mineral processing.

Nickel cyanide permanently loads onto ion exchange resins according to SILMAN (1971) as does cobalticyanide.

SLATER, et al. (1978) tested a fluidized bed continuous ion exchange unit to treat a synthetic mine water containing 56 ppm Cu, 3.5 ppm Ni, 0.3 ppm Co, 1 ppm Fe, and 20 ppm Ca at pH 4 using strong acid resin, Amberlite 200C [54077-23-5] in the sodium form. After a five minute upflow period, loaded resin was transferred to an elution column where a saturated NaCl was used for elution. More information on the results may be available from the authors:

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Gordon Ritcey at CANMET would like to continue these experiments using new resins and the latest CIX concepts which he feels could recover metal values as a resource.

ISUMI, et al. (1976) described a method for recovering heavy metals including cobalt from dilute solutions by foamy complex formation with N-monodecanoyl diethylenetriamine. [N-[2-[C2-aminoethyl)amino]ethyl]decanamide] which forms soluble and foamy complexes with metals.

ZAKIROV, et al. (1981) described the use of polygorskite clays of the Tappok deposit and their use in the treatment of nonferrous metallurgical effluents. Optimal adsorption capacity of the clays for cobalt in simulated wastewater was observed at 16 mg Co/l.

CHIN and TAY (1979) tested Amberlite Resin RI-120 for nickel removal from an acid effluent from a metal finishing plant and found a mass transfer coefficient (ka) of 1.92 g/min-Cm^3. They conclude that chemical precipitation of nickel followed by IX would yield effluents suitable for discharge to the municipal sewer at an estimated cost of S$0.68/$m^3$.

REVERSE OSMOSIS

GOLOMB (1972, 1973) showed in pilot plant studies that plating rinse water could be treated by reverse osmosis with 99.6% rejection of nickel at 1973 cost per 1,000 U.S. gallons of $3.08-$6.08 for relatively concentrated solutions around 1700 mg/l Ni. DONNELLY, et al. (1974) found that the relative efficiency of recovery was dependent on the type of membrane and module used with rejection ranging from 70-98% for plating wastes.

Mining industry effluents are unlikely to contain nickel at levels that justify R.O. treatment unless R.O. is installed for another reason.

Interestingly enough, mine water from the ERPM Hercules Shaft contains 8 ppm Ni and 2.0 ppm Co which, in a pilot scale seeded slurry R.O. test, yielded a product with 0.3 ppm Ni and 0.10 ppm Co.

COBALT AND NICKEL

	Influent (mg/l)	R.O. Product (mg/l)	Removal (%)
Ni	8.0	0.30	96%
Co	2.0	0.10	95%

The highly innovative seeded slurry reverse osmosis technology developed by RESOURCES CONSERVATION COMPANY is described in Chapter 15 and in the trip report on ERPM in Appendix I, also by HERRIGEL (1984).

In this case, the aim of the development program was to find a simple, low cost way to remove TDS from mine water prior to its discharge, and removal of Co, Ni, and other heavy metal ions is purely incidental--yet, nonetheless, it is a good demonstration of the effectiveness of R.O. for Co and Ni removal and concentration.

WILMOTH, et al. (1979) compared lime neutralization, reverse osmosis, and ion exchange for removal of As, Cd, Hg, Ni, Se, and Zn from acid mine drainage. Reverse osmosis and ion exchange were found to be slightly more effective overall than neutralization, but the chemical requirements for IX and the need for subsequent concentrate treatment offset their advantages. It is believed that the seeded slurry R.O. system in conjunction with an innovative tubular R.O. system may make it worthwhile reevaluating R.O. for some applications.

SASTRI (1978) reviewed a process for reverse osmosis removal of nickel from dilute solutions. Subsequently, the same author has been involved in development work in the use of low pressure reverse osmosis for metal recovery from low grade effluents.

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CHAPTER 39

COPPER Cu, LEAD Pb, AND ZINC, Zn

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Copper, lead, and zinc removal are reviewed together as these three base metals often occur in mine and mill effluents together, frequently with iron and other contaminants at a low pH.

Copper, lead, and zinc have some comparable aspects in their chemistry and behavior. For example, they all form hydroxide precipitates, and each forms a sulfide precipitate that is less soluble than its hydroxide. Carbonate chemistry can be used to advantage for the removal of lead to levels below that achievable by straightforward lime or NaOH precipitation.

Zinc and lead form hydroxide complexes, e.g., $[Zn(OH)_3]^-$ which means that beyond a certain pH, the solubility of zinc increases with further addition of hydroxide ions.

The removal of copper, lead, and zinc from solution is discussed in Appendix I in the following trip reports:

Black Mountain Mineral Development Co.
Kidd Creek Mine
Kidd Creek Concentrator and Refinery
Gilman Mine
Homestake Mining Company, Lead, South Dakota
Cominco, Wedge Mine
Waite-Amulet
Cu-Pb-Zn Mine-Mill G
Cu-Pb-Zn Mine-Mill M
Cu-Pb-Zn Mine-Mill B
Lead Smelter B
Heath Steele Mines
Denison Mines Ltd.
AMAX, Mount Emmons

OCCURRENCE OF COPPER, LEAD AND ZINC

The following tables summarize levels of copper, lead, and zinc in effluents encountered in the course of this study and also data extracted from the PEDCO (1983) Survey report to EPA.

SUMMARY TABLE OF Cu, Pb, and Zn IN EFFLUENTS AND PROCESS SOLUTIONS

Operation	Date	Location	Type	Type of Solution	Cu mg/l	Pb	Zn	Fe	pH	Comments
Black Mountain	1983	South Africa	Cu Pb Zn Ag Flotation	Tailings Reclaim	2.7-9.0	2-6	0-3	0-10	5-10	Cr 0-1.3 ppm
Kidd Dreek Mine	1984	Timmins Ontario	Cu Pb Zn Ag Mine	Minewater AMD After LS	LT0.1	---	0.10	0.10	10.30	NH_3 1.2
Kidd Creek Mine	1984	Timmins Ontario	Cu Pb Zn Ag Mine	AMD u/g	---	---	0.10	0.10	8.5	NH_3 12.4
Kidd Creek Concentrator	1984	Timmins Ontario	Zn Refinery	Jarosite Pond	100	1.1	9300	100	2.7	Cd 46 ppm
Kidd Creek Concentrator	1984	Timmins Ontario	Cu Pb Zn Ag Concentrator Refinery	Final Effluent LS	LT0.1	LT0.1	0.1-0.30	---	6.6-8.4	S/S 10
Kidd Creek Concentrator	1984	Timmins Ontario	-Do-	Rock Tailings Decant Before Liming	LT0.1	LT0.1	0.30	3.00	2.70	S/S 2.0, $SO_4^=$ 875 ppm
Gilman Mine	1984	Gilman, CO	Zn Ag Mine	AMD u/ground	1.5-4.0		200-300	50-400	2.8	Mn 100-120 ppm
Gilman Mine	1984	Gilman, CO	Zn Ag Mine	Effluent after LS	0.000-0.018	---	0.5-3.60	0.1-0.04	9.6	Mn 0.09-18.0, Cd 0.001
Homestake Mining Co.	1984	Lead, SD	Gold Cyanidation	Minewater Tailings Decant	0.07-1.60	---	0.01 0.10	0.10-10.00	5.0-6.5	CN_T 0.10-0.50 NH_3 6.0
Homestake Mining Co.	1984	Lead, SD	Gold Cyanidation	After Biological Treatment	0.05		---	---	---	CN_T 0.02 ppm, NH_3 0.5 ppm
Eagle Picher	1982	Schullsburg, Wisconsin	Zinc Mine	Groundwater Recent Mine Area	LT0.10	---	4.87	0.43	---	$SO_4^=$ 2166, Mg 367 ppm
COMINCO, Wedge Mine	1975	New Brunswick	Cu Pb Zn Mine	AMD Raw (Now Abated)	55	---	580	2100	4.2	
COMINCO, Wedge Mine	1975	New Brunswick	Cu Pb Zn Mine	Treated LS	0.25	---	1.60	3.0	9.4	
COMINCO, Wedge Mine	1975	New Brunswick	Cu Pb Zn Mine	Surface Waste AMD	346	---	771	7600	2.1	
COMINCO, Wedge Mine	1985	New Brunswick	Cu Pb Zn Mine	All AMD Avoided		---	---	---	---	Successful Reclamation
NORANDA, Waite-Amulet	1984	Quebec	Abandoned Tailings Cu Pb Zn Mill	AMD Raw	3.36	0.05	20.72	254	2.8	Cd 0.034, Mn 5.12, $SO_4^=$ 2300

Operation	Date	Location	Type	Type of Solution	Cu mg/l	Pb	Zn	Fe	pH	Comments
NORANDA, Waite-Amulet	1984	Quebec	Abandoned Tailings Cu Pb Zn Mill	Treated Effluent HDS	0.02	0.05	0.20	0.30	9.8	Cd 0.005, Mn 0.02, SO_4 938
Denison Mines	1984	Elliott Lake	U_3O_8 Mill	Minewater	1.28	5.05	4.50	300	2.7	U_3O_8=100, Ra 226=40 pCi/l, Ni 0.84, Mn 1.9, SO_4 2050, NH_3 47
Denison Mines	1984	Elliott Lake	U_3O_8 Mill	Tailings Decant LS	0.04					
Denison Mines	1984	Elliott Lake	U_3O_8 Mill	Final Effluent	0.2					
Mine-Mill B.	1984	E. Canada	Cu Pb Zn Mine-Mill	#12 Mine Effluent	0.03	0.07-0.72	0.50-3.49	1.40-2.77	5.5-8.50	Thiosalts 200-900 ppm
Mine-Mill B.	1984	E. Canada	Cu Pb Zn Mine-Mill	#6 Mine Effluent	0.09	0.05 0.54	0.11 3.30	0.40 6.13	8-9	
Mine-Mill G.	1984	Ontario	Cu Pb Zn Mine-Mill	Minewater Raw	5.26	180	260	31	3.60	76 ppm S/S, 5800 ppm TDS
Mine-Mill G.	1984	Ontario	Cu Pb Zn Mine-Mill	Water Treatment Plant Inflow	1.44	---	70.20	680.00	3.5	
Mine-Mill G.	1984	Ontario	Cu Pb Zn Mine-Mill	Water Treatment Plant Effluent (LSHDS)	0.14	---	0.18	0.77	8.9	
Mine-Mill G.	1984	Ontario	Cu Pb Zn Mine-Mill	Receiving Waters	0.07	0.72	0.22	5.00		
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	#4 Minewater Raw	0.8	---	98	---	4.5	
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	Open Pit Drainage	7.50	---	95	---	3.4	
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	Tailings Seepage	2.50	---	14.50	---	3.5	
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	#3 Shaft Water	50.00	---	155	---	4.3	
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	Old Stockpile Drainage	400.00	---	750	---	3.0	

Operation	Date	Location	Type	Type of Solution	Cu mg/l	Pb	Zn	Fe	pH	Comments
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	Average Drainage	23.67	---	119	---	3.9	
Heath Steel Mines	1973	New Brunswick	Cu Pb Zn Mine-Mill	Treated Effluent LS	0.01	---	0.04		10.6	
Lead Smelter A	1984	E. Canada	Lead Smelter	Recycle Plant Water	0.3	10.00	70.00	---	7.0	Cd 100 ppm, As 50 ppm
Lead Smelter A	1984	E. Canada	Lead Smelter	Combined Wastewater	1.0	6.00	7.00	---	7.0	Cd3, As 4.0
Lead Smelter A	1984	E. Canada	Lead Smelter	W Treatment Infow	0.02-0.16	1.0-7.0	10-120	---	4.7	Cd (0.5-50 ppm), As (1.0-140 ppm)
Lead Smelter A	1984	E. Canada	Lead Smelter	W Treatment Effluent LS	0.006-0.07	0.04 0.50	0.3 3.5	---	---	Cd (0.06-4.1 ppm), As (0.5-30 ppm)
Mine-Mill M.	1984	Ontario	Cu Pb Zn Mine-Mill	AMD, Mine Creek	0.01	---	0.30	0.06	6.4	S_2O3 8 ppm, 5.0 S/S
Mine-Mill M.	1984	Ontario	Cu Pb Zn Mine-Mill	Tailings Reclaim Water	0.01	---	5.92	4.70	6.8	S_2O_3 43 ppm, 25.0 S/S
Mine-Mill M.	1984	Ontario	Cu Pb Zn Mine-Mill	W Treatment Effluent	0.01	---	0.76	0.48	10.2	Tr S/S
AMAX, Mount Emmons	1984	Colorado	Zn Mine	AMD Mine	3.0-8.2	1.00	10-115	30-40	---	Cd 0.5, Mn 6-80, Mo LTDL
AMAX, Mount Emmons	1984	Colorado	Zn Mine	AMD Tailings		---	150-300	700	---	Cd 1 ppm, Mn 450, As 1 ppm
AMAX, Mount Emmons	1984	Colorado	Zn Mine	W Treatment Effluent	0.01-0.02	0.001-0.005	0.05		7.8	Mo 0.01, Mn 0.05, S/S 5

PEDCO (1983): Cu, Pb, AND Zn SUMMARY

The U.S. EPA commissioned a huge survey of U.S. mining and milling operations to determine levels of contaminants in minewater, acid mine drainage from tailings, and runoff areas, as well as potentially leachable contaminants from solids by the EP Leach Test which uses acetic acid.

Of the hundreds of samples analyzed for uranium, phosphate, copper, lead-zinc, molybdenum, gold-silver, and taconite recovery operations, most were at extremely low levels for copper, lead, and zinc. Examples of the small percentage where Cu, Pb, or Zn were detected are shown below.

It is concluded that:

1) Considering the levels of copper, lead, and zinc in ores, it is rather surprising to see how low the levels of copper, lead, and zinc are in tailings pond liquid and minewater. Nonetheless, levels are reached which clearly require removal before these solutions can be discharged, but this is not so in many cases.

2) Acetic acid leachate of solids extracted lead which, in most natural occurrences would be fixed as a carbonate or sulfate. Lead forms an acetate complex, but acetic acid does not occur commonly in nature, so the validity of the test is questionable.

3) Within each industry group, there is a wide range of Cu, Pb, and Zn levels in the effluents and leachates which reinforces the need for site specific criteria.

HIGH LEVELS OF EP TOXICITY CONTAMINANTS

IN THE LEAD/ZINC MINING SEGMENT
(mg/liter)

Analytical parameter	District		
	Eastern	Western	Missouri
Lead	5.0[a]	8.8[a], 11.0[b], 16.0[b], 5.5[e]	23.0[c], 39.0[d]

Waste types:
a - Tailings pond settled solids (two occurrences).
b - Fresh tailings (two occurrences).
c - Underground mine waste rock (one occurrence).
d - Mine water pond settled solids (one occurrence).
e - Mine backfilled tailings (one occurrence).

ELEVATED LEVELS OF EP TOXICITY CONTAMINANTS
IN THE LEAD/ZINC MINING SEGMENT
(mg/liter)

Analytical parameter	District		
	Eastern	Western	Missouri
Cadmium	0.65[a]	None	None
Lead	1.2[b], 2.4[b], 1.4[b]	4.6[c], 2.1[d], 1.0[e]	3.6[b], 1.9[f]
Mercury	0.041[c]	None	None

Waste types:
a - Inactive surface mine waste rock (one occurrence).
b - Tailings pond settled solids (four occurrences).
c - Fresh tailings (two occurrences).
d - Mine backfilled tailings (one occurrence).
e - Underground mine waste rock (one occurrence).
f - Coarse tailings dike material (one occurrence).

Source: PEDCO (1983)

HIGH LEVELS OF EP TOXICITY CONTAMINANTS
IN THE GOLD/SILVER MINING SEGMENT
(mg/liter)

Analytical parameter	District	
	Nevada	Other
Lead	None	11.0[a], 17.0[b], 23.0[c], 100.0[c]

Waste types:
a - Underground mine waste rock (one occurrence).
b - Fresh tailings (one occurrence).
c - Tailings pond settled solids (two occurrences).

ELEVATED LEVELS OF EP TOXICITY CONTAMINANTS
IN THE GOLD/SILVER MINING INDUSTRY
(mg/liter)

Analytical parameter	District	
	Nevada	Other
Cadmium	None	0.30[a], 0.36[a]
Lead	None	4.6[b], 4.9[c], 3.7[a]
Mercury	0.043[d]	None
Selenium	None	0.67[d]

Waste types:
a - Tailings pond settled solids (three occurrences).
b - Low-grade ore (one occurrence).
c - Underground mine waste rock (one occurrence).
d - Fresh tailings (two occurrences).

Source: PEDCO (1983)

T = Analysis in Solids; A = Acetic Acid Leachate; W = Water Leachate.

SOUTHWESTERN COPPER

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Leach liquors T	Leached material T	Leached material A	Leached material W
Copper														
Average	1150	2.16	1.76	374	3.13	<0.01	0.13	1190	19.4	34.6	476	1470	12.1	14.3
No. of samples	14	13	8	6	6	1	6	16	16	14	3	6	6	5
Minimum	3.82	<0.0055	0.0004	42.1	0.003		<0.01	174	<0.001	0.003	79	410	0.071	0.022
Maximum	3150	11	11	827	6.45		0.26	7650	240	425	890	3650	45	45
Zinc														
Average	123	0.383	0.0725	66.2	0.469	<0.03	0.0472	137	1.05	0.781	207	235	3.07	3.12
No. of samples	14	13	8	6	6	1	6	16	16	14	3	6	6	5
Minimum	30.5	0.031	<0.003	13	0.06		0.015	0.00	0.004	0.014	170	32.2	0.039	0.052
Maximum	679	1.6	0.25	131	1.3		0.11	378	4.45	3.3	260	353	9.3	7.7
Lead														
Average	159	<0.14	<0.084	<102	<0.082	<0.06	0.14	120	<0.080	<0.08	3.43	157	<0.21	0.38
No. of samples	14	13	8	6	6	1	6	16	16	14	3	6	6	5
Minimum	<102	<0.06	<0.084	<102	<0.072		<0.06	<102	<0.06	<0.06	2.8	131	<0.084	<0.06
Maximum	254	<0.84	<0.084	<102	<0.084		0.36	149	<0.084	<0.17	<4.2	191	<0.84	0.15

OTHER COPPER DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Leach liquors T	Leach material T	Leach material A	Leach material W	Low-grade ore T	Low-grade ore A	Low-grade ore W
Copper																	
Average	589	1.13	1.25	154	1.82	0.017	18	798	7.45	0.217	330	761	17.7	18.4	2750	0.026	0.04
No. of samples	7	7	6	4	4	1	3	7	6	7	1	5	5	4	3	3	2
Minimum	40.3	<0.001	<0.01	61.9	0.39		0.09	2.02	0.01	0.003		219	0.56	1.1	889	<0.01	<0.01
Maximum	2000	6.7	6.38	244	3.4		53	1360	31	<1.35		1970	38	36.4	3580	0.047	0.06
Zinc																	
Average	939	3.54	3.61	68.4	0.43	0.022	213	154	1.52	0.458	12.6	35.9	0.95	1.17	1020	5.38	0.065
No. of samples	7	7	6	4	4	1	3	7	6	7	1	5	5	4	3	3	2
Minimum	33.7	0.032	<0.03	0.87	0.13		0.049	19.1	0.17	0.006		20.9	0.3	0.27	15.0	0.3	0.009
Maximum	2360	17.5	16.4	154	1.1		640	561	6.5	3.05		66.5	2.1	2.1	3010	15.9	1.72
Lead																	
Average	538	<0.081	<0.076	<102	<0.273	<0.004	0.308	138	<0.076	<0.077	2.4	138	0.165	0.174	240	<0.076	<0.072
No. of samples	7	7	6	4	4	1	3	7	6	7	1	5	5	4	3	3	2
Minimum	<102	<0.06	<0.06	<102	<0.004		<0.004	<102	<0.06	<0.06		<102	<0.004	<0.004	112	<0.06	<0.06
Maximum	1510	<0.004	<0.004	<102	<0.84		0.96	250	<0.004	<0.004		367	0.49	0.443	502	<0.004	<0.004

WESTERN LEAD/ZINC DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Underground mine waste T	Underground mine waste A	Underground mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Mine water pond liquid T	Mine backfilled tailings T	Mine backfilled tailings A	Mine backfilled tailings W
Copper														
Average	43.1	0.007	0.008	30.8	0.112	c	0.12	71.6	0.14	0.027	0.48	122	0.008	0.006
No. of samples	2	2	2	3	3	c	1	1	1	1	1	2	2	2
Minimum	<35.1	0.004	0.005	7.97	0.052	c						<35.1	<0.001	<0.005
Maximum	71.1	<0.01	<0.01	55.4	0.22	c						278	0.014	0.007
Zinc														
Average	4820	6.86	0.20	1660	17.6	c	1.9	3870	18.0	0.89	82	4810	3.2	0.255
No. of samples	2	2	2	3	3	c	1	1	1	1	1	2	2	2
Minimum	2000	1.01	0.05	166	1.8	c						856	1.2	0.039
Maximum	7640	7.1	0.36	3360	30	c						7170	5.1	0.49
Lead														
Average	8340	1.02	<0.072	457	10.5	c	0.15	1860	8.8	<0.084	6.3	1750	3.0	<0.082
No. of samples	2	2	2	3	3	c	1	1	1	1	1	2	2	2
Minimum	2970	1	<0.06	287	4.6	c						1660	2.1	<0.084
Maximum	13700	1.03	<0.084	773	16	c						1830	5.5	<0.1

R URANIUM DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Underground mine waste T	Underground mine waste A	Underground mine waste W	Untreated mine water T	Mine water pond liquid T	Mine water pond settled solids T	Mine water pond settled solids A	Mine water pond settled solids W	Low-grade ore T	Low-grade ore A	Low-grade ore W
Lead														
Average	157	<0.064	<0.06	153	<0.074	<0.07	<0.33	<0.084	<102	<0.089	<0.08	195	<0.06	<0.06
No. of samples	6	6	5	8	8	6	3	2	3	3	3	2	2	2
Minimum	<102	<0.06	<0.06	<102	<0.06	<0.06	<0.06	<0.084	<102	<0.084	<0.06	181	<0.06	<0.06
Maximum	180	<0.084	<0.06	280	<0.08	<0.1	<0.84	<0.084	<102	<0.1	<0.1	209	<0.06	<0.06
Copper														
Average	13.4	0.012	<0.01	23.3	<0.006	0.010	0.012	0.251	42.7	0.506	0.009	<7.88	<0.01	<0.01
No. of samples	6	6	5	8	8	6	3	2	3	3	3	2	2	2
Minimum	<0.61	<0.001	<0.01	<0.61	<0.001	0.003	<0.01	0.012	<0.61	<0.001	<0.005	<0.61	<0.01	<0.01
Maximum	48	0.023	<0.01	96.3	<0.01	0.024	0.017	0.49	125	1.5	0.013	<15.1	<0.01	<0.01
Zinc														
Average	65.2	0.06	<0.03	81	0.154	0.026	0.042	0.061	34.9	0.7	0.039	157	0.071	<0.03
No. of samples	6	6	5	8	8	6	3	2	3	3	3	2	2	2
Minimum	26.5	<0.03	<0.03	20.5	0.067	0.008	0.038	0.051	29.9	0.1	<0.03	71.4	0.062	<0.03
Maximum	110	0.12	<0.03	277	0.35	0.045	0.044	0.071	44.1	1.6	0.046	242	0.081	<0.03

AHO PHOSPHATE DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Low-grade ore T	Low-grade ore A	Low-grade ore W
Lead													
Average	109	0.09	<0.084	<102	0.109	c	<0.205	<102	<0.084	<0.084	<102	<0.084	c
No. of samples	14	13	7	2	2	c	3	5	5	2	1		c
Minimum	<102	<0.084	<0.084	<102	0.084	c	<0.084	<102	<0.084	<0.084			c
Maximum	127	0.16	<0.084	<102	0.134	c	<0.42	<102	<0.084	<0.084			c
Copper													
Average	52.3	0.004	0.004	15.3	0.032	c	0.016	68.5	0.053	0.008	63.9	0.007	c
No. of samples	14	13	7	2	2	c	3	5	5	2	1	1	c
Minimum	<0.610	<0.001	<0.001	8.06	<0.001	c	<0.001	57	<0.001	<0.001			
Maximum	128	0.017	0.009	22.5	0.064	c	0.043	107	0.26	0.014			
Zinc													
Average	593	0.689	0.0187	337	1.6	c	0.113	1310	1.74	0.102	1230	0.88	c
No. of samples	14	13	7	2	2	c	3	5	5	2	1	1	c
Minimum	47.8	0.034	0.009	128	1.4	c	0.076	927	1.2	0.024			c
Maximum	1860	1.90	0.0310	545	1.9	c	0.17	2030	2.2	0.18			c

OTHER PHOSPHATE DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W
Copper										
Average	10.9	0.008	0.014	562	<0.001	<0.001	<0.003	<7.01	0.022	0.014
No. of samples	6	6	5	2	2	1	2	5	5	5
Minimum	<0.610	<0.001	<0.001	0.77	<0.001		<0.001	<0.61	<0.001	<0.001
Maximum	24.1	0.016	0.047	1120	<0.001		<0.005	<15.1	0.088	0.051
Zinc										
Average	56.4	0.057	0.026	34.0	0.17	0.025	0.028	47.5	0.101	0.018
No. of samples	6	6	5	2	2	1	2	5	5	5
Minimum	28.1	<0.03	<0.004	7.92	0.11		0.013	30.7	0.069	0.011
Maximum	82.5	0.094	0.046	60.1	0.23		0.042	63.6	0.14	<0.03
Lead										
Average	120	<0.08	<0.08	<102	<0.084	<0.084	0.092	109	<0.087	<0.08
No. of samples	6	6	5	2	2	1	2	5	5	5
Minimum	<102	<0.06	<0.06	<102	<0.084		0.084	<102	<0.084	<0.06
Maximum	143	<0.1	<0.1	<102	<0.084		<0.1	135	<0.1	<0.1

FLORIDA PHOSPHATE DISTRICT

Analytical parameters[a]	Surface mine waste T	Surface mine waste A	Surface mine waste W	Phosphate sand tailings T	Phosphate sand tailings A	Phosphate sand tailings W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Untreated mine water T
	Sample type and treatment[b]													
Lead														
Average	<102	<0.06	<0.06	<102	<0.072	<0.065	<102	<0.078	c	0.12	<102	<0.07	<0.06	<0.084
No. of samples	6	6	6	5	5	5	3	4	c	6	7	7	6	1
Minimum	<102	<0.06	<0.06	<102	<0.06	<0.06	<102	<0.06	c	<0.084	<102	<0.03	<0.06	
Maximum	<102	<0.06	<0.06	<102	<0.084	<0.084	<102	<0.084	c	0.22	<102	<0.1	<0.06	
Copper														
Average	3.75	<0.01	<0.01	1.39	<0.006	<0.008	<0.61	0.043	c	0.06	1.27	0.008	<0.01	0.0890
No. of samples	6	6	6	5	5	5	3	4	c	6	7	7	6	1
Minimum	1.41	<0.01	<0.01	<0.61	<0.001	<0.001	<0.61	<0.001	c	<0.001	<0.61	<0.001	<0.01	
Maximum	9.93	<0.01	<0.01	2.72	<0.01	<0.01	<0.61	0.16	c	0.2	3.63	0.0170	<0.01	
Zinc														
Average	14.2	0.036	<0.03	13.1	0.059	0.027	3.18	0.104	c	0.107	26.1	0.069	<0.03	0.022
No. of samples	6	6	6	5	5	5	3	4	c	6	7	7	6	1
Minimum	4.15	<0.03	<0.03	8.48	0.0435	0.015	<0.82	0.043	c	0.011	8.48	0.026	<0.03	
Maximum	18.4	0.057	<0.03	19.4	0.1	<0.03	7.91	0.15	c	0.36	47.8	0.17	<0.03	

NEW MEXICO URANIUM DISTRICT

Analytical parameters[a]	Surface mine waste T	Surface mine waste A	Surface mine waste W	Untreated mine waste T	Mine water pond liquid T	Mine water pond settled solids T	Mine water pond settled solids A	Mine water pond settled solids W	Low-grade ore T	Low-grade ore A	Low-grade ore W
	Sample type and treatment[b]										
Lead											
Average	110	<0.06	<0.06	0.13	<0.07	103	<0.068	<0.065	112	<0.067	<0.067
No. of samples	4	4	4	1	5	6	6	5	7	7	7
Minimum	<102	<0.06	<0.06		<0.06	<102	<0.06	<0.06	<102	<0.06	<0.06
Maximum	118	<0.06	<0.06		<0.1	103	0.084	<0.084	168	<0.084	<0.084
Copper											
Average	<0.61	0.012	<0.01	0.028	0.012	1.19	0.012	0.0161	6.8	0.016	0.009
No. of samples	4	4	4	1	5	6	6	5	7	7	7
Minimum	<0.61	<0.01	<0.01		<0.001	<0.61	<0.001	<0.01	<0.61	<0.01	<0.001
Maximum	<0.61	0.018	<0.01		0.01	3.14	0.011	0.0405	43.9	0.046	0.015
Zinc											
Average	32	0.067	<0.03	0.5	0.042	34.3	0.20	0.0283	29.3	0.09	0.025
No. of samples	4	4	4	1	5	6	6	5	7	7	7
Minimum	17.8	<0.03	<0.03		0.026	27.7	<0.03	0.0215	12.0	<0.03	0.011
Maximum	49.2	0.13	<0.03		0.093	43.8	0.42	<0.03	71.4	0.14	<0.03

WYOMING URANIUM DISTRICT

Analytical parameters[a]	Surface mine waste T	Surface mine waste A	Surface mine waste W	Untreated mine water T	Mine water pond liquid T	Mine water pond settled solids T	Mine water pond settled solids A	Mine water pond settled solids W	Low-grade ore T	Low-grade ore A	Low-grade ore W
	Sample type and treatment[b]										
Lead											
Average	140	<0.08	<0.08	<0.084	<0.066	<102	<0.084	<0.084	<103	<0.08	<0.066
No. of samples	13	13	12	1	4	3	3	2	4	4	4
Minimum	<102	<0.06	<0.06		<0.06	<102	<0.084	<0.084	<102	<0.06	<0.06
Maximum	292	<0.1	<0.1		<0.084	<102	<0.084	<0.084	<105	<0.1	<0.084
Copper											
Average	12.9	0.020	0.007	0.017	0.014	0.62	0.023	0.010	1.11	0.015	<0.008
No. of samples	13	13	12	1	4	3	3	2	4	4	4
Minimum	<0.610	<0.001	<0.001		<0.01	<0.61	<0.001	0.007	<0.61	<0.01	<0.001
Maximum	44.2	0.104	0.024		0.024	0.65	0.046	0.012	2.59	0.021	<0.01
Zinc											
Average	46.2	0.105	0.022	0.021	0.06	15.6	0.20	0.033	29.4	0.060	0.033
No. of samples	13	13	12	1	4	3	3	2	4	4	4
Minimum	19.3	0.043	0.003		<0.03	10.4	0.13	0.027	13.8	0.042	<0.03
Maximum	109	0.32	0.037		0.16	23.7	0.24	0.039	52.6	0.123	0.043

EASTERN LEAD/ZINC DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Underground mine waste T	Underground mine waste A	Underground mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Mine water pond liquid T	Mine water pond settled solids T	Mine water pond settled solids A	Mine water pond settled solids W
Copper														
Average	5.3	0.075	0.013	11.7	0.010	c	0.07	52	0.079	0.009	<0.006	<15.1	<0.003	<0.003
No. of samples	1	1	1	2	2	c	4	8	8	8	2	2	2	2
Minimum				4.97	<0.003	c	<0.01	<15.1	<0.001	<0.001	<0.001	<15.1	<0.001	<0.001
Maximum				18.4	0.016	c	0.21	154	0.24	0.012	<0.01	<15.1	<0.005	<0.005
Zinc														
Average	88.1	1.22	0.018	1800	3.25	c	1.11	2190	7.15	0.287	0.53	18900	26.9	0.018
No. of samples	1	1	1	2	2	c	4	8	8	8	2	2	2	2
Minimum				211	0.995	c	0.2	1090	2.3	0.026	0.41	382	0.82	0.013
Maximum				3390	5.5	c	3.6	3020	12.3	1.2	0.65	37500	53	0.023
Lead														
Average	<102	0.131	<0.084	<102	<0.096	c	0.082	311	1.29	<0.064	<0.072	106	<0.092	<0.092
No. of samples	1	1	1	2	2	c	4	8	8	8	2	2	2	2
Minimum				<102	<0.092	c	<0.06	<102	<0.06	<0.06	<0.06	<102	<0.084	<0.084
Maximum				<102	<0.1	c	0.15	709	5.02	<0.084	<0.084	110	<0.1	<0.1

MISSOURI LEAD/ZINC DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Underground mine waste T	Underground mine waste A	Underground mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Mine water pond liquid T
Copper											
Average	1330	0.012	<0.001	292	<0.001	c	0.006	69	<0.004	0.017	0.004
No. of samples	1	1	1	2	2	c	2	3	4	4	2
Minimum				134	<0.001	c	<0.001	32.2	<0.001	0.008	<0.001
Maximum				449	<0.001	c	0.012	139	<0.01	0.041	0.006
Zinc											
Average	1300	2.4	0.0645	241	0.57	c	0.84	278	1.97	0.094	0.167
No. of samples	1	1	1	2	2	c	2	3	4	4	2
Minimum				222	0.14	c	0.39	222	1.06	0.052	0.025
Maximum				261	1	c	1.3	313	3.7	0.17	0.31
Lead											
Average	17500	23	<0.084	569	<0.084	c	0.21	384	1.41	0.092	0.127
No. of samples	1	1	1	2	2	c	2	3	4	4	2
Minimum				402	<0.084	c	0.1	331	<0.06	<0.06	<0.084
Maximum				736	<0.084	c	0.32	463	3.6	0.14	0.17

MOLYBDENUM DISTICT

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Underground mine waste T	Underground mine waste A	Underground mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Untreated mine water T	Low-grade ore T	Low-grade ore A	Low-grade ore W
Copper																	
Average	68.7	0.028	0.02	22.1	0.028	0.003	30.8	0.048	c	0.035	29.8	0.024	0.005	0.72	45.4	0.0212	0.004
No. of samples	2	2	2	2	2	2	3	3	c	3	3	3	3	3	2	2	2
Minimum	22	0.014	0.012	<0.61	<0.001	0.003	<8.34	0.022	c	<0.001	7.04	0.016	0.002	<0.001	7.67	0.0065	<0.002
Maximum	115	0.042	0.028	43.5	0.055	0.003	71.6	0.068	c	0.069	68.2	0.037	0.01	26	83.1	0.036	0.007
Zinc																	
Average	45.8	0.08	0.068	177	0.244	0.015	115	0.39	c	0.086	184	0.28	0.029	12	70.1	0.14	0.006
No. of samples	2	2	2	2	2	2	3	3	c	3	3	3	3	3	2	2	2
Minimum	32.1	0.079	0.025	133	0.098	0.009	25.4	0.27	c	0.016	60.3	0.16	0.013	0.082	47	0.11	0.012
Maximum	59.6	0.081	0.11	120	0.39	0.021	260	0.49	c	0.19	308	0.47	0.058	34	93.2	0.16	0.16
Lead																	
Average	156	<0.084	<0.084	241	<0.084	<0.084	171	<0.084	c	<0.0588	152	0.145	<0.084	0.21	160	<0.084	<0.084
No. of samples	2	2	2	2	2	2	3	3	c	3	3	3	3	3	2	2	2
Minimum	<102	<0.084	<0.084	225	<0.084	<0.084	<102	<0.084	c	<0.0084	<102	<0.084	<0.084	<0.084	118	<0.084	<0.084
Maximum	210	<0.084	<0.084	257	<0.084	<0.084	281	<0.084	c	<0.084	200	0.19	<0.084	0.45	203	<0.084	<0.084

NEVADA GOLD/SILVER DISTRICT

Analytical parameters[a]	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Leach material T	Leach material A	Leach material W	Low-grade ore T	Low-grade ore A	Low-grade ore W
Copper																
Average	9.41	0.013	<0.01	3.52	0.12	c	1.3	43.6	0.094	0.178	5.61	0.019	<0.006	3.31	0.016	<0.01
No. of samples	5	5	3	2	2	c	2	4	4	3	3	3	2	2	2	2
Minimum	<0.61	<0.001	<0.01	<0.61	<0.01	c	0.97	4.06	<0.001	<0.0055	5.23	<0.001	<0.001	<0.61	<0.01	<0.01
Maximum	22	0.033	<0.01	6.44	0.24	c	1.63	62	0.35	0.52	5.86	0.046	<0.01	6.01	0.021	<0.01
Zinc																
Average	148	0.177	<0.03	101	0.42	c	15.8	452	0.408	0.018	104	0.25	<0.016	53.4	0.141	<0.03
No. of samples	5	5	3	2	2	c	2	4	4	3	3	3	2	2	2	2
Minimum	63.3	0.062	<0.03	56.3	0.13	c	14.4	62.2	0.305	0.007	93.7	0.11	<0.003	20.7	0.042	<0.03
Maximum	212	0.27	<0.03	146	0.7	c	17.1	871	0.685	<0.03	124	0.45	<0.03	86.1	0.24	<0.03
Lead																
Average	123	<0.07	<0.06	<102	<0.072	c	0.22	200	<0.077	<0.072	104	<0.076	<0.072	106	<0.06	<0.06
No. of samples	5	5	3	2	2	c	2	4	4	3	3	3	2	2	2	2
Minimum	<102	<0.06	<0.06	<102	<0.06	c	<0.06	<102	<0.06	<0.06	<102	<0.06	<0.06	<102	<0.06	<0.06
Maximum	163	<0.084	<0.06	<102	<0.084	c	0.38	427	<0.084	<0.084	107	<0.084	<0.084	110	<0.06	<0.06

OTHER GOLD/SILVER DISTRICT

Analytical	Sample type and treatment[b]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Underground mine waste T	Underground mine waste A	Underground mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Low-grade ore T	Low-grade ore A	Low-grade ore W
Copper																
Average	<15.1	0.002	0.012	101	0.036	0.0048	16.6	3.07	c	11.6	116	0.203	0.0713	78.2	0.031	0.012
No. of samples	2	2	2	3	3	3	3	3	c	4	5	5	4	3	3	2
Minimum	<15.1	<0.001	<0.001	30	<0.005	0.002	3.55	0.013	c	0.47	4.35	<0.001	<0.001	<3.61	0.008	0.008
Maximum	<15.1	0.003	0.024	166	0.07	<0.0115	31.1	8.8	c	24	282	0.51	0.18	142	0.051	0.016
Zinc																
Average	15.7	0.084	0.072	895	2.73	0.133	93.7	10.5	c	37.2	1200	15.4	11.6	1110	1.61	0.058
No. of samples	2	2	2	3	3	3	3	3	c	4	5	5	4	3	3	2
Minimum	15.6	0.057	0.059	107	<0.004	0.018	45.8	0.14	c	0.99	67.8	0.077	0.004	32.1	0.22	0.005
Maximum	15.7	0.11	0.084	1650	4.4	0.2	132	22	c	82	3710	43	41	2070	3.1	<0.11
Lead																
Average	157	<0.084	<0.084	1840	5.3	<0.084	227	5.7	c	0.095	3210	25.4	0.93	7600	1.89	<0.084
No. of samples	2	2	2	3	3	3	3	3	c	4	5	5	4	3	3	2
Minimum	<102	<0.084	<0.084	<102	<0.1	<0.084	<102	<0.084	c	<0.084	<102	<0.084	<0.084	120	<0.084	<0.084
Maximum	212	<0.084	<0.084	3900	11	<0.084	426	17	c	0.13	8150	100	3.4	15500	4.6	<0.084

TACONITE

Analytical parameters[a]	Sample type and treatment[a]: Surface mine waste T	Surface mine waste A	Surface mine waste W	Fresh tailings T	Fresh tailings A	Fresh tailings W	Tailings pond liquid T	Tailings pond settled solids T	Tailings pond settled solids A	Tailings pond settled solids W	Untreated mine water T	Low-grade ore T	Low-grade ore A	Low-grade ore W
Copper														
Average	<19.8	0.003	0.002	<11.5	0.005	c	0.0082	<15.1	0.018	0.003	<0.008	<30.3	0.008	<0.016
No. of samples	13.0	13	6	4	4	c	4	8	8	6	2	4	4	2
Minimum	<15.1	<0.001	<0.001	<0.61	<0.001	c	<0.001	<15.1	<0.001	<0.001	<0.005	<15.1	<0.001	<0.001
Maximum	<75.7	0.009	0.004	<15.1	0.011	c	0.026	<15.1	0.13	0.012	<0.01	<75.7	0.019	<0.0315
Zinc														
Average	32	0.034	0.010	8.9	0.089	c	0.029	12.3	0.044	0.015	0.023	17.8	0.058	0.007
No. of samples	13	13	6	4	4	c	4	8	8	6	2	4	4	2
Minimum	14.6	0.013	0.007	3.74	0.042	c	0.024	3.68	0.000	0.008	0.016	15.4	0.034	<0.003
Maximum	56.2	0.054	0.013	16.2	0.14	c	0.03	17.2	0.11	0.024	<0.03	19.7	0.077	0.011
Lead														
Average	116	<0.084	<0.084	<102	<0.084	c	<0.092	<102	<0.088	<0.084	<0.08	<102	<0.084	<0.084
No. of samples	3	13	6	4	4	c	4	8	8	6	2	4	4	2
Minimum	<102	<0.084	<0.084	<102	<0.084	c	<0.084	<102	<0.084	<0.084	<0.06	<102	<0.084	<0.084
Maximum	144	<0.084	<0.084	<102	<0.084	c	<0.1	<102	<0.112	<0.084	<0.1	<102	<0.084	<0.084

COPPER

Eh-pH diagrams for copper given by GARRELS and CHRIST (1964) suggest that copper oxide or hydroxy-carbonate minerals would tend to limit the solubility of copper in aerated water at pH 7.0 to about 64 mg/l. At pH 8.0, the solubility would be about one tenth as great or about 6.4 mg/l. Copper solubility is generally lower in reducing systems than in oxidizing systems, especially if reduced sulfur species are present.

Copper is a widely distributed element, and the amounts of copper reported in river water by DURUM and HAFFTY (1963) are within the general range predicted from the solubility calculated by GARRELS and CHRIST (1964).

Besides the natural occurrence of copper, the metal is used extensively in water treatment equipment and in the fabrication of pipe, valves, and pumping equipment. Small amounts of copper sulfate are commonly added to water stored in reservoirs to inhibit algal growth. Most of the higher concentrations reported by DURFOR and BECKER (1964) for public supplies were in water which had been impounded in storage reservoirs and treated in this way.

High concentrations of copper up to hundreds of ppm may occur in acid mine drainage from open pit and underground mine workings, ore dumps, or mill tailings. Copper contents in ground and surface water can be high in areas where ore bodies occur. MALIUGA (1950) found an average of 200 mg/l Cu in water from a mineralized region in the southern Urals of the U.S.S.R., but one would not have to go that far to find elevated copper levels in AMD. Geochemical literature contains much data on copper concentrations in water from such areas.

Concentrations of copper in the Great Lakes are dependent on local inputs. In parts of Lake Superior and elsewhere, copper concentrations are shown to rise in the spring. Modal copper concentration in upper lakes offshore are less than 2.5 ug/l with 95% of the measurements below 5.0 ug/l. Water intakes to the lakes varied between 2 and 60 ug/l, probably influenced by local industrial and municipal sources.

Sediments in Lake Erie deposited in pre-colonial times contain about 27 ug/g copper compared with 57 ug/g for recent sediments indicating that man's activities account for 50% of the total input of copper in Lake Erie according to KEMP, et al. (1976).

WILLIAMS and MINK (1975) analyzed the levels of Cu, Pb, Zn, Cl, F, Ca, Cd, Fe, K, Mg, Mn, Na, and Sb in the inflow and effluent from the settling ponds of seven mines which produce lead, zinc, and silver in Idaho. The outflow from five settling ponds that received only effluent from the concentrating process were acceptable, but the outflows from two ponds that received concentrator effluent plus acid mine drainage and wastes

from various processes contained "high" concentrations of F, Cd, Cu, Pb, Zn, and Sb according to the Idaho Bureau of Mines and Geology, Moscow, Idaho.

A typical analysis of water from the Burra-Burra Mine, Ducktown, Tennesee, dated 1911, from HEM (1970) shows a typical acid mine drainage analysis from a copper mine:

	mg/l
SiO_2	56
Aluminum	433
Iron	2,178
Manganese	0.2
Copper	312
Zinc	200
Calcium	68
Magnesium	41
Sodium	23
Potassium	20
Bicarbonate	0
Sulfate	6,600
Chloride	0.1
TDS	9,990
Acidity as H_2SO_4	130

Total copper in water is usually in the form of insoluble particulates, soluble complexes, and soluble Cu^{2+} ions. The proportion of each form depends on the amount of particulate and soluble complexing agents. These agents, according to STIFF (1971), may be materials such as humates or carbonates.

PATTERSON (1975) reported copper levels in effluents as follows:

Process	Copper Concentration mg/l	Reference
Copper Ore Extraction	0.28-0.33	TALLMANGE (1965)
Gold Ore Extraction	20	HALLOWELL, et al. (1973)
Acid Mine Drainage	3.2	HILL (1972)
Acid Mine Drainage	3.9	HILL (1972)
Acid Mine Drainage	0.12	HILL (1972)
Acid Mine Drainage	51.6-128.0	LARSEN, et al. (1973)

In the course of this investigation, recycled process solutions, mine drainage effluents, and treated effluents were encountered with compositions shown at the front of this chapter. Metals, Pb, Zn, Fe, and pH, are shown to provide perspective. It is concluded that:

- Acid mine drainage and surface drainage where copper is present can reach levels in the hundreds of ppm. Some mines where mine drainage has a high pH, e.g., Kidd Creek Mines, never see copper above 0.1 ppm as it is precipitated by the water in the mine. Underground sludges contain 2-3% copper at times.

- Treated effluents contain low copper values, generally below 0.1 ppm and often as low as 0.01 ppm.

- Ammonia is a powerful complexing agent, and it is not detected from the data whether relatively high ammonia levels in minewater prevent copper from being precipitated by lime. This does not appear to be the case.

- In recycled mill solutions, especially in copper-lead-zinc flotation plants, soluble copper must not be allowed to build up. Copper is an activator for sphalerite and, if present in mill solutions, will cause sphalerite to float in the primary separation where Cu-Pb is floated as a semi-bulk rougher ion while sphalerite is depressed. At one Cu-PbZn mine-mill in British Columbia, the presence of a small amount of oxidized copper ore in the mill feed wreaked havoc with separations achieved in the mill due to copper solubilization.

In the course of this investigation, copper was encountered in the following metallurgical process solutions, effluents, acid mine drainage, etc:

LEAD

The chemistry of lead in natural waters has been indicated in Eh-pH diagrams by GARRELS and CHRIST (1964). Over most of the water stability region, the oxidation state of lead is Pb^{++}, and the most likely control of solubility in oxidizing systems is the carbonate, cerussite. Lead sulfate $PbSO_4$ is relatively insoluble and will control lead in oxidizing systems, especially those associated with sulfide mines where sulfate is always abundant in waters that come into contact with ore, tailings, and wasterock. In the presence of sulfides in water, lead sulfide precipitates with a solubility around 2 mg/l. The carbonate, hydroxide, phosphate chloride, sulfide, and sulfate of lead all have very low solubilities in water.

The ONTARIO MOE (1979) reported median lead offshore values of less than 1.0 ug/l in Great Lakes waters. A median value of 3.7 ug/l of lead for public water supplies was

reported by DUFOR and BECKER (1964), although lead was not detected at all in many samples. The median value for North American rivers reported by DURUM and HAFFTY (1963) was 4.0 ug/l. The wide use of lead as a gasoline additive and its dispersal in engine exhaust has considerably increased the availability of lead for solution in rainfall and fresh water but, according to HEM (1970), the importance of that effect was not known except, of course, in the banning of new cars that use leaded fuels.

Lead contained in zinc flue dusts used as fertilizer additives is added to soils as a plant food despite the fact that lead, even at 1.0 mg/l in the nutrient solutions, is toxic to plants. A common problem in wetlands is lead pellets ingested by wildfowl where just 5-6 pellets are lethal.

Metal mining and concentrate smelting introduce lead into the environment although the levels encountered in minewater were surprisingly low. Lead smelter recycle water contained 10 ppm lead, probably mostly in the form of suspended solids which are reduced to 0.04-0.50 mg/l on lime addition and settling.

Significant lead values have been found in minewater. One example is municipal water pumped from an abandoned mineshaft in Australia which was used as a municipal water supply infiltration gallery and was reported by the AUSTRALIAN DEPT. OF MINES (1962). MILL (1972) reported the following lead levels in acid mine drainage at low pH values where lead would be predominantly in soluble form:

Source	pH	Lead (mg/l)
Tailings Pond	2.0	0.67
Mine Drainage	2.6	0.30
Mine Drainage	3.2	2.5
Mine Drainage	-	0.02

ZINC

Zinc occurs commonly as sphalerite, a sulfide mineral. Zinc is commonly present in carbonate rocks, and its geochemistry has been described by WEDEPOHL (1953).

The weathering of zinc minerals in contact with air releases zinc ions. HEM (1970) showed an example of acid mine drainage from the Victor Mine, Joplin, Missouri, that contained 345 mg Zn/l in 1917.

Data gathered during this RANDOL investigation showed zinc at 9300 mg/l in a Jarosite pond solution, and 0.10-800 mg/l in some acid mine drainage flows. A mine does not have to be a base metal mine to have zinc in its minewater--for example, an Elliot Lake uranium

minewater contained 4.50 mg/l zinc, and gold-silver cyanidation plants use zinc to precipitate the precious metals, allowing the zinc to go into solution as a cyanide.

Zinc is a widely used metal and can be dissolved from galvanized pipe, fences, and construction steel in many forms and uses. It may also be present in industrial waste and is added as a nutrient supplement in fertilizers and animal feed.

The solubility constant for zinc hydroxide quoted by SILLEN and MARTELL (1964) is around 10^{-17} at 25°C. According to HEM (1970), the equilibrium activity of Zn^{++} at pH 8.00 in the presence of $Zn(OH)_2$ is about 650 mg/l. As pH increases, the solubility passes through a minimum and then increases as $[Zn(OH)_3]^-$ is formed. The solubility of zinc carbonate is in the same range as the hydroxide, and concentrations of zinc in solution at well above 1 mg/l can be stable at neutral pH.

Zinc is often present in natural waters at concentrations well above that which would be in equilibrium with $Zn(OH)_2$ or $ZnCO_3$. In southwestern Wisconsin, some springs near known ore deposits contained 1500 mg/l Zn in contrast to background levels of around 10 mg/l.

At a reclaimed minesite in Quebec, galvanized articles in the burned garbage dump of the former operation and residential area introduced enough zinc to percolating solutions to necessitate diversion of runoff from the area to minimize uptake of zinc from this area.

Zinc also enters the environment through the burning of fossil fuels containing zinc and in effluents from synthetic fabric treatment, e.g., rayon.

According to the ONTARIO MOE (1979), modal concentrations of zinc offshore in the Great Lakes are less than 10 ug/l with concentrations ranging from 1.0 ug/l to 28 ug/l. At water intakes to the lakes, zinc concentrations were considerably higher, e.g., 178 ug/l at Buffalo.

WATER QUALITY CRITERIA, CU, PB, AND ZN

Water quality criteria to protect fresh and marine aquatic life as summarized by NORANDA RESEARCH are tabulated on the previous pages.

The EPA (1980) objectives to protect freshwater aquatic life is a log function:

Copper

$$[Cu] = e^{(0.94\ [\ln \text{hardness}]\ -1.23)}$$

This computes as follows:

Hardness	50 mg/l	200 mg/l $CaCO_3$
[Cu] Max.	12 ug/l	43 ug/l

Lead

$$[Pb]\ Max. = e^{(.22\ [in\ hardness]\ -0.47}$$

This computes as follows:

Hardness	50 mg/l	200 mg/l $CaCO_3$
[Pb] Max.	74 ug/l	400 ug/l

Zinc

$$[Zn]\ Max. = e^{(0.83\ [in\ hardness]\ +\ 1.95}$$

This computes as follows:

Hardness	50 mg/l	200 mg/l $CaCO_3$
[Zn] Max.	102 ug/l	570 ug/l

Cu (ug/L) COPPER

Summary of North American Water Quality Criteria for Copper

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		0.01 (96-hr LC50)	0.1 (96-hr LC50)	24-hr mean 5.6	2	<5.0	Non-detectable	--	50-300	--	20
MAX. PERMISSIBLE LIMIT		--	--	e(0.94 (ln (hard))-1.23	--	5.0	5-10	20	--	20	0.1 96-hr LC50
PROTECTION OF MARINE LIFE											
OBJECTIVE		<10.0 0.01 (96-hr LC50)	0.1 (96-hr LC50)	24-hr mean 4.0	50*	--	--	--	50-300	--	--
MAX. PERMISSIBLE LIMIT		50.0	--	23.0	--	--	--	--	--	--	--
PUBLIC WATER SUPPLY		1,000	1,000	1,000	500	1,000	10-50 (obj) 1,000 (max per. limit)	20	--	1,000	1,000
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	500	(1,000)	--	1,000	500	--	--	--	--	500
	IRRIGATION	50	--	--	200-5,000	--	--	--	--	--	200

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.

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9. British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries.

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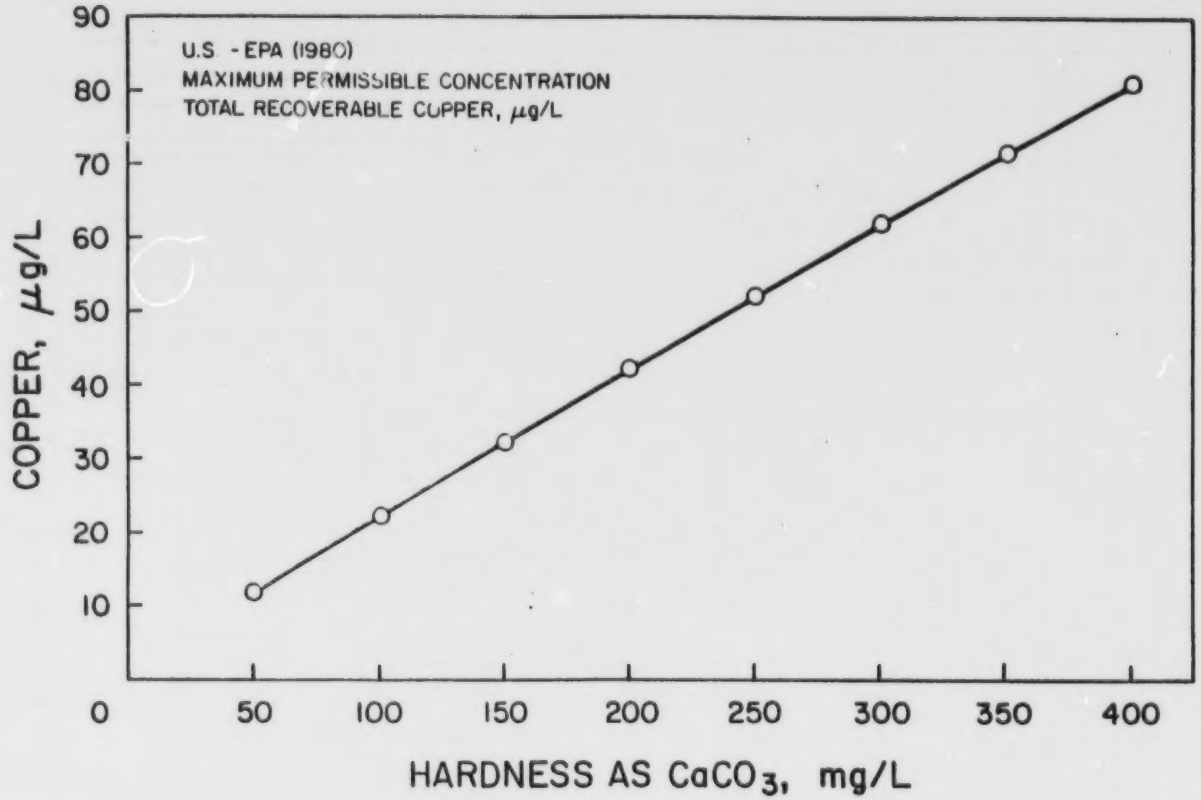
U.S. - EPA (1980)
MAXIMUM PERMISSIBLE CONCENTRATION
TOTAL RECOVERABLE COPPER, μg/L
COPPER, μg/L
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300
350
400
HARDNESS AS $CaCO_3$, mg/L

1(a)

Pb (ug/L) LEAD

Summary of North American Water Quality Criteria for Lead

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1980	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9,**] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE						Alkalinity mg/L / [Pb] <20 / <5 20-40 / <10 40-80 / <20 >80 / <25					
OBJECTIVE		--	.01 (96-hr LC50)	24-hr mean $e^{(2.35 (\ln (hard))-9.48)}$	5(soft water) 10(hard>95 mg/L)		ND	--	50-200	--	--
MAX. PERMISSIBLE LIMIT		30	--	$e^{(1.22 (\ln (hard))-0.47)}$	30	5, 10, 20, 25	1300	50	--	50	30
PROTECTION OF MARINE LIFE											
OBJECTIVE		<10	--		<50 *	--	--	--	50-200	--	--
MAX. PERMISSIBLE LIMIT		50	--	--	--	--	--	--	--	--	--
PUBLIC WATER SUPPLY		50	50	50	250 or 50	50	N.D. (Obj) 50-100 (limit)	(50)	--	50	50
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	100	(50)	--	500 (Horses present) 1000 (Horses absent)	100	--	(50)	--	--	100
	IRRIGATION	5,000	(50)	--	5,000	5,000	--	(50)	--	--	5,000

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Lead, EPA 440/5-80-057.
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6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
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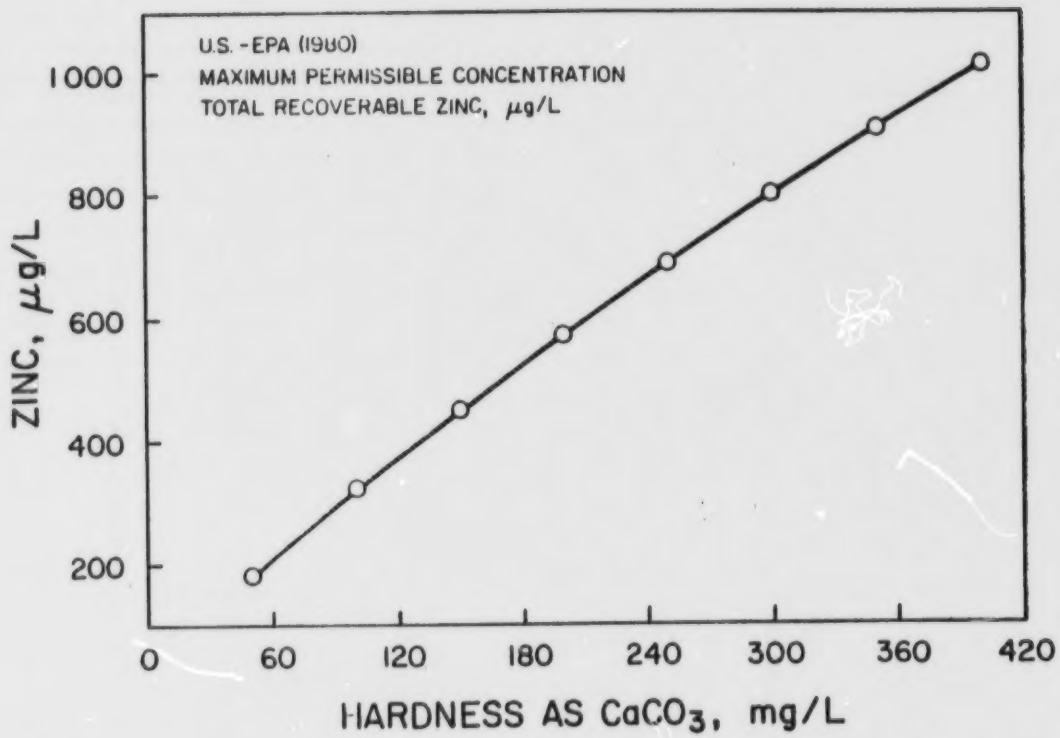
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9. ** British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries. (Receiving water objectives not available)
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.


U.S. -EPA (1980)
MAXIMUM PERMISSIBLE CONCENTRATION
TOTAL RECOVERABLE ZINC, μg/L
ZINC, μg/L
1000
800
600
400
200
0
60
120
180
240
300
360
420
HARDNESS AS CaCO3, mg/L

Zn (ug/L) ZINC

Summary of North American Water Quality Criteria for Zinc

WATER USAGE	EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE				[Zn] / Hardness (mg/L): 50 / 0-120; 100 / 120-180; 200 / 180-300; 300 / >300						
OBJECTIVE	0.005 X the 96-hr LC50	0.01 X the 96-hr LC50	24-hr mean 47		<30	10-50	<50	200-1,000	--	0.01 X the 96-hr LC50
MAX. PERMISSIBLE LIMIT	--	--	(0.83 (ln (hard))+1.95		30	30-1000	50	--	50	--
PROTECTION OF MARINE LIFE										
OBJECTIVE	<20.0 0.01 X the 96-hr LC50	--	24-hr mean 58.0	<100*	--	--	--	200-1,000	--	--
MAX. PERMISSIBLE LIMIT	100.0	--	170.0	--	--	--	--	--	--	--
PUBLIC WATER SUPPLY	5,000	5,000	5,000	5,000	5,000	1000-5000	(50)	--	5,000	5,000
AGRICULTURAL WATER SUPPLY — LIVESTOCK WATERING	200		--	50,000	25,000	--	(50)	--	--	25,000
AGRICULTURAL WATER SUPPLY — IRRIGATION	2,000-10,000		--		25,000	--	(50)	--	--	2,000

Compiled by NORANDA

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.

2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.

3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Zinc, EPA 440/5-80-079.

4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).

5. Environment Canada. 1980. Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances, Zinc.

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11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

ENVIRONMENTAL SENSITIVITY TO Cu, Pb, AND Zn

Copper

It would appear that the 2.0 ug/l Canadian objective for fresh water copper levels is very strict, as may be the U.S. EPA 24-hour limit objective of 12-43 ug/l copper for fresh water and 4 ug/l for marinewater.

The objectives appear to be based on laboratory bioassay tests in which Cu^{2+} ions were added to laboratory water rather than real life waters which contain complexing agents such as carbonate, phosphate, amino acids, humic acid, lignins, and suspended organic and inorganic materials according to STIFF (1971).

Critics have commented on the need to distinguish between total and ionic copper in setting environmental objectives.

The ONTARIO MOE (1979) recognizes the various ways in which copper is present in water and recognizes that methods of distinguishing between toxic and non-toxic copper have not been applied in laboratory studies which are based on total copper introduced as cupric ions.

In public water supplies, copper presents an aesthetic rather than toxicity problem. The U.S. drinking water standard is set at 1,000 ug/l to control taste (U.S. PHS, 1962).

Concentrations of copper that are toxic to organisms vary considerably with hardness and alkalinity of water because concentrations used during short-term LC 50 tests are close to the limits of solubility.

Freshwater algae are sensitive to copper. Generally, 200-800 ug/l inhibit algal life functions according to WONG (1975).

NIELSON, et al. (1969) showed that photosynthesis of Chlorella pyrenoidosa was reduced 60 percent by only 20 ug/l copper, and that toxicity of copper varied with exposure time, light intensity, initial cell concentration, and composition of the medium. Copper and nickel synergistic effects on algae have been noted as well as heavy metal tolerance by STOKES and HUTCHINSON (1975).

Numerous aquatic species were adversely affected at copper levels between 4-15 ug/l. Reproduction of Daphnia magna were reduced 16 percent at 22 ug/l and 50% at 35 ug/l after three weeks in Lake Superior at 45 ug/l hardness.

Atlantic salmon (Salmo salar) avoided 2.4 ug/l copper in the laboratory and, in a famous experiment in a New Brunswick river, a spawning run of adult salmon was reversed when copper and zinc levels were 19 an 240 ug/l according to SPRAGUE, et al. (1965).

The ONTARIO MOE (1979) shows numerous references to evidence of damage to trout, bluegills, and minnows at copper levels of around 10-20 ug/l.

Testwork suggests no food chain bioaccumulation in the muscle of fish and shellfish.

EATON (1973) found that low levels of Cd and Zn, if present with 5-7 ug/l copper, will have an adverse effect on fathead minnow reproduction.

It is recognized that very much more needs to be learned about copper toxicity in its various modes of occurrence, but it is also clear that copper even at very low levels has a detrimental effect on aquatic life.

Lead

Lead toxicity is highly dependent on the alkalinity of water. Toxicity decreases with increasing alkalinity. Lead forms insoluble compounds in water including carbonate, hydroxide, phosphate, chloride, and sulfates which precipitate it from solution. The percentage of lead that is precipitated when a solution is added to Lake Ontario water was found to be:

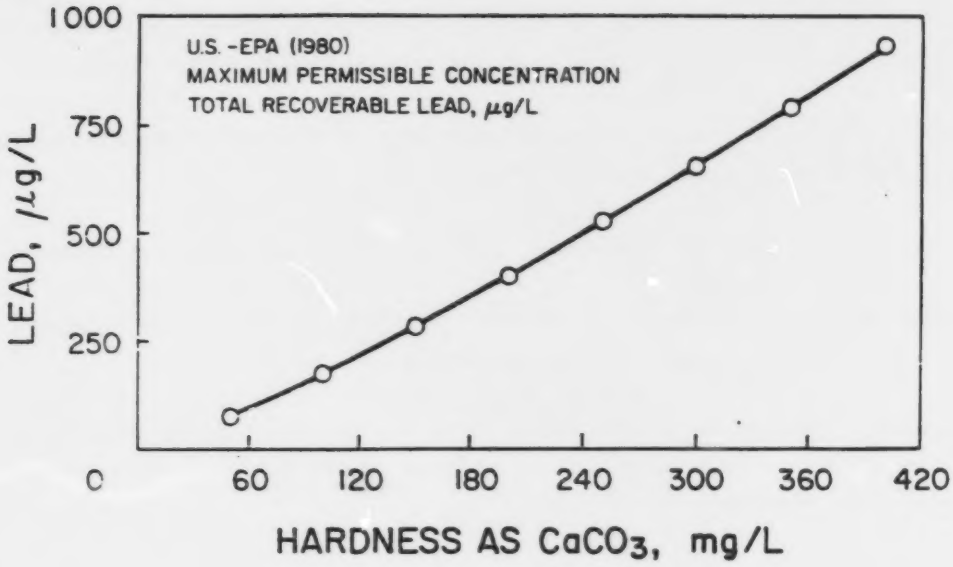
Concentration Added	Degree Precipitated
100 mg/l Pb	98% Plus in 24 Hours
10 mg/l Pb	70% Plus in 24 Hours
1 mg/l Pb	10% in 24 Hours

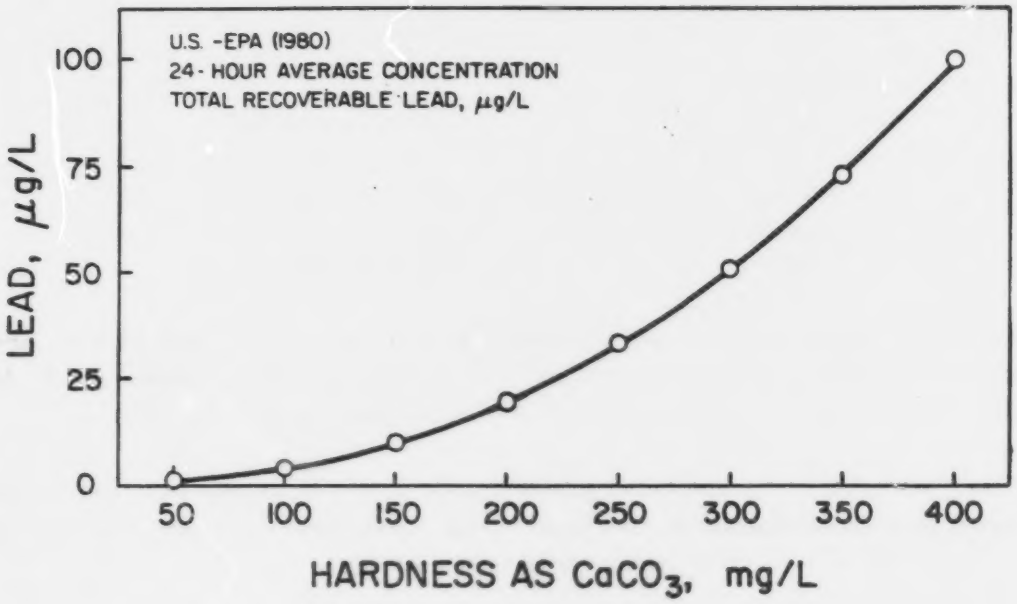
For example, a hardness of 24.0 mg/l, alkalinity of 22.8 mg/l $CaCO_3$, and pH 6.91, about 100 percent of lead present below 100 mg/l is in dissolved form. Above pH 8, lead solubility is less than 10 ug/l regardless of alkalinity (HEM and DURUM, 1973).

Total lead concentration in unpolluted inland Ontario waters is usually less than 10 ug/l, and modal lead concentrations in the upper Great Lakes waters are less than 1.0 ug/l offshore with 95% of all samples containing less than 3.0 ug/l.

Lead is not essential for plant and animal growth and is quite toxic. BOWEN (1966) rated lead as very toxic to plants, even below 1 mg/l in nutrient solutions.

LEAD


U.S. -EPA (1980)
MAXIMUM PERMISSIBLE CONCENTRATION
TOTAL RECOVERABLE LEAD, µg/L
LEAD, µg/L
1000
750
500
250
0
60
120
180
240
300
360
420
HARDNESS AS CaCO3, mg/L


U.S. -EPA (1980)
24- HOUR AVERAGE CONCENTRATION
TOTAL RECOVERABLE LEAD, µg/L
LEAD, µg/L
100
75
50
25
0
50
100
150
200
250
300
350
400
HARDNESS AS CaCO3, mg/L

Just 5-6 shot pellets ingested orally are lethal to a mallard and 12-25 to a Canada goose (NRCC, 1973), and toxicity varies with diet.

Lead is extremely toxic to humans and animals, and the recommended maximum level for lead in livestock watering is 100 ug/l (NAS/NAE, 1973).

Because of a variation in hardness and alkalinity, the Ontario MOE objective for lead is different for each lake, e.g.:

Lake	Hardness (mg/l)	Alkalinity (mg/l)	Safe-Unsafe (Pb ug/l)
Superior	44	41	15-25
Huron	94	75	21-38
Michigan	119	--	25-46
Erie	123	91	25-48
Ontario	135	90	26-52

It is recognized by the ONTARIO MOE (1979) that the effects of lead methylation in lake sediments may reduce the toxicity of lead, but this had yet to be demonstrated or proven.

Mining industry observers have commented that the Canadian objectives of 5-30 ug/l lead, depending on water hardness, are reasonable based on the documentation available, but the U.S.A. EPA level of 0.75 ug at 50 mg/l hardness - 20 ug/l at 200 mg/l hardness do not seem to be substantiable.

Water hardness and alkalinity affect the toxicity of lead, and pH greatly affects both the solubility and the toxicity of lead.

Zinc

Zinc is an essential element for both plants and animals. Zinc is necessary for reproduction, growth, the formation of DNA and RNA, promotes wound healing, and has several other important roles in human and animal health.

Zinc toxicity to land plants is very rare. Zinc is non-toxic to man, even up to 40,000 ug/l Zn in water. The U.S. drinking water recommendation is based on taste at 5000 ug/l (NAS/NAE, 1973).

Concentrations of zinc inhibiting freshwater algae growth range generally between 1,000-10,000 ug/l according to WONG (1975); however, some algae species are much more sensitive and are affected at around 200 ug Zn/l.

Aquatic invertebrates are more sensitive to zinc than algae. Daphnia magna are affected in increasing degrees between 70 and 158 ug/l according to BIESINGER and CHRISTIANSEN (1972).

Fish are more sensitive to zinc than other aquatic organisms. Cases of complete mortality at 267 ug/l zinc and 0-29% mortality at 75 ug/l Zinc have been observed.

There is evidence that if the eggs if rainbow trout are pre-exposed to zinc, then safe-unsafe concentrations were 135-251 ug/l zinc according to GOETTL, et al. (1973).

It is believed that hatcheries in Colorado producing trout fry to stock Rocky Mountain streams in areas affected by acid mineral drainage pre-expose the trout eggs to metals in order to acclimatize the fish.

Avoidance of zinc may also prevent the reproduction of Atlantic Salmon. In the laboratory, juvenile salmon avoided 54 ug/l zinc while in the field, migration of adults was prevented by 240 ug/l Zn (SPRAGUE, et al., 1965) when there was also 19 ug/l copper present in the field test.

Zinc toxicity appears to vary with concentrations of other metals such as Cu and Cd. Concentrations of zinc causing sublethal harm to aquatic biota do not appear to vary significantly with hardness or alkalinity according to the ONTARIO MOE (1979), but the EPA found a definite link between zinc toxicity and hardness.

Bioaccumulation effects of zinc in fish muscle appears minimal although zinc in the muscle of seven species of fish which, in Lake Huron contained 4.69 ug/g Zn, contained 36.01 ug/g zinc in Toronto Harbor. The maximum accumulation of zinc in fish is in the gills and kidneys. In fish killed by zinc uptake, the ratio of zinc in gills to zinc in bones was dramatically increased.

Very low zinc level criteria levels of 30 ug/l in Ontario Lakes were established because of the great sensitivity of fish to low levels of zinc in water. Receiving stream guidelines of 30-570 ug/l Zn as maximum permissable concentrations have been selected by different regulatory agencies in North America. Observers feel that acclimatization has not been property taken into account.

REGULATIONS AND PERMITS - Cu, Pb, AND Zn

Levels of Cu, Pb, and Zn stipulated as maxima in permits for mines and mills encountered during this investigation are summarized below.

It is clear that there is a wide variation from one operation to the next and that most permits are considerably more lenient than the objectives set by regulatory bodies for these three metals. One reason for this is that the objectives are for the receiving waters, and the permit is written for the effluent being discharged.

It is important to note that most of the U.S.A. has to meet zero discharge for mills and tailings although minewater may be discharged subject to permits such as those shown below.

REGULATIONS AND PERMITS

		COPPER-LEAD-ZINC		
		Cu	Pb	Zn
U.S.A.				
CLIMAX MOLYBDENUM MINE	24 Hour Max.	0.10	---	0.20 ppm
1981 Permit, Colo. Dept. of Heath	30 Day Ave.	0.05	---	0.10 ppm
COTTER CORPORATION Schwarzwalder Mine Golden, Colorado Colorado Dept. of Health NPDES		0.005	0.032	0.05 ppm
HOMESTAKE MINING COMPANY Lead, South Dakota NPDES	Daily Max.	0.009	0.28	0.02 ppm
HOMESTAKE MINING COMPANY	Daily Max.	0.30	0.10	1.5 ppm
McLaughlin Gold Project California NPDES Permit	30 Day Ave.	0.15	0.05	0.75 ppm
Mount Emmons, Colorado NPDES	Daily Max.	0.04	0.15	0.60 ppm
New Mexico Water Quality Control Commission, August 27, 1971		0.05	0.05	0.10 ppm
NORANDA GREY EAGLE Northern California RWQCB Order 84-108		0.20	-	0.01 ppm
RCRA 1980 40 CFR 440	Max. Grab	0.10	0.40	1.00 ppm
Subpart B for Copper Mining Effluents - Temporarily Suspended by Beville Ammendment	30 Day Ave.	0.05	0.20	0.50 ppm
ST. JOE MINERALS	Daily Max.	-	-	187 lb/d
Zinc Smelter Monaca, Pennsylvania (1984 Permit)	Daily Ave.	-	-	62.5 lb/d

REGULATIONS AND PERMITS (Continued)

		Cu	Pb	Zn
U.S.A. (Continued)				
Typical Arizona Copper Concentration Permit, Late 1970's	24 Hour Max.	1.0	-	2.0 ppm
	30 Day Ave.	0.50	-	1.0 ppm
Brazil				
State of Rio de Janeiro		0.5	0.5	1.0
State of Sao Paulo		1.0	0.5	5.0
State of Minas Gerais		0.5	0.1	1.0
Canada				
BRUNSWICK MININC NB Cu, Pb, Zn	30 Day Ave.	0.30	0.20	0.50
COMINCO LTD. Con Mine Gold Northwest Territories	Max. Grab	0.60	0.40	1.00
	30 Day Ave.	0.30	0.20	0.50
DENISON MINES LTD. Uranium Ontario - Elliott Lake		0.60*	0.40*	1.0*
FALCONBRIDGE Onaping Operations		1.0	1.0	-
GIANT YELLOWKNIFE MINES Northwest Teritories	Max. Grab	1.60	0.40	1.00
	30 Day Ave.	0.80	0.20	0.40
KEY LAKE URANIUM Saskatchewan	Max. Grab	0.60	0.40	1.0
	30 Day Ave.	0.30	0.20	0.5

* 1.00 mg/l Max Total for Cu, Pb, and Zn.

REGULATIONS AND PERMITS (Continued)

		COPPER-LEAD-ZINC		
		Cu	Pb	Zn
Canada (Continued)				
WEDGE MINE	Max. Grab	0.45	0.30	0.75
New Brunswick	30 Day Ave.	0.30	0.20	0.5
Cu, Pb, Zn				
WESTERN MINES LTD. BC	Max.	0.30	0.10	0.50
Cu, Pb, Zn				
1975 Permit				
South Africa				
Government Gazette, 5 April 1962				
General Standard	Max. Grab	1.00	1.00	5.00 ppm
Special Standard	Max. Grab	0.02	0.10	0.30 ppm
Sweden				
Guideline Only (No Fixed Limits)				
Example of One Case	Max. 1 mg/l Combined Cu, Pb, Zn, Cd, As, Hg			
Public Water Supply				
South Africa Drinking Water				
SABS 241-1971				
	Recommended Max.	1.00	0.05	5.00 ppm
	Maximum Allowable	1.50	0.10	15.00 ppm
U.S.A. Public Water Supply		1.00	0.05	5.00 ppm
Canadian Public Water Supply		0.50	0.05	5.00 ppm

METALLURGICAL INTERFERENCES OF COPPER, LEAD, AND ZINC

Copper

Copper has been found to interfere in metallurgical operations in several ways. The most common is in the recovery of gold and/or silver by cyanidation of ores, concentrates, or calcines containing cyanide soluble copper.

For each mole of cyanide soluble copper in the gold-bearing feed, at least five moles of sodium cyanide must be added to be able to leach gold effectively. Some gold ores are so rich in cyanide soluble copper that 10-12 Kg NaCN/t is required to recover this gold by cyanidation, while an equivalent amount of copper cyanide complex is dissolved. Several gold ores have been rendered uneconomic in this way. Two highly innovative new process technologies are now offering promising solutions to the problem. First is a cost effective way to recover cyanide from copper cyanide in solutions or pulps. The other is an oil agglomeration physical recovery process for very fine gold particles from high copper ores.

Even ores with low levels of copper result in relatively high concentrations of copper in cyanide solution in the pulp when barrens are recycled. Ultimately, a level is reached at which the base metal sulfides interfere with zinc precipitation of gold. When this occurs, copper and other base metals are bled from the system in a so called barren bleed. Since the barren bleed contains high levels of copper and other base metals as well as cyanide, this barren bleed represents an effluent disposal problem. Numerous gold mills around the world dispose of barren bleed solutions in one way or another.

Another interesting effect of soluble copper on metallurgical circuits is in complex sulfide flotation circuits. A typical arrangement is to float a Cu-Pb sulfide concentrate in a semi-bulk float while depressing sphalerite in this primary recovery step.

Copper sulfate is commonly used as an activator for sphalerite in the subsequent flotation of zinc.

If copper gets into solution in the recycled process water or for any other cause, then there is a good possibility that the selectivity of flotation will be seriously impaired. Problems of this sort are described in the trip report on BLACK MOUNTAIN MINING AND DEVELOPMENT CO. in Appendix I. In this case, extensive recycle of water resulted in a buildup of copper ions in process water.

McTAVISH (1985) described a similar situation where it was virtually impossible to recover cleanly separated concentrates from a copper-lead-zinc ore. These metallurgical problems occurred at NORANDA's Goldstream project in British Columbia despite extensive pilot testwork which gave no reason to anticipate them. Finally, it was found that a thin layer

of the open pit ore near the surface contained enough water soluble-copper to introduce enough soluble copper with mill feed to do severe damage. Since open pit ore was mined in "slices," there was a continual source of the trouble-causing oxidized layer which was blended with underground ore and deeper open pit ore. Soluble copper levels of 5-10 ppm were measured in the process solution. In this case, the problem was solved by isolating the water soluble oxide copper ore which represented but a tiny fraction of total feed and ultimately, design tonnages, recovery, and grade were achieved for all three concentrates before Goldstream shut down due to metal market conditions.

More information can be obtained about this most interesting problem and the simple answer that was found from:

NORANDA MINES LTD.
Goldstream Mine Site
Post Office Box 2970
Revelstoke, B.C. V2C 250
(604) 837-9312
S. McTavish

Although the root of the problem at Black Mountain and at Goldstream is probably quite different, in both cases soluble copper had a similar effect on the metallurgy of not too dissimilar copper-lead-zinc ore treatment.

Lead and Zinc

No serious metallurgical problems were encountered as a result of zinc and/or lead in solution. If zinc levels get too high in gold cyanidation circuits, then this contributes to a foul liquor and necessitates a barren bleed. Lead in high pH values will invariably precipitate as a carbonate or sulfate before it becomes a nuisance metallurgically.

Lead nitrate or lead acetate is often added in gold milling circuits that contain soluble sulfides as a means of controlling cyanide consumption and improving recovery.

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TREATMENT FOR COPPER, LEAD, AND ZINC

Each of these metals can be removed from solution using the same basic processes, e.g., precipitation by hydroxide or sulfide, and ion exchange. The response to each process is somewhat different for each of the metals, however. There are several frontier processes which have the potential for development into useful and economical processes.

During the course of this investigation, which focuses on the mining and mineral processing industry, the most commonly employed process encountered at this time is lime precipitation and settling although ion exchange is in use to recover an economical copper resource from an effluent at El Teniente, Chile. Sulfide precipitation on a commercial scale is employed at BOLIDEN MINERAL AB's Skellefteham smelter operation. Attempts to recover zinc economicaly by ion exchange have been a technical success but an economic failure. Of the three metals, lead appears usually to be the least troublesome in mining and metallurgical solutions, probably because of the frequent presence of sulfate, carbonate, and chloride ions in the mine-mill environment which precipitate lead.

Although, in many cases, copper, lead, and zinc levels in mine-mill effluents (after lime precipitation) comply with effluent discharge permits currently in force, there is clearly still pressure on and by regulators to lower the permissible dischargable effluent limits. In some cases, even existing limits are met only with difficulty. Improved technology is needed to further improve performance of effluent treatment to meet the more demanding permits such as the Colorado Dept. of Health's permit for the COTTER CORPORATION's Schwarzwalder minewater which required 0.005 ppm Cu, 0.032 ppm Pb, and 0.05 ppm Zn. This also requires improved understanding of the practical limitations and process improvement possibilities that can be considered. Although the BEVILLE Amendment has temporarily suspended the applicability of the Federal RCRA rules on hazardous waste disposal to mine-mill wastes, several states are enacting their own solid waste disposal regulations which are as or more strict. There is still a significant gap between national objectives for fresh receiving waters and the levels that can be achieved in treated effluents. Litigation is also in progress in which the mineral processing industry is calling for a more lenient regulatory stance.

Performance of plants treating effluents for copper, lead, and zinc removal that were encountered in this investigation are summarized in the following table.

SUMMARY OF WATER TREATMENT PLANTS (mg/l)

Operation	Type	Effluent Treatment	Inflow	Outflow
AMAX Mt. Emmons	Zn Reclaimed Mine	LF	Cu 3-5 Pb 1.0 Zn 10-100	0.01 0.05-0.3 0.05
Boliden Metall	Pb Smelter	L, Su, S	Cu 3 ppm Pb 35 ppm Zn 34 ppm As 156 ppm	LT 0.01 ppm 0.05 LT 0.1 4 ppm
Canadian Lead Smelter B.	Pb Smelter	LS	Cu 1.0 Pb 6.0 Zn 7.0 Cd 3.0 As 4.0	Cu 0.02 Pb 0.15 Zn 1.50 Cd 0.60 As 10-15
Cotter Corp. Schwarzwalder	Minewater Uranium	S, IX	Cd 0.002 Cu 0.02 Pb - Zn -	0.0004 0.005 0.005 0.05
Denison Elliott Lake	U_3O_8 Mine Drainage	LS	pH 2.7 Cu 1.28 Pb 5.05 Zn 4.50	pH 8.2 Cu 0.02 Pb 0.10 Zn 0.02
Giant Yellowknife	Gold	CLS	Cu 6.87 As 12.1 Zn 0.1 CN 8.6	Cu 0-08 As 0.14 Zn 0.05 CN 0.20
Gilman 1982 Colorado	Mine Drainage Pb, Zn, Ag	LS	Cu 1.5-4.0 Pb - Zn 130-300 Mn 80-453	Cu 0.01 Pb 0.003 Zn LT 1.0 Mn 1-12 ppm

SUMMARY OF WATER TREATMENT PLANTS (mg/l) (Continued)

Operation	Type	Effluent Treatment	Inflow	Outflow
Homestake Lead, SD	Gold Mine/Tails	BiO	Cu 0.1-1.50 Zn 0.1-0.50 NH_3 1.0-6.50 CN_T 2.0	0.05 0.50 0.02
Jabiluka Uranium	U_3O_8 Tailings/ Raffinate	LS	Cu 15-100 Pb Zn	Cu 0.30 mg/l
Kidd Creek Concentrator	Tails Decant		pH 2.7 Cu LT 0.10 Pb LT 0.10 Zn LT 0.30	pH 6.0 Cu LT 0.10 Pb LT 0.10 Zn 0.10
Kidd Creek Mine	Surface Drainage		pH 7.3 Zn 4.8	pH 10.3 0.10
Noranda Mattabi	Cu, Pb, Zn Tailings Return	LS	pH 6.8 Cu 0.01 Zn 5.92	pH 10.2 Cu 0.01 Zn 0.76
Ontario Cu,Pb,Zn Mill-Mine G.	Cu, Zn, Pb Tails Seepage	LS (HDS)	Cu 1.44 Zn 49.50 Fe 294.00 pH 3.7	0.17 0.06 0.35 8.6
St. Joe Minerals Monaca, PA	Zinc Smelter Effluent	LSF	Cd 2.4 Pb 2.6 Zn 14.5	Cd 1.02 Pb 0.45 Zn 0.55
Vaal Reefs South Africa	LS		Variable Mix	Cu LT 1.0 Pb LT 1.0 Zn LT 1.0
Waite Amulet Quebec	Reclaimed Mine-Millsite	LS (HDS)	pH 2.8 Cu 3.4 Pb 0.05 Zn 20.72	9.8 0.02 0.05 0.02

SUMMARY OF WATER TREATMENT PLANTS (mg/l) (Continued)

Operation	Type	Effluent Treatment	Inflow	Outflow
Wedge Mine 1975 New Brunswick	Cu, Pb, Zn	LS	pH 4.2	pH 9.4
			Cu 55	0.025
			Zn 580	1.6
Wedge Mine 1985	Reclaimed	Nil	No Drainage	

CRITERIA FOR WATER TREATMENT SELECTION

Technology is one way to approach the water treatment problem to remove or recover unwanted copper, lead, zinc, and other contaminants. In all cases, the selection of such technology must be on the basis of the following criteria:

- It must be appropriate for the scale of operation contemplated.
- The technology must be appropriate for the concentrations of metals in the feedwater that is to be treated and must be capable of meeting the effluent requirement that must be met.
- The technology must be compatible with other contaminant removal processes that may have to be integrated into the system.
- The technology should not add other unwanted contaminants which do not meet effluent discharge limits or which would cause metallurgical interference if the product water is recycled to the mine or mill.
- Optimum performance must take into account not only solubility aspects, but also precipitate removal efficiency and disposal thereof.
- The process must be affordable and safe to operate.

The second approach to solving effluent treatment problems and reducing costs is through prevention. This means reducing the volume of effluent generated in the first place either through reducing drainage into the site, segregation of water on the site and cascaded use, etc., or reducing the opportunities for contaminants to get into the water in the first place and, finally, making more provision for water recycling. Some extremely innovative, yet simple, ideas have been encountered in this respect.

The following is a list of phenomena of interest and potentially useful observations on a variety of technologies that have been applied for treatment of effluents and/or process waters containing copper, lead, and zinc. Several phenomena have an important impact on technology selection and implementation from a practical chemistry point of view:

1. Hydroxide precipitation can be achieved by lime addition or through use of more expensive sodium hydroxide or soda ash. For precipitation to be effective, complexing agents must first be removed. Different complexing agents have different effects on each metal's solubility.

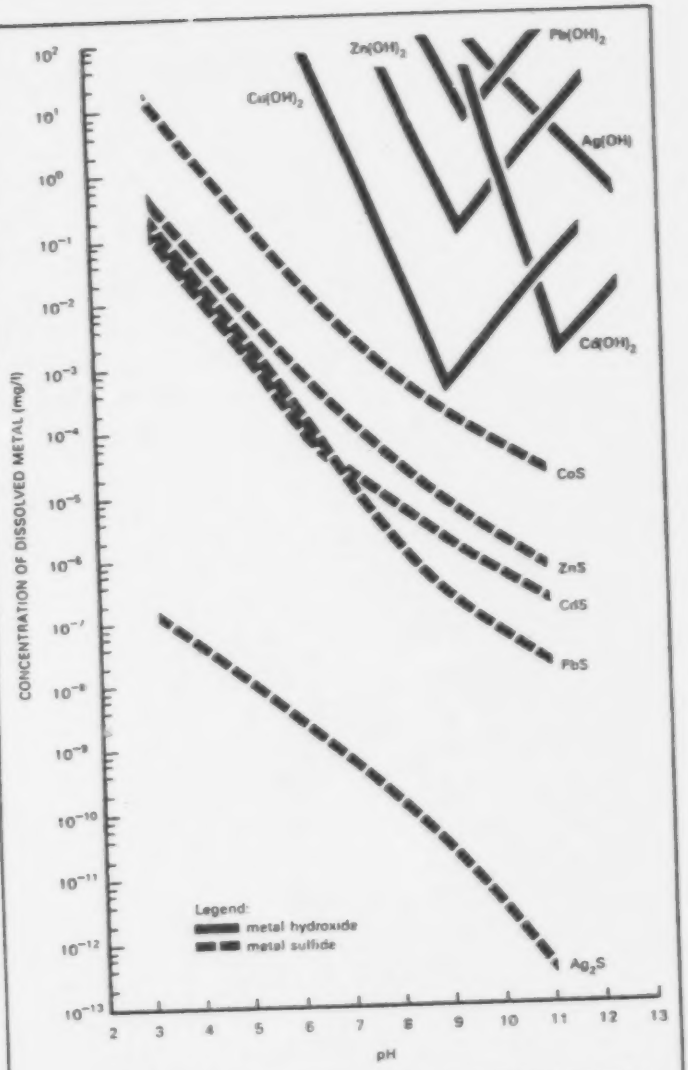
2. Next, each metal has an optimum pH at which its solubility is a minimum and, above which, the solubility of the hydroxide increases. For example, above pH 10.5, zinc

solubility increases due to formation of $[Zn(OH)_3]^-$. Since more than one of these metals are usually removed together, the optimum pH for removal of one of them may not be the optimum for the other metals that must be removed.

3. Co-precipitaion effects, particularly with iron, e.g., by $Fe_2(SO_4)_3$ or $FeSO_4$ addition often enhances removal of these metals when precipitation by OH^- addition is used.

4. After precipitation, the removal of metal values from solution to meet regulatory limits may not be possible by straightforward settling (decanting) due to difficult-to-settle precipitates. In such cases, more sophisticated clarification methods may be called for--possibly in conjunction with more sophisticated precipitation techniques, some of which are already in use in the mining industry.

5. Sulfides of copper, lead, and zinc are less soluble than hydroxides over a broader pH range even extending in the acid region.



Note.—Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modern Alkaline Cooling Water Treatment," in *Industrial Water Engineering* (p. 31), Jan.-Feb. 1973.

6. When employing hydroxide precipitation, complexing agents may compete to keep metals in solution. These are usually not strong enough to compete with sulfide precipitation, however. Complexing agents are not the same for each of the three metals. For example, the following table shows complexing cations which are known to interfere with hydroxide precipitation:

Metal	Complexing Agent
Copper	Cyanide CN^-, Ammonia NH_3, Humic Acids.
Lead	Humic Acid, Ammonia.
Zinc	Chromate $CrO_4^=$, Dichromate $Cr_2O_7^=$, Cyanide CN^-, Hydroxide above pH 10.5, Humic Acid.

7. Disadvantages of lime precipitation have been cited as:

- High lime costs.
- The need for pH adjustment.
- High volume of precipitate sludge produced especially if $SO_4^=$ ions are present.
- Low value of metals in the sludge rendering it less attractive for metal recovery and more expensive to dispose of.

8. At Jabiluka Uranium, Northern Territory, Australia, LEVINS (1979) reported levels of 15-100 ppm Cu in decanted effluent including raffinate from acidic uranium leaching operations in the Alligator Rivers Region of Northern Territories. After adjustment to pH 8 with lime, copper was precipitated to 0.3 mg/l. The acid solution contained 2-5,000 mg/l Fe which, no doubt, aided in the Cu removal by co-precipitation effects.

9. A summary of treatment processes for effluents from mainly metal finishing operations as presented by PATTERSON (1975) is presented below showing that even for these small-scale water treatment operations, levels below 0.3-0.5 ppm Cu are seldom achieved except by special processes.

Summary of Effluent Copper Concentrations after Precipitation Treatment.

Source and Treatment	Initial Copper conc. (mg/l)	Final Copper conc. (mg/l)	Reference
Metal Processing (Lime)	204-385	0.5	29
Nonferrous Metal Processing (Lime)	—	0.2-2.3 (prior to sand filtration)	30,31
Metal Processing (Lime)	—	1.6-7.8 (prior to sand filtration) 0.0-0.5 (after sand filtration)	32
Electroplating (caustic, Soda Ash + Hydrazine)	6.0-15.5	0.09-0.25 (sol.) 0.30-0.45 (tot.)	33
Machine Plating (Lime + coagulant)	—	2.2	34
Metal Finishing (Lime)	—	0-1.2 (ave. 0.19)	35
Brass Mill (Lime)	10-20	1-2	17
Plating	—	0.02-0.2	36
Plating (CN oxidation, Cr reduction, neutralization)	11.4	2.0	37
Wood Preserving (Lime)	0.25-1.1 (range)	0.1-0.35	38
Brass Mill (Hydrazine + NaOH)	75-124	0.25-0.85	16
Silver Plating (CN oxidation, Lime, FeCl,	30 (ave.)	0.16-0.3 (with sand filtration)	13

SOURCE: PATTERSON (1975)

29	NYQUIST and CARROLL (1959)	17	TALLMANGE (1965)
30, 31	STONE (1967), STONE (1972)	36	METAL FINISHING J. (1971)
32	OGAWA, et al. (1972)	37	CHALMERS (1965)
33	MARTIN (1973)	38	TEER and RUSSELL (1972)
34	HANSEN and ZABBAN (1959)	16	VOLCO (1971)
35	WATSON (1954)	13	NEMEROW (1973)

10. Copper as cupric oxide forms from the hydroxide which has a minimum solubility between pH 9.0-10.3 of 0.01 mg/l Cu. Fred Stevens of Lancy International, Zelienople, Pennsylvania, pointed out that at 43°C', copper precipitates as CuO rather than $Cu(OH)_2$. Copper oxide is much less soluble than $Cu(OH)_2$.

11. Copper as cupric can seldom be removed by hydroxide (lime) additions to its theoretical solubility because of poor separation of colloidal precipitates, slow reaction ratio, pH fluctuations, and the interference of other ions in solution. PATTERSON (1975) compared results of several metal finishing effluent treatment plants and found that hydroxide precipitation yielded effluents of 0.1-7.8 ppm Cu without filtration and 0.16-0.5 ppm with filtration.

12. Cuprous oxide forms a very dense easy-to-settle and easy-to-handle sludge of 40-60% solids according to the VOLCO BRASS CO. (1971), CROWLE (1971), and JACKSON (1972).

Treatment of cupric wastewater with hydrazine or some other reducing agent plus sodium hydroxide reduces copper to cuprous form and is recommended by several

authors for the treatment of metal finishing effluents, VOLCO (1971), CROWLE (1971), JACKSON (1972), and CURRY (1972). Surely the same would be achieved more easily with SO_2?

According to VOLCO (1971), such a system can be operated at pH 7-8, and a full-scale system has been reported in operation using the "integrated treatment" method in which copper was removed from a brass mill effluent by hydrazine and NaOH addition from 75-124 mg/l to 0.25-0.85 ppm.

In a second metal finishing application described by MARTIN (1973), the addition of caustic and soda ash to pH 9.5-10.5 with 300-700 mg/l hydrazine resulted in copper reduction from 6-16 ppm to 0.09-0.25 ppm soluble copper and 0.30-0.45 ppm total copper.

13. MURUYAMA, et al. (1972) studied copper removal from municipal wastewater enriched to 5.0 mg/l copper. Various combinations of lime and ferrous sulfate addition were examined for treatment effectiveness in a 4 gpm pilot plant. After chemical addition, flocculation, and settling, the effluent was sand filtered and passed through activated carbon columns. Compositions of the treated effluent are summarized in the following table as presented by PATTERSON (1975). It is noteworthy that the best removal of copper occurred at pH 6.0 with the addition of ferrous sulfate only rather than at higher pH with lime neutralization. Could the ferrous iron possibly be reducing cupric to cuprous resulting in improved removal of copper as cuprous oxide?

Treatment of Copper Wastewater

Process	Chemical Addition	pH	Effluent Copper (mg/l) (carbon column
Iron Only	43 mg/l $FeSO_4$	6.0	0.155
Low Lime	260 mg/l $Ca(OH)_2$, 20 mg/l $FeSO_4$	10.0	0.170
High Lime	800 mg/l $Ca(OH)_2$	11.5	0.352

14. BOLIDEN has observed unexpectedly low Cu/thiosulfate ratios in their tailing pond effluents, and it was speculated that copper may be reduced by thiosulfate from cupric to copper metal thereby removing it from solution. The above evidence of precipitaion of very insoluble cuprous oxide now offers an alternative.

15. In the treatment of gold mill effluents, e.g., barren bleed or tailings pond decant solution which contains copper that is complexed by cyanide, several methods of cyanide detoxification have been developed which also remove copper as a precipitate, e.g.:

Alkaline Chlorination	Giant Yellowknife	See Appendix I
INCO SO_2-Air	Scottie Gold Mine	DEVUYST, et al. (1984)
$FeSO_4 + Na_2S$	Cominco Con Mine	Appendix I
Bacterial	Homestake Mining Co., Lead, SD	Appendix I, MUDDER and WHITLOCK (1984)

16. Since copper is toxic to algae and some bacteria, caution should be used when considering the use of biological processes for copper removal, e.g., algae in meander systems for polishing or where bacterial removal of cyanide and copper is contemplated in the presence of high levels of copper. Nevertheless, low levels of copper, in the order of 0.15-1.5 ppm appear to be successfully reduced to ppb levels in the HOMESTAKE biological process for cyanide removal using rotating biological contactors. See the trip report on HOMESTAKE MINING COMPANY, Lead, South Dakota, in Appendix I.

17. Most of the objections to lime precipitation can be overcome when using the high density sludge process which is described in Chapter 24 on acid mine drainage treatment. The Bethlehem Mines Panther Valley Operation, one of many where the BETHLEHEM STEEL CORP. employs the HDS process, and COMINCO's application of HDS at Kimberly and Brail, B.C., are described. Further descriptions are included in Appendix I trips reports on:

    NORANDA MINES, Waite-Amulet
    Cu-Pb-Zn Mine-Mill G
    KROMDRAAI Coal Operation, South Africa
    ERPM, RAND MINES LTD., South Africa

    The principle of HDS is to recycle thickener underflow sludge consisting of precipitated metal hydroxides which is first mixed with lime before being added to feedwater to the plant.

    Examples of base metal removal in the course of HDS treatment are:

		Influent	Treated Effluent
NORANDA, Waite-Amulet	Cu	5-15 mg/l	LT 0.02
	Pb	-	-
	Zn	40-85 mg/l	0.20
	Cd	0.05-0.20	LT 0.005

COPPER-LEAD-ZINC

			Influent	Treated Effluent
Mine-Mill M	Ontario	Cu	LT 0.01	LT 0.01
		Pb	0.06	0.02
		Zn	3.14	0.1-0.3
NORANDA, Les Mines Gallen, Quebec		Cu	0.26	0.039
		Pb	-	0.160
		Zn	530	0.45
COMINCO, Kimberly, BC		Cu	0.15	LT 0.05
		Pb	5.0	LT 0.01
		Zn	22	LT 0.20

Major advantage of the HDS process is that the sludge generated has a high solids content, up to 40-50% if desired. It is therefore compact and more easily disposed of. In addition, BETHLEHEM INTERNATIONAL ENGINEERING CORP. has developed a way of mixing the sludge with a pozzolon to yield a stable waste material that passes the EP toxicity test (U.S. EPA, 1978) and is suitable for disposal in sanitary landfill sites. Secondly, metals are precipitated to lower levels from solution by the HDS process to form a non-amphoteric precipitate. Precipitation to low levels, usually less than 0.01 mg/l Pb and Cu, occurs at lower pH values than the optimum pH for conventional lime precipitation.

More details on this very powerful metal precipitation process are obtainable from:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18016
(215) 694-2424
Telex: 847417
Jim Forand
Stewart T. Herman

COMINCO LTD.
200 Granville Street
Vancouver, B.C. V6C 2R2
(604) 682-0611
Walter Kuit

NORANDA MINES LTD.
Horne Division
BP 4000
Noranda, Quebec J9X 5B6
(814) 762-7764
Bernard Brooks

18. Cross Flow Filtration/Sludge Recycle

The section on acid mine drainage also describes results achieved when a sludge recycle arrangement was tested in conjunction with NaOH precipitation of metals from acid mine drainage from the Argo Tunnel together with the Wannamaker Continuous Concentrator which is a form of a crossflow filtration device. Results were as follows:

	AMD	pH Treated Effluent
pH	3.4	pH 8.3
Cu	14 mg/l	0.025 mg/l
Pb	0.13 mg/l	0.035 mg/l
Zn	63.0 mg/l	0.070 mg/l

More information on this test project is contained in HOLM and SIMPSON (1981) or may be requested from:

COLORADO DEPT. OF NATURAL RESOURCES
Mine Land Reclamation Division
1313 Sherman Street
Denver, CO 80203-2273
(303) 866-3567
J. David Holm

19. Jet Aeration Precipitation with NaOH

BARRETT, HAENTJENS & CO. is one of several companies working on the development of an innovative method for metals precipitation from acid solutions using a turbojet mixer which achieves lower levels of metal in the treated effluent than conventionally possible with very low capital investment. More information is provided above in Chapter 24 may be requested from:

BARRETT, HAENTJENS & CO.
225 North Cedar Street
Hazelton, PA 18201
(717) 455-7711
David Ackerman

20. SCHILLER and KHALAFALLA (1983) in U.S. Patent Application US 325269AO, March 18, 1983, describe the removal of heavy metals from water by an improved process employing dry powdered reactive MgO added dry directly to the effluent. The resulting precipitate, which contains Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, settles rapidly to a small volume from which purified water is easily decanted, thereby overcoming the major obstacle of removing precipitate particles from suspension in treated effluent water.

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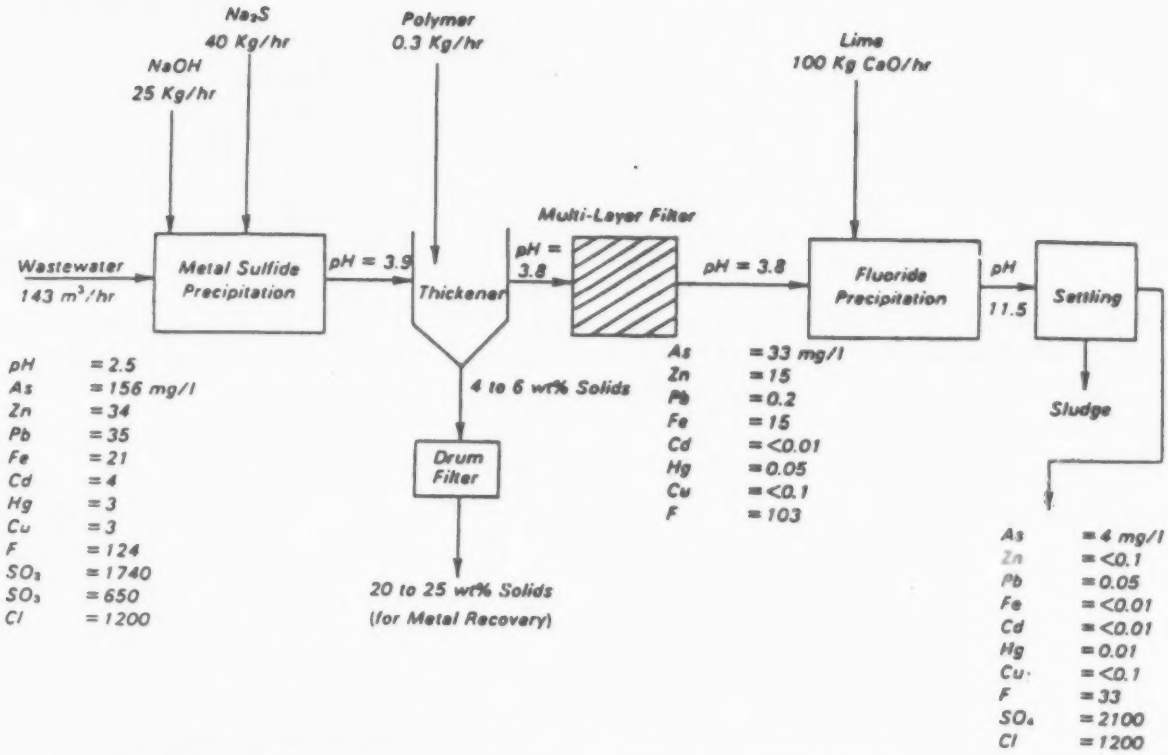


Typical residual metal concentrations obtained by full-scale test run (Boliden Metall).

Removal of Metals by Sulfide Precipitation and by Sulfide Precipitation Followed by Lime Precipitation (Full-Scale Process)

Component	% Removal: Sulfide Precipitation*	% Removal: Sulfide + Lime Precipitation**
As	67-87	96-99
Zn	51-75	99
Pb	97-99	97-99
Cd	99	99
Cu	>90	>90
Hg	99	99
Fe	2-26	>99
Fluoride	0	70-78

gold recovery effluent from 20 mg/l to below the detection limit by sulfide precipitation. They also found that similar results were attainable by co-precipitation with alum.

LARSEN, et al. (1973) used a two-step lime addition to pH 5 to precipitate iron and aluminum and then barium sulfide addition at pH 6.5 to precipitate heavy metals. Copper was reduced from initial levels of 50-115 mg/l to below 0.5 mg/l. LARSEN and ROSS (1976) described the same process, now called the DRI process, which was tested for treatment of acid mine drainage for the removal of Fe, Al, Cu, Pb, Zn, Hg, and Cd in Colorado. Attempts to locate the authors who were employed at the Denver Research Institute when the work was carried out were unsuccessful.

22. Sulfide precipitation processes are used to treat effluents from the large copper smelter and metallurgical works of BOLIDEN at Skellefteå, Sweden. BLYTHE, et al. (1981) described the operation and performance of the sulfide precipitation process at BOLIDEN which is complicated by the need to remove arsenic, which requires a two-stage process as arsenic sulfide is precipitated only at low pH. Results of the BOLIDEN installation are summarized in the following diagram from which it can be seen that:

- Copper is precipitated as a sulfide along with arsenic at pH 3.8. Lead is also precipitated but not as quantatively and, at the low pH, zinc is poorly removed.

- The addition of lime and settling drops zinc and lead to below 0.1 mg/l and 0.05 mg/l respectively.

It is clear that sulfide precipitation is very effective for base metal removal. Additional information is available from:

BOLIDEN METALL AB
Skellefteå, Sweden
Rolf Swedberg

D. BHATTACHARYYA
Chemical Engineering Dept.
University of Kentucky
Lexington, KY 40506-0046
(606) 257-2798

23. MIKHNEV, et al. (1978) described the use of a solution of sulfide in $Ca(OH)_2$ to precipitate heavy metals from metallurgical plant effluents. The Cu, Ni, and Fe were precipitated at pH 5.2, 7, and 7-9 respectively. The degree of removal depended little on temperature in the range 20-80°C. The treatment at final pH 7.5-8 decreased the metal values in solution as follows:

	Cu	Pb	Zn
			COPPER-LEAD-ZINC
Before Treatment (mg/l)	70	80	10
After Lime-Sulfide (mg/l)	0.10	0.01	0.01

The precipitate contained Cu at 12%, Ni at 12%, and CaO at 20% as NiS, CuS, and $CaSO_4$ $2H_2O$, as well as S. Significally, the use of $Ca(OH)_2$-S solution in the place of $Ca(OH)_2$ increased the clarification rate by 50-100%.

24. It is rumored that the GENERAL ELECTRIC R & D GROUP has patented a process for metals precipitation which uses a combination of lime and sulfide.

Information has been requested from:

GE RESEARCH & DEVELOPMENT CENTER
Post Office Box 8
Schenectady, NY 12301
(518) 385-8247

A similar process employing calcium polysulfide precipitation and two stages of precipitation and filtration has been described by Italian workers COCHECI, et al. (1983).

25. The latest regulations for primary zinc refineries in the U.S.A. specify levels that will necessitate the use of Na_2S precipitation unless the AMC litigation against the EPA is successful in reversing the regulation. Most U.S. zinc smelters have looked into sulfide precipitation and have probably conducted some experiments which form the basis for their objections to the requirement that sulfide precipitation be used.

One of the major arguments may be that in generating a sulfide precipitate of base metals, a hazardous waste is generated that requires special disposal arrangements.

One of these companies with whom industry may be able to discuss the merits of sulfide precipitation is:

ST. JOE MINERALS CORPORATION
Post Office Box A
Monaca, Pa 15061
(412) 774-1020
Tom E. Janeck
Director-Corporate Environmental Programs
John M. Cigan
Senior Executive Met. Engineer
Charles A. Brockmiller
Consultant

26. According to BHATTACHARYYA (1985 personal communication), one of the problems of the low pH sulfide precipitation is excessive cost of Na_2S reagent when sulfite

$SO_3^=$ is present and the efficient removal of metal sulfides by settling and filtration. Especially, copper forms a very finely divided sulfide precipitate which is difficult to remove. Another problem mentioned is the less effective removal of metals that form weaker sulfides when chelating agents or complexing agents such as cyanide are present.

Additional discussion of sulfide precipitation for copper removal is included in the following references:

LANTZ (1979)
U.S. EPA (1980, April)
U.S. EPA (1980, June)
BHATTACHARYYA, et al. (1979)
BHATTACHARYYA, et al. (1978)
LARSEN, H.P. and ROSS, L.W. (1976)
SCHLAUCH and EPSTEIN (1979)
ROBINSON and SUM (1980)
YELIGAR, et al. (1981)
SCOTT, M.C. (1979)

One of the most innovative aspects of sulfide precipitation is the PERMUTIT COMPANY's patented SULFEX process which employs a sludge blanket type clarifier with a sludge blanket of freshly prepared FeS which offers several advantages in the sulfide precipitation of metals. SCOTT (1979) reports that the SULFEX process can reduce copper from solution to below 0.01 ppm and zinc to below 0.05 ppm. Although the sulfide precipitate generated using the SULFEX process is reported by SCOTT (1979) to pass the EPA (1978) leach test, questions remain as to the long-term stability of the precipitates in landfill conditions where they may be subject to bacterial attack.

Although there is no record of the SULFEX process having been used for mine-mill effluents, the process appears to have considerable merit. More information can be obtained from:

THE PERMUTIT COMPANY, INC.
Post Office Box 355
Paramus, NJ 07652
(201) 967-6000

27. A variation on the SULFEX process which, however, does not employ the blanket type clarifier to contact solution with FeS is COMINCO's patented process for cyanide detoxification in which freshly generated FeS is employed to precipitate cyanide and also to precipitate heavy metals from the effluent of gold ore cyanidation. The

process is employed at the CON MINE at Yellowknife, Northwest Territories, and is described in a trip report in Appendix I. A copy of the U.S. Patent is included in the chapter on cyanide detoxification (KUIT and BABCOCK, 1981). SCOTT (1984) reported that copper was reduced from 50 mg/l to 0.3 mg/l and zinc from 155 to 0.04 mg/l by their treatment process which is pH dependent and, in this case, perates at pH 7.5.

28. PATTERSON (1975) mentions evaporative recovery as a means of treating copper bearing effluents containing 100-500 mg/l Cu. The copper residue has an economic value if it can be recycled or sold. This process does not appear to be economically attractive in the levels found in mine and mineral processing effluents.

29. Ion Exchange

Ion exchange is capable of achieving very high levels of copper removal, particularly from dilute wastes. Copper removal by ion exchange from 1.02 mg/l to less than 0.03 mg/l has been reported by BOTHAM and BRYSON (1953). The initial cost of an ion exchange system depends on the required resin volume. For dilute wastes, flow rate will be the limiting factor while resin exchange capacity dictates the volume for more concentrated systems.

PATTERSON (1975) points out that to be cost effective compared with other treatment processes, the copper values must be recovered. This also implies that ion exchange will be more favorable where the copper concentration in the effluent is relatively high--i.e., more usable copper to recover.

30. CHEM. ENG. (1971) describes the treatment of copper rinse solutions containing 70 mg/l ammonia. A selective ion exchange resin (Amberlite 1R120, Rohm and Haas) reduced copper from 45 mg/l to undetectable levels. Ammonia was dropped from 70 mg/l to 1 mg/l.

More information on further commercial developments for selective copper removal from low pH effluent solutions is likely to be available from manufacturers of the innovative ion exchange resins such as:

ROHM & HAAS COMPANY
Independence Mall West
Philadelphia, PA 19105
Dr. Gerald D. Button
Technical Manager
(215) 592-3698
Dr. Jim Clovis
Marketing Manager
(215) 592-2817

DOW CHEMICAL COMPANY
1691 North Swede Road
Larkin Laboratory
Midland, MI 48640

DOW CHEMICAL U.S.A.
Post Office Box 5818
Denver, CO 80217
(303) 773-8800
Scott Josif

NADEN and WILLEY (?) reviewed solid ion exchange as a means of reducing the cost of copper recovery. David Naden is employed at:

DAVY McKEE LTD.
Bowesfield Lane
Stockton on Tees
England TS18 3HA
(0642) 67108

He pointed out the problem of poor Fe^{+++}/Cu^{++} selectivity of aminodiacetic acid resins which would require the scrubbing of ferric ions or removal by converting ferric to ferrous with SO_2. A table showing properties of commercially available resin types from his paper follows:

Commercially Available Resin Types

Resin Type	Name	Copper Adsorption pH	Fe Adsorption pH	Ca.Mg.Al Adsorption pH
1. Strong Acid (Sulphonic Acid)		0-14	0-14	0-14
2. Weak Acid (Carboxylic Acid)		>3.5	>3.5 Cu^{2+} Replaces Fe^{2+}	>5
3. Weak Base		~4	Fe^{2+} Not Absorbed; Fe^{3+} >1.5	Not absorbed
4. Strong Chelating Amido Diaceticacid	Rohm & Haas XE318 Dowex XFS 4132 Lewatit TP207 Dowex A1 Zerolit S1006	>1.5, Cu^{2+} & Fe^{3+}	>3.0	>6
Phosphonic Acid	Duolite ES63	>1	>1 Fe^{2+} & Fe^{3+}	absorbed
Amidoxime	Duolite CS346	>3.0	>1.5 Fe^{2+} & Fe^{3+}	Not absorbed
5. Inorganic Gels Zirconium Phosphate		1.0 - 1.5	Fe^{2+} >1.5; Fe^{3+} 1-1.5	Al^{3+} >1.5
Zirconium Phosphate Selectivity	$\frac{Cu}{Fe^{3+}} = 3.8$ $\frac{Cu}{Fe^{2+}} = 11$ $\frac{Cu}{Al^{3+}} = 12$			

Copper-Selective Ion-Exchange Resin with Improved Iron Rejection

Robert R. Grinstead
Dow Chemical U.S.A.
Western Division Research & Development Laboratories
Walnut Creek, Calif.

A new chelating ion-exchange resin with lower affinity for iron improves the efficiency of copper leaching. The resin is readily regenerated with dilute sulfuric acid or ammonia.

The properties of two chelating ion-exchange resins, FS 4195 and XFS 4196, which are selective for pper over most of the commonly encountered metal ns,[1,2] particularly ferric iron, have been reported eviously. The characteristics of XFS 4196 were de-ned for use in the processing of copper leaches to ectrowinning cell feed, in that regeneration can be complished with dilute sulfuric acid.

This paper will describe a new resin, designated FS 43084, which exhibits an increase of several fold copper/iron (III) selectivity, while retaining the er absorption characteristics of the original XFS 96. The basic characteristics of XFS 43084, in-uding distribution equilibria of a number of other etal ions besides copper and iron, and some kinetic ta, will be reported here. Performance in column plications will be described in a second paper[3].

EXPERIMENTAL METHODS

Equilibrium data for metal-ion absorption, were determined by uilibrating resin and solution for at least 16 hr., a time which s shown to be more than adequate for equilibrium to be achieved. e resin was eluted, either with dilute sulfuric acid or ammonium droxide, and both aqueous phases were analyzed by atomic-sorption spectrometry.

Resin loading data, unless otherwise stated, are expressed on the sis of the wet settled volume of the acid form of the resin, which s arbitrarily defined as the form in equilibrium with 0.1 N sul-ric acid. In some cases, volumes of resin were measured for ex-riments; in others, air-dried resin was prepared and measured by weight. In the latter cases, data were converted to a volume basis by use of the appropriate density and moisture contents.

In some cases, a value of the maximum copper capacity has been used. This value was determined by equilibration of resin with a copper sulfate solution containing 10 g Cu/l at its natural pH. The value so obtained is usually somewhat less than calculated by assuming one copper to be chelated per amine group. A major reason for this is the fact that 10-15% of the amines contain quaternized nitrogen atoms, which destroys their chelation ability.

Table I: Properties of XFS 4196 and XFS 43084 Resins*

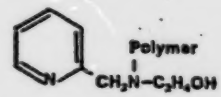
	XFS 4196	XFS 43084
sh size	−16 + 40	−16 + 40
ong base capacity, eq/l	0.08	0.07
ximum copper capacity, g/l	37	40
content, %	55	46
mt pK_a**	4.5	3.9
ume change, acid → base, %	−19	−13

e are based on sulfate salt form of resin
0.10 N Na_2SO_4 Solution

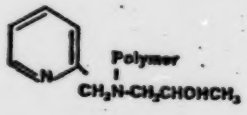
GENERAL PROPERTIES OF XFS 43084

Table I gives some basic physical and chemical properties of XFS 43084. Data for XFS 4196 are given for comparison. Capacity properties of the two resins are similar. XFS 43084 does exhibit a somewhat lower water content and a smaller volume change from acid to base forms. It also exhibits a slightly lower apparent pK_a, as will be shown.

The general structure of resins of this type has been described in patents which were recently issued[4,5] and is based on picolylamine (2-aminomethylpyridine). The resins are macroporous polystyrene/divinylbenzene copolymers to which has been attached a chelating functional group. The structures of the active groups in the two resins are:



XFS 4196
N-(2-hydroxyethyl)-picolylamine
HEPA



XFS 43084
N-(2-hydroxypropyl)-picolylamine
HPPA

Absorbed copper ions are presumably coordinated not only to the two nitrogen atoms of the structure, but also to the oxygen of the hydroxyl group. Evidence for the participation of the hydroxyl exists in the fact that in acid solutions of the monomeric chelators, HEPA is a stronger chelating agent for copper than the unsubstituted picolylamine by a factor of about six[7].

BASE STRENGTHS OF THE RESINS

Because the functional groups are amines and have basic properties, the resins will exist in a protonated or salt form in contact with acid solutions, and in a neutral or free base form in alkaline solutions. Both the resin volume and its kinetic performance depend on the form of the resin, and it is important to determine the pH

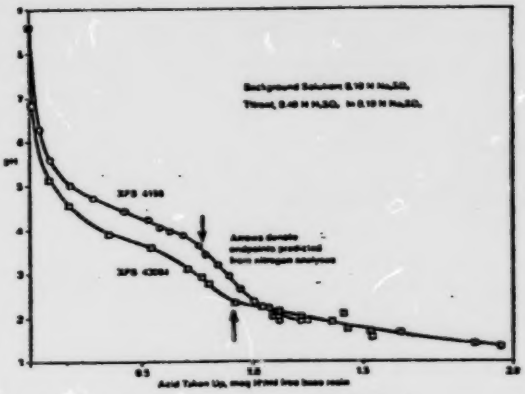


Figure 1. Titration curves of resins.

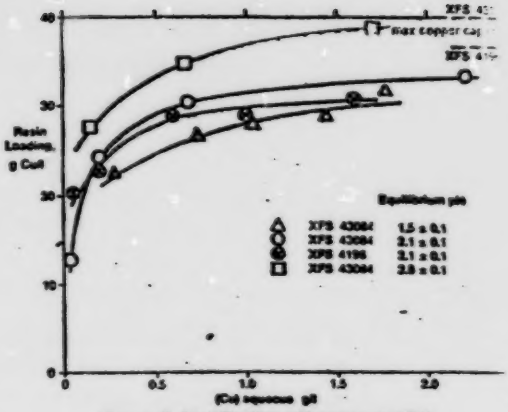


Figure 2. Distribution of copper at pH 2.

range over which this transformation occurs. This is done by acid titration of the free base form of the resin, data for which are shown in Figure 1. Because of the slow achievement of equilibrium, each point represents a separate experiment, which was equilibrated for 16 hrs. The amount of acid actually taken up by the resin was determined by subtracting the acid remaining in the external solution from the total acid added to the system.

Protonation of both resins is clearly indicated by a buffer region with pK_a's in the region of pH 4-5, culminating in definite though imprecise endpoints in the general region predicted by nitrogen analyses of the resins. These points (shown by arrows) represent the total exchange capacity, as determined by nitrogen analyses, reduced by the amount of strong base capacity (quaternized amine). Lack of precise agreement is probably due mainly to impurities in the original chelating agent used to make the resin. Agreement is, however, sufficient to characterize the protonation reaction as involving one proton per functional group in the pH region above about 2.5 to 3. Below pH 2, further protonation occurs, but it is not possible to distinguish between two possible mechanisms: (1) protonation of the pyridine ring nitrogen; and (2) protonation of sulfate ion to bisulfate. It is likely that both are occurring, since more than one additional proton appear to be taken up in this region.

A volume change of the resin also occurs during the protonation. After the endpoint region is reached, in the vicinity of pH 3, no further volume change is observed, at least out to the end of the titration curve shown.

ABSORPTION EQUILIBRIA OF COPPER AND IRON

Since in copper leaches the most troublesome impurity is ferric iron, and since the absorption of these two species is somewhat interrelated, it is useful to examine their behavior together. Several variables are important, in particular pH and concentration of the metal ions. The distribution of cupric ion between sulfate solutions and XFS 43084 is shown in Figure 2 for three pH values in the normal range of leach solutions. Comparable data for the pH 2 series for XFS 4196 are also shown for comparison, and are quite similar.

Distribution of ferric iron for XFS 43084 is shown in Figure 3. In the absence of copper, the iron loads readily up to a level of about 22 g Fe/l (about 0.4 moles/l, which is about half of the total ion exchange capacity of the resin. If iron were absorbed by a chelate mechanism, one would conclude that one iron is being shared between two chelating groups. We believe, however, that iron is absorbed by an anion exchange mechanism involving the sulfate anion, presumably in the same way as occurs with non-chelating, strong-base anion exchange resins.

The second curve was obtained in the presence of a fixed amount of copper, giving the resin loadings (in g Cu/l) shown by the numerals at each point. Aqueous equilibrium copper concentrations were all 0.7 ± 0.05 g Cu/l.

The effect of iron on copper loading is rather minimal and is in fact undetectable below about 4 g Fe/l. The effect of copper on iron absorption in this range, however, is quite marked, causing a reduction in iron distribution coefficient of 4-5 fold.

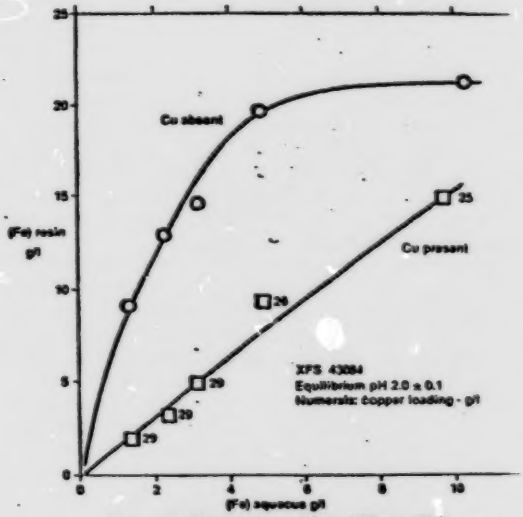


Figure 3. Distribution of iron (III) at pH 2.

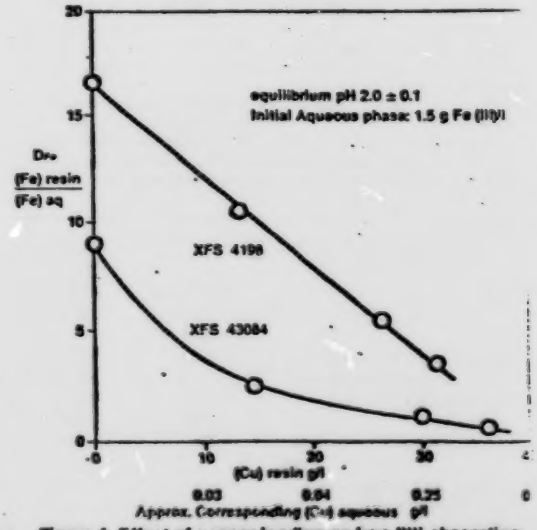


Figure 4. Effect of copper loading on iron (III) absorption.

effect of copper is shown in a different manner in Figure 4, the distribution coefficient of iron is plotted as a function per resin loading. The data for XFS 4196 are shown for com-n, and the higher selectivity of XFS 43084 is clearly evident, ting to about fourfold at typical copper loading levels. The selectivity, if defined as the ratio of distribution coefficients er/iron) is about 30 for XFS 43084 in the range of resin load-t 30 g Cu/l, as compared to about 8 for XFS 4196. This selectivity provides a double advantage for rejecting iron: only about one-fourth as much iron will load on a copper-g resin; second, the reduced distribution tendency of iron any type of a scrubbing operation more effective by the same

bably the most important variable governing metal ion ab-on is pH. The source of this dependence lies, of course, in the basicity of the resins. In its simplest form, the absorption of al ion by the resin can be expressed as follows:

$$M^{+m} + \overline{R \cdot nH^+} \rightarrow \overline{MR^{+m}} + nH^+ \;;$$

$$K' = \frac{(\overline{MR^{+m}})\,(H^+)^n}{(\overline{R \cdot nH^+})\,(M^{+m})} \qquad (1)$$

R represents the resin structure, and barred species are in sin phase. This is obviously not a complete expression of the ption process, since if m≠n, then some sulfate species must er into or out of the resin to maintain electrical neutrality. ch a situation, K' will, strictly speaking, not be a constant, ill depend upon the sulfate concentrations in both the resin olution phases. However, if one works in systems where the e concentration does not change appreciably, K' will be constant.

shall define the Conditional Absorption Constant, K, by llowing expression:

$$K = \frac{K'}{(H^+)^n} = \frac{(\overline{MR^{+m}})}{(\overline{R \cdot nH^+})\,(M^{+m})} \qquad (2)$$

thus a parameter which depends upon pH, and can be used strate the dependency of metal ion absorption as a function this expression, the quantities containing the metal ion ermined by analysis. Determination of the unused resin es a knowledge of the total capacity, which is obtained from tion loading experiments.

Figure 5 are shown plots of K for both copper and iron (III) unction of pH. The direct dependence of copper absorption on nforms to that predicted by the equation, although the depen-is somewhat greater than first power over most of the range. is presumably due to the fact that in this range (mainly pH 2), more than one proton exists in the unloaded resin. The for XFS 43084 and XFS 4196 are quite comparable, as was n earlier in Figure 2.

e iron data for the two resins appear nearly identical, in con-to the behavior depicted in Figure 4. The identity is more ent than real, since the curves in Figure 5 at pH 2 are sepa-by a factor of about 2, with the XFS 43084 exhibiting the iron absorption. This is about the same factor observed in e 4 at the zero-copper point.

KINETICS OF EXCHANGE

hough equilibria are of fundamental importance in characteriz-resin, the rate at which equilibrium is achieved is at least as tant, perhaps more so, from a practical point of view. Kinetic rmance can be measured in a variety of ways, but because of omplexity of ion exchange equipment, it is difficult to relate e laboratory kinetic data to column performance. It is possible, er, to observe qualitatively some important aspects of kinetics tal exchange.

e important aspect is the difference between kinetics of ab-on by the acid and base forms of the resin. It is well known water-treating technology that weak-acid and weak-base are relatively slow when used in their un-ionized forms. characteristic is usually ascribed to the fact that in these lack of a charged species reduces the affinity of the resin , which results in a smaller volume of the un-ionized form correspondingly restricted space through which exchanging s can diffuse. This effect was observed for XFS 43084 by ng out batch contacts with copper and iron solutions, monitor-he concentration in the aqueous phase, and calculating the

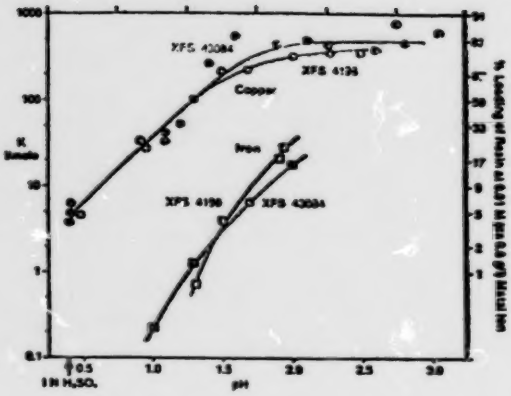


Figure 5. pH profile for copper and iron (III).

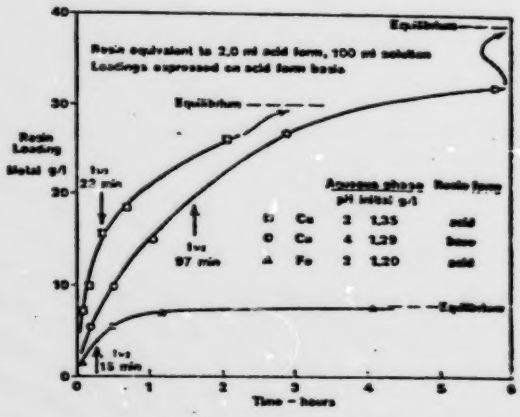


Figure 6. Rate of copper and iron (III) absorption by XFS 43084.

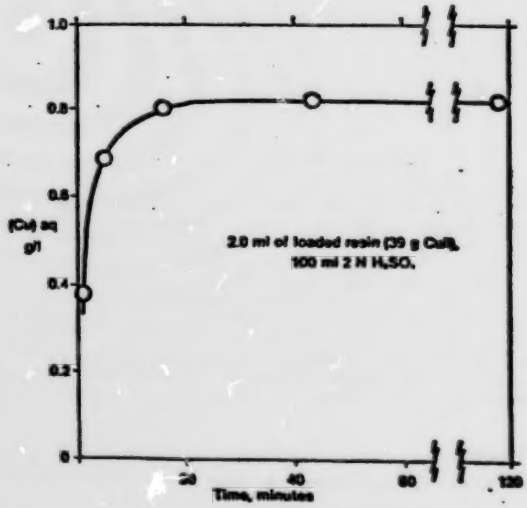


Figure 7. Rate of elution of copper.

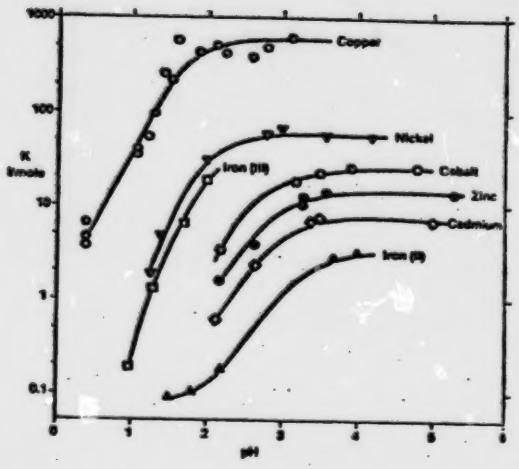


Figure 8. pH profiles for some metal ions.

Table II: Metal Ion Absorption by XFS 43084*

Species	pH	Equilibrium concentrations, g/l: Solution	Resin	K,l/mol
Cu	2.1	0.68	30	500
Fe (III)	2.0	0.87	8.6	18
Ni	2.0	0.80	10.1	29
	3.0	0.75	16	64
Co	2.2	0.93	1.7	3.2
	3.5	0.85	8.4	22
Cd	2.2	0.89	0.3	0.6
	5.0	0.87	3.3	7.2
Zn	2.2	1.06	1.0	1.5
	3.6	0.98	7.1	14
Al	3.7	0.71	0.3	0.7
Mg	6.3	0.90	0.33	0.6
Ca	6.3	0.19	0.38	3.2
Fe (II)	2.2	1.25	0.14	0.18
	4.0	1.13	2.1	3.1

*Resin: solution volume ratio = 1.2/100; initial aqueous concentrations, 1g/l metal except Ca, which was 0.2 g/l

resin loading by difference. Data for these experiments are shown in Figure 6 for absorption and Figure 7 for elution of copper.

Two points deserve mention. First, the rate of copper absorption is much faster for the acid form of the resin. If the half-times (i.e., the time to reach half of the equilibrium loading) are compared, the acid form is over four times as fast as the base form. The second point is that iron absorption is somewhat faster than copper under the same conditions (about 18 minutes vs. about 22 minutes for copper).

Elution of copper by 2N sulfuric acid, a typical eluant, is much more rapid than absorption, as Figure 7 shows. A half time was found to be about 1.5 minutes, some 15 times faster than for absorption. The greater exchange rate is probably mainly the result of the relatively high acid concentration.

Although not studied in detail here, copper can also be readily eluted from XFS 43084 with aqueous ammonia, just as with XFS 4196. This provides an additional flexibility in terms of the form of the final concentrate which can be obtained.

ABSORPTION OF OTHER METALS

Typical equilibrium absorption data for XFS 43084 are given in Table II for several common metals of potential interest in metallurgical operations. Additional data are shown in Figure 8 for most of these metal ions. In all cases the curves exhibit the typical rise in the value of K through the region in which the resin protons are ionizing, reaching a plateau at high pH. Of the metal ions commonly encountered in copper dump leaches only copper and ferric iron exhibit appreciable absorption below pH2. Certain anionic species can be absorbed, however, as was reported earlier. Besides ferric iron, which is mainly absorbed via an anion exchange mechanism, uranyl ion is also absorbed, as well as species such as molybdate, chromate, and vanadate(1).

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1. R. R. Grinstead, W. A. Nasutavicus, R. M. Wheaton, and K. C. Jones, "New Selective Ion-Exchange Resins for Copper and Nickel," *International Symposium on Copper Extraction and Refining, Vol. II*, 105th AIME Annual Meeting, Las Vegas, Nevada, Febr. 1976.
2. K. C. Jones and R. R. Grinstead, "Properties and Hydrometallurgical Applications of Two New Chelating Ion Exchange Resins," Chemistry and Industry (Aug. 6, 1977) 537-541.
3. K. C. Jones and R. A. Pyper, "Copper Recovery from Acidic Leach Liquors by Continuous Ion-Exchange and Electrowinning," to be published in Journal of Metals, April, 19
4. K. C. Jones and R. M. Wheaton, "Recovery of Non-Ferrous Metals from Acidic Liquors with a Chelate Exchange Resin in Presence of Iron(III)," U.S. Patent 3,990,924, December 21, 1976.
5. R. R. Grinstead and W. A. Nasutavicus, "Water Insoluble Chelate Exchange Resins Have a Crosslinked Polymer Matrix and Pendant Thereto a Plurality of Methylenepyridine Groups," U.S. Patent 4,031,038, June 21, 1977.
6. R. R. Grinstead and W. A. Nasutavicus, "Water Insoluble Chelate Exchange Resins from Aminopyridines and Process for the Selective Extraction of Valuable Metals Using the Same," U.S. Patent 4,098,867, July 4, 1978.
7. L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

ABOUT THE AUTHOR

Robert R. Grinstead is an Associate Scientist in the Western Division Research Department of Dow Chemical U.S.A. He graduated in chemistry from University of California at Berkeley in 1946, and obtained his PhD in Chemistry from the California Institute of Technology in 1950. He joined Dow at that time, participating in the development of the solvent-extraction and ion-exchange processes now used in the uranium industry. His interests since then have included mechanisms of model enzyme redox systems, the recovery of minerals and metals from brines and other raw materials sources, waste water recycling, and air- and water pollution control processes. His current interests center primarily around applications of metal chelate chemistry, of which the chelate resins described here are a principal outgrowth. He is a member of the editorial board of the Journal *Hydrometallurgy*.

31. In 1984, a large solvent extraction plant was commissioned to recover copper values from minewater at the El Teniente Mine in Peru.

	Water Flow Rate	Copper Production
Minimum	250 m^3/h	Less than 1,000 tpa Cu
Nominal	612 m^3/h	4060 tpa Cu
Maximum	900 m^3/h	4611 tpa Cu

At nominal flow rates and less, the plant operates in a conventional counter current two-stage extraction and two-strip mode. For higher flowrates, the plant is connected with the two extraction units in parallel. This caters for the seasonal variation in flow and tenor of copper concentration which reputedly can rise as high as 2 g Cu/l. More information can be requested from the designers and constructors of this innovative plant:

DMC ENGINEERS & CONSTRUCTORS
Division of Davy McKee Corp.
Post Office Box 5500
San Ramon, CA 94583
(415) 838-1166
Telex: 337635
Dr. M. A. Cocquerel
Vice President, Technology

32. Attempts have been made to regenerate gold and silver cyanidation barren bleed solutions by removing contaminating metals from the cyanide stream. No known commercial application of this process has been identified to date.

33. The COTTER CORPORATION at their Schwarzwalder Mine, Golden, Colorado, employs a highly innovative continuous plug flow ion exchange system to treat minewater as described by PALMER, et al. (1984).

Although designed primarily to remove uranium from 2-7 ppm to meet the effluent discharge regulation of 0.06 mg/l U_3O_8 max., the system also had to meet a 30-day average maximum 0.005 ppm Cu. Analyses of the feedwater effluent are compared with the Colorado Dept. of Health permit as reported by PALMER, et al. (1984).

	Feed mg/l	IX Effluent mg/l	Discharge Permit 30d Ave. (mg/l)
Uranium (dissolved)	2-7	LT 0.010	0.060
Cadmium	0.002	0.0004	0.0004
Copper	0.02	0.005	0.005

	Feed mg/l	IX Effluent mg/l	COPPER-LEAD-ZINC Discharge Permit 30d Ave. (mg/l)
Lead	-	0.005	0.032
Zinc	0.0026	0.05	0.05
Radium pCi/l	50-100	5	5
Sulfate	800	800	N.A.
Chloride	60	60	N.A.
Barium	-	1.0	1.0
Arsenic	-	0.050	0.050

The above results, which reduce copper and cadmium levels to 5 ppb and 0.4 ppb respectively were achieved using a 500 U.S. gpm continuous downflow ion exchange system with the following parameters:

Flow Rate:	500 U.S. gpm
Column Diameter:	4-7 Feet
Number of Stages:	Two Downflow Adsorption Stages in Series; One Downflow Elution Column
Resin Depth:	6-7 Feet
Column Height:	12 Feet
Elution:	13% H_2SO_4
Eluate:	12 g U_3O_8/l
Resins:	Dowex Rohm & Haas Anion Exchange Diamond Shamrock Duolite AIOID Anionic
Resin Loading:	To 35 g U_3O_8/l

More details are provided in the Appendix I trip report and in the PALMER, et al. (1984) paper. The innovative ion exchange system was designed and installed by:

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Alec Himsley
President
Al Peterson

34. PATTERSON (1975) referred to the innovative counter-current continuous regeneration system which yields high tenor eluates with 3-4 N copper. There are several similar counter-current systems for elution which can be considered. Some are upflow, and others are downflow. Some are fluid-bed while others are plug flow. Although not many have been used as yet for copper, lead, or zinc recovery, these systems as employed for low-grade uranium recovery could be considered if needed. RANDOL (1980) has provided details of all the major CIX (continuous ion exchange) systems available that could be considered for this purpose, although the RANDOL study was oriented toward uranium recovery.

35. Ion Exchange - Zinc Recovery

At METSEP (PTY) LTD., Germiston, South Africa, an ion exchange plant was installed in the mid-1970's to recover zinc from pickle liquor acid. Despite the relatively high tenor of the feed solution, this process was a technical success but an economic failure. The plant is owned by WOODALL DUCKHAM LTD., a U.K. company with South African partners.

36. Electrolytic Recovery

Direct electrolytic recovery of copper metal is said to be possible (PATTERSON, 1974) from relatively concentrated waste solutions. According to JACKSON (1972), treatment of dilute solutions (less than 2 g/l) using conventional electrolysis is impractical because of high power consumption. Normally, some form of preconcentration such as ion exchange is needed. SIMPSON and THOMPSON (1950) refer to direct electrowinning of copper from acid leach solution from an ore in which the regenerated sulfuric acid electrolyte is recycled. This application is applicable to concentrated solutions and would not be not applicable to typical mine and mineral processing solutions and effluents.

According to VOLCO BRASS (1971), the proper control of electrolysis current can eliminate the problem of other metals plating out. Again, this is an interesting phenomenon but applicable to concentrated metal finishing solutions.

PATTERSON (1975), SILMAN (1971), JACKSON (1972), and the AMERICAN ELECTROPLATING SOCIETY (1969) described a process which claimed to make electrolytic treatment of dilute copper cyanide solutions economically attractive. The process consists of a fluidized semi-conducting carbon bed across which a potential is applied. The large surface area per unit of volume, which provided a low-current

density on the electrode surfaces but a high current density across the cell, reduced the power consumption. The system was built for small-scale application for plate shops but never found commercial application in treating mine and/or mill effluents. ENVIRON. SCI. TECHNOLOGY (1970) carried an article in which it was claimed that 20 mg/l CN is reduced to 0.5 mg/l, and 40 mg/l is reduced to below 1.0 mg/l for roughly 5% of conventional treatment costs at about 100 times the rate of conventional electrolysis treating wastes of similar strength as inserted below.

RESOURCE CONTROL, INC. of West Haven, Connecticut, was shown in the article as the vendor, but in 1985 no record of this company in West Haven, Connecticut, or in any directory could be found.

37. During the early 1980's, the CANADA DEVELOPMENT CORP. financed development of an electrolytic equipment item for cyanide removal or recovery of metals from dilute effluent solutions. The basis of the development by HSA REACTORS LTD. was to use a very high surface area carbon fiber cathode. However, in 1984, HSA REACTORS LTD. was liquidated. The equipment had been tested on barren bleed regeneration from gold cyanidation operations at CAMPBELL RED LAKE MINES in Ontario. Again, this technology appears more appropriate for smaller flows associated with plating wastes than high volume mine and mill effluents.

38. Several universities continue to work on low-level metal removal by electrolysis, generally using high surface area electrodes or fluid bed electrodes of one form or another. One of these workers is:

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Dept. of Chemical Engineering
University of the Witwatersrand
Johannesburg 2001

It is noted in the table of Test Plant Results included in the paper by BRYSON and DARDIS (1980) inserted below that even with the high surface area electrode operating on a small demonstration scale, the effluents are still around 1 mg/l for Cu, Pb, and Zn--clearly not low enough to be of much use in meeting effluent requirements for the close of the 20th century.

Electrolysis speeds up waste treatment

New electrical process hastens destruction of contaminants in liquid plating wastes

A new wrinkle to the chemical industry's ancient art of electrolysis may provide those who have been seeking a cheap, simple means for treating dilute liquid wastes with just the technique they've been looking for. At least Stauffer Chemical Co.'s specialty chemicals division thinks so. The division has just reached an agreement which will give it exclusive rights to market a new electrolytic process developed by Resource Control, Inc. (West Haven, Conn.), to the metal finishing industry.

Stauffer, as a supplier of chemical products for the plating industry, had been looking for some time for an effective, low-cost way to treat dilute plating wastes, so that its customers in the industry would have a practical means for dealing with a growing water pollution problem. At the same time, Resource Control, Inc. (RCI), a relatively small company without a large marketing force, was seeking outlets for its new process which previously proved effective in treating plating wastes at several U.S. sites.

Waste problem

The metal processing and finishing industries produce large volumes of dilute wastes. These arise in the rinsing operations carried out to remove chemicals from metal parts. Since there may be as many as 15 separate steps in a finishing operation, a typical shop has numerous rinse water streams, each contaminated by different chemicals. Commonly, the chemical contaminants which must be removed before the water is discharged are cyanide, hexavalent chromium and heavy metals (silver, cadmium, zinc, copper, etc.).

The usual way of removing the contaminants is by chemical treatment: Cyanides are oxidized by sodium hydroxide and chlorine, the chromium cation is reduced by sulfur dioxide, and metal bearing wastes are chemically neutralized to precipitate the metal as an insoluble salt.

New twist

Although electrolysis has been used in the past to treat metal finishing wastes, it has been found to be a slow and costly method. Generally performed batchwise, the oxidation and reduction reactions necessarily have been slow because the electrical resistance of the waste is high, particularly when the concentration of contaminants becomes small and the liquid is ionized only slightly.

RCI has managed to overcome the problem of high resistance by using a cell in which the space between anode and cathode is packed with carbonaceous material. (The exact nature of the material is not being revealed, but RCI says that it is cheap enough to be discarded after several months of use, consists of small particles, and takes up only 50% of the available cell volume.)

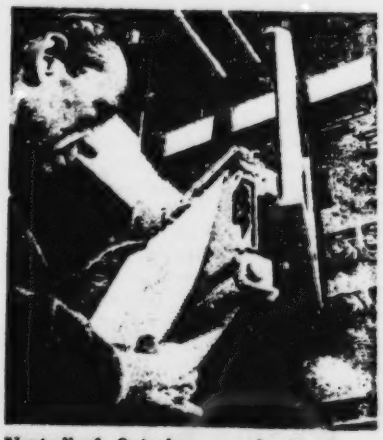
Avery Smith, president of RCI, refers to the bed as semiconductive. For some reason, the presence of the particles does not short-circuit the anode and cathode, as might perhaps be expected. What does happen, or so RCI believes, is that each individual particle gains, at different parts of its surface, a positive and a negative charge. Oxidation and reduction of contaminants in the waste then take place at the anodic and cathodic sites on each particle. The result is that the amount of current flowing is essentially independent of the conductivity of the waste, and the chemical reactions which destroy the contaminants take place more quickly (more than 1000 times as fast, RCI claims) than in conventional electrolysis using the same applied voltage (typically, 12 volts d.c.). Power costs are cut, too.

The new system is capable of reducing the concentration of cyanide ion in a waste stream from 20 p.p.m. to less than 0.5 p.p.m. with a corresponding reduction in copper content (in the case of copper cyanide plating) from 40 p.p.m. to less than 1 p.p.m. Similar reductions in hexavalent chromium are claimed by the company, which also has calculated that the system costs 95% less to operate than conventional chemical treatment.

RCI presently is manufacturing mobile, easily installed units rated at either 5 or 10 gallons per minute. These sizes are deemed adequate for the average metal finishing shop, but larger units can be custom built, according to RCI. Capital outlay called for is less than $20,000 for the typical shop.

Applications

RCI's Smith is enthusiastic about the possible uses of his company's electrolytic technique for the treatment of a wide variety of liquid wastes—in fact, any waste where the contaminants are capable of being oxidized or reduced to a harmless or easily disposable form. Whether the method will find wide application, of course, remains to be seen, but, if its attractive economics in the metal finishing field can be taken as a guide, it certainly will be a competitor to better established waste treatment processes.



Neutralized. *Stripchart records pH of metal plating wastes after electrolysis*

Treatment of Dilute Metal Effluents in an Electrolytic Precipitator

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Abstract

Excessive concentrations of metals in industrial effluents may adversely affect the performance of sewage purification works. Although there is existing technology for treating these effluents, it has not found wide application due to costly equipment and chemicals and the absence of sufficient space on most plants. In this paper the feasibility of removing these metals from dilute solutions by electrolytic precipitation using a particulate electrode is investigated.

Based on laboratory investigations a test plant was constructed which was compact, did not require the addition of chemicals and could be operated by unskilled personnel. The plant was installed at an electroplating works on the Witwatersrand and was extremely successful in treating wash waters containing copper, nickel chromium and zinc.

Introduction

The harmful effects of heavy metals on human and animal life have been known for a very long time: for instance, lead poisoning was probably first recognised by Hippocrates (370 BC) and mercurialism was described by Pliny (AD 29) in his writings on the diseases of slaves (Hunter, 1975). It is only in recent years, however, that public concern, spurred by such incidents as outbreaks since the early 1950's of minamata disease (the deformation of the foetus in the womb due to mercury absorbed by the mother), has led to the introduction of strict legislative standards governing exposure to heavy metals and the discharge of effluents containing these metals.

Such effluents are produced by a broad spectrum of sources which include the metal refining, metal plating, tanning, chlor-alkali, anodising and automotive industries. The wastes contain a wide range of metal ions including arsenic, antimony, cadmium, chromium, copper, lead, manganese, mercury, silver, selenium and zinc. Electroplating effluents can also contain additional quantities of extremely toxic cyanide compounds. The magnitude of the problem may be gauged by the fact that it is estimated that at least 10 000 tons of copper are discarded in electroplating rinse waters in the U.K. annually (Tseug and Mahmood, 1977) and in the United States the value of nickel and chromium lost in plating wastes, has been conservatively estimated at 50 60 million dollars per year (Cherry *et al.*, 1975). In 1973 losses of chromium and nickel in the Johannesburg municipal area alone were estimated to cost a quarter of a million rands (Funke and Coombs, 1973).

Toxic effects of metals have been observed at very low levels (Funke, 1973; Nemerow, 1971) and can pose problems during treatment in conventional sewage works where, above certain threshold concentrations, they can disasterously inhibit the bacterial action of the sludge digestion process. Even when the metal concentration of the raw sewage is low enough for efficient removal, the metals could still be concentrated to levels in excess of 1 000 mg/ℓ in the sludge discarded by the works and would make the sludge unacceptable as a nitrogenous fertiliser for crops or grazing (Coker and Davis, 1978).

Treatment Methods

Treatment of metal effluents is likely to be most effective at the source of the pollution where the concentration is highest. The conventional method consists of essentially three stages. The cyanide content is oxidised to nitrogen and sodium bicarbonate with sodium hypochlorite. Hexavalent chromium is reduced to the trivalent form using reagents such as ferrous sulphate, sodium metabisulphite or sulphur dioxide. Finally, neutralisation by addition of sodium hydroxide or lime for acid solutions or sulphuric acid for alkaline solutions, takes place. The metal hydroxide precipitates thus produced are then dewatered by settling or filtration. The resulting sludge (containing 10–50% solids) is dried and either dumped or incinerated.

Alternative treatment methods include ultrafiltration, reverse osmosis, electrodialysis, ion exchange, solvent extraction and cementation with scrap iron (Mantle, 1976). Other less well known methods which may be used are foam fractionation, complexing with polyelectrolytes and adsorption of organometallic complexes on activated carbon (Mulligan and Fox, 1976; Young, 1975).

The methods of metal removal considered above, while they might succeed in producing a treated effluent of sufficiently high quality, suffer from a common drawback, namely that it is generally difficult to recover the metal from the waste stream without further treatment. Electrolysis, on the other hand, has the proven capability of producing metal directly from effluents in a form suitable for recycling.

The conventional flat plate electrochemical cell has been used for many years for treating relatively concentrated solutions. Silver is routinely recovered in this way from photographic wastes (Nemerow, 1971), and in the electroplating industry such cells are used for the oxidation of cyanides and the regeneration of chromic acid (Kuhn, 1971). When the concentration of most metal ions is less than about two grams per litre, however, plating efficiency drops dramatically and unless the current density is progressively reduced, competing reactions eventually dominate.

The poor performance at low concentrations of conventional cells is due to mass transfer limitations. As the current density is increased, more and more reactant is consumed, until a point is reached where the concentration of the reactant at the electrode surface becomes zero. The rate of deposition then becomes limited by the rate of diffusion to the electrode and any further increase in current density or decrease in reactant concentration must result in some competing reaction (usually that of hydrogen evolution) becoming significant. The designer of a cell intended for operation at low concentrations must therefore either specify a very low current density (and consequently a

very high surface area) or must reduce the resistance to mass transfer by stirring or by some other means.

The particulate bed electrode cell, in which the conventional plate electrode is replaced by a three dimensional fixed or fluidised bed of conducting material satisfies both requirements (Pickett, 1979). The surface area per unit volume can be very large and mass transfer from the solution pumped through the bed is enhanced by the very nature of the cell construction. The cell current is supplied to the bed by a current feeder which may be either a backing plate or a wire grid inserted into the bed.

Experimental

Laboratory-scale fixed and fluidised-bed cells were tested with a variety of effluents. Although the fluidised-bed proved to be slightly more efficient in most cases it required fairly tight control on the flow-rate. This type of cell also had to be operated in a vertical position to obtain uniform fluidisation. The fixed-bed electrode did not suffer from either of the above restrictions and it was decided that this system would be preferable to use on a plant where there is a lack of skilled operating personnel. All subsequent work was restricted to the fixed-bed type of equipment.

Figure 1 shows diagrammatically the essential components of a cell and flow system which were designed specifically to reduce the concentration of nickel from 20 mg/ℓ to less than 2 mg/ℓ at a flow-rate of 180 ℓ/h and a current of 30 A. The dimensions of the packed sections were L = 1 900 mm, B = 350 mm and W = 5 mm. The packing consisted of crushed graphite which was sieved to a size range of 1,2 mm to 1,7 mm. The cell was tested on site at an electroplating works near Johannesburg where it was used to treat the wash water from various plating lines. The results are summarised in Table 1.

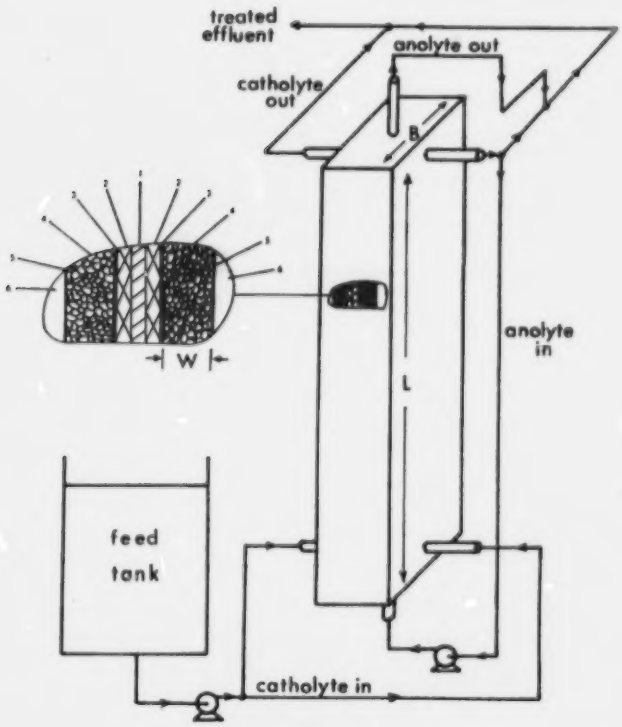

Figure 1
Electrolytic Precipitator:
1. Lead Anode
2. PVC mesh spacer
3. Anion permeable membrane
4. Graphite particles
5. Current feeder plate
6. Fibre glass reinforced plastic body

TABLE 1
TEST PLANT RESULTS

Solution Treated	Metal Removed	Concentrations (mg/l) Inlet	Outlet	Flowrate (l/h)	Current (A)	Voltage (V)	C.E. (%)
NCW	Ni	22,6	1,5	180	30	5,4	12
NCW	Cr	13,5	1,0	180	30	5,4	12*
ACW	Cu	57,5	0,9	360	40	5,0	28
ZCW	Zn	16,2	1,5	360	20	3,5	22

NCW = nickel and chromium wash
ACW = acid copper wash
ZCW = zinc cyanide wash
C.E. = overall current efficiency.
*The current efficiency for chromium is based on the reaction $Cr^{6+} + 3e \rightarrow Cr^{3+}$

Discussion and Conclusions

The results show that the test plant was able to achieve greater than 90% reduction in nickel concentration even though the effluent solution contained chromium as well. The plant also performed very well in treating copper and zinc effluents where it was possible to double the flow-rate while maintaining an acceptable outlet concentration.

It may thus be concluded that the electrolytic system proposed can be used to remove a variety of metals from dilute solutions in equipment which is compact and has a low operating cost in terms of power requirements. It also has the potential for economically recovering metals in re-saleable form. These aspects, however, have not yet been studied in detail and hence a comparison of costs with other treatment methods is not possible at present.

Acknowledgement

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39. Cementation

Cementation of copper onto a bed of scrap iron is useful for recovery of copper from both concentrated and dilute effluent streams and has been described by DEAM, et al. (1972), HILL (1972), CIANCA (1972), JESTER and TAYLOR (1973), CASE (1974), ANDERSON and HOLLINGWORTH (1972), and JACKSON (1972). By oxidation-reduction reaction, copper cements onto the iron with sacrificial iron going into solution. PATTERSON (1975) refers to one plant in which copper averaging 80 mg/l (range 34-220 mg/l) was reduced to an average effluent of 0.33 mg/l (range 0.2-90.84 mg/l Cu). The copper can be recovered as essentially pure metal representing a significant offsetting savings to treatment costs.

40. FAULKNER (Undated) points out that the cost of cementation recovery of 1 lb. Cu depends on the amount of ferric iron in solution and the Fe^{3+}/Cu^{2+} ratio because ferric ions also consume iron scrap. He describes a process whereby, with the use of SO_2 and activated charcoal, the ferric ions can be inexpensively reduced to ferrous prior to contacting the scrap iron with the solution to be treated.

CALGON CORPORATION

PITTSBURGH ACTIVATED CARBON
DIVISION OF CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.
CALGON CENTER, BOX 1346, PITTSBURGH, PA. 15230

CONTROLLING IRON AND ACID COSTS IN THE PRODUCTION OF CEMENT COPPER WITH SULFUR DIOXIDE AND ACTIVATED CARBON

W. D. Faulkner

Familiarity with activated carbon in the metallurgical field started with its use to extract gold and silver from chloride, and later, cyanide solutions. In the mid '50s its use to remove molybdenum from acid uranium circuits became an established practice. As in the case of molybdenum and uranium, activated carbon can selectively adsorb metals from solution making it a useful tool in extractive metallurgy.

Activated carbon can also function as a catalyst. It is in this capacity that the copper industry, or more specifically, the phase of the industry dealing with leaching and cementation, is interested. The reaction of primary importance is the catalytic reduction of ferric iron in pregnant leach liquors by sulfur dioxide. The purpose of this paper is to present the practical and economic implications of using this approach to eliminating the detrimental effects of ferric iron. Before presenting details on the system, perhaps some background on activated carbon would be of interest.

Activated carbon differs from other forms of carbon such as coke, graphite, carbon black, etc., in its structure and internal surface area. X-ray studies have shown that activated carbons are composed of randomly dispersed graphitic-like crystallites of submicroscopic dimensions. Each crystallite is composed of a number of layers and each layer contains carbon atoms arranged in a pattern identical to that in a poly-nuclear aromatic compound. In the case of activated carbons the distance between the layers are greater than that for graphite. A structure of this kind leads to a very complex network of fine pores and consequently a very great internal surface area.

The total surface area of commercial carbons range from 600 to 1400 square meters per gram and have internal pore volumes ranging from 0.6 to 1.0 cc/g. This means that one pound of carbon can provide more than 100 acres of surface area.

Examples of established catalytic applications are the production of phosgene from carbon monoxide and chlorine and in the dechlorination water. It is also used to support the catalysts used in the manufacture of vinyl acetate and vinyl chloride monomers.

Our discussions here are pertinent to dump, heap, and vat leaching operations where cementation is used to extract copper values from solution. Since the tailings solutions after cementation are normally returned to the leaching areas because of water shortages or pollution considerations, the following discussions are presented with this in mind.

Theoretically 0.88 pounds of iron are required to precipitate 1.0 pounds of copper

$$CuSO_4 + Fe \rightarrow Cu + FeSO_4 \quad (1)$$

The actual iron consumption for most of the U. S. operations fall in the range of 1.3 to 2.8 lbs. Fe/lb. Cu. The presence of ferric iron in the pregnant solutions accounts for much of the excess iron by the reaction

$$Fe_2(SO_4)_3 + Fe \rightarrow 3FeSO_4 \quad (2)$$

This reaction proceeds at a much faster rate than reaction (1) and it is not possible to get a reasonable copper recovery before the ferric reduction is complete. Reaction (2) actually accounts for 5 to 50% of the total scrap consumption in the industry.

The attack of acid on the scrap constitutes another source of consumption by

$$H_2SO_4 + Fe \rightarrow H_2 + FeSO_4 \quad (3)$$

This reaction is much slower than reactions (1) and (2) but in most plant operations the reaction essentially goes to completion before the solutions exit from the precipitation section. More will be presented on this subject later.

To reduce one pound of ferric costs 1.38¢ assuming a scrap cost of $55/T. This may be a substantial cost depending upon the Fe^{+++}/Cu^{++} ratio in solution. Also, better than 95% of the iron dissolved during each cycle precipitates out in the dumps and is suspected of imparing leaching efficiency by blinding mineral surfaces.

A lower cost ferric reductant other than scrap iron would have a direct economic advantage and an indirect advantage of reducing the iron load in the recycled solutions. Although sulfur dioxide would be cheaper it does not react swiftly enough to be practical. With the aid of activated carbon it does. The reaction is as follows:

$$Fe_2(SO_4)_3 + 2H_2O + SO_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (4)$$

When an amount of SO_2 stoichiometric to the Fe^{+++} is added to the solution and passed through a column of activated carbon, the effluent contains no ferric iron and all of the SO_2 is consumed. The retention time in the carbon bed is a matter of minutes.

The SO_2 requirement is 0.57 lb./lb. Fe^{+++}. The source of SO_2 will establish the cost. Estimates of $15/T for SO_2 produced from pyrite and $28/T from elemental sulfur have been advanced. These correspond to reduction costs per pound of ferric of 0.44¢ and 0.80¢, respectively, versus the 1.38¢/lb. with scrap iron. Purchased liquid SO_2 is also a possibility.

You will note from reaction (4) that H_2SO_4 is one of the products. For each pound of ferric reduced, 1.75 lbs. of H_2SO_4 are generated.

The presence of this acid raises a question. Although ferric iron is being eliminated from the system, won't the advantage be negated by the attack of the generated acid on the scrap? If no control over solution residence time in the precipitation section is exercised, the answer is 'yes'. However with proper control, the effect can be minimal.

To show that this is possible, the following test was conducted. A synthetic pregnant solution of the following composition was prepared:

Ferric iron	10	g/l
Ferrous iron	40	g/l
Copper	3.1	g/l
H_2SO_4	17.5	g/l

The solution was divided into two lots. The first was used as prepared. Stoichiometric SO_2 was introduced into the second and passed through a bed of Pittsburgh Type SGL 8 X 30 mesh Activated Carbon. Both solutions were then contacted with iron filings and monitored for copper qualitatively. When the concentration of Cu^{++} became less than 0.1 g/l, the iron was removed. The iron consumption was 2.66 lb./lb. Cu for the "as prepared" solution. The reduced solution gave an iron factor of 1.16 lb. Fe/lb. Cu even though it contained 35.0 g/l H_2SO_4.

It should be emphasized that these results were obtained under laboratory conditions in which the iron was removed from the system as soon as cementation reaction was complete. Similar results in plant practice will require similar control.

The acid in the tailings solution has potential economic appeal, since many operations add acid before returning the solutions to the leaching areas.

In the precipitation section itself, the presence of acid should result in a faster rate of copper precipitation. Since the pH of the solutions would not rise to the 3.2 plus area, the cement product should be higher grade due to the absence of precipitated iron salts.

The efficiency of the activated carbon is a function of the pore structure, internal surface area, and mesh size. After evaluation of several carbons we have recommended Pittsburgh Type SGL in an 8 X 30 mesh range. Field tests to date show no loss in catalytic efficiency of Type SGL with time.

Solution temperature does influence the ferric and SO_2 reaction. A synthetic solution was prepared and divided into two lots. Stoichiometric SO_2 was added to both solutions and run through carbon beds at identical rates. The only difference was temperature. The ferric reduction was 91% complete at 25° C. but only 62% was reduced at 5° C. For 100% reduction, the maximum retention time in the carbon reactor under extreme conditions is 15 minutes. Generally, retention times of 5 to 10 minutes will give complete reduction.

Slimes are commonly present in the pregnant liquor. Since such large solution flows are involved, filtration would be expensive. Granular carbon is an efficient filter media for suspended solids in packed beds. If the carbon reactor is operated downflow, then a backwash to remove solids would be required periodically.

We feel the practical approach to the slimes problem is to operate the system upflow with the carbon free to expand. A high density carbon will permit a solution linear velocity sufficient to carry the slimes through the carbon bed without washing granular carbon over the top. For Pittsburgh Type SGL 8 X 30 mesh, the flow rates are 7 to 12 gpm/ft.^{2} depending on the solution temperature and the settled carbon bed depth is 8 to 10 ft., again depending upon temperature.

The carbon reactor itself is quite simple. Wood tanks or acid-resistant concrete vats can be used. It is necessary to have a good liquor distributor in the bottom of the bed to prevent short-circuiting of solution. Generally, the carbon will be supported on graded gravel. The net result is possibly a wooden tank, perforated filter tile, graded gravel, and activated carbon. So far we have seen no evidence of the need to regenerate or replace the carbon.

In studies to date, purchased or essentially pure sources of SO_2 and plant liquors have been used. No poisoning of the carbon has been observed. With pyrite being a logical source of SO_2, we wanted to check possible poisons from that source, such a arsenic, antimony, lead and zinc. Lead was not tested due to its low solubility in high sulfate systems. To a synthetic pregnant solution, the others were added in amounts of 0.1 g/l each. Stoichiometric SO_2 was added and a total of 314 column volumes were run through a carbon bed. The percent reduction remained constant throughout the run. This is a good indication that there should be no significant difference in carbon efficiency with roaster gas.

The following example is presented to show the potential significance of the SO_2 reduction system. The plant conditions are:

Copper production	60 tons/day
Flow to precipitation section	10,000 gpm
Acid addition to tails	4 lbs./lb. Cu precipitated
Delivered scrap cost	$55/Ton
Delivered acid cost	$15/Ton
SO_2 from pyrite	$15/Ton
Pregnant solution assay, g/l:	
Fe^{+++}	1.8
Fe^{++}	2.5
Cu^{++}	1.0
H_2SO_4	0.3

It is assumed the 0.3 g/l H_2SO_4 is consumed under present conditions and a total of 0.45 g/l would be consumed in the reduced solution.

The pertinent calculations regarding iron and acid for this plant with and without SO_2 reduction are given in the following table.

		Standard Practice	With SO_2 Reduction
Fe Factor	lb. Fe/lb. Cu	1.95	1.14
Fe^{++} in Tails	grams/liter	6.25	5.44
H_2SO_4 in Tails	grams/liter	0.0	3.0
Acid addition required	grams/liter	4.0	1.0
Fe Cost per day	Dollars ($)	6430	3770
SO_2 Cost per day	Dollars ($)	0	926
H_2SO_4 Cost per day	Dollars ($)	3600	900
Total Cost per day	Dollars ($)	10030	5596
Savings/1000 gpm/yr.	Dollars ($)		159624

You will note the savings in acid are as great as the savings in scrap. Whether full credit can be taken for the acid generated will depend on previous practice and attitude regarding acid addition.

SUMMARY

The profitability of leaching low grade or waste rock for copper is strongly dependent on acid and scrap iron requirements. As dumps age, the copper content of the pregnant liquor tends to lower and the iron level climbs. Due to bacterial and chemical oxidation, much of the dissolved iron reports in the pregnant liquor as ferric. This results in increased scrap consumption. At some point in time, the dumps are closed down when the solution grade does not justify the chemical and operating costs of recovery. Much of the scrap and acid costs can be offset by reducing the ferric with SO_2 which also generates sulfuric acid. Granular activated carbon is an expedient catalyst.

To take full advantage of the acid generated, control over retention time of solutions in contact with scrap iron is mandatory. Several types of precipitators are in use. The cone-type developed by Kennecott Copper Corporation would seem the most advantageous; however, one launder system employing SO_2 and activated carbon is in operation and the results to date are encouraging.

41. Electrodialysis

BOVET (1970) has claimed that electrodialysis is economically feasible for the treatment of process solutions and rinse waters from plating and metal finishing operations and for the treatment of acid mine drainage. ANDERSON, et al. (1971) reported energy requirements of 10 kWh per 1,000 U.S. gallons for electrodialysis and indicated that membrane fouling can be a serious problem.

More information about recent demonstration of electrodialysis reversal EDR for desalination of acid mine drainage at a Witwatersrand mine in 1984 can be requested from:

PROCESS SYSTEMS (PTY) LTD.
Box 1042
Johannesburg 2000
(011) 802-4230
Ralph Jones
Managing Director

PROCESS SYSTEMS is the South African representative of the leading EDR system manufacturer in the world:

IONICS, INC.
65 Grove Street
Watertown, MA 82172
(617) 962-2500
Telex: 922-473
Bill Katz

42. Reverse Osmosis

GOODLOE (1984), HERRIGAL (1984), and RESOURCES CONSERVATION CO. (1981) described the seeded slurry reverse osmosis process demonstrated at two sites, one for acid mine drainage water recovery at the ERPM mine, RAND MINES LTD., Brakpan, South Africa (a Witwatersrand gold mine) and one other non-mining application.

The combination of an innovative low-cost tubular R.O. system developed in South Africa with the seeded slurry concept where a slurry of gypsum crystals, which precipitate from the R.O. concentrate, is recycled back into the feedwater to prevent membrane fouling. This has made it possible to achieve excellent recoveries in the high 90% range from feed that is close to saturation with gypsum.

Although the purpose of the desalination plant was to demonstrate water recovery, the system also reduced levels of Cu, Pb, and Zn significantly as can be seen from the following results:

COPPER-LEAD-ZINC

	Feedwater	Recovered Product
Cu	0.3 mg/l	LT 0.01 mg/l
Pb	0.1 mg/l	LT 0.02 mg/l
Zn	2.0 mg/l	0.10 mg/l
pH	4	5

It appears that the seeded slurry reverse osmosis system very effectively removes copper, lead, and zinc to very low levels from acid mine drainage even at acidic pH values. It would be interesting to see how this process would perform on solutions with somewhat higher base metal levels.

This technology is said to cost around RO.50/m³ ($0.25/m³) to operate in South Africa (about U.S. $1.00/1000 gallons).

More information on this highly innovative breakthough technology is available from:

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Reams R. Goodloe
Sales
Russell Vandenberg
Vice President
Tom Wolfe
Research & Development

Precipitation

43. Soluble lead is usually removed from solution by precipitation and decantation including lime or caustic to precipitate lead hydroxide; soda ash to precipitate lead carbonate and phosphate to lead phosphate. Alum and ferrous and ferric sulfate coagulation have also been reported for lead treatment, as has ion exchange.

    In precipitation processes, lead is normally precipitated as the carbonate $PbCO_3$ or the hydroxide $Pb(OH)_2$.

44. Literature reports conflicting values of pH optima for lead precipitation as a hydroxide with the following being suggested:

Author	pH Recommended for Lead Precipitation
DEAN, et al. (1972)	pH 6.0
MILL, R.D. (1972)	pH 6.0-7.0
METAL FINISHING J. (1971)	pH 8.7-9.3
NETZER, et al. (1975	pH to 10.0
NILSSON (1971)	pH to 10.0
HEM and DURUM (1973)	pH 9.2-9.5 (Theoretical)
DAY, et al. (1974)	pH 9.2-9.5

NETZER, et al. (1975) found in bench scale tests that at the optimum pH 10.0, a residual lead value of 0.5 mg/l was achieved.

According to HEM and DURUM (1973), theoretical calculations indicate that the most efficient lead hydroxide precipitation occurs at 9.2-9.5.

45. HAAS and MILLER (1972) surveyed eight battery manufacturers' wastewater treatment and found that simple sedimentation was relatively ineffective in removing particulate lead. Data on four plants employing pH adjustment and sedimentation (for three of them) indicates that:

- Improved effluent quality was achieved at higher pH and longer settling times.
- Plant D, with no settling, had a very poor quality effluent.
- Plant D also uses ammonium hydroxide to raise the pH which results in a high soluble lead level. Ammonium is ineffective for lead precipitation because of lead amine complex formation.
- The best effluent was obtained by addition of caustic soda t pH 7.0 followed by 24-hour settling.

Treatment Practice and Effluent Lead Levels from Battery Plants

Plant	Treatment Chemical	pH	Settling Time (hr)	Effluent Lead (mg/l) Dissolved	Suspended	Total
A	Lime	6.8	30	0.30	0.18	0.48
B	Caustic	5.5	1	0.6	1.0	1.6
C	Caustic	7.0	24	0.02	0.02	0.04
D	Ammonia*	7.8	0	1.9	22	23.9

* Used for pH adjustment.

46. According to literature references, ammonia complexes lead and inhibits its precipitation from solution.

47. Solubility of lead carbonate is dependent on both treatment pH and carbonate concentration. For a fixed carbonate dosage, a broad range of pH (8.0-9.2) provides consistent treatment according to HEM and DURUM (1973) and DAY, et al. (1974). Precipitation by sodium carbonate addition plus sand filtration yielded an effluent with total lead at 0.2-3.8 mg/l and soluble lead of 0.1 mg/l at pH 6.4-8.7.

48. Pilot testwork by MARUYAMA, et al. (1972) demonstrated the importance of effective solid removal. An effluent with 5 mg Pb/l was precipitated by lime and $FeSO_4$ and then settled and filtered through a dual media filter. The results show lead values an order of magnitude lower after filtration compared with sedimentation alone.

Lead Removal by Precipitation and Sedimentation plus Filtration

Treatment Chemical	Treatment pH	Effluent Lead Concentration (mg/l)	
		Sedimentation	Filtration
Ferric Sulfate at 45 mg/l Fe	6.0	0.25	0.030
Lime at 260 mg/l + Ferric Sulfate at 20 mg/l Fe	10.0	0.25	0.029
Lime at 600 mg/l	11.5	0.20	0.019

49. Precipitation of dissolved lead by dolomite ($CaCO_3$, $MgCO_3$) as lead carbonate has been described by VOZNESENSKIC, et al. (1940). Lead wastewater was filtered through a calcined dolomite bed which precipitated dissolved lead. The dolomite filters were regenerated by backwashing with water to remove the lead carbonate formed in the process.

50. The reaction of lead with dolomite yielding insoluble lead carbonate results in very little lead reaching receiving streams from southeastern Missouri lead mines according to WIXSON, et al. (1969), JENNETT and WIXSON (1971), and BOLTER, et al. (1972). The lead mineralization occurs in a dolomitic hostrock, and the mill tailings contain ground dolomite. As the mill tailings are channeled through sedimentation basins and a meander system prior to release of the waste effluent, dolomite plus reacted lead carbonate are readily removed. Heavy metals precipitation is encouraged in the settling lagoons by the slightly basic nature of the waste at pH 7.5-8.2

JENNETT and WIXSON (1977) described the treatment of effluent from ST. JOE MINERALS' Fletcher Mine and Mill in which the minewater used to be treated in a series of five sedimentation ponds, and the effluent from the last pond is recycled to the milling operation resulting in a dramatically reduced heavy metal discharge to the receiving waters.

51. The Missouri new lead belt meander system also contains a thriving biological metals removal system. Plants, algae, and bacteria all contribute in the process to polish the effluent.

The Missouri Lead Study edited by WIXSON (1977) showed clear evidence of lead uptake to 4-5 mg/g (dry weight) of algae at the discharge point to the receiving stream which dropped to around 100 ppm within a mile or so from the tailings dam. Average water quality characteristics at the meander effluent stream were found by ERNST to be as follows as reported in WIXSON (1977):

	Cu	Pb	Zn
Dissolved Max.	0.015	0.025	0.08
TOTAL Max.	0.015	0.10	0.10
Dissolved Ave.	0.01	0.025	0.034
TOTAL Ave.	LT 0.01	0.038	0.034
Dissolved Min.	LT 0.01	LT 0.025	0.01
TOTAL Min.	LT 0.01	LT 0.025	0.01

This data shows the effectiveness of both the carbonate ore system and the biological polishing pond considering the large scale production of lead from the operation for which the above data describe the effluent.

52. At ST. JOE MINERALS' zinc smelter-refinery at Monaca, Pennsylvania, cadmium, lead, and zinc are precipitated by lime from the plant effluent and runoff waters to achieve the following results which are also reported in a trip report in Appendix I:

Influent	Ave.	1-Day Max.	30-Day Max.
Zn mg/l	14.5	77.2	21.3
Cd mg/l	2.5	16.7	3.9
Pb mg/l	2.6	16.0	4.0
Discharge After Lime, Settle, Filter			
Zn mg/l	0.55	3.34	0.75
Cd mg/l	0.19	1.02	0.22
Pb mg/l	0.17	0.45	0.12

The process employed to achieve these effluents includes settling followed by lime addition, settling in a clarifer, and multi-media filtration. Flocculant is used.

John M. Cigan of ST. JOE MINERALS pointed out that the low lead values are due to carbonate precipitation. There is adequate $CO_3^=$ in solution due to CO_2 uptake into the water from the air to precipitate lead; however, after a rainstorm, some Na_2CO_3 can be added if needed.

53. Lead Precipitation as Phosphate

CRANDELL and RODENBERG (1974) and ROHRER (1971) reported the use of sodium phosphate Na_3PO_4 to precipitate lead phosphate. The solubility of lead phosphate is determined by treatment pH and phosphate dosage. Treatment conditions are specified to exceed pH 7.0 with up to three times excess sodium phosphate added (3.7 pounds sodium phosphate per pound lead). This may result in excess phosphate levels. At pH 7.2-7.2, lead values were reduced to 0.2-0.6 mg/l total lead and 0.1 mg/l soluble lead.

54. Organic lead compounds generated, for example, in a tetraethyl lead plant did not respond to lime precipitation according to NOZAKI and HATOTANI (1967) but could be removed on strong acid cation exchange resins. Reductions of organic lead from 130-140 mg/l to 0.02-0.53 mg/l Pb were reported using ion exchange. The organic lead compounds were eluted from the resin by caustic soda.

55. Precipitation and removal of inorganic lead is facilitated by addition of ferrous sulfate according to ROBB (1961) and as noted above where ferrous sulfate is added in several lead treatment plants. Lime and ferrous sulfate were added to precipitate and coagulate lead leached from a nearby mine into a municipal water supply as described by J. INST. MUNICIP. ENG. (1957).

Alum coagulation at pH 6.8-7.0 has also been reported to coagulate lead from 17 to 1.3 mg/l according to NILSSON (1971).

56. Ion Exchange Removal of Lead

Successful ion exchange treatment has been claimed for both organic and inorganic lead. A study on treatment of an ammunition industry waste showed reduction of lead from 6.5 to 0.1 mg/l by precipitation. Ion exchange treatment of the effluent at pH 5.0-5.2 with a phosphoric acid resin reduced lead to 0.01 mg/l according to SHANNON (1973).

Elsewhere, an effluent level of 0.002 mg/l lead was achieved (LIEBIG, et al., 1943) although RANDOL INTERNATIONAL LTD. would question the ability to analyze to such a low detection limit in 1943.

Organic lead reductions from 140 mg/l to 0.02-0.50 mg/l Pb were claimed by NOZAKI and HATOTANI (1967) using a strong acid cation exchange resin.

57. A Summary of Reported Lead Treatment Processes and Efficiencies as extracted from PATTERSON (1975) is provided here:

Summary of Reported Lead Treatment Processes and Efficiencies.

Treatment	pH	Lead Concentration (mg/l) Initial	Lead Concentration (mg/l) Final	Percent Removal	Reference
Ion Exchange	5.0-5.2	0.1	0.01	90	15
Ion Exchange[a]		0.055	0.0015	97.3	28
Ion Exchange[a]		126.7-144.8	0.020-0.53	99.9+	16
Lime + Sedimentation		0.31	<0.1	97+	10
Lime + 30-hr Sedimentation	6.8		0.48		2
Caustic + 1-hr Sedimentation	5.5		1.6		2
Caustic + 24-hr Sedimentation	7.0		0.04		2
Ammonium Hydroxide	7.8		23.9		2
Lime + Ferric Sulfate + Sedimentation[a]	10.0	5.0	0.25	95	25
+ Filtration[a]		5.0	0.029	99.4	
Lime + Sedimentation[a]	11.5	5.0	0.20	96	25
+ Filtration[a]		5.0	0.019	99.6	
Lime + Sedimentation		6.5	0.1	98.5	15
Lime[a]	9.0-9.5	5.0	0.01-0.03	99+	23
Caustic + Soda Ash[a]	9.0-9.5	5.0	0.01-0.03	99+	23
Dolomite + Sedimentation	7.5-8.2	0.04	0.022	45	12
		0.018-0.036	0.038	+	
		0.051	0.030	42	
		0.098	0.055	44	
Sodium Carbonate + Filtration[a]	6.4-8.7	10.2-70.0	0.2-3.6	82-99+	3
Sodium Phosphate + Filtration[a]	7.2-7.5	3.0-5.0	0.2-0.6	83-93	3
Ferric Sulfate + Sedimentation[a]	6.0	5.0	0.25	95	25
+ Filtration[a]		5.0	0.03	99.4	
Ferrous Sulfate + Sedimentation	10.4-10.8	45	1.7	96.2	17

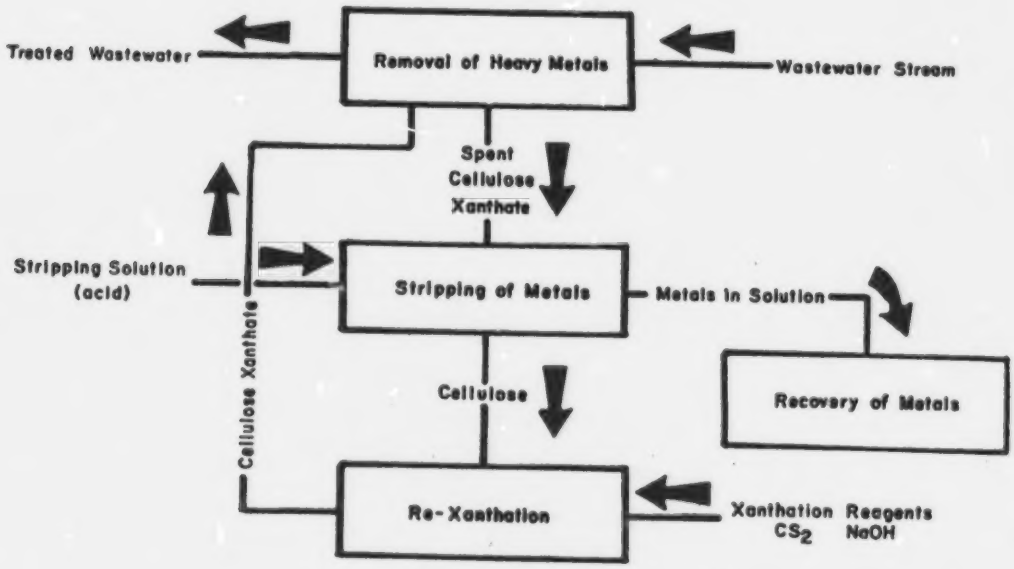
[a] Pilot Plant Results

15	SHANNON (1973)	25	MARUYAMA, et al. (1972)
28	LIEBIG, et al. (1943)	23	DAY, et al. (1974)
16	NOZAKI and HATOTANI (1967)	12	BOLTER, et al. (1972)
10	JENNETT and WIXSON (1971)	3	CRANDALL and RODENBERG (1974)
2	HAAS and MILLER (1972)	17	ROBB (1961)

58. HANWAY, et al. (1976) showed that metals in effluent samples could be reduced to 0.01 mg/l lead and 0.06 mg/l copper using starch xanthate to precipitate metals. Although the volume of the precipitated starch xanthate residue was small in comparison with that generated by conventional metal preciptation, the characteristics of the sludge were not particularly favorable. Sedimentation rates were slow, and the supernatant was often turbid and, on filtration, the residue clogged the filter media. The filter cake was sticky and had a moisture content of 60-80% water. The precipitate did not lend itself to metal stripping and re-xanthating. Adjustment of the pH to 8 with lime or caustic improved the results somewhat.

These authors discussed the advantages of using cellulose xanthate for metal removal because of its fibrous nature and the possibility of recyling the substrate. At a

xanthate dosage of 90 ppm, residual values of lead and zinc in an industrial wastewater could be reduced to 30 ug/l or less after 15-30 minute contact time. The residues settle rapidly to a pulp that filters readily leaving a clear supernatant and filtrate. A schematic of their proposed treatment scheme is shown below



Flowsheet of Cellulose Xanthate Process for Heavy Metal Removal.

Although the use of reusable cellulose xanthates appears to be intelligent and potentially practical, no users on a commercial scale have been identified, and there is no way to obtain comments on the pitfalls encountered with such a system.

WING, et al. (1974) described how the starch xanthate recovery properties could be dramatically improved using a cationic co-precipitant Poly (vinyl benzyl trimethyl ammonium chloride) PVBTMAC. It was shown that heavy metals could be dramatically removed from a synthetic solution, even at low pH. For example,

Metal	Concentration of Metal Ion mg/l	pH of Solution	Volume Starch Xanthate PVBTMAC Solution (1%) Added	Residual Metal Concentration ug/l
Cd^{++}	56.2	3.1	4.65 ml	8
Cr^{+++}	26.0	4.5	3.45 ml	52
Cu^{++}	31.8	3.0	4.50 ml	12
Pb^{++}	104.0	8	4.60	8
Hg^{++}	100.0	3.2	4.70	3.8
Ag^{++}	54.0	3.2	4.52	3
Zn^{++}	32.7	3.3	4.10	3,300

It is undersood that the work on starch xanthate with polymer addition has continued. Information has been requested from:

MR. ROBERT E. WING
Northern Regional Research Center
Agricultural Research Service
U.S. Dept. of Agriculture
1815 North University
Peoria, IL 61604
(309) 685-4011
Dr. Robert E. Wing

The PVBTMAC used in the development work was an experimental resin QX-2611.7 manufactured by the DOW CHEMICAL COMPANY, Midland, Michigan.

59. Another frontier treatment technology of potential interest, although to date inadequate information on cost has been made available to determine whether it could be considered for use in mine-mill effluent or process water treatment, is the DEVOE-HOLBEIN technology.

DEVOE-HOLBEIN (CANADA) LTD. has formulated experimental compositions which are capable of very specific metal removal and the removal of metals to extremely low levels. For example:

Metal	D-H Composition Used	Starting Concentration	Treated Water Concentration
Cd	B1	10 ppm	0.1 ppb
Cu	W-3	38.1 ppm	LT 1.0 ppt
Cu	A-1	381 ppm	3.8 ppt

Metal Cation	g Metal Removed per Liter DX-2000
Ag^{+1}	300
Au^{+1}	550
Cd^{+2}	155
Cu^{+2}	89
Pb	Not Shown
Zn^{+2}	91

The chelation compound DX-2000 is not designed for solution polishing to below 0.30-2.0 ppm levels. It is designed for macro removal of metals that are complexed and, therefore, do not precipitate easily using other processes.

The same company also manufactures an insoluble starch xanthate product designed for solution polishing for which a technical data sheet is shown below.

POLLUTION TECHNOLOGY SYSTEMS, INC. also offers design and engineering services along with their process. More information is available from:

POLLUTION TECHNOLOGY SYSTEMS, INC.
3015 Benton Street
Garland, TX 75042
(214) 272-4010
Mike Coward
Manager, Systems Engineering

61. RANDALL, et al. (1975) of the U.S. Dept. of Agriculture were granted U.S. Patent 3,925,192 for the removal of metal ions from water using formaldehyde-modified nut waste, e.g., peanut shells. Removal of mercury, silver, nickel, and lead to sub-ppm levels was demonstrated, but it is not clear what volume of water can be treated by a ton of modified nut waste. Possibly, the nut waste and formaldehyde provide organic energy for anaerobic bacteria that convert sulfates to sulfide and may be the mechanism?

    45 g formaldehyde modified hemlock bark was able to remove lead to less than 0.3 ppm from 60 l of solution containing 20 mg/l Pb.

62. Industrial effluent treatment for zinc removal has been achieved using precipitation and ion exchange. The most common precipitation method is by lime precipitation or precipitation with caustic. Generally, treatment is not for zinc alone.

63. Cyanide or chromate are often present with zinc in plating wastes and cyanide with zinc in many gold or leaching operations. Cyanide and chromate must be removed before zinc can be precipitated as a hydroxide.

POLLUTION TECHNOLOGY SYSTEMS, INC.

2922 BENTON STREET
GARLAND, TEXAS 75042
(214) 272-4010

INDUSTRIAL WASTEWATER MANAGEMENT PRODUCTS AND SERVICES

TECHNICAL DATA SHEET

NOMENCLATURE:

DX-2000

GRADE:

Technical

TYPICAL PROPERTIES:

Physical Form	Yellow Liquid
Specific Gravity	1.140 @ 30 C
pH	10.5
Solubility	Soluble in Water
Concentration	40 percent

CONTAINERS:

500 Net Pounds/55 Gallons
Phenolic Lined

USES:

DX-2000 is a buffered organic material that effectively precipitates complexed or chelated cationic heavy metal concentrations of 10 mg/l or greater from difficult-to-treat industrial process waters. The product is effective over a pH range of 3 to 11. Residual heavy metal concentrations following treatment with DX-2000 are usually well below local, state and EPA-NPDES discharge limit permit requirements.

APPLICATION:

Batch or continous flow injection of predetermined dosage for maximum heavy metal cation removal from process aqueous solution containing constituents greater than 10ppm. Thoroughly mix, allowing adequate contact time. Cationic polymer may aid in sludge settling and removal. Sludge is removed by filtration, clarification or centrifuge. Effective cation heavy metal removal over a pH range of 3-11. Adjustments in dosage and pH may optimize effectivness and economics.

RECOMMENDED DOSAGE:

Metal Cation	Grams of Metal Removed per liter DX-2000 (1)
Ag^{+1}	300
Au^{+1}	550
Cd^{+2}	155
Co^{+2}	83
Cu^{+2}	89
Fe^{+2}	78
Hg^{+2}	280
Mn^{+2}	77
Ni^{+2}	82
Zn^{+2}	91

NOTE: (1) Based on Molecular Weight Theoretical Capacity.

TECHNICAL DATA SHEET

POLLUTION TECHNOLOGY SYSTEMS, INC.

2922 BENTON STREET
GARLAND, TEXAS 75042
(214) 272-4010

INDUSTRIAL WASTEWATER MANAGEMENT PRODUCTS AND SERVICES

NOMENCLATURE:

Insoluble Starch Xanthate
ISX/5-CM

GRADE:

Technical

DESCRIPTION:

ISX/5-CM is a yellow colored highly crosslinked xanthate starch in powder form with a light pungent odor.

PARTICLE SIZE:

20 Microns, aqueous solution

COMPOSITION:

Sulfur Total	18 Percent
Sulfur Xanthate	12 Percent
Ash (Sodium & Magnesium)	18 Percent
Caustic	14 Percent
H_2O	35 Percent

TYPICAL PROPERTIES:

Stored	45 F	6 Months
Stored	70 F	3 Percent(1)

NOTE: (1) Xanthate sulfur reduction in 7 days.

CONTAINERS:

Standard unit 25 & 250 pounds net.

USES:

Instantaneous heavy metal cation removal upon contact from industrial and mining process and wastewaters. As an inexpensive final polish of singular or combined heavy metal cations of less than 10ppm in aqueous solution.

APPLICATION:

Filter precoat, batch or slurry. Easily dewaters to less than 50 percent by volume. Recommended pH 3-11 with maximum effectiveness at a pH of approximately 7 for most heavy metal cations. Recommended weight capacity ratios of ISX/5-CM for heavy metal cations in aqueous solution are as follows:

Ag^{+1}	Silver	6.5:1
Au^{+1}	Gold	3.5:1
Cd^{+2}	Cadmium	12.0:1
Co^{+2}	Cobalt	23.0:1
Cr^{+3}	Chromium	40.0:1
Cu^{+2}	Copper	21.0:1
Fe^{+2}	Iron	24.0:1
Hg^{+2}	Mercury	7.0:1
Mn^{+2}	Manganese	25.0:1
Ni^{+2}	Nickel	23.0:1
Pb^{+2}	Lead	6.5:1
Sn^{+2}	Tin	12.0:1
Zn^{+2}	Zinc	21.0:1

Dependent on end user specific needs, variations of pH and ISX/5-CM weight capacity ratios will optimize product efficiency.

PTS 1153

64. Settling efficiency of zinc hydroxide precipitate affects effluent concentrations with significant improvement if the effluent is filtered after decantation.

65. Sulfide precipitation at pH 2 has been reported to achieve "complete removal" of zinc from an electrolytic nickel recovery system by BANERJEE and BANERJEE (1952).

Sodium sulfide treatment of a gold ore refining waste initially containing zinc at 42 mg/l achieved precipitation to 1.16 mg/l at a treatment pH of 7 according to ROSEHART and LEE (1972). Treatment of the same waste by caustic at pH 10 reduced zinc to 0.02 mg/l.

66. LARSEN, et al. (1973) reported that treatment of acid mine drainage containing 122-294 mg Zn/l by lime addition to pH 5.0-5.5 for Al and Fe precipitation followed by sulfide addition at pH 5.5-6.4 produced variable zinc levels in the effluent ranging from 0.20-30.0 mg/l, indicating that sulfide precipitation of zinc may not always be straightforward.

67. DUPONT's Kastone process employing copper catalyst, hydrogen peroxide, and stabilizers oxidizes cyanide and promotes the formation of metal oxides rather than hydroxides which, in small metal finishing plants, are more easily filtered.

On the other hand, CHAMBERLAIN and ANDERSON (1971) were able to demonstrate selective zinc removal from 6 to 0.4 mg/l from cooling tower blowdown.

PATTERSON (1975) concluded that lime precipitation of zinc can generally achieve levels below 1 mg/l, although assurance of consistant removal of the precipitate from the effluent may require sand filtration and adequate pH control.

68. Ion exchange can be used as a recovery method for zinc at very high concentrations although no cases are known where this is economically used on a commercial scale except at viscous rayon plants where zinc is present at very high levels. For mining and metallurgical operations, IX would be most unlikely to be useful except possibly for polishing of a final effluent. Laboratory studies by KANTAWALA and TOMLINSON (1964) found that at flow rates of 2.5 gal/hr/ft^2, ion exchange was less effective than lime precipitation for zinc removal.

WILMOTH, et al. (1979) reported that reverse osmosis and ion exchange were slightly more effective than neutralization for removal of As, Cd, Cu, Hg, Ni, Se, and Zn.

69. The demonstration seeded slurry reverse osmosis system installed at ERPM (RAND MINES, South Africa), although installed to demonstrate water recovery, did reduce zinc from 2 ppm in the feedwater to 0.1 ppm Zn in the product demonstrating that

zinc can be effectively removed by reverse osmosis at pH 4-5 through a cellulose acetate membrane. More information on seeded slurry R.O. can be obtained from

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Tom Wolfe

70. As mentioned above in the discussion on copper and lead removal, very low levels of zinc can be achieved in effluents treated by starch or cellulose xanthates and also with the compositions of DEVOE-HOLBEIN (CANADA), INC., which in tests have achieved removal of zinc to below 20 parts per trillion.

71. HERMAN (?) described the use of the high density sludge HDS process to drop soluble copper, cadmium, zinc, nickel, and lead to below 0.1 ppm at a single pH level while generating a sludge with in excess of 20% solids compared with 1% solids by conventional neutralization.

72. ST. JOE MINERALS reported removing zinc by lime precipitation from 27 ppm Zn and 1.65 ppm Pb in the feed stream to 2.6 ppm Zn and 1.5 ppm Pb in the reactor clarifier overfow and to 0.11 ppm Zn and 0.17 ppm Pb in the SVG overflow at pH 9.

73. COCHECI, et al. (1983) reported purification of effluents from a nonferrous metallurgical operation by precipitation with calcium polysulfide and simultaneous recovery of useful metals.

74. <u>Ion Flotation</u>

ISUMI, et al. (1976) described removal of heavy metal ions, i.e., Cu, Pb, Zn, Ni, Cd, Co, and Mn, which were recovered from real and simulated waste waters by a foam separation method using N-decanoyl diethylenetriamine [N-[2-[(2-aminoethyl) amino]ethyl]decanamide]. The reagent forms soluble and foamy complexes with the metals.

In this process, Cu and Zn are recovered from the precipitate. The supernatant is filtered, neutralized, and treated again with Ca polysulfide and refiltered to give an effluent that meets disposal standards.

75. IKEBE (1974) described an interesting chemical scheme for removal of heavy metal ions from metallurgical and mining effluents.

Heavy metal ions, especially Cu^{2+} and Hg^{2+}, are sequestered with a dealkyldithiocarbamic acid and are treated with NaOH and Na_2S or two equivalents of the metal dialkyldithiocarbamate in a suspension of the salt with a pulp concentration of 1-3

mole/l to produce a scum of CuS or PbS. The sulfide scum is separated either by precipitation or flotation and after regeneration, the dialkyldithiocarbamate ion is recycled. The process is useful in treating waste water containing heavy metal ions, and the dialkyldithiocarbamate can be recovered quantitatively and recycled.

The use of NaOH in this process improves the separation efficiency by preventing the formation of colloidal CuS. Thus, $Cu[S(S)CNEt_2]_2$ was suspended in one l water (pulp density 5×10^{-2} mole/l), and 2 g NaOH were added and stirred. Na_2S at one mole/l was then added, and the CuS formed was removed by precipitation. When one equivalent of Na_2S was added, approximately 100% of the $NaS(S)CNEt_2$ was recovered. The light yellow liquid recovered had a pH of 12.8 and contained only 1-2 ppm Cu. The recovered liquid could be recycled for additional Cu removal. When NaOH was not used in a similar process, 100% of the $NaS(S)CNEt_2$ was recovered, but about 35% of the colloidal CuS was also present in the recovered liquid.

The author, according to Chemical Abstracts CA 83(8):65183V, is employed at the SUMITOMO CHEMICAL COMPANY in Japan.

76. KAIDA, et al. (1978) described a bench scale treatment of mine effluent containing iron, copper, Cd, and zinc. The process employs catalytic air oxidation of ferrous to ferric ions using $NaNO_2$, fractional precipitation of $Fe(OH)_3$, neutralization, coagulation and sedimentation, flotation, and sludge treatment. The concentration of heavy metals in the effluent was reduced from 549 mg/l to 0.91 mg/l for Zn; 4.92 to 0.04 mg/l for Cd, Cu and Fe were not detected in the treated effluent. The unusual aspect of this process is the oxidation of Fe^{2+} to Fe^{3+} at low pH and the removal of Cu and Fe to their detection limit if the claim is accurate.

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.)	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon (U.S.)	0.05841
Milligrams per liter	Tons per acre-foot	.001360
Tons per acre	Metric tons per hectare	2.217
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Gallons (Imperial)	Gallons (U.S.)	1.2009
Acre-feet	Gallons	325,851
Acre-feet	Cubic feet	43,560
Cubic feet	Cubic meters	.028317
Cubic feet	Gallons	7.481
Cubic meters	U.S. Gallons	264.2
Cubic meters	Imp. Gallons	220.0
1,000 m^3/d	I gpm	152.8
1,000 m^3/d	U.S. gpm	183.6
U.S. gallon	Cubic meter	0.3785

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Summary

Cyanide is metallurgically the most suitable lixiviant for the leaching of gold and silver from many ores and concentrates and gold from calcines after the roasting of otherwise refractory sulfide concentrates. Cyanide is also used as a depressant in the selective flotation of sulfide minerals, for example in the depression of pyrite from base mineral sulfides, and in the separation of copper-lead and copper-molybdenum sulfide flotation bulk concentrates.

Cyanide also usually occurs as a metallurgical contaminant in groundwater around aluminum cell potlines as a result of interaction between air and the carbon electrodes. 200 ppm cyanide as ferrocyanide was detected in groundwater around a typical potline. Cyanide is generated in the manufacture of coke and processes have been or are being developed for its removal from effluent streams in which it occurs.

At a current cost of US$0.40 - $0.80/lb depending on location, cyanide is used in relatively small dosages (Average 1-1.5 lbs/ton ore) and offers a significant economic advantage over other leaching reagents for the conventional leaching of gold and silver. Without the development of cyanide as a leaching means, it is possible that the full potential of the Witwatersrand - a major source of the world's accumulated gold supply - might never have been reachable.

Cyanide also offers the definite environmental advantage of being "biodegradable" under favorable climatic conditions and there is evidence that cyanide does not persist for a

long time in the environment (HUIATT, 1984). Yet the lethal toxicity of cyanide in large doses to mammals and its use in executions or dramatic suicide attempts has set cyanide apart from other equally or more toxic reagents and invokes a degree of unjustifiable paranoia in the minds of those not familiar with its use.

Although low levels of cyanide generally encountered in metallurgical operations and treated with appropriate respect are not difficult to handle safely without accident or injury to humans, levels as low as 0.1 ppm and below of free cyande are shown to be very detrimental to aquatic life. Much more insight and knowledge is needed as to the environmental effects and "non-effects" of cyanide in the forms in which it occurs in effluent streams to determine what levels and forms can safely be tolerated in nature. Meanwhile, regulations controlling the discharge of cyanide and complex cyanides in effluents are in several countries not yet clearly formulated.

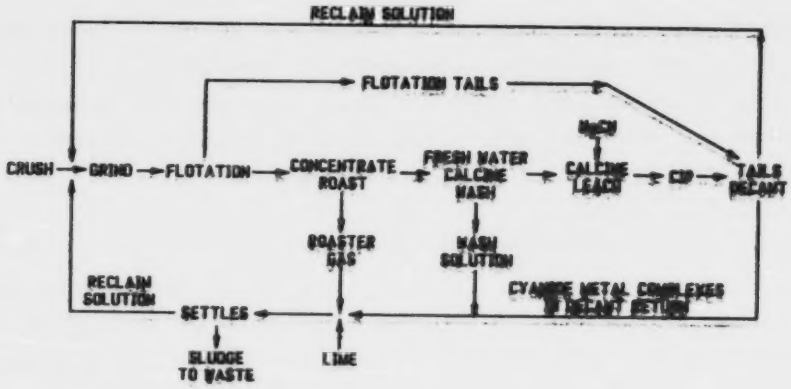
This section of the report deals with how cyanide can be decomposed or removed from metallurgical effluents and tailings. Control of and understanding the environmental and process effects of cyanide requires accurate analyses, and it is essential therefore to review the various analytical methods that are available, the sources of interference and what the results obtained by each method mean. There is likely to be continued controversy and debate as to the merits of existing regulatory limits or what additional limits need to be set and on which method of analysis the limits should be based. For this reason cyanide analysis is discussed here in some depth.

There are several cyanide removal processes available and it is important to gain an insight into what species are removed, what byproducts are generated and how well the processes work in practice compared with laboratory tests. Climate, regional regulatory requirements and the nature of effluent chemistry as well as the receiving waters all have an effect on the applicability of the various cyanide decomposition and removal processes. Finally it is necessary to gather and review data on the cost and performance of several of these processes installed in actual plant conditions.

Some argue that environmental toxicity data presented so far are meaningless due to the uncertainties in analysis methods, and because cyanide used in the toxicity test is dosed to synthetic solutions that do not represent real mine effluents. Others have recently produced a large amount of data on toxicity of cyanide and complex cyanide which they have presented as compelling evidence. The data available on the whole subject is presented here with the intention of remaining impartial and without making any recommendations as to how it should be regulated.

Complete books have and will be written on the subject, meanwhile the most pertinent points considered to be of practical value on cyanide treatment processes are discussed under the following headings:

- Cyanide in metallurgical effluents
- The advantages of cyanide
- Regulations governing cyanide in tailings and effluents
- Motivation to remove cyanide from effluents
- The chemistry of cyanide
- Analytical determination of "cyanides"
- Methods for removing or destroying "cyanides"



Cyanides in Metallurgical Effluents

The greatest use of cyanide in mineral processing is for gold leaching. Free world consumption of cyanide for this purpose amounts to a guestimated 75,000 tons per year of sodium and calcium cyanides combined.

Canada for example, in 1979, produced around 60 tons of gold by treating 6.2 million tons of ore per year consuming 2,820 tons of sodium and calcium cyanide annually. This works out to 17,000 tons ore per day requiring 7,700 Kg sodium and cyanide daily according to SCOTT & INGLES (1981).

By far the largest amount of cyanide used for gold processing is consumed in South Africa where a guestimated 130,000 tons per year of calcium and sodium cyanide was consumed in this industry in 1983, nearly all of it in the giant Witwatersrand and Orange Free State gold mines. In this generally arid country water is recycled on a macro scale yet cyanide contamination problems even there where the gold mining industry forms the nucleus of the industrial heartland of the country, could be rated as minimal, if any.

Cyanide in gold and silver leaching effluents occur in several streams. Firstly, some cyanide remains in the leached tailings from the gold plant and is pumped to the tailings impoundment with the tailings or, if backfill is practiced, some may return underground with the sand fraction of mill tailings. Table 1 shows the wastewater

characteristics of minewater and tailings impoundment water from the Homestake Mine as reported by WHITLOCK, Terry I., and MUDDER, James L. (1984).

Data on gold mining effluents from seven gold mines in Ontario as reported by MILGRAM (1982) are shown in Table 2.

Table 3 reports data on cyanide and thiocyanate as they appeared in the proceedings of a comprehensive Workshop Proceedings edited by HUIATT, et al. (1982).

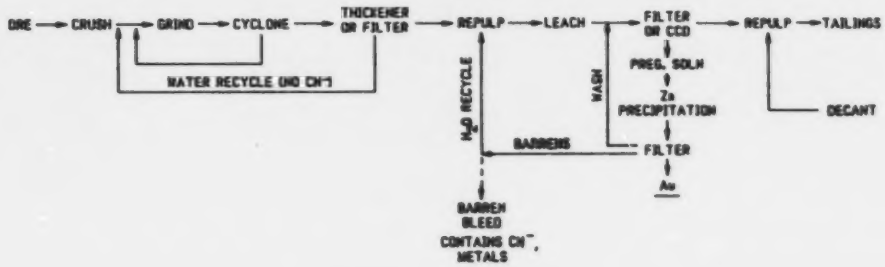
Table 4 lists water quality data for several additional Canadian mills as well as one South African gold plant effluent.

Influence of Metallurgical Process on Cyanide Levels

Several process selection decisions have a significant effect on the cyanide levels in gold and silver recovery tailings and effluents. The most significant of these is the extent to which cyanide bearing solutions are recirculated.

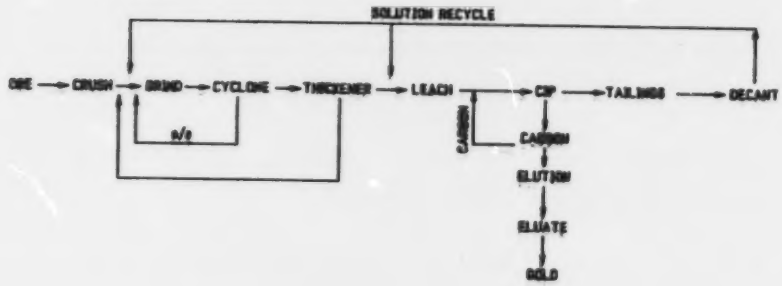
1) Conventional Leach - Merrill-Crowe Zn Precipitation

Non-cyanide grinding circuit
Cyanide leach circuit
Filtration or CCD washing recovers 99% Au and CN^-
Repulp of tailings with tailings return water

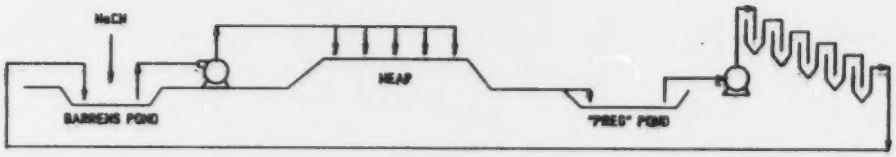


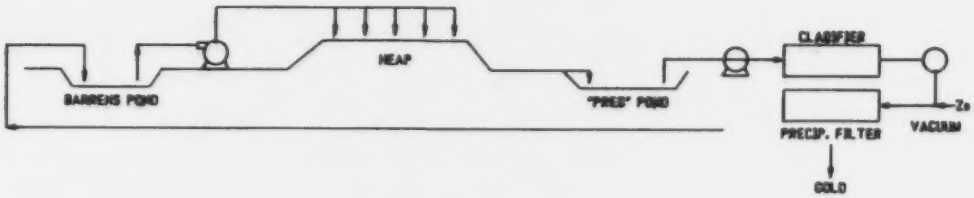
2) Carbon in pulp

Crush
Grind with or without cyanide
Leach with or without carbon
Tailings to tailings pond without washing



3) <u>Heap leaching</u>





In the first and third basic process flowsheets it will be noted that the opportunity exists to recycle cyanide with the recirculating leach solution.

In the case of the conventional leach/Merrill-Crowe process it is possible to maintain the grinding circuit as cyanide free. After leaching and solid/liquid separation gold and soluble cyanides are washed from the pulp and after gold is recovered the barren solution is returned to the front end of the leach. As undesirable soluble salts build up to a point that they interfere with the process the system is bled and solution made up with fresh water. The extent of the barren bleed depends on the nature of the ore.

In the carbon in pulp process which is more applicable to gold ores than silver, the cyanide present in the leach pulp advances through the CIP step to tailings. There is some recycle of cyanide possible in tailings return water but mostly it is lost through natural or biodegradation.

When the gold or silver ore contains cyanide-soluble copper then an excess of cyanide over that required to complex the copper must usually be added to leach gold and silver. Since copper cyanide reports as "free" cyanide, usually 5 moles cyanide are added per mole copper to find the correct amount needed. For example, the Battle Mountain operations of Duval Corp. treating a copper rich ore use 2 Kg NaCN/ton ore compared with the industry average of 0.7 Kg/t (1.5 lbs NaCN/t). Noranda Grey Eagle Mines with a higher copper level uses about 4 Kg NaCN/t ore.

As copper cyanides build up in the solution due to recycling of solution then it reaches a point at which it interferes with zinc precipitation of gold and silver. Then the "poisoned" cyanide solution historically called foul liquor is partially purged from the system as a barren bleed and made up with fresh solution.

In general CIP is more applicable for high copper and nickel ores than the Merrill-Crowe conventional process. However, to make the carbon adsorption process work best it is then necessary to maintain an excess of cyanide in solution - which ends up in the tailings. Also, because of the high copper values the tailings solution cannot be recycled to the leaching step without expensive special steps which are not currently known to be cost effective.

Consequently tailings from CIP circuits are likely to be higher in cyanide than tailings from the conventional agitation leach and zinc precipitation processes even for the treatment of normal free milling ores low in copper and nickel.

TABLE O
Cyanide Consumption Estimates

	Year	Reference	Tons/day Ore	Kg cyanide/d	Kg cyanide ton ore	tons cyanide/ year
Ontario Total	1983	1	10,000	4,166		1,520 tpa
Canada Total	1979	2	17,000	7,700		2,820 tpa
Est.	1985	2	35,000	15,900		5,800 tpa
OK Tedi	1984	3	17,000	8,500	0.5 Kg/t	3,102 tpa
USA						
Noranda Grey Eagle	1984	4	500	2,000	4.0 Kg/t	730 tpa
Duval Battle Mtn.	1984	5	3,500	7,000	2.0 Kg/t	2,555 tpa
South Africa Total	1984		301,000		0.28 Kg/t	30,800 tpa
Total "Free" World	1984	est.				75,000 tpa

References

1. MILGRAM (1984) MOE, Ontario
2. SCOTT & INGLES (1981) 1985 est. less 10,000 tpd for Cons Cinola
3. LAMMERS J. M. (1984)
4. Public Document "Program to Control Cyanide Seepage"
5. TODD & ANDERSON (1984)

Table 1

HOMESTAKE MINE WASTEWATER CHARACTERISTICS

PARAMETER	MINEWATER[1]	TAILINGS IMPOUNDMENT WATER[1]
Thiocyanide	1.0 - 16.0	110.0 - 240.0
Total Cyanide	.10 - .50	7.00 - 30.00
Method-C Cyanide	.02 - .10	4.00 - 20.00
Iron	.10 - 10.00	1.50 - 6.00
Copper	.07 - 1.60	1.40 - 6.00
Nickel	.01 - .04	.20 - .40
Zinc	.01 - .10	.01 - 1.50
Ammonia-N	5.0 - 6.0	less than 1.0
Phosphorous-P	trace	trace
pH	5.0 - 6.5	7.00 - 9.5
Temperature (F°)	70 - 85	34.70

1 - All values in mg/l except temperature and pH.

Note: The actual wastewater ratio is varied throughout the year from 70/30 mine/tailings impoundment wastewater ratio in the winter to 50/50 mine/tailings impoundment wastewater ratio in the summer.

Source: WHITLOCK & MUDDER (1984)

Table 2

ONTARIO GOLD MINING EFFLUENTS

The following data summary calculated from seven mine/mill complexes gives representative averages for each of the parameters listed. The data are simple arithmetic averages with exclusion of erratic numbers. All units are expressed in ppm with the exception of Hg which is expressed in ppb.

DATA SUMMARY

PARAMETER	DECANT	RANGE	MINE WATER BLEED	RANGE	BARREN	RANGE
HCN*	1.2	0.01 - 12.5	0.01	0.01 - 2.0	334	40 - 750
K	-	-	-	-	35	26 - 50
Ca	77.8	39 - 510	351	65 - 760	406	150 - 940
Na	-	-	-	-	657	210 - 1160
Cl	86	32 - 130	46	26 - 68	503	82 - 1230
Cd	0.01	0.01 - 0.005	0.01	0.005 - 0.01	0.01	0.005 - 0.01
Co	0.04	0.02 - 0.58	0.04	0.01 - 0.11	0.50	0.09 - 1.5
n	-.09	0.01 - 1.8	0.15	0.01 - 0.42	0.05	0.01 - 0.18
Mg	23.6	6.0 - 36	98	0.25 - 170	0.19	0.10 - 0.4
Fe	0.65	0.44 - 2.2	0.78	0.11 - 2.8	3.3	0.1 - 10.0
Pb	0.06	0.03 - 0.1	0.06	0.06 - 0.1	0.08	0.06 - 0.2
As	0.069	0.003 - 4.9	0.06	0.012 - 0.25	0.94	0.011 - 4.0
Cu	1.05	0.01 - 17	0.08	0.01 - 420	29.1	9.7 - 390
Zn	0.16	0.02 - 20	0.08	0.01 - 48	40.1	1.5 - 94
Cr	0.05	0.004 - 0.08	0.05	0.02 - 0.08	0.06	0.02 - 0.08
P	0.05	0.04 - 0.08	0.04	0.04 - 0.18	0.5	0.04 - 1.1
Hg	0.07	0.02 - 0.11	0.05	0.02 - 0.09	0.03	0.02 - 0.05
Ti	0.32	0.02 - 10	0.15	0.04 - 0.1	0.03	0.02 - 0.04
Ni	0.47	0.02 - 2.28	0.17	0.04 - 3.8	12.7	2.4 - 140
Ag	0.03	0.01 - 0.04	0.02	0.005 - 0.4	0.04	0.01 - 0.06
Ba	0.16	0.02 - 0.15	0.1	0.04 - 0.2	0.36	0.03 - 1.1
Mo	0.11	0.02 - 0.37	0.4	0.02 - 1.6	1.4	0.04 - 5.2
Li	0.019	0.005 - 0.01	0.01	0.01 - 0.02	0.01	0.005 - 0.01
Al	0.32	0.20 - 0.45	0.26	0.08 - 0.47	0.68	0.2 - 0.63

* Total CN expressed as HCN

Source: MILGRAM (1982)

Table 3

CHEMICAL ANALYSES OF CANADIAN GOLD MILL BARREN SOLUTIONS AND TAILINGS POND EFFLUENTS [1,2]

Plant	Solution	Volume[3]	Fe	Ni	Zn	Cu	CN	S.S	SCN
A	Barren		35.7	2.9	17.9	73.0	220.0	-	180
	Effluent	200,000	0.6	0.4	0.82	2.4	13.0	17	
B	Barren		21.4	10.0	62.5	6.7	300.0	-	54
	Effluent	516,000	8.2	0.7	0.70	1.1	3.3	37	
C	Barren		0.4	1.7	84.1	11.0	610.0	-	400
	Effluent	1,500,000	0.3	0.1	0.20	2.3	6.8	24	
D	Barren		0.1	0.3	13.9	6.1	86.0		42
	Effluent	7,200,000	N.A.	0.4	0.19	0.3	0.3	10	
E	Barren		0.1	9	31.0	29.0	74.0		50
	Effluent	1,678,000	N.A.	0.2	0.13	0.5	1.2	19	
F	Barren		0.8	3.1	12.0	300.0	310.0		N.A.
	Effluent	915,000	N.A.	1.8	0.60	16.0	26.5	53	

1. Units in mg/1 unless otherwise noted.

2. The above analyses are for grab samples taken in 1978. Arsenic was found in the waste barren solution from Canadian ores in the range of 0.01 to 0.13 mg/1. The range reported in the final tailings effluent was 0.01 to 21.4 mg/1.

3. Imperial gallons per day (IGPD).

Adapted from HARRISON 1979; cited by SCOTT 1981

Source: HUIATT et al. (1982).

Table 4

GOLD MILL TAILINGS

	1	2	3	4	5	6	7	8	9	10
pH	9.5	9.5	10.5	9.8		9.0		8.0	11.0	8.0
Cu	55	0.4	62	0.5	35.0	1-10	17	0.2-2	20	1-5
Pb										
Fe	80	0.4	35	0.2	1.5	LT 0.5	0.7	0.02-0.3	6	0.3
Cd										
Ni	35	1.6	50	0.2						
Hg										
Zn	35	LT 0.2	78	0.2	66	0.5-2	18	LT 0.1	90	0.01-0.2
CN avail.										
CN_T	890	1.6	665	0.7	450	0.1-2	115	0.1-1.0	240	0.1-0.3
NaCNS										
As										
Co										
TSS										
Flow										

1. Campbell Red Lake Barren Bleed before treatment as reported by DEVUYST et al. (1984)

2. Campbell Red Lake (1) Barren Bleed after treatment by SO_2 process DEVUYST et al. (1984)

3. Campbell Red Lake Barren Bleed before treatment as reported by DEVUYST et al. (1984)

4. Campbell Red Lake (2) Barren Bleed after treatment by SO_2 process DEVUYST et al. (1984)

5. Scottie Gold Garren Bleed before treatment DEVUYST et al. (1984)

6, Scottie Gold Barren Bleed (5) treated by SO_4 DEVUYST et al. (1984)

7. Scottie Gold Mill Tails before treatment DEVUYST et al. (1984)

8. Scottie Gold Mills Tails (7) treated by SO_2 process DEVUYST et al. (1984)

9. Dupont Baker Lake sump & mill tails untreated DEVUYST et al. (1984)

10 Dupont Baker Lake sump & mill tails treated by SO_2 process DEVUYST et al. (1984)

Table 4 (Continued)

GOLD MILL TAILINGS

	11	12	13	14	15	16	17	18
pH	11.00	9.6	9.0	8.7	10.1	8.2	7.7	8.8
Cu	350	5-15	13-15	0.5-5	130	0.8	0.1	6.87
Pb								
Fe	75	0.1-0.3	1.0-3.2	0.1-0.3	16.7	18.7	1.5	-
Cd								
Ni				5.1	0.2	0.05	1.23	
Hg								
Zn					84.6	0.7	0.2	0.10
CN avail.								
CN_T	1500	3-10	11-19	0.3-2	400	0.5	1.3	8.6
NaCNS								
As					11.0	0.5	5.1	12.1
Co								
TSS					12.2	24,000	840	-
Flow (Igpd)					71K	655K	220K	1,100K

11. Carolin Mines barren bleed Untreated DEVUYST et al. (1984)

12. Carolin Mines barren bleed treated by SO_2 DEVUYST et al. (1984)

13. Carolin Mines mill tails & treated barren DEVUYST et al. (1984)

14. Carolin Mines final tailings after SO_2 treatment to pond DEVUYST et al. (1984)

15. Giant Yellowknife barren bleed before treatment HALVERSON & CROSS (1984)

16. Giant Yellowknife tailings before treatment HALVERSON & CROSS (1984)

17. Giant Yellowknife minewater before treatment HALVERSON & CROSS (1984)

18. Giant Yellowknife tailings pond before treatment HALVERSON & CROSS (1984)

Table 4 (Continued)

GOLD MILL TAILINGS

	19	20	21	22	23
pH	7.7		11.9	11.6	10.5
Cu	0.08	1-10	11.6	1.11	1.11
Pb			LT 0.05	LT 0.05	LT 0.05
Fe	1		0.84	0.85	0.88
Cd			LT 0.005	LT 0.005	LT 0.005
Ni	0.11	1-15	0.5	0.67	LT 0.05
Hg			0.52 mg/l	0.04 mg/l	0.01 mg/l
Zn	0.05	10-30	1.11	1.09	0.13
CN avail.			39.0	38.5	3.3
CN_T	0.20	50-80	39.0	38.5	3.3
NaCNS		40-70			
As	0.14		LT 0.003	LT 0.003	LT 0.003
Co		0.1-1.0			
TSS	1.2		LT 1.0	LT 1.0	5.0
Flow	1,100K	0.01-0.04 Au			

19. Giant Yellowknife tailings decant after treatment HALVERSON & CROSS (1984)

20. South African Gold Plant effluent - Stilfontein GOLDBLATT (1959)

21. Le Mine Doyon, Quebec Tailings Pond HOPE (1984)

22. Le Mine Doyon, Quebec Final Effluent HOPE (1984)

23. Le Mine Doyon, Quebec After dilution Russeau Lac Billot HOPE (1984)

Table 4 (Continued)

GOLD MILL TAILINGS

	19	20	21	22	23
pH	7.7		11.9	11.6	10.5
Cu	0.08	1-10	11.6	1.11	1.11
Pb			LT 0.05	LT 0.05	LT 0.05
Fe	1		0.84	0.85	0.88
Cd			LT 0.005	LT 0.005	LT 0.005
Ni	0.11	1-15	0.5	0.67	LT 0.05
Hg			0.52 mg/l	0.04 mg/l	0.01 mg/l
Zn	0.05	10-30	1.11	1.09	0.13
CN avail.			39.0	38.5	3.3
CN_T	0.20	50-80	39.0	38.5	3.3
NaCNS		40-70			
As	0.14		LT 0.003	LT 0.003	LT 0.003
Co		0.1-1.0			
TSS	1.2		LT 1.0	LT 1.0	5.0
Flow	1,100K	0.01-0.04 Au			

19. Giant Yellowknife tailings decant after treatment HALVERSON & CROSS (1984)

20. South African Gold Plant effluent - Stilfontein GOLDBLATT (1959)

21. Le Mine Doyon, Quebec Tailings Pond HOPE (1984)

22. Le Mine Doyon, Quebec Final Effluent HOPE (1984)

23. Le Mine Doyon, Quebec After dilution Russeau Lac Billot HOPE (1984)

Table 4 (Continued)

GOLD MILL TAILINGS

	24	25	26	27	28	29	30
pH	7.4	5.9-6.5	7.9	7.7	9.74		
Cu				2.85	0.09	41.9	0.14
Pb				0.17	0.08		
Fe							
Cd							
Ni							
Hg							
Zn				3.27	0.43		
CN avail.							
CN_T	0.5	0.5		4.72	0.18	68.3	0.13
NaCNS							
As							
Co							
TSS	43	16	7				
Flow		750m³/h	1666m³/h				
TDS	3101	3352	1939				
$CaCO_3$ Hardness	1869	1981	984				
$SO_4^{=}$	1834	2051	984		380		
Cl^-	136	136	170				
F	1	1	1				
Na	190	182	210				
K	36	46	9				
$PO_4^{=}$	1	1	1				
Cl_2					+0.1 mg/l		

24. ERGO, South Africa Tailings Dam decant water after repulping old gold tailings, then flotation of gold and pyrite, then U leach in sulfuric acid
25. ERGO, discharge of plant effluent to stream "Complex" Water
26. "Sallies" Minewater Witwatersrand Mine Drainage pumped as feedwater to ERGO
27. Final Effluent Untreated, Western Mining Myra Falls Cu-Pb-Au Flotation ECCLES (1977)
28. Final Effluent Treated, Western Mining Myra Falls Cu-Pb-Au Flotation ECCLES (1977)
29. Chlorination Plant Feed Dec. 1975 ECCLES (1977)
30. Chlorination Plant Product Dec. 1975 ECCLES (1977)

THE EFFECTS OF CYANIDE-BEARING, GOLD TAILINGS DISPOSAL ON WATER QUALITY IN THE WITWATERSRAND, SOUTH AFRICA

by
Adrian Smith , Alison Dehrmann and Rob Pullen

INTRODUCTION

The workshop on "Cyanide in Mineral Processing" held in Salt Lake City in February 1982 identified the following problems with respect to the fate of cyanide in the environment:

> "Limited information is available on the fate of cyanide from leaching and flotation operations in soils, aquifers, and/or old tailings dumps. Temperature, natural oxidants, sunlight, bacteria, organic and inorganic materials, type of soils, water chemistry, mineral constituents of tailings, permeabilities of soils and tailings, type of cyanide compound, concentration of the cyanide compound, rate of migration of cyanides, and materials of construction and design of leach pads and tailings ponds all have an effect on the ultimate fate of cyanide in the environment. Accurate knowledge of the fate of cyanide is necessary if meaningful, practical regulations are to be established for monitoring or controlling mineral process effluents. Nearly all regulations are now handled on a site-specific basis. Any information concerning fate of cyanides and related compounds will be of considerable value to the mine operator and to the monitoring agency."

For the past two years, Steffen Robertson and Kirsten have been cumulating information on the levels of cyanides in tailings, surface waters and near-surface groundwaters associated with cyanide-bearing gold tailings disposal from Witwatersrand, South Africa. In addition, cyanide data has been collated from the drilling and monitoring of tailings impoundments allowing the construction of a cyanide profile through the tailings mass. It is believed that these data will serve as a useful adjunct to data from North America tailings disposal operations.

The collection of data is not complete. This paper represents a presentation of the data available as of November 1984 and may be considered an interim statement of results. Due to the confidential nature of individual data, no specific sources have been identified and remain entirely anonymous. This does not detach from the value of the data which are considered to represent the Witwatersrand area as a whole.

Steffen, Robertson & Kirsten (B.C.) Inc., Vancouver, Canada.
Steffen, Robertson & Kirsten (Mining) Inc., Johannesburg, South Africa.

BACKGROUND

It is almost one hundred years since the first gold was mined in 1886 on the Witwatersrand, the "ridge of white waters", in the Transvaal Highveld of South Africa. Mining on the Witwatersrand, the principal centre of the South African gold mining industry, has resulted in the accumulation of over 300 tailings impoundments through the area. The majority of the mills producing these tailings used sodium cyanide in the gold extraction process and hence there is normally a residual quantity of unused cyanide reporting to the process tailings.

The combination of geology and climatic regime on the Highveld are such to have produced a groundwater regime over a significant part of the area where two principal aquifers are formed:

- a deep, regional aquifer (in the Transvaal dolomites) bearing good quality groundwater; and
- a near-surface, sometimes non-perennial aquifer, which is normally in hydraulic continuity with the surface waters of the area, when they are present.

The latter aquifer, developed due to the intense weathering of the surficial rocks of the Witwatersrand, is highly permeable and relatively vunerable to surface pollution sources. Slow leakage may or may not occur from this near-surface aquifer to the deeper, regional groundwater. The disposal of cyanide bearing, gold tailings can represent a potential pollution threat to both aquifer regimes by direct runoff, erosion of tailings and seepage from the tailings impoundments themselves.

REGULATORY CONTROL

Discharge of cyanide-bearing effluents or seepage from mining and milling operations is covered by regulations made under the Water Amendments Act 1984 (No. 9330), or, if discharge is made to a potable water resource, in terms of the South African Bureau of Standards (SABS 241-1971) specifications.

Discharge is regulated in terms of total cyanide levels. The general effluent standards specify a total cyanide level of 0.5 mg/L, while the potable water standards are 0.01 mg/L "recommended" limit and 0.2 mg/L "maximum allowable" level. These are broadly similar to both World Health Organization and U.S. Public Health recommendations.

MONITORING PROGRAMS

All the current and past cyanide monitoring has been done as and when time and resources have permitted, in addition to the regular water quality monitoring programs Steffen Robertson and Kirsten undertake. The collection of data has not been as complete as is possible, but efforts have been made to encompass the following variations in good tailings disposal (see overleaf):

- operational, recently-decommissioned and older, abandoned tailings impoundments;

- milling operations which extract uranium in addition to gold, the two elements occurring together in some of the Witwatersrand ore;

- vertical variation within the tailings mass; and

- variation in the interstitial waters in the tailings and in the associated near-surface groundwater adjacent to the tailings impoundment.

The results of the monitoring program are tabulated in the subsequent section. These data are from:

- an operational impoundment, $\pm$ 5 years in age;

- an operational impoundment, $\pm$ 10 years in age;

- a recently-decommissioned impoundment (within the last 5 years), approximately 20 years in age; and

- an abandoned dam, > 20 years in age.

The cyanide profiles through the deposited tailings are results of drilling two impoundments, both of which have been abandoned in the last ten years.

All data are for total cyanide. They were determined by using prescribed South African Bureau of Standards methods which are essentially the same as those monthly in use in North America.

CYANIDE MONITORING RESULTS

Cyanide monitoring data have been collated in five tables. These are:

- Table 1: total cyanide in the tailings system for a gold/uranium mill;

- Table 2: cyanide profile in interstitial water in a decommissioned tailings impoundment;

- Table 3: chemistry of oxidised, intermediate and reduced zones in tailings impoundments (mean values);

- Table 4: comparison of cyanide (total) in tailings impoundments and near-surface groundwater: (mean and range); and

- Table 5: comparison of total cyanide levels in near-surface groundwater with general groundwater composition.

TABLE 1

TOTAL CYANIDE IN MILLING SYSTEM FOR A GOLD/URANIUM MILL

	RANGE	MEAN	REMARKS
DISCHARGE FROM GOLD PLANT	—	±9	PRIOR TO U PLANT
DISCHARGE AT THICKENERS	0.05–0.08	0.06	MOSTLY PRESENT AS THIOCYANATE
POOL AT TOP OF DAM	—	<0.01	ADJACENT TO DECANT TOWER
SOLUTION TRENCH	—	<0.01	—
RETURN WATER DAM	—	<0.01	USED FOR WATER STORAGE ALSO

1. NEAR-GROUND AND DEEP GROUNDWATER CARRY <0.01 TOTAL CYANIDE ALSO.

TABLE 2

CYANIDE PROFILE IN INTERSTITIAL WATER IN A DECOMMISSIONED TAILINGS IMPOUNDMENT

BOREHOLE	PIEZOMETER NO.	DEPTH m[2]	TOTAL CN mg/l
A	1	11	0.16
	2	17	0.21
	3	25	0.57
B	1	27	1.54
	2	30	0.16
	3	47	<0.01[4]
C	1	18	0.22
	2	22	2.92
	3	26	0.35
D	1	19	N/S[3]
	2	24	1.09
	3	28	1.86

1. CYANIDE DISCHARGE CONCENTRATION VARIED BETWEEN 8-19 mg/l DURING OPERATION.
2. TOTAL HEIGHT OF TAILINGS IMPOUNDMENT, 32m (104 ft).
3. N/S, NO SAMPLE.
4. SAMPLES TAKEN BELOW 32 m ARE IN THE SEDIMENTS BELOW THE IMPOUNDMENT.

TABLE 3

CHEMISTY OF OXIDISED, INTERMEDIATE AND REDUCED ZONES IN TAILINGS IMPOUNDMENTS (MEAN VALUES)

	PH	TDS	SO_4	Fe*	Mn	TOTAL CN
OXIDISED ZONE 0-3m	6.6	3350	1850	47	4	0.6
INTERMEDIATE ZONE 3-15m	6.6	3600	2210	21	11	2.0
REDUCED ZONE 15-35m	6.6	2850	1600	8	20	0.9

1. PH; UNITS OTHEWISE ALL VALUES IN mg/l.
2. TOTAL CYANIDE IN NEAR-SURFACE GROUNDWATER BELOW IMPOUNDMENT WAS 0.08 mg/l (MEAN VALUE).
3. TWO IMPOUNDMENTS ± 20 YEARS OLD.
4. SAMPLE TOTAL = 149

* TOTAL IRON

TABLE 4

COMPARISON OF CYANIDE (TOTAL) IN TAILINGS IMPOUNDMENTS AND NEAR-SURFACE GROUNDWATER (MEAN AND RANGE)

DECRIPTION OF DAM	TAILINGS RANGE	TAILINGS MEAN	GROUNDWATER RANGE	GROUNDWATER MEAN
1 OPERATIONAL DAM ± 5 YEARS AGE	—	0.25	—	<0.01
2 ABANDONED DAM <20 YEARS AGE	—	(0.1?)	0.03-0.04	0.04
3 RECENTLY DECOMMISSIONED DAM ± 20 YEARS AGE	0.6-2.9	1.3	<0.01-0.16	(0.08)
4 OPERATIONAL DAM ± 10 YEARS AGE	—	<0.01	—	<0.01

TABLE 5

COMPARISON OF TOTAL CYANIDE LEVELS WITH GROUNDWATER COMPOSITION

DESCRIPTION OF DAM	TOTAL CN	TDS	SO_4	Fe	Mn	PH
① OPERATIONAL DAM ± 5 YEARS AGE	<0.01	712	317	0.1	15	6.8
② ABANDONED DAM >20 YEARS AGE	0.04	500	400	34	69	2.9
③ RECENTLY DECOMMISSIONED DAM ± 20 YEARS OLD	0.08	300	70	4	0.8	5.8
④ OPERATIONAL DAM ± 10 YEARS	<0.01	500	—	—	—	7.5
⑤ "BACKGROUND" WATER QUALITY	<0.01	250	50	0.1	0.1	7.8

1 ALL VALUES IN mg/l, EXCEPT PH; UNITS

ANALYSIS OF MONITORING DATA

The data which follow the progress of cyanides from the gold extraction plant through to the water return facility at a mill with both gold and uranium extraction facilities, given in Table 1 illustrate that disposal of tailings from such mills may not represent a cyanide pollution to water resources. While a typical total cyanide level of 9 mg/L is discharged from the gold plant, the discharge at the thickners after the uranium plant is less than 0.1 mg/L, the bulk of which is believed to be in the form of thiocyanate. The cyanide is apparently either destroyed or otherwise lost in the uranium extraction process, which may involve solvent extraction, ion exchange, precipitation or a combination of these processes. For the remainder of this passage through the disposal facility, the aqeous phase associated with the tailings reports cyanide levels less than detection at < 0.1 mg/L. In addition, there is no remobilization of cyanide, should it report to the solid phase of slurried tailings, as both the near-surface groundwater and the regional aquifer adjacent to this impoundment were found to carry levels of cyanide less than 0.1 mg/L also.

The cyanide profile with respect to interstitial waters in a gold only tailings impoundment is given in Table 2. The interstitial water is taken to be typical of any seepage which may be discharged from the base of the impoundment to the groundwater regime. Given that the cyanide levels in the tailings slurry varied between 8-19 mg/L during operations at the mill, the maximum value in the interstitial water is

now less than 3 mg/L. Therefore either the cyanide has decomposed during or after discharge, or it is being held on/in the solid phase of the tailings.

The actual cyanide profile is of interest. The upper portion of the profile to 20 m depth (66') is depleted in cyanide with values less than 0.22 mg/L. Between 20 m and 28 m (92'), the total cyanide levels increase and are in the range of 0.4-3 mg/L CN. These levels may decrease below this depth, although there is only one value of 0.16 mg/L to support such a conclusion. By comparison, the interstitial water in the sediments below this impoundment give cyanide levels less than 0.01 mg/L indicating no cyanide contamination from the impoundment.

In a second tailings impoundment, about 150 samples of interstitial water were taken from three distinct chemical zones within the tailings mass. These chemical zones - oxidised, intermediate and reduced - have been described in detail by Smith et al (1982, 1983). Table 3 illustrates the general chemistry of the three zones together with their respective total cyanide levels. These data are mean values, at least twenty samples being taken from each chemical zone.

In general, there is not a great variation in the major ion chemistry of the waters of the three zones. While the pH values are the same, the TDS and sulphate values are slightly higher in the intermediate zone and lower in the reduced zone as compared with the upper, oxidised zone. There is, however, a very clear increase in manganese levels with depth in the interstitial water coupled with antipathetic behaviour of total iron. Cyanide values then follow the major ion pattern, with highest values occurring in the intermediate zone (average value, 2.0 mg/L).

In addition, it should be noted that while the lower, reduced tailings have an interstitial water cyanide level of 0.9 mg/L, the near-surface groundwater below and adjacent to the impoundment have a mean total cyanide level of only 0.08 mg/L.

The data comparing cyanide in interstitial tailings waters with groundwater (Table 4) and cyanide in groundwater with the general groundwater chemistry (Table 5) can be considered together. Cyanide levels from the tailings examined vary from < 0.01 mg/L to about 3 mg/L with a mean value probably less than 1 mg/L. Known discharge levels for gold only mills are up to 20 mg/L and therefore the cyanide is either being destroyed prior to being held in the interstitial water within the tailings or combined with the tailings itself. Once the interstitial water is lost from the impoundment to the near-surface groundwater, it appears at levels no greater than 0.08 mg/L and, on average, less than 0.03 mg/L. Again, this may be fixation onto a solid phase or decomposition of the cyanide itself, with the addition of dilution by cyanide-free groundwater.

GENERAL DISCUSSION

From the foregoing data analysis, the following observations require some further discussion and possible explanation:

- the relatively low levels of total cyanides in interstitial tailings water, despite significantly higher cyanide discharge levels; and
- the apparent lack of contamination of the groundwater regime, even in close proximity to the impoundments.

It is suggested that there are several possible processes which may be responsible for the breakdown and/or fixation of the cyanide, removing from the aqeous system in the tailings and preventing groundwater contamination. These are:

- the method of tailings disposal: the so-called "semi- dry" or "sub-areal" disposal technique;
- the prevalent climatic conditions;
- the presence of partially or wholly oxidised iron in the tailings; and
- the presence of iron in the highly weathered, semi-lateritic or lateritic near-surface aquifer.

Sub-areal tailings disposal seeks to optimize tailings/water ratios, permitting the impoundment to be constructed by a self-build technique without the requirement of a water-retaining dam, as commonly practiced in North America. Lower water volumes on the impoundment result in smaller seepage volumes and hence limited solute transport. In addition, the presumed free cyanide-bearing tailings liquid is held in a very shallow pool on top of a dam and is readily available for interaction with available oxygen and solar radiation.

The Witwatersrand, at 2000 m (6000 ft.) in the Transvaal Highveld, has an "ideal" climate for maximizing natural cyanide oxidation; a mean yearly temperature of 15°C (60°F), in excess of 290 sunshine days per year - with only 5-10 cold days/nights, moderate but high intensity rainfall and high summer temperatures. The duration of high levels of incoming radiation resulting from the altitude and cold-free days/nights promote conditions for natural oxidation of cyanide, which are maximized by extensive area, shallow depth pool of liquid held on top of the tailings impoundment.

Pyrite, or residual pyrite, which may form between 0.5% and 5% of the tailings is subject to strong oxidation in the tailings, as evidenced by the red-brown iron minerals which form on the surface of the tailings, from the essential grey material which is deposited initially. The evidence for fixation, and hence attenuation, of cyanide by formation of iron species is documented in the literate (see discussion in Chapter 4, Huialt et al, 1983) and an active oxidation

system which is in chemical disequilibrium, such as a tailings impoundment, has significant potential for immobilization of free cyanide species from the aqeous phase.

A similar potential which exists to a limited extent is the near-surface aquifer below the tailings impoundment itself. Almost without exception, the mineralogy of this aquifer, derived from quartzitic, dolomite or shale types of strata, compromises some iron minerals. Again, this provides a mechanism for cyanide removal, attenuation and fixation.

SUMMARY

A number of observations on the dearth of cyanide contamination from cyanide bearing, gold tailings disposed on the Witwatersrand, South Africa, can be made: These are:

- despite cyanide discharge levels from gold plants of up to 20 mg/L cyanide (and perhaps significantly more), there is little available total cyanide in interstitial waters in gold tailings impoundment, the general level being about 1 mg/L;

- There is little evidence of cyanide contamination of the groundwater regime below or adjacent to gold tailings disposal facilities, the general total cyanide levels in near-surface groundwater being about 0.03 mg/L; and

- a combination of the sub-areal/semi-dry method of tailings disposal, the climate of the Witwatersrand which greatly facilitates oxidation, ultraviolet radiation involved cyanide decomposition, and the availability of iron species for cyanide complexation may be processes which contribute to cyanide reduction prior to seepage discharge to the groundwater regime.

REFERENCES

Huialt, J.L., Kerrigan, J.E., Olson, F.A. and Potter, G.L. (1983) - Proceedings of a Workshop on Cyanide From Mineral Processing Sponsored by NSF, Grant PAG 8119007, USBM and Industry.

Smith, Adrian, Oehrmann, A.A. and McPhail, G. (1982 and 1983) - Internal Reports: Steffen, Robertson and Kirsten (Mining) Inc., Johannesburg, South Africa.

THE CONCENTRATION OF THE COMPLEX CYANIDES IN FLOTATION TAILINGS

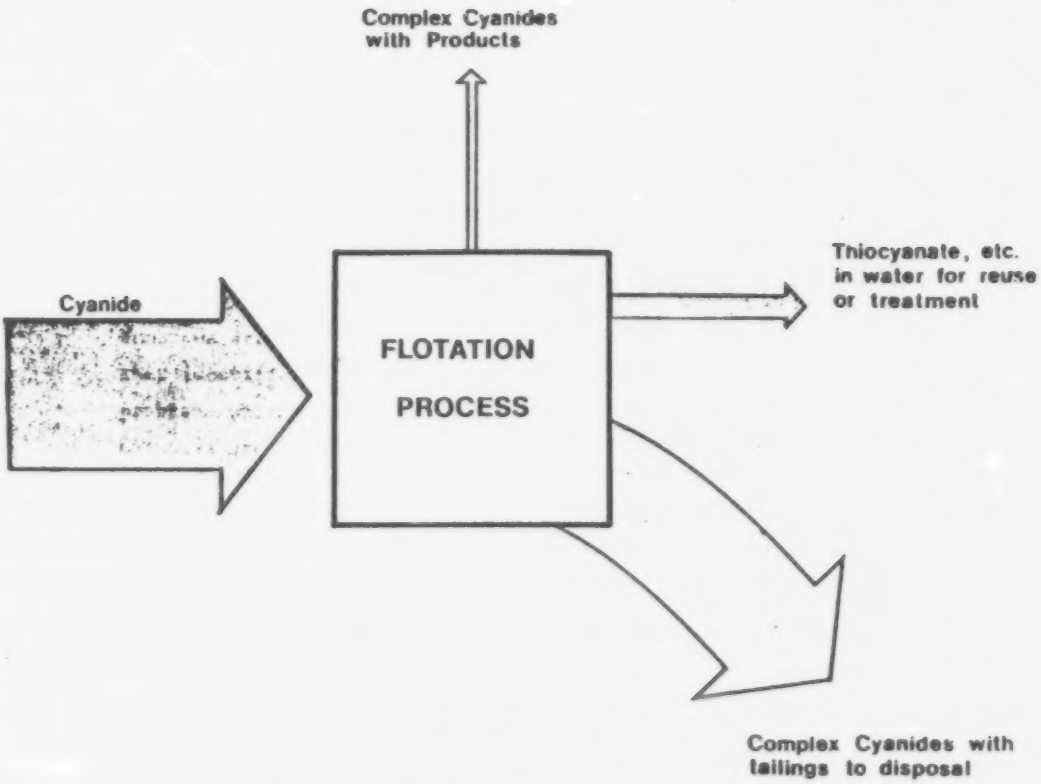
The factor of the concentration of complex cyanides in flotation tailings was not found in any of the Canadian or other documentation. Concentration may not have been addressed due to difficulties in assessing levels of cyanide as they occur in flotation tailings as was discussed in an earlier section.

Recent studies by the Bureau of Mines in the States, of tailings from flotation processes utilizing cyanide have been unable to find cyanides in flotation tailings. This finding may be an analytical sensitivity problem since the expected levels are extremely low. It may also be indicative of the stability of the complex cyanides...as the U.S. background study (USEPA Report No. 560/6-76-012) on cyanides stated "... the cyanide is absorbed strongly on the surface of the minerals..."

Although concentration data is absent in some key U.S. literature, other U.S. EPA documents can be used to estimate the maximum probable concentrations of cyanide in the tailings. In a U.S. EPA study (Contract No. 68-03-2552) of mineral mine operations using, or potentially using, cyanide as a depressant in flotation, the rates of usage of cyanide usage rates it is possible to calculate the maximum possible concentrations of cyanide at these surveyed plants. Table 3.1 presents a summary of those estimates.

In order to place this concentration in perspective, a complex cyanide (sodium ferrocyanide) is approved for use in table salt at a level of 13 parts per million and road salts spread on highways as deicers contain up to 350 parts per million of complex cyanides (sodium ferrocyanide and ferric ammonium ferrocyanide).

Since the cyanide used in the selective flotation process is carefully controlled by metering in weak solutions to selectively react with the surface of a small portion of the ore, it is improbable that concentrations of complex cyanides would significantly vary from



FATE OF CYANIDE IN FLOTATION SYSTEMS

TABLE 5

ESTIMATED MAXIMUM PROBABLE
CONCENTRATION OF CYANIDE TAILINGS[1]

PLANT NO.	MINE TYPE	CYANIDE ADDED LB/TON	ORE PROCESSED TONS/DAY	PROBABLE CONCENTRATION OF CYANIDE IN TAILINGS PPM
A	Cu/Mo	0	60,000	0
B	Cu/Mo/Ag	0	92,000	0
C	Cu	0	50,000	0
D	Cu	0	42,000	0
E[2]				
F[2]	Cu/Mo/Others	0.02	105,000	5
G[2]				
H[4]	Lead/Zinc/Cu	0.05	5,000	10
I[4]	Lead/Zinc/Cu	0.05	7,500	10
J[4]	Lead/Zinc/Cu	0.05	5,000	10
K[4]	Lead/Zinc/Cu	0.05	2,500	10
L	Lead/Zinc/Cu	0.02	4,200	1
M	Lead/Zinc	0.01	6,500	5
N	Zinc/Copper	0.1	7,000	35
O[3]	Zinc	0.0-0.02	6,500	≤ 5
P[3]	Zinc	0.0-0.02	3,200	≤ 5
Q[3]	Zinc	0.0-0.02	1,900	≤10

1. Data from US EPA Contract No. 68-03-2552.
2. Plants E, F and G reported as one facility
3. Intermittent usage; estimated using ore feed as tailings estimate since ore: Tailings ratio is approximately 1:1.
4. Suppress zinc and iron; zinc recovered due to intermittent iron suppression.

those indicated in Table 3.1. Furthermore, since some cyanides are converted in the flotation circuit by oxidation to cyanates or thiocyanates and may not report to the tailings, and due to other factors, these estimates may be somewhat high.

No reports of measurements of the level of cyanides were found in the literature. During discussions with U.S. Bureau of Mines, however, the estimate was made that possibly eighty percent of the cyanide ended up in the tailings (Ref. 3.1).

It can be calculated, however, what the maximum possible level of cyanide in the tailings is by knowing the rate at which the cyanide is added to the cell on a pounds per ton of ore basis and knowing the approximate tailings generated per ton of ore. Consideration will, however, have to be given to several other factors in common experience at flotation sites. They are:

- Intermittent use of suppressant.
- Loss of cyanide in flotation cell.
- Possibility of "overdosing" or "underdosing" reagents.
- Loss of cyanide on floated products.
- Use of suppressed minerals as products that are not blended with tailings.

FACTORS AFFECTING CYANIDE CONTENT IN TAILINGS

In the U.S. EPA's study (Ref 3.2) dealing with use of sodium cyanide in flotation, several of the mineral flotation plants studied used cyanides intermittently. This type of intermittent operation would lead to a dilution of cyanide content in tailings by discharge of non-cyanide containing wastes. Similarly, some mines add cyanide to only a portion of their flotation cells resulting in dilution proportional to the tailings generated in the treated cells as a fraction of the entire tailings (Ref. 3.3).

Cyanide will react with other flotation reagents, such as xanthate, to yield thiocyanates which do not end up in the tailings (Ref. 3.4). This loss would further reduce the calculated concentration maximum based solely on pounds of cyanide per ton of feed.

Since small amounts of cyanide are used to control flotation products (0.001 to 0.1 lb/ton) the flotation process becomes a "policeman" to determine if too much or too little suppressant is being added. As recognized in U.S. EPA's work (Ref. 3.5) the dosage of cyanides must be critically controlled to produce an acceptable product. The same argument applies for underdosing.

Some cyanide is carried out of the process with the flotation mineral product rather than the tailings. This loss would further reduce the concentration calculated on a pounds per ton of feed basis.

Tailings from one flotation circuit often become flotation products in the next flotation circuit. The cyanide preferentially reacted with the flotation product does not report to the tailings diluting the levels further.

Since feed rates of suppressant are in terms of pounds of cyanide per dry ton of ore, the water in tailings dilutes the concentration further.

PERCENT SOLIDS IN TAILINGS

With all these factors considered it is a conservative estimate to use the numbers in Table 3.1 in summary which have only been adjusted for tailings affected. Figure 3.1 shows the relative concentration of cyanide in common materials as a method of gauging the relative concentration in the flotation tailings.

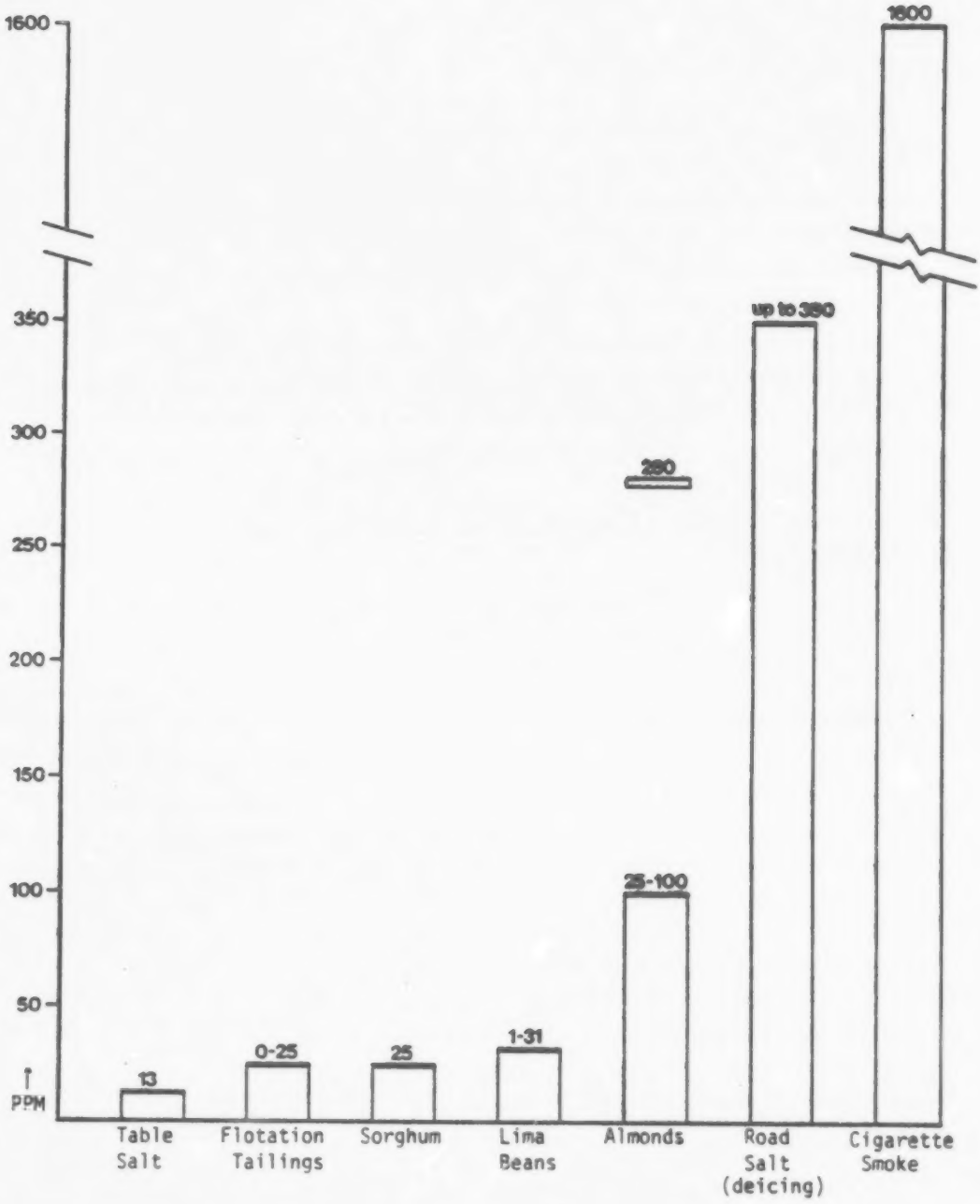


FIGURE 3.1 Cyanide content of various materials.

REFERENCES

3.1 Private Communication. Mr. Jerry Huiatt 7/2/80 U.S. Bureau of Mines.

3.2 Treatability of and Alternatives for Sodium Cyanide for Flotation Control. Phase II. Contract No. 68-03-2552. January, 1980. p. 14. USEPA.

3.3 Flotation, M.C. Fuerstenau AIME 1976 p. 1172

3.4 Edisbury, V. Engineering Mining Journal. Vol. 12 1967 p. 17.

3.5 The Manufacture and Use of Selected Inorganic Cyanides US EPA 560/6-76-012 p. 105 January 1976.

3.6 Mine and Mill Wastewater Treatment. Report EPS 3-WP-75-5 December, 1975. Environmental Protection Service. Environment Canada. p. 47.

THE ADVANTAGES OF CYANIDE

1) Cyanide for gold and silver leaching from "normal" ores requires very small doses at a relatively low concentration.
Typical concentrations in gold mill leach solutions would be 0.015-0.1% NaCN 150-1000 ppm and typical consumption would be about 1 lb/ton. Consumption can, however, be very much higher when the ore contains cyanide soluble copper minerals e.g., NGEMI 8 lb CN per ton ore consumption.

2) Cost of cyanide is relatively inexpensive at $0.40 - $0.80/lb depending on location.

3) Cyanidation yields better leach recoveries than most other lixiviants for gold and silver. The term "refractory" gold or silver ores refers to those from which the precious metals are not readily leachable by cyanide.

4) Industry is familiar with the use of cyanide and the precautions that need to be taken.

5) Cyanide is biodegradable especially in warm climates. Even if there was to be environmental impact on surface waters due to cyanide use this impact will not continue for a long period after the mine-mill shuts down - unlike acid mine drainage or seepage from sulfidic ore tailings which could persist for hundreds of years.

DISADVANTAGES OF CYANIDE

1) Cyanide also dissolves base metals and iron and these are held in solution as cyanide complexes.

2) Cyanide is toxic and does require special handling precautions. These are not difficult, however.

3) Free cyanide, some complexed cyanides and their degradation products are toxic to aquatic life at very low levels.

4) The regulations as to what levels of cyanide are permissible in effluents in the USA are not clear cut.

5) There remains some general confusion as to appropriate analytical techniques for low level cyanide in effluents and analytical interferences. There are now techniques of analysis which overcome these interferences but regulatory limits are set based on standardized analytical methods which do not include the latest improvements.

6) Comparison of toxicity data for cyanides requires careful qualification of the analytical methods used for the analysis and careful evaluation of their meaning - the problem of comparing apples and oranges exists.

7) Cyanide leaks, however small, can be sure of getting a bad press.

The Denver Post/Sunday, Sept. 23, 1984

Associated Press

Cyanide in Chicago well water

Joe Walker holds a glass of well water at his home on Chicago's far South Side Thursday after he learned that the water is tainted with cyanide. An official said Friday the source of the contamination found in two wells hasn't been pinpointed. None of the nine residents who use the wells had drunk the water, the official said. Said Walker, 'It eats my pipes up, and I know it would eat me up.'

CONTRAVERSIAL ASPECTS OF CYANIDE

1) How toxic are ferrocyanide and ferricyanide complexes or their degradation products? Should ferrocyanide be included in the cyanide level limits set for effluents? Should an analysis method be used to report total cyanide if it does not detect ferrocyanide?

2) How effective is natural degradation of cyanide in effluents in different climates?

REGULATIONS CONCERNING CYANIDE IN TAILINGS AND EFFLUENTS

Regulations governing cyanide containing effluent disposal in various gold and silver mining centers of the world have not yet been finalized. Comparison of regulated limits are complicated by the need to qualify the analytical method specified for its determination, which vary from country to country.

In some parts of the world with warm year-round climates such as South Africa and Fiji, for example, natural degradation of cyanide in solutions occurs as long as there is an adequate retention time in an impoundment. The South African drinking water standard SA Bureau of Standards second version 241 of 1971 set a recommended maximum of 0.2 mg/l CN and a maximum of 0.3 mg CN/l. The South African proposed standard for effluents in the Witwatersrand were published in government Notice No. R553 Table 2 by the Department of the Environment and set cyanide "and related components" at 0.05 mg/l.

In South Australia where gold was mined in the foothills around Adelaide, cyanidation was prohibited anywhere within the rainfall catchment area which provides the city of Adelaide with its water supply. In Brazil, individual states have set their own limits for cyanide at 0.2 mg/l. Sweden has no general fixed cyanide limits, but one operation must meet 0.5 mg free CN and has set a target of 0.2 mg/l for July, 1986.

In other parts of the world, notably North America, much more attention is focused on this aspect of gold and silver mining. In the cold northern winters, cyanide is not naturally destroyed and fisheries are much more important than in some of the other mining areas.

In general, North America has also become much more conscious of environmental protection in recent years than most other gold producing countries. Also, in parts of the USA and Canada, gold recovery plant effluent or tailings runoff does get into the river and lake water system. Considering the L50 lethal effects of cyanide in excess of 0.038 ppm on fish, and the highly developed fisheries resource of some North American inland waters, there is a clear need for responsible control of cyanide entering the inland water system. On the other hand much of the gold mining areas are in desert or semi-desert climates where there are no fisheries near the operations so there is a clear need for site specific limits which do not require unnecessary treatment costs.

Consequently, cyanide destruction techniques and disposal in mill tailings and effluents have been of major interest to the gold and silver mining industry as well as State and Federal licensing and environmental protection authorities. Unfortunately the technology for cyanide destruction in pulps and solutions and what can be acheived in operating

plant conditions was not well established. Improved analytical techniques and a better understanding of the meaning of the results are still being developed.

CYANIDE REGULATIONS

In the USA the EPA is working on a national limit for cyanide in effluents. Individual states may enforce the Federal (EPA) standard when it is fixed or may impose stricter rules on their own.

According to an EPA document "Cyanides: Ambient Water Quality Control" PB 296792 (1979), the EPA proposed an ambient quality criteria for free cyanide in effluents. To protect fresh water aquatic life, the criterion was set at 0.0014 ppm CN^- as a 24 hour average with a concentration not to exceed 0.038 ppm at any time. For the protection of human health the ambient water quality criterion is 0.0200 ppm. Federal RCRA regulations concerning effluents from leaching operations do not appear to regulate cyanide for the time being. It seems likely however, that EPA will include cyanide in the regulations they are working on for the preservation of groundwater quality.

There are four sets of Federal regulations in the USA which will ultimately be relevant to cyanide in effluents and tailings levels. Then each state has its own laws pertaining to effluent and tailings discharge or containment which are contained in the permit required to operate a mine-mill complex.

The Federal rules of consequence are:

1) NPDES regulations for discharge to surface waters, lakes and navigable waterways, rivers, etc.

2) Resources Conservation and Recovery Act RCRA governing hazardous waste disposal which have temporarily been suspended from applicability to mining and milling wastes. These are under review and will likely be reapplied to mining and milling in some form in the future. As originally promulgated, cyanidation mills for gold and silver recovery were required to be zero discharge.

3) A new set of groundwater protection laws under development by the EPA but not yet enacted.

4) The CERCLA Superfund laws under which each company that disposes of solid waste must contribute to a fund which is to be used to clean up existing threats to the environment and under which sites which lead to future environmental damage c[illegible] repaired by the government and billed to the company that caused th[illegible]

In most gold mining areas of the USA, for example in Nevada, Utah, California, Eastern Oregon, etc., the arid climate offers high evaporation rates and makes it easier to control runoff to prevent it from getting into permanent rivers and lakes. Many milling operations also are able to operate on a zero discharge basis. This is possible when the ores contain low levels of cyanide-soluble base and heavy metals. When the ores are not "clean" these species will build up in a mill that recirculates tailings water until a certain amount of solution must be bled from the circuit. In an arid climate even this should present little problem as the solutions can be evaporated so that no cyanide bearing solutions need escape to the environment. However, once cyanide salts are evaporated to dryness in a tailings pile or leached heap it may last forever because natural degradation seems to work only for solutions. It was reported that the state of California in 1981 did not accept the zero discharge concept and were insisting on cyanide destruction of cyanide in effluents even when solutions are recycled from the tailings pond. Their position may have changed since then. Homestake Mining Company's McLaughlin project will be a zero discharge operation and it is known that the state of California has insisted on double linings of the tailings pond and numerous additional measures.

In high rainfall areas, or cases such as Homestake Mining Company's Lead S. D. operations, where excess mine water and decanted tailings pond water are discharged to a creek, strict regulations governing allowable cyanide limits in the effluent are enforced.

Certainly at Noranda Grey Eagle Mines Inc. operation near the Klamath River in Northern California the determination of low levels of cyanide unexpectedly in the seepage from their tailings dam resulted in a major concern to the California Regional Water Quality Control Board and expensive mitigating action by the company even though no known environmental damage occurred. Even though rainfall exceeds precipitation at this site, it is designated for zero discharge of even treated effluent which has to be irrigated to dispose of it.

Water effluents from Homestake's Lead S. D. operation were restricted to 0.02 ppm total cyanide according to their state permit which they have worked very hard to try and meet. Judging by past penalties that have been imposed on Homestake for non-compliance, it is clear that the regulations have been enforced even before practical methods have been developed to achieve the legislated limits. This does not seem reasonable, and it was rumored that the limit may be raised to 0.08-0.10 ppm or whatever can be shown to be an environmentally acceptable level achievable with the best technology available. Homestake has been developing an in situ bioassay technique for site specific species in their effluent stream as one way of improving the monitoring of environmental toxicity of their treated effluent. This may well prove so successful as to form the basis for a modification in the way future limits are set and regulated.

At Superior Oil Company's heap leaching operation at Stibnite, Idaho, the heaps after gold has been recovered by cyanide leaching, must be rinsed to remove cyanide which is

destroyed with a hypochlorite solution. Hypochlorite is generated at the site from liquid chlorine and lime. Before tailings can be disposed of in the disposal site, free cyanide in the "off" solution must be reduced to below 0.2 ppm. When the tailings are placed on the disposal area, they are spread out in a 1 foot layer allowing further oxidation of cyanide by aeration and sunlight. Here is a case where no solutions are deliberately discharged as effluent but where cyanide destruction techniques are mandated because of the possibility of precipitation runoff from the area to a nearby tributary of the Salmon River, a sport fishing paradise. It is reputed that in Nevada, on the other hand, regulations are more easily satisfied. Nevada recognizes its dependence on the mining industry and is familiar with the use of cyanide in metallurgical processes that have been used in the state for many years without obvious damage. Zero discharge operations are often possible, and there are negligible inland fish resources near most mines that could be affected by cyanide. Even so, the Battle Mountain operation of Duval spends a lot of money chlorinating their CIP pulp discharge to the tailings area in the valley below the mine. Other operations such as at Pinson Mining Co., Freeport Gold, and many more have so far operated on a zero discharge basis.

The U.S. rgulatory situation with respect to cyanide in gold and silver mine effluents is still emerging, and it will vary from state to state.

The U.S. Environmental Protection Agency still has not issued Federal regulations regarding cyanide and thiocyanate in effluents. However, as mentioned above, regulations are likely after the impact of mining on groundwater has been evaluated. The U.S. EPA Best Practicable Technology guidelines published in 40 Federal Register 51722, November 6, 1975, under 40 CFR 440.22 indicate a maximum of 0.02 mg/l total cyanide.

The U.S. EPA is apparently shifting the regulation of mining and metallurgical effluents from a federal responsibility to a state responsibility. Each state is now formulating its own set of rules. This has resulted in a delay in the crystallization of what the final regulations are to be and a great range in the limits themselves from state to state. Each state may impose tichter limits if they wish as long as they are not less stringent than the federal limits which have yet to be announced. Because the local state regulators are inexperienced in many cases with mining waste and effluents, the result has sometimes been to demand ridiculous or ill-conceived requirements, and excessive delays in securing permits for heap leaching test projects, for example, let alone for commercial operations.

California is regarded as a trend setting state, and their emerging regulations with respect to cyanidation tailings, even for heap leaching operations, although still to be finalized, are extremely strict.

The Federal RCRA regulations concerning hazardous waste disposal have been temporarily suspended for mining waste. However, the state of California Hazardous Waste

Regulations have been enacted and in several aspects are even more strict than the Federal RCRA that is being reconsidered for mining.

The state of Washington and Montana are also said to be following California with respect to tight effluent limits and strict mine/mill operating permits.

Apart from the tightness of limits imposed on effluent discharge, a major factor in the economics of developing a new mine and mill in the USA today is the long delay required in processing permits that are required from many different regulatory authorities. Several mining companies claim that these factors are already driving investment away from mining ventures in the USA at this time.

EXAMPLES OF SOME U.S. EFFLUENT REGULATIONS

Homestake Mining Company
Lead, South Dakota

Comparison of the Homestake NPDES effluent permit with the Federal BPT regulation and the State Water Quality Standards for a fishery.

Parameter	BPT Limit (40 CFR 440.22)* mg/l	WQS Limit mg/l	Permit
Total Suspended Solids	30	10	10
Arsenic	N/A	0.38	0.38
Cadmium	0.1	0.00025	0.00025
Chromium	N/A	0.85	0.85
Copper	0.1	0.009	0.009
Lead	0.4	0.28	0.28
Mercury	0.002	0.001	0.001
Nickel	N/A	1.25	1.25
Silver	N/A	0.001	0.001
Zinc	1.0	0.020	0.020
Cyanide	0.02	**	0.02
pH	6 to 9	N/A	6 to 9

* 40 Fed. Reg. 61722 (Nov. 6, 1975).

** "Quality Criteria for Water," United States Environmental Protection Agency (July

CN (ug/L) CYANIDE

Summary of North American Water Quality Criteria for Cyanide

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9,**] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		0.05 of the 96-h LC50	--	24-hr mean 3.5	5.0*	5.0	Non-detectable	10	100-500	--	--
MAX. PERMISSIBLE LIMIT		5.0	5.0	52	--	--	5.0	--	--	10	5.0
PROTECTION OF MARINE LIFE											
OBJECTIVE		<5.0 0.01 of the 96-h LC50	--	<2.0 (recommendation only)	5.0*	--	--	--	100-500	--	--
MAX. PERMISSIBLE LIMIT		10.0	5.0	<30 (recommendation only)	--	--	--	--	--	--	--
PUBLIC WATER SUPPLY		200	--	200	200	200	200, 50	(10)	--	10	10
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	--	--	--	--	--	--	(10)	--	--	--
	IRRIGATION	--	--	--	--	--	--	--	--	--	--

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.

2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.

3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Cyanide, EPA 440/5-80-037.

4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).

5. Environment Canada. 1981. Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances, Preamble.

6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.

7. Goulin, D. et Halo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.

8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.

9. British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries. **(Receiving water objectives not available).

10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.

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1976), indicated that an instream value of 0.005 mg/l total cyanide would be necessary to protect fresh water aquatic life. With the available dilution ratio, this would require and effluent limitation of approximately 0.017 mg/l.

Source: EDELMAN & WALLINE

PAPUA, NEW GUINEA

Effluent from OK Tedi is discharged to a river (Tabubil?). Free cyanide levels in the river are limited by regulation to 5 ppb (0.005 ppm). There is a 200 fold dilution of effluents in the river which means that the effluent should never exceed 1 ppm.

BRAZIL

In Brazil, each state has its own effluent discharge limits. For cyanide, the limit is 0.2 ppm (not clear whether free or total cyanide).

US EPA 40 CFR 440 Sub part B
Effluents from Copper Mining Operations

	Maximum Grab Sample	Average daily Sample for 30 days max
Suspended Solids	30.0	20.0
Cu	0.1	0.05
Pb	0.4	0.2
Hg	0.002	0.001
Cd	0.01	0.05
CN	0.02	0.01
Zn (mines only)	1.00	0.50
pH	6 to 9	6 to 9

Note: This limit is probably part of the RCRA regulations that are currently in abeyance under the Beville Amendment.

CANADIAN CYANIDE EFFLUENT REGULATIONS

In Canada, there is currently not yet a Federal limit set for cyanide in effluents, and the responsibility for developing a national standard rests with ENVIRONMENT CANADA. The levels set by ENVIRONMENT CANADA will be the basis for a minimum national standard although the individual provinces may set more stringent standards and will be responsible for enforcing the regulations.

ENVIRONMENT CANADA's mandate is to set permissable effluent limits based on what can be achieved by demonstrated technology. They are now evaluating the performance of various plant scale tests for cyanide destruction by several techniques to determine their performance. In the meantime, ENVIRONMENT CANADA has not yet set the national standard and the Provinces are permitting gold plants on a case-by-case basis. Every major new gold mill in Canada since 1980 has installed an effluent treatment plant, however. Each province has its own licensing authority which sets limits for cyanide in effluents. However in comparing these it is important to note where the sampling point is specified to be. For example in several Ontario gold operations the sampling point for effluent analysis may be 1 - 2 miles downstream from the effluent discharge point from the pond. SCOTT (1984).

In Canada, regulations affecting effluent discharge from mining and metallurgical operations are part of the Fisheries Protection Act. This gives some idea of the importance given to inland fisheries in Canada - where 37% of the world's fresh water is located.

There are still three schools of thought as to how cyanide in effluents should be controlled:

1) Free Cyanide

Free cyanide is the most available form of cyanide toxicity. However, silver and copper cyanides are also toxic. Another difficulty is that there is still much debate as to how to measure free cyanide levels.

2) Total Cyanide

Total cyanide measurements include iron cyanide which is not toxic, although it can photodecompose to yield free cyanide. This becomes more of a factor for decanted effluent flowing in shallow streams at the headwaters of major fishery rivers.

A national level set to control on the basis of total cyanide would have to be quite high because it should allow a certain amount of iron cyanide which would not be

regarded as harmful. In cases where cyanide occurs as free cyanide such a total cyanide level would probably be too high.

3) Total Cyanide & Free Cyanide

A combination of total cyanide and available cyanide standards. This would allow some iron cyanides while providing a stricter control of free cyanide and other available cyanides. For example, such a standard might end up as 0.1 ppm maximum available cyanide and 0.5 total cyanide. Such a double standard would, however, be more difficult to enforce.

Before setting any regulations, ENVIRONMENT CANADA evaluated performance by three plants employing alkaline chlorination in British Columbia and the alkaline chlorination plant at Giant Yellowknife Mines Ltd. Meanwhile three of the alkaline chlorination plants in British Columbia have been replaced by SO_2 - air cyanide removal or shut down or stopped using cyanide.

A consulting firm, namely KERR, PRIESTMAN & ASSOCIATES of Victoria, B. C., was commissioned to monitor the three alkaline chlorination plants in British Columbia and prepare a report. A summary of their report is attached hereto.

Other methods such as Inco's SO_2-Air cyanide destruction process are also being evaluated, but by 1984 the toxicity of effluents from this process had still to be quantitatively determined.

ENVIRONMENT CANADA expected to have completed the technical assessment of commercial techniques for cyanide destruction by June 1983 and the National Standard for cyanide in mine effluents was to be published no sooner than the end of 1983. However this did not materialize.

It has been pointed out that Carolin Mines Ltd. in British Columbia was shut down for a period of time in 1982 by the British Columbia Government on account of a fish kill ascribed to cyanide in their effluent. One of the requirements in the operating permit for Carolin Mines is that the water in their effluent discharge must not be toxic to fish. After retrofitting SO_2-Air in their existing system Carolin Mines stopped cyanide leaching and shipped their flotation concentrate to a smelter as dictated by a change in their ore.

ENVIRONMENT CANADA has become a center for information on cyanide measurement and on techniques for and effectiveness of cyanide destruction, in conjunction with a task force on gold mining established to include mining industry representatives. Their approach has been professional and has adopted an attitude of finding out what can be achieved within practical and economic limits. Direct contact with this organization

is an excellent source of up-to-date information far in excess of the space available here:

ENVIRONMENT CANADA
Water Pollution Control Directorate
Environment Protection Service
Place Vincent Massey
Hull, Quebec K1A 1C8
Jim S. Scott, Chief
John C. Ingles
(819)997-3582

Examples of Limits for Cyanide - Canada
(mg/l)

		Type of Standard	Maximum Average	Maximum Grab
1.	Canadian Federal Government	National Standard CN Limit still under review - none issued.		
2.	Giant Yellowknife Mines, NWT NWT Water Control Board.			
	Total Cyanide	O	1.5	3.00
	Available CN^-	O	0.4	0.80
3.	Cominco Ltd., Con Mine NWT			
	Total CN_T	O	1.5	3.00
	Available CN^-	O	0.4	0.80
4.	Province of Ontario Water Quality Objective CN_T	G	0.005	0.005
5.	Ontario Drinking Water Goal CN_T	R	0.01	0.01
6.	Ontario Drinking Water Grounds for Rejection	R	0.20	0.20
7.	Western Mines Ltd. (1977) British Columbia	O	0.50	0.50

O: Obligatory Limit in permit
R: Recommended Limit
G: Goal

Motivation to Remove Cyanide from Effluents:

- To meet regulatory effluent discharge limits.

- To recover cyanide values in some instances.

The difficulty in meeting effluent regulatory limits for cyanide depends on the limits to be met, the metallurgical process employed, the nature of the ore treated, and the climate in which the operation is located, as well as the nature of the tailings impoundment.

Recovery of cyanide from effluent solutions could potentially be economically attractive in cases where very high levels of cyanide soluble metals such as copper or nickel are present in the ore which build up in level until they interfere with the process. Some cyanide recovery processes potentially make it feasible to recover cyanide, metal values and water. Although this has been accomplished on a test basis recently and on a commercial scale many years ago, no present day commercial installations are known. In very many cases cyanide is recovered by virtue of the internal recirculation and segregation of solutions within the plant or the recovery of some cyanide values in the tailings decant solutions.

TOXICITY OF CYANIDE

Cyanide is acutely toxic to fish at concentrations ranging from 0.05 - 0.1 ppm according to several researchers: HERBERT & MERKINS (1952); BURDICK et al. (1958); CAIRNS & SHEIER (1958); DOUDOROFF (1956); TURNBULL et al. (1954); LIPSCHUETZ & COOPER (1955); and WASHBURN (1948).

Industry argues that the levels that prove toxic under laboratory conditions are tested under conditions that are not representative of field conditions. In this respect the work that HOMESTAKE MINING COMPANY is currently undertaking with flow through tests should be very useful when finally published.

PROCESS REQUIREMENT

Where cyanides are to be destroyed ahead of an environmentally sensitive stream it should be borne in mind that if such a plant works perfectly for 99 plus percent of the time, then that is great. However, if it upsets only once, effluent damage would likely be as serious as if it were not installed at all - i.e., it is not average performance that counts, but the likelihood of occasional failure to meet minimum standards.

Consequently cyanide destruction plants must be reliable all the time to be useful and provision should be made for recycling of solutions that do not meet the discharge criteria during plant upsets. In this respect a continuous on-line cyanide monitoring device is under development by Witteck Development which could prove very useful if its detection limits are low enough.

WITTECK DEVELOPMENT, INC.
2640 South Sheridan Way
Mississauga, Ontario
Canada L5J 2M4
(416) 823-7381
Telex: 06-982328
Peggy Witte, President

MUDDER & WHITLOCK (1984) monitor thiocyanate rather than cyanide because it is more easily monitored at higher levels. They have developed an automated CNS^- monitor for use at Lead.

A second aspect to be considered, as pointed out by MUDDER & WHITLOCK (1984) is that several processes that destroy cyanide do not destroy harmful byproducts of the destruction, for example, ammonia. Nor do they remove environmentally undesirable metals such as copper, required to catalyze some cyanide destruction process. Even if ammonia is not a byproduct of cyanide destruction several mine effluents contain ammonia introduced by underground blasting. The effluent treatment process should be appropriate for the site specific conditions of climate, solution chemistry and the environment in which the plant is located.

TOXICITY EFFECTS OF CYANIDE

An enormous effort has been made to develop appropriate cyanide destruction techniques and experience is showing that the overall toxicity of the treated solution may be more important from an environmental point of view than extremely low free and total cyanide levels. MUDDER (1984) will present a paper on "Development of Site Specific Discharge Criteria through Toxicological Testing," reflecting the major efforts over several years that HOMESTAKE MINING COMPANY has put into trying to resolve cyanide effluent issues.

CHEMISTRY OF CYANIDE

The environmental behavior of cyanides as well as the performance and meaning of cyanide analyses by various analytical techniques are better understood when the chemistry of cyanide and cyanide metal complexes is understood.

Similarly the stability of various cyanide metal complexes is the basis for understanding why some complex metal cyanides are less easily decomposed than others in detoxification processes.

The chemistry of cyanides is discussed in depth by HUIATT et al. (1982), SCOTT & INGLES (1981) and MILGRAM (1984) as well as the series of INCO papers culminating with

DEVU ST, CONARD & HUDSON (1984). All of which are essential documents to anyone seriously interested in cyanide.

Some of the most fundamental tables of data describing cyanides are inserted here as a guide.

CYANIDE DESTRUCTION

Fortunately in much of the world where gold and silver are recovered by cyanidation the climate is hot or evaporation exceeds precipitation to such an extent that a zero discharge operation is possible. In hot climates natural degradation of cyanide is relied upon by producers of about 70% of the free world gold production or more. In several parts of the USA regulations for tailings disposal mandate lined tailings and evaporation ponds and zero discharge.

Cyanide destruction becomes important in climates where precipitation exceeds evaporation to the extent that a bleed to the environment cannot be avoided or where the ore treated contains so much cyanide soluble copper or nickel that the solutions cannot be recycled.

Unfortunately, the companies that must treat cyanide in their effluents, with the notable exception of Giant Yellowknife Mines Ltd. and Homestake Mining Company seldom include discussions of this important cost item in published papers describing their operations.

Prior to installation of an alkaline chlorination plant to detoxify effluent and especially tailings pulps it is highly recommended that the earlier installations be visited to learn what pitfalls can be avoided in advance.

In selecting an appropriate cyanide destruction process it is essential to perform pilot tests on actual pulps or solutions. This is impossible to simulate on a pilot scale before an actual operation that recycles solutions is brought on stream.

Several factors need to be considered when selecting such a process.

1) The effectiveness in removing CN_T^- and CN_C^- from solutions. Will it safely meet the regulated limits including ferrocyanides?

2) Does the CN^- treatment process add other toxic elements that then have to be removed by further treatment steps, e.g., Cl_2, NH_3, Cu, NH_2Cl?

3) Does the CN^- treatment process perhaps have an added advantage in removing other undesirable species such as Cu, Ni, As, etc.?

4) Can CN^- treatment be integrated in some way with an incremental resource recovery, e.g.,

- Carbon columns to destroy residual Cl_2 and recover Au?.
- Precipitate CuCN - float recovery and regeneration of CN^- for reuse?
- Recycle CN^- solutions after electro-removal of Cu.

5) Do regulations call for removal of CNS^- and CNO^-? If so, can the process achieve this?

6) Is the process upset-proof or upset-prone?

7) Is the process affordable and appropriate for operation at the proposed location?

8) Since most often it is during winter that CN removal is not helped by natural biodegradation the process performance at the operating temperatures must be considered.

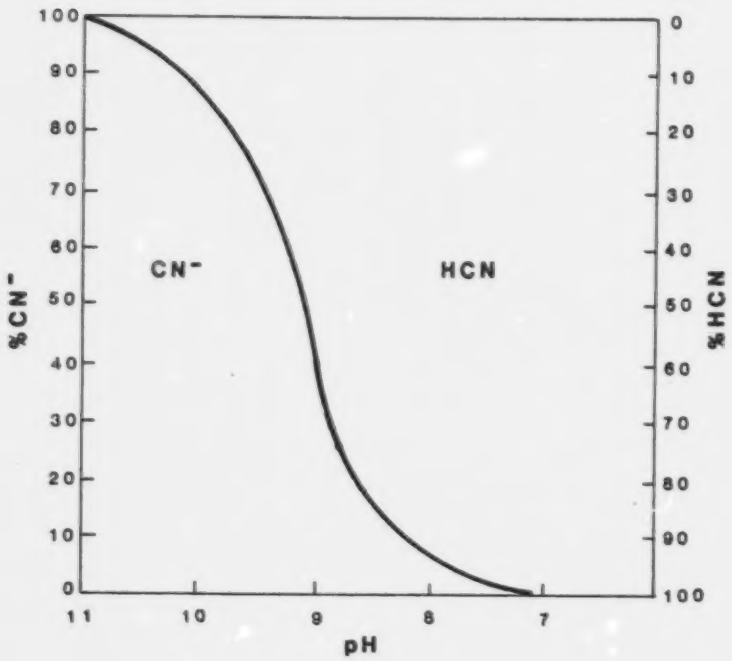
TABLE 6

SOLUBILITIES OF FERROCYANIDES AND FERRICYANIDES

Name	Formula	Solubility g/l (T°C)
Ammonium Ferricyanide	$(NH_4)_3Fe(CN)_6$	very soluble
Ammonium Ferrocyanide	$(NH_4)_4Fe(CN)_6 \cdot 3H_2O$	soluble
Barium Ferrocyanide	$Ba_2Fe(CN)_6 \cdot 6H_2O$	1.7g (15°)
Cadmium Ferrocyanide	$Cd_2Fe(CN)_6 \cdot xH_2O$	insoluble
Calcium Ferrocyanide	$Ca_2Fe(CN)_6 \cdot 12H_2O$	868g (25°)
Cobalt Ferricyanide	$Co_3\ Fe(CN)_6{}_2$	insoluble
Cobalt Ferrocyanide	$Co_2Fe(CN)_6 \cdot xH_2O$	insoluble
Copper (I) Ferricyanide	$Cu_3Fe(CN)_6$	insoluble
Copper (II) Ferricyanide	$Cu_3\ Fe(CN)_6{}_2 \cdot 14H_2O$	insoluble
Copper (II) Ferrocyanide	$Cu_2Fe(CN)_6 \cdot xH_2O$	insoluble
Iron (II) Ferricyanide	$Fe_3\ Fe(CN)_6{}_2$	insoluble
Iron (III)Ferricyanide	$Fe\ Fe(CN)_6$	---
Iron (II) Ferrocyanide	$Fe_2\ Fe(CN)_6$	insoluble
Iron (III) Ferrocyanide	$Fe_4\ Fe(CN)_6{}_3$	insoluble
Lead Ferricyanide	$Pb_3\ Fe(CN)_6{}_2 \cdot 5H_2O$	slightly soluble
Magnesium Ferrocyanide	$Mg_2Fe(CN)_6 \cdot 12H_2O$	330g
Manganese (II) Ferrocyanide	$Mn_2Fe(CN)_6 \cdot 7H_2O$	insoluble
Nickel Ferrocyanide	$Ni_2Fe(CN)_6 \cdot xH_2O$	insoluble
Potassium Ferricyanide	$K_3Fe(CN)_6$	330g (4°)
Potassium Ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	278g (12°)
Silver Ferricyanide	$Ag_3Fe(CN)_6$	0.00086 (20°)
Silver Ferrocyanide	$Ag_4Fe(CN)_6 \cdot H_2O$	insoluble
Sodium Ferricyanide	$Na_3Fe(CN)_6 \cdot H_2O$	189g (0°)
Sodium Ferrocyanide	$Na_4Fe(CN)_6 \cdot 10H_2O$	318.5g (20°)
Strontium Ferrocyanide	$Sr_2Fe(CN)_6 \cdot 15H_2O$	500g
Thallium Ferrocyanide	$Tl_4FE(CN)_6 \cdot 2H_2O$	3.7g (18°)
Tin (II) Ferricyanide	$Sn_3\ Fe(CN)_6{}_2$	insoluble
Tin (II) Ferrocyanide	$Sn_2Fe(CN)_6$	insoluble
Tin (IV) Ferrocyanide	$SnFe(CN)_6$	insoluble
Zinc Ferrocyanide	$Zn_2Fe(CN)_6$	insoluble

Source: Weast, 1969

EFFECT OF pH ON DISSOCIATION OF HYDROGEN CYANIDE



THE NATURE OF TOXICITY OF COMPLEXED CYANIDES

IN FLOTATION TAILINGS

SUMMARY

The acute toxicity of free cyanide (molecular HCN and ionic CN^- is well documented. Free cyanide inhibits oxygen metabolism by binding to metal constituents of certain enzymes within cells. The most sensitive enzyme inhibited by free cyanide is cytochrome oxidase. When this enzyme is inactivated by free cyanide, oxygen utilization by the cells is prevented and cell death results. Cells with high oxygen demands, such as those of the Central Nervous System, are most sensitive to oxygen deprivation. Cells can detoxify low levels of free cyanide by coverting it to less toxic or nontoxic intermediates. The primary detoxification pathway is the reaction of free cyanide with thiosulfate to produce thiocyanate which is then slowly eliminated from the body in urine.

Complexed cyanides, especially those associated with flotation tailings, are generally considerably less toxic than free cyanides. However, complexed cyanides undergo varying degrees of dissociation when in solution which release free cyanide. The degree of toxicity of solutions of complexed cyanides is largely dependent upon the amount of free cyanide present. However, other factors may contribute to toxic effects as well, such as the metals themselves, e.g. copper-cyanide complexes. Whereas the level of toxicity is largely dependent on the amount of free cyanide present as a result of dissociation, the degree of dissociation for any given complex is highly variable depending on conditions. Also, for many metallocyanide complexes, no concensus exists among investigators as to the amount of dissociation under any given set of conditions because of the wide range of factors that can potentially effect the dissociation constants.

Certain complexes that are more readily dissociated in aqueous solution than iron complexes (e.g., zinc-tetracyanate, etc.) are reported as highly toxic because of the availability of free cyanide. These toxic complexed forms are not expected to be found in flotation tailings. Complexes with the cyanide group tightly bound (e.g., iron-cyanide, cobalt-cyanide) have a low toxicity and are considered nontoxic by most investigators. Copper, nickel, silver, and other metallic cyanide complexes undergo moderate degrees of dissociation relative to iron cyanides. Numerous factors affect the degree of dissociation. e.g., pH, temperature, dissolves oxygen concentration, and thus markedly influence toxicity levels.

Within flotation tailings, the more stable complexes predominate (e.g., iron-cyanides) due in part to operational practices associated with ore extraction procedures (e.g., cyanides are used to react with iron pyrites to depress them). The cyanides are frequently used to preferentially react with iron containing minerals such as pyrites to preferentially suppress them by forming iron cyanides at the surface. In the EPA reference document, The Manufacture and Use of Selected Inorganic Cyanides, page 1, the reference is made to iron complex cyanides: "Cyanide in this form is not particularly toxic nor hazardous to handle because of the great stability of the iron cyanide radical ion toward dissociation and oxidation-reduction reactions."

Inasmuch as the iron complex cyanides are more stable, thermodynamics would indicate that they would preferentially form over the less stable metal cyanides. Thus complexed cyanides associated with flotation tailings, in addition to being present in low concentrations, are relatively non-hazardous. Some complexed cyanides are used as food additives (e.g., sodium ferrocyanide). Several grams of complexed cyanide (i.e., sodium ferrocyanide) have been swallowed repeatedly by would-be suicides without apparent ill-effect. A case is reported in which disposal of cyanide wastes in a gravel pit near Cologne, Germany resulted in ground water contamination by complexed cyanide (i.e., potassium hexacyanoferrate); however, tests revealed that the complexed cyanide was relatively innocuous, so the water supply was not shut down.

There is conflicting information reported regarding the hazards associated with the iron-cyanide complexes because of their tendency to undergo photodecomposition. However, in flotation tailings, photodecomposition of iron-complexes would not produce significant amounts of free cyanide because light is not transmitted through the solid phase of the tailings. Additionally, the low concentration of iron cyanides and the fact that not all the iron cyanide would photolytically decompose at once make this degradation problem insignificant.

Complex and free cyanide appears to have an unusually low degree of chronic toxicity. The effects are either lethal or the free cyanide is detoxified by the organism. Almost no information is reported on the chronic toxicity of complexed cyanides. There is no reported evidence that cyanide is mutagenic, teratogenic, or carcinogenic. This finding is collaborated by the EPA which in March 1979 published the following statement

in their Ambient Water Quality Criteria report for Cyanide.

> "...there is no evidence that chronic exposure to cyanide results in teratogenic, mutagenic, or carcinogenic effects."

RATIONALE FOR THE ESTABLISHMENT OF ONTARIO'S PROVINCIAL WATER QUALITY OBJECTIVES

September, 1979

Ontario
Ministry of the Environment

CYANIDE

OBJECTIVE

Concentrations of free cyanide in unfiltered water samples should not exceed 5 micrograms per litre for the protection of aquatic life.

RATIONALE

Cyanide is one of the simplest and most readily formed organic compounds. Cyanide and derivatives are almost universally present where life and industry are found. Besides being very important in a number of manufacturing processes, they are found in many plants and animals as metabolic intermediates which generally are not stored for long periods to time.

Common forms of cyanide in effluents are metal cyanide complexes, hydrocyanic acid, and the free cyanide ion formed primarily from dissociated simple cyanide salts. The cyanide form present in the aquatic environment is largely pH dependent. Most of the free cyanide exists as HCN at pH values of natural waters, with the fraction increasing rapidly as the pH of the solution decreases. When simple cyanide salts dissociate in aqueous solution, the cyanide ion combines with the hydrogen ion to form hydrocyanic acid, which is highly toxic to aquatic life. Chemically, the cyanide ion behaves similarly to the halide ions -- chloride, fluoride, bromide and iodide.

The cyanide ion combines with numerous heavy metal ions to form metallocyanide complexes. The stability of these anions is highly variable. Those formed with zinc and cadmium are not stable; dissociation and production of hydrocyanic acid in near neutral or acidic environments is rapid. In turn, some of the metallocyanide anions are extremely stable. Cobaltocyanide is difficult to destroy with highly destructive acid distillation in a laboratory. The iron cyanides are also very stable but exhibit the phenomenon of photodecomposition, and in the presence of sunlight the material dissociates to release the cyanide ion, thus affecting toxicity; at night the reaction may reverse to produce a less toxic environment.

A wide variety of organic compounds may contain cyanide functional groups. These compounds belong to a class of organic chemicals called nitriles, none of which dissociates to liberate cyanide ions or molecular HCN. In addition, there are also complex organic acids, alcohols, esters, and amides that contain the cyanide radicals. These organic compounds are used for numerous products or may be a waste by-product. Their toxicity, persistence, and chemistry in the aquatic environment are not well known except for a few specific compounds.

Cyanide toxicity is essentially an inhibition of oxygen metabolism, i.e., rendering the tissues incapable of exchanging oxygen. The cyanogen compounds are true non-cumulative protoplasmic poisons (can be readily detoxified) since they arrest the activity of all forms of animal life. Cyanide shows a very specific type of toxic action. It inhibits the cytochrome oxidase system which facilitates electron transfer from reduced metabolites to molecular oxygen. The ferric iron-porphyrin molecule responsible for the catalytic action of cytochrome oxidase is the reactive site where cyanide combines with ferric (Fe(III)) iron atoms to form a reversible complex. Other enzymes containing a metal porphyrin molecule, e.g., peroxidases and xanthine oxidases, are also strongly inhibited by cyanide. Only undissociated HCN inhibits the consumption of oxygen in the tissues, causing cellular asphyxia (historic anoxia) by attaching itself to the iron of the prosthetic group of the enzyme cytochrome oxidase.

Hydrocyanic acid can be rapidly absorbed and carried in the plasma but does not combine with hemoglobin because its iron atom is divalent (ferrous). Instead, cyanide combines with methemoglobin, a mildly oxidized form of hemoglobin in which the iron atom is trivalent (ferric). Methemoglobin, which cannot carry oxygen, normally represents only a small fraction of the total hemoglobin. Since it forms an irreversible and innocuous complex with cyanide, it is an active cyanide detoxifying agent. Amyl nitrite and other agents can be used to increase the level of methemoglobin to counteract cyanide toxicity. A few of the ways in which cyanide can be metabolized within a pattern of normal physiology are by the production of thiocyanate, with amino acids, oxidation to carbon dioxide and formate, etc. The conversion of only free cyanide and not organically bound cyano groups to thiocyanate (SCN-) by action of the enzyme rhodanase is considered to be the primary method of detoxification of cyanide. Rhodanase is absent from blood and skeletal muscle, but is abundant in the liver. Thiocyanate is eliminated irregularly and slowly in the urine.

The action of cyanide on the respiration of the cell and the primary methods of detoxification of cyanide have been noted above. However, it should be pointed out that cyanide does not completely abolish cellular respiration. It is possible that a small amount of residual respiratory activity is made possibly by cytochrome-b activity, since this substance does not require the cyanide-susceptible cytochrome oxidases. An alternative explanation of residual respiratory activity of the cyanide-poisoned system is found in the action of the flavin aerobic dehydrogenases, which can transfer hydrogen to molecular oxygen without the cytochrome system.

The persistence of cyanide in water is highly variable. This variability is dependent upon the chemical form of cyanide in the water, the concentration of cyanide, and the nature of other constituents. Cyanide may be destroyed by strong oxidizing agents such as permanganates and chlorine. Chlorine is commonly used to oxidize strong cyanide solutions to produce carbon dioxide and

ammonia; if the reaction is not carried through to completion, cyanogen chlorine may remain as a residual and this material is also toxic. If the pH of the receiving waterway is acid and the stream is well aerated, gaseous hydrogen cyanide may evolve from the waterway to the atmosphere. At low concentrations or toxicity and with acclimated microflora, cyanide may be decomposed by microorganisms in both anearobic and aerobic environments or waste treatment systems.

A review of the available pertinent data on the acute toxicity of simple cyanides to fish reveals that the minimum lethal (threshold) concentrations of free cyanide from data obtained from experiments ranging from 12 minutes to 10 days with brook trout, Salvelinus fontinalis (Karsten, 1934); rainbow trout, Salmo gairdneri (Herbert and Merkens, 1952); brown trout, Salmo trutta (Burdick et al., 1958); bluegills, Lepomis macrochirus (Doudoroff et al., 1966); and fathead minnows, Pimephales promelas (Doudoroff, 1956), are reported to be 50, 70, (60 determined concentrations) 70, 104, 150 and 180 ug/L as cyanide, respectively. The minimum lethal threshold concentration is the concentration nearly or barely tolerable for individuals of average resistance when the exposure thereto is indefinitely prolonged.

Research at the University of Minnesota has revealed that the minimum lethal threshold concentrations, as determined from continuous flow bio-assays in which routine analyses for cyanide were performed, are generally lower than the above reported values. In addition, the acute data with fish indicate that, in general, juveniles are more sensitive to HCN than younger life history stages, and that their sensitivity is increased with reduction in dissolved oxygen concentration and with lowering of temperature. Over the temperature range of 25°C to 8°C the lethal threshold concentration (LTC) for juvenile bluegills (Lepomis machrochirus) was determined to decrease linearly from 130 to 58 ug/L HCN. Should the above linearity persist to lower temperature - not as yet experimentally determined - the calculated LTC values at 5, 3, and 1°C would be 41, 32 and 23 ug/L HCN respectively.

In review it can be concluded that free cyanide concentrations in the range from 50 to 100 ug/L as cyanide have proven eventually fatal to many sensitive fishes and levels much above 200 ug/L probably are rapidly fatal to most species.

Downing (1954), Cairns and Scheier (1958), and Burdick et al. (1958) have shown that the toxicity of free cyanide increases with any reductions in dissolved oxygen below the 100 percent saturation levels. Cairns and Scheier (1958) observed that even periodic lowering of dissolved oxygen decreased the tolerance of bluegills to cyanide.

Contradictory information from the literature indicates that uncertainty exists between the relationship of toxicity of simple cyanides to fish and the pH of the test solution. However, since undissociated hydrogen cyanide has been demonstrated to be the toxic cyanide species in simple cyanide solutions, changes in the pH of natural waters below a value of about 8.3 should have no measurable effect on the acute toxicity of simple cyanides to fish. There is no apparent relationship between toxicity to fish and the alkalinity and hardness of the dilution water.

Cyanide is acutely toxic to most fishes at concentrations ranging from 50 to 200 ug/L (Herbert and Merkens, 1952; Burdick et al., 1958; Cairns and Scheier, 1958; Doudoroff, 1956; Turnbull et al., 1954; Lipschuetz and Cooper, 1955; Washburn, 1948).

Some information on chronic or sublethal effects of cyanide is also available. Leduc (1966) found increased intestinal secretions in the fish, Cichlasoma bimaculatum, at concentrations as low as 20 ug/L and reduced swimming capability at concentrations of 40 ug/L. Costa (1965) reported that three common species of fish detected and avoided cyanide concentrations of 26 ug/L in approximately one hour or less. Exposure to a cyanide concentration as low as 10 ug/L reduced the swimming ability or endurance of brook trout, Salvelinus fontinalis (Neil, 1957). Growth, or food conversion efficiency of coho salmon, Oncorhynchus kisutch, was reduced at hydrogen cyanide concentrations of 20 ug/L. Small freshwater fish of the family Cichlidae exposed to a cyanide concentration of 15 ug/L lost weight more rapidly than the control fish in water free from cyanide (Leduc, 1966).

Survival and growth tests of 56 days duration on young of the yellow perch (Perca falvescens) and newly hatched bluegill fry (Lepomis machrochirus) performed at the University of Minnesota indicate that with the bluegill fry significant mortality occurred after about one month at all levels above 26 ug/L HCN. With the yellow perch, a marked effect on growth and survival was observed at about 45 ug/L, and at 64 ug/L survival was approximately 50 percent (Broderius, 1975). Chronic tests were also performed by Broderius in 1975 from egg through reproduction and into the second generation of fathead minnows (Pimephales promelas) and through reproduction and hatching with brook trout (Salvelinus fontinalis). For the fathead minnow it was observed that HCN levels above 40 ug/L decreased growth rate through 84 days.

A significant reduction in fecundity was noted at HCN levels greater than 18 ug/L. Mean percentage hatch was significantly decreased at levels of 40 ug/L HCN and higher. When the combined effect of egg production and fertility (percentage of egg hatch) were calculated at about 50, 120, 180, 250, and 330 ug/L HCN, effective reproduction was approximately 65, 59, 35, 24, and 21 percent of the controls respectively. From the brook trout chronic data, it can be calculated that at about 50, 100 and 300 ug/L HCN effective reproduction was about 80, 50, and 30 percent of the controls respectively.

Based upon chronic effects on fish growth and reproduction, an objective of 5 ug/L free cyanide as HCN is recommended.

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SOURCE

The above rationale information was taken from "Appendix A, Water Quality Objectives Subcommittee Report, Great Lakes Water Quality 1975", pages 95-100, International Joint Commission, 1976.

Table 7

STABILITY OF METAL-CYANIDE COMPLEXES

Source: HUIATT et al (1981)

COMPLEX ION	STABILITY CONSTANT[1/]
$Cr(CN)_6^{3-}$	10^{33}
$Cr(CN)_6^{4-}$	10^{21}
$Fe(CN)_6^{4-}$	$10^{35.4}$
	10^{47} [2/]
$Co(CN)_6^{4-}$	10^{50}
$Ni(CN)_4^{2-}$	10^{30}
$Pd(CN)_4^{2-}$	10^{42}
$Pt(CN)_4^{2-}$	10^{40}
$Cu(CN)_2^{-}$	$10^{23.9}$
$Cu(CN)_3^{2-}$	$10^{29.2}$
$Cu(CN)_4^{2-}$	$10^{30.7}$
$Ag(CN)_2^{-}$	$10^{20.4}$
$Ag(CN)_3^{2-}$	$10^{21.9}$
$Au(CN)_2^{-}$	10^{37}
$Au(CN)_4^{-}$	10^{85} (estimate)
$Zn(CN)_4^{2-}$	10^{21}
$Cd(CN)_4^{2-}$	10^{19}
$Hg(CN)_4^{2-}$	10^{39}

[1/] Source unless otherwise noted is from Sharpe (1976)

[2/] Taken from Ph.D. Dissertation of Broderius, 1973.

Table 8

STABILITY OF METAL CYANIDE COMPLEXES

Source: GRIGORAOVA & LENAHAN (1983)

Metal M	Complex M-CN	Stability Constant Ka
Zn^{2+}	$Zn(CN)_4^{2-}$	10^{17}
Cd^{2+}	$Cd(CN)_4^{2-}$	10^{18}
Ag^{1+}	$Ag(CN)_2^{1-}$	10^{20}
Fe^{2+}	$Fe(CN)_6^{4-}$	10^{24}
Cu^{2+}	$Cu(CN)_4^{2-}$	10^{25}
Fe^{3+}	$Fe(CN)_6^{3-}$	10^{31}
Au^{1+}	$Au(CN)_2^{1-}$	10^{38}
Ni^{2+}	$Ni(CN)_4^{2-}$	10^{41}
Au^{3+}	$Au(CN)_4^{1-}$	10^{56}
Co^{3+}	$Co(CN)_6^{3-}$	10^{64}

The stability constant of hydrogen cyanide (HCN) in aqueous solution is:

$$Ka = 4,93 \times 10^{-10}$$

TABLE 9

ESTIMATED CAPABILITIES OF PROCESSES FOR CYANIDE REMOVAL FROM GOLD MILL EFFLUENTS*

(Adapted from HUIATT et al. (1982) and MUDDER & WHITLOCK (1984)

	Suitability for removal of												
			Zinc and Cadmium complex cyanides		Copper and Nickel complex cyanides								
Process	CN^- and HCN	CN_T	metal	cyanide	metal	cyanide	Ferro cyanide, $Fe(CN)_6$	Thio-cyanate, CNS	Ammonia	Metals	Products	Requires further treatment	Patent Protected
Natural degradation	yes	no	partial	partial	no	no	no	partial			decant	yes	
Acidification/ Volatilization/ Reneutralization	yes	yes	yes	yes	yes	yes	yes	partial	no	no	1) treated effluent	yes (a,b)	
									no	no	2) recycle cyanide solution	no	
Alkaline Chlorination	yes	no	yes	yes	yes	yes	no	yes	yes	yes, expensive (i)	treated effluent	may (b)	
Ozonation	yes		yes	yes	yes	yes	with UV irradiation	yes	---	no	treated effluent	may (b)	

TABLE 9

Process	Suitability for removal of: CN^- and HCN	CN_T	Zinc and Cadmium complex cyanides: metal	Zinc and Cadmium complex cyanides: cyanide	Copper and Nickel complex cyanides: metal	Copper and Nickel complex cyanides: cyanide	Ferro cyanide, $Fe(CN)_6$	Thio-cyanate, CNS	Ammonia	Metals	Products	Requires further treatment	Patent Protected
Ion Exchange													
1) untreated resin	no		yes	yes	yes	yes	yes	possible	---	yes, partial	1) treated effluent	no	
2) untreated resin, pretreated solution	yes		yes	yes	yes	yes	yes	possible	---	yes, partial	2) waste re-generating solution	yes (c)	
3) CuCN-treated resin	yes		yes	yes	yes	yes	yes	possible	---	yes, partial	3) recycle cyanide solution	no	
Activated Carbon													
1) granular, fixed bed	no		partial	partial	yes	yes	yes	?	---	no	treated effluent	yes (d)	
2) granular, copper treated fixed bed	partial		yes	yes	yes	yes	yes	?	---	no	1) treated effluent	may (d)	
											2) strip solutions	yes (d,e)	

TABLE 9

Process	Suitability for removal of: CN^- and HCN	CN_T	Zinc and Cadmium complex cyanides: metal	Zinc and Cadmium complex cyanides: cyanide	Copper and Nickel complex cyanides: metal	Copper and Nickel complex cyanides: cyanide	Ferro cyanide, $Fe(CN)_6$	Thio-cyanate, CNS	Ammonia	Metals	Products	Requires further treatment	Patent Protected
Bacterial (acclimatized pseudomonas paucermobilis)	yes		yes	yes	yes	yes	yes	yes	yes	yes	bicarbonates, sulfates nitrates no ammonia generated	no, except possible polishing (1)	yes Homestake
SO_2/Air	yes		yes	yes	yes	yes	yes	no	no	yes	CNO, Me_2 $Fe(CN)_6$	(1)	yes INCO
Activated Carbon, copper-treated, with aeration													
1) granular, fixed bed	yes		yes	yes	yes	yes	partial	?			treated effluent	may (b)	
2) powdered, once through	yes	yes	yes	yes	yes	yes	yes	?			1) treated effluent	no	
											2) cyanide-free slidge	no	
Ion Flotation	partial (e)		partial	partial	yes	yes	yes	?	no	partial	1) treated effluent	may (d)	
											2) sludge	yes	

TABLE 9

Process	Suitability for removal of: CN^- and HCN	CN_T	Zinc and Cadmium complex cyanides: metal	Zinc and Cadmium complex cyanides: cyanide	Copper and Nickel complex cyanides: metal	Copper and Nickel complex cyanides: cyanide	Ferro cyanide, $Fe(CN)_6$	Thio-cyanate, CNS	Ammonia	Metals	Products	Requires further treatment	Patent Protected
Electrochemical													
1) for cyanide recovery HSA Reactors (k)	no (h)		yes	no	yes	no	no	no	no	yes	1) partially regenerated cyanide solution (for recycle)	may	
											2) metal-bearing strip solution	yes (g)	
2) for cyanide destruction	partial to most		yes	partial to most	yes	partial to most	no	yes	no	yes	1) treated effluent	may (b)	
											2) metal-bearing strip solution	yes (g)	
3) Electro chlorination	yes		yes	yes	yes	yes	no	yes	no	yes	1) treated effluent	may (b)	
											2) metal-bearing strip solution	yes (g)	

TABLE 9

Process	Suitability for removal of												
	CN^- and HCN	CN_T	Zinc and Cadmium complex cyanides		Copper and Nickel complex cyanides		Ferro cyanide, $Fe(CN)_6$	Thio-cyanate, CNS	Ammonia	Metals	Products	Requires further treatment	Patent Protected
			metal	cyanide	metal	cyanide							
Hydrogen Peroxide Copper Catalyzed	yes		yes	yes	partial	partial	no	no	no	no	treated effluent	may (b)	
Hydrogen Peroxide Copper Catazyzed with $FeCl_3$ addition for Residual Metal Removal	yes		yes	yes	yes	yes	yes	no	no	yes		(h)	Dupont
Prussian Blue Precipitation	yes		yes	yes	yes	yes	yes	no	no	yes	Ferri Ferro cyanide precipitate	may (m)	yes Roy Neville
Fresh FeS	yes		yes	yes	yes	yes	no	no	no	yes	treated effluent	may (m)	yes Cominco Permutit
Wet Oxidation	yes		?	?	?	?	?	?	?	?			

TABLE 9

ESTIMATED CAPABILITIES OF PROCESSES FOR CYANIDE REMOVAL FROM GOLD MILL EFFLUENTS*

(Adapted from HUIATT et al. (1982) and MUDDER & WHITLOCK (1984)

a) Extra filtration step both before and after liming, if copper, nickel and ferrocyanide levels are high; requires strong acid for ferrocyanide destruction.

b) Supplementary treatment (e.g. activated carbon) if ferrocyanide level high.

c) Treatment (e.g. liming) to recover metals for disposal.

d) May require pretreatment to convert all cyanide to copper or iron complexes.

e) Depends on prior conversion to ferrocyanide.

f) Thiocyanate and ferrocyanide build-up, and water-balance considerations will necessitate bleed stream requiring further treatment.

g) Strip solution may be regenerated electrolytically, recovery in metals as powder.

h) Cyanide is recycled instead.

i) Is-20g Cl_2 is needed to decompose 1g NH_3.

j) MUDDER & WHITLOCK (1984) Pilot plant recudes CN_T to 0.35 mg/l and free CN to 0.05 mg CN/l.

k) HSA reactors reputedly in liquidation.

l) Depending on regulatory CN_T and CN limits in effluents.

m) Ferrocyanide removed only if the Prussian Blue precipitate is settled, floated or filtered from solution.

NOTE: The response "Yes" in this matrix means that there is a reaction and that levels of the metal or species referred to will be reduced. It does not necessarily mean, however, that levels can be reduced sufficiently to meet present or future permit levels or that the levels can be reduced at an affordable cost. Further discussion is provided in the text.

* The estimates of performance capability presented in this table are based on literature data for feed solutions from many different sources. The final cyanide concentration that can be achieved, and the cost of treatment in any particular case, can only be determined by actual tests.

ANALYTICAL DETERMINATION OF CYANIDES

The determination of "free" cyanide in mill solutions using silver nitrate with various indicators is well established although subject to several interferences. The most common indicator is potassium iodide but a much more convenient endpoint is obtained using 2-5 drops of 0.03% acetone solution of 5-[p(Dimethylamino)-benzylidene]-rhodanine. Cas No. 536-17-4, Eastman Kodak No. 2648. This indicator is used and recommended by Kappes, Cassiday & Associates, Reno Nevada.

The DuPont Company has developed a modification of the "free" cyanide field titration method so that it will also include copper and nickel cyanides which are environmentally undesirable. Their method involves reacting the sample first with a small amount of zinc dust to release cyanide from the copper and nickel complexed form before the silver nitrate titration which is precise down to around 1 ppm. Work is in progress to see whether this adaptation will be applicable also to the potentiometric cyanide specific electrode determination and the HACH rapid colorimetric method reportedly precise down to 0.1 ppm CN. More information will be available at the December cyanide conference in Tucson and from: Frederick W. DeVries, E. I. DuPont de Nemours & Co., Wilmington, DE.

The determination of cyanide at the very low levels of interest in tailings and effluents approaching or below regulatory limits is no straightforward matter. Several different techniques have been proposed and the literature on the subject has become somewhat confusing as illustrated when reading the exentsive literature survey on the subject by POHLANDT et al. (1983). A further complicating factor is that in making determinations of cyanide in a sample to determine whether the effluent meets a certain limit, there is not much point in using one preferred method if the limit is based on another method which is the one used by the regulatory authority. Still, if as in this case, the standard method on which a regulatory limit is based can be shown to be non-reproducible or subject to serious interferences by other species in the solution, then it becomes important to find an improved method of analysis which eventually can replace the current standard method. POHLAND (1984) described a powerful new ion chromatography method for the determination of different cyanide-metal complexes in solution.

MUDDER & WHITLOCK (1984) and MUDDER (1984) propose to overcome all argument and uncertainty by installing a site specific in situ bioassay program which would determine whether or not the effluent or treated effluent is toxic to ecological species of concern to the particular location.

The Wastewater Technology Centre in Burlington, Ontario carried out a systematic survey of methods for "free" and "total" cyanide determination in Wastewater in 1981. This review by CONN (1981) confirmed that the standard sulfuric acid distillation technique for "total" cyanide determination as it appears in the APHA-AWWA "Standard Methods" is

subject to interference by thiocyanate and sulfide. Ways to avoid this interference by simple modification of the technique have been suggested.

GRIGOROVA & LENAHAN (1983) do not believe that CNS^- interferes with the cyanide analysis but they suggest other modifications of the method to overcome interference by-sulfides.

MUDDER & WHITLOCK (1984) also undertook extensive research to evaluate and develop reliable methods for cyanide analysis and found the "total" cyanide analysis method in "Standard Methods" to be subject to interferences which could be overcome by minor modification.

If there is uncertainty about the reliability of "total cyanide" analysis, then, the uncertainty is greater when it comes to "free" cyanide or "available" cyanide analysis because then it depends very much on which metal cyanide complexes are measured and which are not, or only partially detected. This depends on the precise details of the process. One way of overcoming this would be to settle for "that free and complexed cyanide as determined by method X" based on which it is agreed by convention to determine toxicological effects and set effluent limits. A start has been made in this direction in the USA in the ASTM Methoc C determination which is gaining acceptance.

The key to understanding cyanide analysis and what results of determinations by the different techniques mean is to understand basic chemistry and in particular to understand the range in metal cyanide complex stabilities ranging from $[Cd(CN)_4]^{2-}$ with a stability constant of 10^{19} to $[Au(CN)_4]^-$ with an estimated stability constant of 10^{85} which on the table presented in HUIATT et al. (1982) in Table 7 and 10^{18} and 10^{56} respectivey by GRIGOROVA & LENAHAN (1983) in Table 8.

Tables 7 and 8 of metal cyanide stability constants as they appear in HUIATT (1982) and GRIGOROVA & LENAHAN (1983) were inserted above. It is remarkable how many discrepancies there are, nevertheless the grouping of stabilities would agree, i.e.:

Less Stable Metal Cyanide Complexes	Zinc Cyanide Cadmium Cyanide Silver Cyanide
More Stable Metal Cyanide Complexes	Ferrous, Ferric, Cupric Cyanide Complexes
Most Stable Cyanide Complexes	Gold, Nickel, Cobalt Cyanide Complexes

The less stable the complex, the easier it will be to dissociate it using acid and to distill the resulting HCN off with free cyanide for determination.

Some of the confusion about cyanide analysis is due to differences in interpretation in what should be included in the term "free" cyanide. Should it include only the species HCN and free CN^- ions, or should it include some of the various weaker cyanide metal complexes such as those of zinc, cadmium and silver, for example, and if so which ones.

It is hoped that this question will be resolved in the forseeable future. This was a topic at the 1984 Cyanide Conference to be held in December in Tucson, AZ.

TOTAL CYANIDE ANALYSIS

"Total" cyanide analysis refers to all free cyanide, HCN and all complexed cyanide including iron cyanide complexes.

APHA-AWWA & ASTM METHOD

The most commonly referred to method for "total" cyanide is that published by the American Public Health Association in "Standard Methods for the Examination of Water and Wastewater." This method is the same as the ASTM method for "total" cyanide.

This method employs decomposition of free and complexed cyanides in the presence of added magnesium chloride which catalyzes their decomposition. The liberated cyanide is quantitatively distilled off as HCN and condensed in a solution of chloramine T which converts it to cyanogen chloride. The cyanogen chloride then forms a red-blue dye on addition of a pyridine-barbituric and reagent which is quantitatively determined by photometric absorbance compared against standard solutions.

It has been found that the above method is subject to interferences:

- Sulfides are decomposed in sulfuric acid and form H_2S which is distilled with the HCN and cause a high reading.

- CNS has been found by CONN (1981) and others to give a high reading although this could not be confirmed by tests carried out by LUDZACK et al. (1954) and GRIGOROVA & LENAHAN (1983).

- MUDDER & WHITLOCK (1984) found that the above method was subject to interferences.

- GRIGOROVA & LANAHAN (1983) found that the APHA "Standard" method does not give a quantitative determination of all the iron and gold cyanide complexes present in the sample and will under read total cyanide in some samples.

Several improvements in the APHA-AWWA-ASTM method have been developed and are in use.

1) MUDDER & WHITLOCK (1984) described the use by HOMESTAKE MINING COMPANY, Lead, S. D. of the "Standard" method modified to use phosphoric acid H_3PO_4 in the place of sulfuric acid to avoid interferences. They find this technique accurate and reproducible down to total cyanide levels of 0.02 mg/l with a standard deviation of 0.01 mg/l.

2) GRIGOROVA & LANAHAN (1983) describe the use of the "Standard Method" and that prescribed by the South African Dept. of the Environment which uses $HgCl_2$ as catalyst in the place of $MgCl_2$. They find that the addition of $Cd(NO_3)_2$ at 0.5% to the sample solution ahead of acidification will prevent any sulfides from interfering by precipitating cadmium sulfide which must also be filtered ahead of acidification.

   GRIGOROVA & LANAHAN (1983) also substitute H_3PO_4 for sulfuric acid.

   GRIGOROVA & LANAHAN (1983) have shown that gold cyanide complexes which are not quantitatively determined when using the "Standard Methods" or ASTM or South African Government Gazette Method, can be quantitatively determined if zinc is added with the acid during the reflux step. However, since the use of zinc with sulfuric acid results in the generation of some H_2S which interferes with the determination as discussed above, these analysts replace sulfuric acid with phosphoric acid.

   When using zinc, however, it is found that not all the ferric cyanide complex is dissociated, so when ferrocyanide and ferricyanide are to be included in the determination as well, this method is not totally suitable.

3) According to CONN (1982 personal communication), two procedures have been tested by the Wastewater Technology Centre at Burlington, Ontario, and confirmed as reliable for determination of total cyanide in solution including iron cyanides without CNS^- interference: -

   - Distillation with HCl and hydroxylamine hydrochloride with addition of $CdCl_2$ to prevent $S^=$ distillation.

This technique was developed as a modification to the standard distillation method used in the past by KNECHTEL & CONN (1980).

- Distillation of cyanide in the presence of tartaric acid as developed by Noranda Mines Ltd., has been shown to measure total cyanide including iron cyanides and to avoid CNS^- interference. This has been confirmed by the Wastewater Technology Centre, according to CONN (1982 personal communication).

  It is believed that Homestake Mining Company determine total cyanide using phosphoric acid, which also measures iron cyanides while avoiding CNS^- interference.

In each of these cases, after distillation subsequent steps are the same as the standard technique involving conversion to cyanogen chloride CNCl by reaction with chloramine-T at a pH less than 8, followed by formation of a red-blue dye on the addition of pyridine-barbituric acid reagent. The concentration is then determined by measurement of the absorbance at 578 nm and compared against standard solutions.

The method and equipment used for the photometric step in the determination, are the same as that described in "Standard Methods for the Examination of Water and Wastewater", 14th Edition, edited by MARY ANN FRANSON and published by:-

AMERICAN PUBLIC HEALTH ASSOCIATION
1015 Eighteenth Street NW
Washington, DC 20036

The South African regulated limit refers to "cyanide and related compounds" although the method listed for their determination in the South African Government Gazette measures only "total cyanide" and then imperfectly. Clearly the South African Government intended to include complexed and free cyanide but <u>not thiocyanate and cyanate</u> in "related compounds" as was interpreted by GRIGOROVA & LENAHAN (1983).

GRIGOROVA & LENAHAN (1983) point out that thiocyanate on acidification is converted to ammonia and is not reported in the "total cyanide" analysis:

$$2NaCNO + H_2SO_4 + 4H_2O = (NH_4)_2\ SO_4 + 2NaHCO_3$$

GRIGOROVA & LENAHAN (1983) do not find that thiocyanate interferes with cyanide analysis. They refer to a test by LUDZACK, F. J.; MOORE, W. A. and RUCHHOFT, C. C. (1954) in which thiocyanate and cyanate were refluxed for two hours in a cyanide blank solution without yielding any reading for cyanide. Since their work was dated 1954 long before there was an interest in cyanide determination at current ppb levels, possibly these authors were testing interference at a much higher detection limit for cyanide, and

the tests should be redone. That a low level interference might occur was also indicated by CLYSTERS & ADAMS (date unknown).

WEAK ACID DISSOCIABLE CYANIDE

The ASTM Procedure D-2036-81 Method C is gaining ground at least in the USA for determination of free and metal complexed cyanides with the exception of iron complexed cyanides, as a means of determining toxic cyanide levels.

The ASTM Method C has been found to give satisfactory detection limits, accuracy and precision and to be free of significant interferences when applied on Homestake effluent solution according to WHITLOCK & MUDDER (1984).

ASTM METHOD C

This method uses acetic acid and sodium acetate buffered at pH 4.5 and zinc acetate for the dissociation of metal cyanide complexes. Apart from this detail the method is believed to be identical to the "Standard Methods" technique.

There are numerous other techniques for analyzing cyanide. For example, PALMER & SKARSET (1981) described the Determination of Free Cyanide using a Microdiffusion Technique followed by a Pyridine-barbituric Acid Photometric Finish. This measures HCN, CN^- and cyanide in weak cyanide complexes such as cadmium, lead, manganese and zinc cyanide.

Complexes of copper, iron, nickel and silver are not dissociated into free cyanide at the microdiffusion at pH 7. Cyanate, sulfide and thiocyanate do not interfere and the method is claimed to be sensitive down to 5 ppb with a standard deviation of less than 10%.

The caustic solution containing CN^- is neutralized with acid phosphate solution and chloramine T is added to oxidize CN^- to CNCl which reacts with pyridine and then with barbituric acid to form a purple dye whose wavelength of maximum absorbance is 580 nm.

Full color development takes 12 minutes after addition of pyridine-barbituric acid solution and the color is stable for 50 minutes. Calibration curves are linear to 0.3 ppm.

As and when regulations on allowable limits on cyanide in effluents emerge, they will also have to specify how the cyanide analyses are to be carried out.

INCO METHOD FOR CYANIDE ANALYSIS

Inco uses three techniques for cyanide determination in conjunction with their cyanide destruction method.

1) Analysis of total cyanide by distillation of an acidified sample in the presence of HCl - hydroxylamine hydrochloride as described by CONN (1981). This technique is used for periodic check analyses.

2) Picric acid addition and spectrophotometric analysis determination of the weak acid dissociated cyanide measures free cyanide, HCN and cyanide associated with Ni, Cu, Zinc, etc. The only complexed cyanide not measured is that occuring as a complex with iron and cobalt. This method is described by ZATKA (1980).

   Before carrying out this analysis calcium is added to precipitate excess $SO_3^=$ as $CaSO_3$ otherwise $SO_3^=$ forms a color compound with the picric acid, which gives a positive photometric response. The calcium is added to the solution until no more $CaSO_4$ is precipitated and the picric acid is added to the supernatant solution, which gives a normal color development. This takes a few minutes to develop.

   When there is $SO_3^=$ present in solution, a color forms immediately the picric acid is added, which gives a clue to the presence of the interference.

3) Total iron in solution is analysed by AA. There are 6 moles of cyanide per mole of Fe analyzed. In terms of ppm by weight, this means that for each ppm of Fe analyzed there will be close to 3 ppm of cyanide as iron cyanide.

   The cyanide as iron cyanide determined by method 3 added to weak acid dissociated acid by method 2 give total cyanide by easy to analyze techniques. The sum of these two results invariably correspond well to total cyanide determined by method 1 described by CONN (1981).

In reviewing the finer points for selection of analytical techniques for cyanide determination at these levels, it is helpful to call on the advice of others who have been evaluating the processes for years:

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THE DETERMINATION OF CYANIDE IN WATERS

by B. Grigorova and W. Lennhan

Cyanide is a toxic substance. That is neither a masterpiece of understatement nor the utterance of an idiot. The fact is (and it is in facts that, as scientists, we are supposed to deal) that the toxicity of cyanide is no greater than that of many substances commonly, and casually, used, with little or no thought to their toxicity. Many indeed are subjects of jokes; such as hydrogen sulphide, the toxicity of which is similar to that of hydrogen cyanide. Nobody but a homocidal, or suicidal, maniac would dream of mischievously planting a "bomb" to produce the stink of bitter almonds. The word cyanide has about it a dread mystique. More than any other word it conjures up spectres of death. It is the stuff that bad dreams are made on.

And yet cyanide is an essential reagent in many technological processes: in the metallurgical industry, especially in the metallurgy of gold, it is of particular importance. Indeed it is more than doubtful if the Witwatersrand would ever have achieved its spectacular potential had it not been for the discovery of the cyanide process.

And yet, again, despite its popularity as a poison and its scientific significance; the chemistry of cyanide seems to have been, until recently, somewhat superficially understood. Paradoxically, perhaps, the reason can be found in the spectacularity of its effectiveness in all aspects of its application.

Furthermore, both the simplicity of techniques by which its metallurgical application can be controlled and the dread with which its deathly attribute is abhorred have led to a confusion, and even to a misuse of elementary terminology. This is probably the most serious single problem in the analytical chemistry of cyanide.

The Metallurgist talks of "free" and "total" cyanide when he really means "free" and "total available" cyanide. The Environmentalist talks of "total" cyanides (or "cyanide and related compounds") while he need only interest himself in cyanide and <u>some</u> of its complexes. The Analytical Chemist strives, as is his custom, to satisfy all his clients.

In the context of this symposium however, we must obviously confine ourselves to the environmental aspects of the problem. And, as we see them, these aspects, apart from the procedures which we shall discuss, are three-fold:

1) All official regulations, of which we are aware, demand the specification of "total" cyanide in water and effluent; yet we are unaware of any method by which true total cyanide can be determined.

2) All but one of the metallo cyanide complexes (cobalt) can be determined by techniques to be described in this presentation; yet officially prescribed methods are generally less effective: neither the procedure authorized by the South African Department of the Environment nor that of the American Public Health Association is capable of effecting complete dissociation of the iron and gold cyanide complexes.

3) Many of the cyanide complexes are so stable that their toxicity is negligible. Thus it is not only the terminology that is questionable: one wonders if the results derived by the official analytical procedures constitute a valid measure of the toxicity of the water or effl-

Be that as it may, the practicing environmental chemist is committed to the analytical control of the environment, and to principles embodied or implied in the relevant legislation. But it is the wise chemist who knows his own terminology. And he would be well advised to be wiser still; and to ensure that terms such as "total" appear, in his report, within the security of quotation marks.

THE DETERMINATION OF CYANIDES IN THE HYDROMETALLURGICAL PROCESSING OF GOLD

by

C. POHLANDT

The determination of cyanides in cyanidation processes is of considerable importance for several reasons.
For example, excessive consumption of the reagent must be prevented for economic reasons; the chemistry of the process must be controlled for efficient operation; and, most important of all, environmental pollution must be avoided. Depending on the pH value of a solution, cyanide can be present as the molecular acid (HCN), as ionic cyanide, or as metal complexes of widely varying stability. Classical methods for the determination of cyanide are invariably tedious and time-consuming, and are rarely suitable for the rapid analysis of large numbers of samples.

Ion chromatography has gained increasing acceptance in the determination of a large variety of anions and, with an amperometric instead of a conductivity detector, it is eminently suitable for the determination of cyanides[1]. For the determination of 'free' or 'available' cyanide, the sample simply needs to be diluted and to be injected into the chromatographic system. With a weakly alkaline mobile phase containing ethylene diamine, excellent separation of the cyanide from most other anions, including common interferents such as sulfide and thiocyanide, is obtained. The method is fast, precise, and reasonably accurate, and as little as 50 µg of cyanide ion per litre can be

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Cyanide and the Environment Conference, University of Arizona. Dec. 1984

reliably determined. Weak metal cyanide complexes, for example those of cadmium, zinc, and nickel, are decomposed in the alkaline environment of the chromatographic system, whereas strong cyanide complexes, for example those of iron, gold, and cobalt, remain intact and are retained on the anion-exchange separator.

'Total Cyanide'

The determination of 'total' cyanide requires the decomposition of strong metal cyanide complexes. Classical methods of determination require boiling under reflux with acids, usually followed by a distillation step. At the Council for Mintek Technology (Mintek) it was considered that an attractive alternative approach would be to combine ultraviolet irradiation, which results in the photo-ionization of strong cyanide complexes, with the ion-chromatographic procedure. It was established that, in 3 per cent hypophosphorous acid (50 per cent), all the metal cyanide complexes except that of cobalt decompose completely if they are irradiated for 2 to 3 minutes. Various mercury lamps were tested as irradiation sources. Those with a maximum radiation output at wavelengths longer than 300 nm were preferred because thiocyanate was not decomposed, whereas the recovery of cyanide from the hexacyano cobaltate complex improved. It was established also that a more powerful lamp, i.e. a 400 W instead of the 100 W mercury lamp originally used, further improved the decomposition of the cobalt complex (i.e. 50 per cent), and 96 to 100 per cent of the cyanide present was reproducibly recovered from a mixture of stable complexes. Photo-ionization is complex, and the oxidation-reduction reactions involved need to be carefully controlled if

reliable analytical results are to be obtained. For example, the irradiation of an aqueous solution of ionic cyanide in the absence of reducing agents results in the quantitative formation of harmless cyanate within 3 minutes. Metal complexes, on the other hand, decompose slowly with the simultaneous appearance of cyanide and cyanate ions. Therefore, pollution of the environment with so-called 'stable' cyanide complexes must be avoided, since irradiation by sunlight would result in the continuous production of small amounts of cyanide over long periods of time, which could be harmful to marine life.

Individual Cyanide Complexes

Recently the Dionex Corporation, U.S.A., issued a series of application notes describing the separation of the complexes of cobalt from gold (I) and gold (III), and also the separation of iron (II) from iron (III) by mobile-phase ion chromatography (MPIC)[2]. This procedure utilizes the principles of ion-pair chromatography, and uses a suppressor device to reduce the conductivity of the mobile phase prior to conductimetric detection.

Metallurgical processes that involve the use of resins or carbons frequently suffer from the 'poisoning' of such materials by, for example, metal cyanide species that cannot be eluted under normal stripping conditions. It follows that a knowledge of the kind of complexes present in the system is of considerable importance.

A method based on the information issued by Dionex has been developed that enables the cyanide complexes of copper, nickel, cobalt, iron (III) or iron (II), and gold to be separated (Figure 1). The determination of the

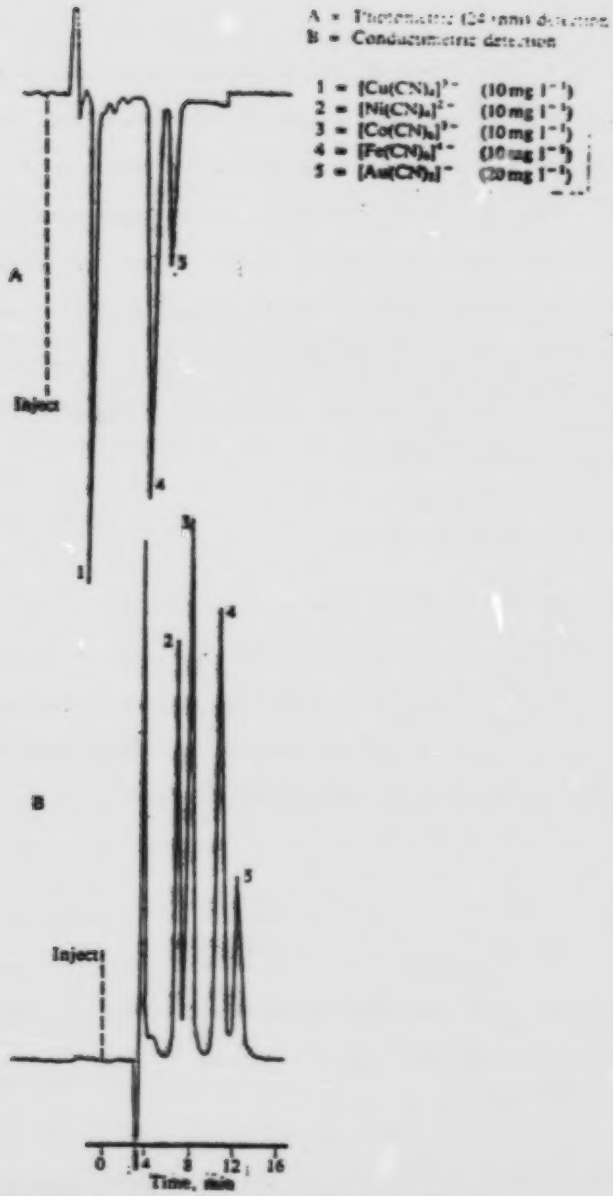

FIGURE 1. The separation of five individual metal cyanide complexes

copper complex that, due to decomposition in the suppressor, could not be detected conductimetrically, was achieved by simultaneous photometric detection at 240 nm. Calibration graphs for the various complexes were found to be linear over the concentration ranges 0.2 to 10 $mg.l^{-1}$; the gold (I) complex was the least sensitive. The separation of the two iron complexes, as claimed by the Dionex Corporation, could not be verified under any experimental conditions. Iron (II) and iron (III) cyanides were found to decompose rapidly when exposed to daylight, and additional peaks due to decomposition products were observed in the chromatogram. Daylight also had a pronounced effect on the hexacyano cobaltate (III) complex, resulting in the formation of the aquo-pentacyano cobaltate (III) complex. Since it is the latter complex that was previously identified[3] as causing resin poisoning, it is of significance that the proposed procedure is able to distinguish between the two cobalt complexes.

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DETERMINATION OF CYANIDES IN DRINKING AND NATURAL WATERS, AND INDUSTRIAL EFFLUENTS

Cyanide has long been know to man for its toxicity. Although that fact, cyanides are widely used in the mining, electroplating, steel, gas, food and many other industries. It is not surprising, therefore, that the cyanide content, often is high in effluents and in the atmosphere.

Before we go any further on the subject, lets distinguish the different forms in which cyanide may appear.

Cyanide, depending on the pH value, occurs as molecular hydrocyanic acid (HCN), cyanide ions (CN^-), metal cyanides ($M(CN)_x$) which are sparingly soluble in water, but form a variety of highly soluble alkali-metallic cyanide complexes in the presence of alkali cyanides. The alkali-metallic cyanides can be expressed by the formula: $AyM(CN)_2$, where A represents the alkali, M represents the heavy metal (copper, cobalt, cadmium, nickel, iron, gold, silver, zinc, etc.) x is equal to the valence of A taken y times, plus the balance of the heavy metal. The initial dissociation of these soluble alkali-metallic cyanides is expressed by the equation (I):

$$A_yM(CN)_x \longrightarrow yA \quad + \quad M(CN)_x^{y-}$$

Depending on several factors, pH being one of them, the dissociation can continue with liberation of the CN^- radical and consequent formation of the highly toxic hydrogen cyanide (HCN).

In the aqueous solutions, therefore, there are cyanide radicals (CN^-), hydrocyanic acid (HCN) and metallo-cyanic radical $(M(CN)_x^{y-}$.

In analytical chemistry we discuss the terms "free" and "total" cyanide.

"Free" cyanide represents the content in solution of the hydrocyanic acid (HCN), the simple alkali cyanides (NaCN or KCN) and some unstable alkali-metallic cyanides, such as $Na_2Zn(CN)_4$ and $Na_2Cd(CN)_4$.

The term "total" includes that mentioned above plus all metallo-cyanide complexes.

The extreme toxicity to human and equatic life, of the molecular hydrogen cyanide (HCN), formed in solutions of cyanides, by the hydrolytic reaction of CN^- radical with water is well known.

Although metallo-cyanide complexes are undoubtedly far less toxic, than the CN^- ions and the molecular hydrogen cyanide, it is possible, that under certain conditions, CN^- ion liberates from these complexes. They are, therefore, a potential hazard and as such, they must be subject to a careful determination and elimination from the effluent waters.

Depending on their stability constant and pH values, metallo-cyanide complexes tend to ionize and convert to the toxic form of cyanide ion or hydrogen cyanide. The zinc and cadmium complexes are totally dissociated in strong alkaline solutions, as well as in any ordinary pH in natural waters. They can be considered, therefore, as acutely toxic.

The increasing stability of some metallo-cyanide complexes is expressed in Table I.

TABLE I

THE INCREASING STABILITY OF SOME METALLOCYANIDE COMPLEXES

Metal (M)	Complex ((M-CN)	Stability Constant Ka
Zn^{2+}	$Zu\ (CN)_4^{2-}$	10^{17}
Cd^{2+}	$Cd\ (CN)_4^{2-}$	10^{18}
Ag^{1+}	$Ag\ (CN)_2^{1-}$	10^{20}
Fe^{2+}	$Fe\ (CN)_6^{4-}$	10^{24}
Cu^{2+}	$Cu\ (CN)_4^{2-}$	10^{25}
Fe^{3+}	$Fe\ (CN)_6^{3-}$	10^{31}
Au^{1+}	$Au\ (CN)_2^{1-}$	10^{28}
Ni^{2+}	$Ni\ (CN)_4^{2-}$	10^{41}
Au^{3+}	$Au\ (CN)_4^{1-}$	10^{56}
Co^{3+}	$Co\ (CN)_6^{3-}$	10^{64}

The stability constant of hydrogen cyanide in aqueous solutions is (II):-

$$Ka = 4,93 \times 10^{-10}$$

Bearing in mind the extreme toxicity of cyanide and the behaviour of the complex cyanides, it can easily be understood, why the waters for domestic supply and the effluent waters from mines and industries are subject to stringent regulation of their cyanide content. By the South African standard regulations, the recommended limit of cyanide concentration in waters used for domestic purpose is 0,01 mg/L as CN^- and the maximum permissible level is 0,2 mg/L as CN^-, for the industrial effluents, the level of "cyanides and related compounds" is max. 0,5 mg/L as CN^- by the government regulations. The toxic level for fish is 0,03 mg/L CN^-.

It seems to be a lack of recognition of the fact that relatively innocuous compounds are counted in the official methods of analysis.

The regulations must, however, be based on the knowledge of cyanide chemistry and stability of the metallo-cyanide complexes. Regulations based on the simplistic idea, that all cyanides are dangerous, are economically damaging and should be challenged.

For example, the acute toxicity to fish of diluted solutions containing copper or silver cyanide complexes is due mainly or entirely to the toxicity of the undissociated ions. Another paradoxal fact is that the use of sodium ferrous-cyanide ($Na_4Fe(CN)_6 \cdot 10H_2O$) is permitted in food industry as anti-caking agent, and in the same time the analtyical chemist strives to find the most satisfying method to obtain the ferro-cyanide contained in the sample.

The extreme stability of the iron-cyanide complexes in a natural environment is also a well known fact; their photo-decomposition is very low in deep, turbed and shaded waters and the loss of the hydrogen cyanide to atmosphere and its bacterial and chemical destruction, prevents the increase of HCN concentration in waters to harmful levels, practically classifying them as non-toxic.

There is another controversial fact: by the Government Regulations, the permissible level in industrial effluents is for "cyanide and related compounds", but the method suggested by the S.A. Government Gazette and the American Public Health Association do not determine them. The content of thiocyanates (SCN^-) and cyanate (CNO^-) is very limited, and the toxic dose level for KSCN is 760 mg/kg or 76 times lower than the cyanide toxicity.

On acidification, CNO^- will be converted to ammonia, according to the reaction (III).

$$2NaCNO + H_2SO_4 + 4H_2O \longrightarrow (NH_4)_2SO_4 + 2NaHCO_3$$

On the thiocyanate role in the cyanide determinations, there are two controversial opinions.

Some authors are suggesting, that thiocyanate interferes with the analysis of cyanide.

The second opinion on this subject, which incidentally is the opinion of the authors of this paper, is that thiocyanate does not interfere.

In their work "Determination of cyanides in water and waste samples", Ludzack, Moore and Ruchhof show that thiocyanate (SCN^-) and cyanate (CNO^-) do not interfere with the determination of "total" cyanide. In the experiment performed by them, a 500 mg/L of KSCN and KCNO respectively were added to the distillation flask and refluxed for 2 hours following the cyanide determination procedure. The results reported in both tests were "NIL" cyanide (CN^-) concentration in mg/L.

Clysters and Adams in their work "Potentiometric determination with the silver sulphide membrane electrode", show that thiocyanate only at very high concentrations of 1 per cent will interfere with the direct reading of cyanide containing solutions; in other words the determination of "free" cyanide. Thiocyanate at this level (1 per cent) does not occur in any fresh natural waters or industrial effluent.

A test on the effect of the thiocyanate on the cyanide determination was performed at AARL.

Three 50 ml portions of potassium auro-cyanide standard solution, with cyanide concentration of 100 mg/L CN^-, were mixed with different volumes of potassium thiocyanate standard solution, with thiocyanate content of 100 mg/L SCN^-.

The solutions were refluxed for two hours, following the modified cyanide distillation procedure, suggested by AARL.

The results obtained, are expressed in Table II:-

TABLE II

EFFECT OF THIOCYANATE ON THE CYANIDE DETERMINATION

Thiocyanate Concentration in the Analysed Solution as SCN^- (mg/L)	Cyanide Concentration as CN^- (mg/L)	
	Added to the analysed solution	Obtained after distillation
50	100	93
67	100	91
80	100	100

From the results in Table II, it can be observed, that thiocyanate in concentration up to 80 mg/L SCN^- does not interfere with the "total" cyanide determination.

A really disturbing interference on cyanide determinations, "free" and "total", occur when sulphides (S^{2-}) are present in the analyte.

In most instances, the distillation procedure eliminates the interferences, but, when sulphide is present in the solution to be analysed, it is distilled as hydrogen sulphide gas (H_2S), which interfere with the following analytical procedure, ion-selective electrode measurement, or argomtometric titration.

Sulphide also converts the cyanide to thiocyanate, the reaction greatly accelerated at elevated pH value.

Removal of sulphides, as soon as the sample is collected, and before its stabilisation with sodium hydroxide, therefore, is essential.

A 0,5 solution of cadmium nitrate $Cd(NO_3)_2$ is added to precipitate the sulphide. The yellow precipitate of cadmium sulphide (CdS) that forms is filtered. The complete precipitation of sulphide is tested with lead acetate paper.

An excess of cadmium nitrate should be avoided, to prevent the possibility of formation of additional cyanide complexes.

Historically, the generally accepted treatment of cyanide containing industrial and mine effluents, is by alkaline chlorination (Reaction IV):

$$CN^- + Cl_2 \xrightarrow[>9,0]{pH} CNCl + NaCl$$

The first product of the chlorination is highly toxic cyanogen chloride (CNCl), but in alkaline media, the reaction proceeds by hydrolysation of the cyanogen chloride to the cyanate ion (CNO^-) which has a very limited toxicity (Reaction V):

$$CNCl + 2NaOH \longrightarrow NaCNO + NaCl + N_2O$$

The chlorination process is relatively fast, but depends greatly on dissociation of the cyanide complexes.

Metal cyanide complexes, such as cobalt, gold, iron and nickel do not dissociate to any degree. The chlorination process, therefore, does not eliminate their presence but their resistance to chlorination and lack of toxicity, overlap.

As many cyanides are unstable under certain conditions, the cyanide determinations should be performed on receipt of the sample. If this is not possible, the sample should be treated immediately for sulphide elimination, followed by addition of sodium hydroxide to raise the pH value to 12,0.

Bottle with sample must be kept in a dark, cool place.

A holding time of 24 hours only, is recommended.

The high toxicity of "free" cyanide for animals and human beings, together with its wide spread industrial application creates a need for a sensitive and selective method, capable of detecting cyanide concentrations at the 0,01 mg/L level.

The relatively stable metallo-cyanide complexes, although not showing typical cyanide toxic properties, are still potentially dangerous and classified by most health organisations together with the toxic form of cyanide.

An application of a very sensitive method for their analysis, therefore, is essential.

From the discussion on cyanide toxicity and the health regulations on drinking waters and industrial and mine effluents, it is obvious, that a procedure for determination of the "total" cyanide concentration in water samples should be employed. And yet, the method suggested by the Government Gazette and the American Public Health Association, cannot ensure the complete decomposition and therefore, determination of auro-cyanide, cobalt-cyanide and ferric-cyanide.

In the "Annual Book of ASTM Standards", part 31, Water, edition 1981, published by the American Society for Testing and Materials, the following statement can be found:-

"The cyanide in some cyano-complexes of transition metals: that is cobalt, gold and platinum is not completely determined by these methods".

The method suggested by the American Society for Testing and Materials is the same, as the one described by the American Public Health Association. The procedure proposed by the South African Government Gazette is very similar to the American Standard Methods.

They consist of one hour reflux of the analyte with sulphuric acid and catalyst to help the dissociation of the metal complexes.

The APHA suggests the use of magnesium chloride ($MgCl_2$) as a catalyst, which is very effective on the iron complexes dissociation.

The S.A. Government Gazette uses the same method and includes mercuric chloride ($HgCl_2$) as the catalyst, and a longer reflux time.

Both procedures fail to decompose completely the gold, cobalt and iron cyanide complexes, an event that can be observed from Table III:-

TABLE III

THE RECOVERY OF SOME STABLE METALLO-CYANIDE COMPLEXES AFTER DISTILLATION PROCEDURE SUGGESTED BY THE S.A. BUREAU OF STANDARDS AND THE AMERICAN PUBLIC HEALTH ASSOCIATION

Metal complex	Cyanide Concentration as CN^- (mg/L)	Recovery of the Cyanide as CN^- (%)
$K_4Fe(CN)_6$	100	88,9
$K_3Fe(CN)_6$	100	82,6
$KAu(CN)_2$	100	49,1
$K_3Co(CN)_6$	100	20,3

The accurate detection of the auro-cyanide complex, if not of great importance for the American environment, is of major interest to the South African society. Due to the gold mining industry, the South African effluents contain a significant amount of gold cyanide complexes. An accurate method for their detection is, therefore, essential.

As the existing procedures yield unsatisfactory results, work to solve this problem was undertaken in AARL.

A modification of the reflux-distillation procedure was established with excellent results for the determination of the auro-cyanide complex. A 100% recovery of potassium auro-cyanide $KAu(CN)_2$ was achieved.

The procedure involves two hours reflux of the cyanide complex solution, with ortho-phosphoric acid and addition of zinc powder to the known catalysts ($MgCl_2$ and $HgCl_2$).

Some of the data obtained by application of this modified technique, can be observed from Table IV.

TABLE IV

THE RECOVERY OF GOLD-CYANIDE COMPLEX AFTER DISTILLATION PROCEDURE SUGGESTED BY ANGLO AMERICAN RESEARCH LABORATORIES

Analyte	Cyanide Concentration present as CN^- (mg/L)	Mean of cyanide Concentration obtained as CN^- (mg/L)	Recovery of Cyanide conc. (%)
$KAu(CN)_2$	1000	1000,66	100,07
$KAu(CN)_2$	100	100,84	100,84
$KAu(CN)_2$	80	80,18	100,22
$KAu(CN)_2$	25	25,40	102,40

This technique was used for analysis of metallurgical plant samples, which explains the high concentration of auro-cyanide in the solutions used for the test.

The replacement of sulphuric acid with ortho-phosphoric acid was essential to prevent its eventual reduction, when zinc powder as catalyst is used. This can evolve hydrogen sulphide which is absorbed, together with the hydrogen cyanide, in the alkaline solution.

A test to observe this event was performed. Results obtained are expressed in Table (V):-

TABLE V

THE POSITIVE INTERFERENCE OF SULPHURIC ACID, ON CYANIDE DETERMINATION, WHEN THE Zn REDUCTION PROCEDURE IS INVOLVED

Type of mineral acid used for distillation	Recovery of the cyanide concentration as CN^- (%)
H_2SO_4	102,3
H_3PO_4	100,5

As the hydrogen sulphide interferes in positive way, higher results, when sulphuric acid is used, were obtained.

The second reason for replacing the sulphuric acid was based on suggestion made by Serfass, Freeman, Dodge and Zabban, that sulphuric acid reflux procedures yield better results when iron-cyanide complexes are included in the analyte.

Once, the auro-cyanide complex problem was solved, as it can be expected in science, a new problem arose. Zinc salts render the iron cyanide complexes insoluble, therefore it is possible, that the zinc powser will act as anti-catalyst with respect to the iron-cyanide complexes.

An experiment was performed which confirmed our fears. Work to overcome this new problem is proceeding, but the data is still not sufficient, to draw a final conclusion. Anyhow it is certain, that a prolonged reflux-distillation procedure, for the dissociation of iron-cyanide complexes is essential.

There are three different techniques for determination of the cyanide content after the digestion procedure: argentometric titration suitable for concentrations higher than 10 mg/L CN^-, the spectrophotometric method and ion-selective electrode procedure for low cyanide concentrations.

There are a few advantages of the ISE procedure to the spectrophotometric method:

1. When the colourimetric method is employed, the cyanide from the solution reacts with chloramine-T to form the very toxic gas cyanogen chloride (CNCl). Its toxicity exceeds greatly that of the cyanide.

2. When colour measurement is performed, the 8-15 minutes interval for absorbance reading is critical. Even with a specified time of 8-15 min., there is a slight change in absorbance (standard methods for the Examination of Waters and Waste Waters; APHA, AWWA, WPCF).

3. Ion-selective electrode measurement is fast with good accuracy and precision. Sixty to eighty cyanide determinations per day can be performed, when the computerised Phillips PW 9416 Ion-Selective Analyser is used.

4. No previous knowledge of the cyanide concentration, of the sample to be analysed is necessary when ISE and the standard addition procedure is used; as it covers a very wide concentration range from 0,01 up to 100 mg/L CN^-.

The ISE procedure has advantages also to the argentometric titration method, when "free" cyanide is analysed and p-dimethylaminobenzylidenerhodanine is used; which incidently is the best available indicator for cyanide determination.

The interferences of copper (Cu) on titrimetric determination was investigated at AARL. It was found, that the argentometric method can tolerate the present of 1,5 mg Cu only, in the solution to be analysed. Copper and other heavy metals do not effect the ISE procedure.

At this stage of investigation on the chemistry of the metallo-cyanide complexes, we still cannot suggest a procedure which will ensure the dissociation of all possible metallo-cyanide complexes.

The analytical chemist still faces the dilemma for the right choice of decomposition technique for cyanide complexes. A knowledge of the type of the solution to be analysed, for indication of the probable existance of certain metallo-cyanide complexes, as well as knowedge of the behaviour of those complexes under the digestion conditions, are the answers to the problem.

JOHANNESBURG
13th June, 1983
BG/LN

CYANIDE
(Colorimetric–Chloramine-T, Pyridine-Pyrazolone)

1. Scope and Application

1.1. This method is applicable to the determination of cyanide in surface, waste and sea water. When the distillation assembly described is used the method is sensitive to about 2 μg/L.

2. Principle and Theory

2.1. Distillation of the sample in the presence of sulphuric acid converts complex cyanides into hydrocyanic acid, HCN. The HCN gas is absorbed in a solution of sodium hydroxide and the cyanide is determined colorimetrically.

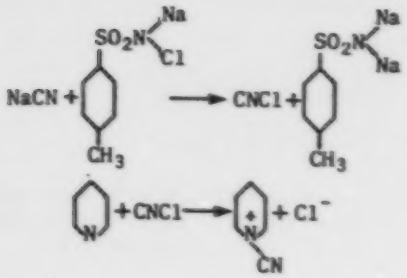
Equations:

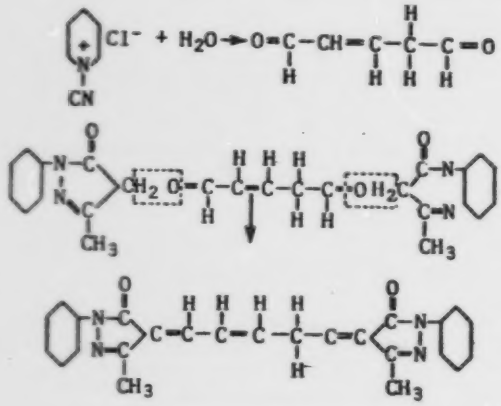
$$Fe(CN)_6^{4-} + 6H^+ \longrightarrow 6HCN + Fe^{2+}$$

$$HCN + NaOH \longrightarrow NaCN + H_2O$$

2.2. In the colorimetric measurement, the cyanide in the sodium hydroxide solution after distillation is converted to cyanogen chloride, CNCl, by reaction with chloramine-T, $CH_3C_6H_4SO_2NClNa \cdot 3H_2O$. The CNCl then forms a blue dye on the addition of pyridine-pyrazolone ($C_{10}H_{10}N_2O$) reagent and the absorbance is measured at 620 nm.

The reaction may be expressed by the following equations (ref. 11.4):





3. Interferences

3.1. Sulphides interfere and should be removed prior to distillation (see section 5).

3.2. Other interfering substances are removed by distillation.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a 2-L plastic bottle and analyzed as soon as possible after collection.

4.2. Samples should be preserved by addition of sufficient NaOH to raise the pH to 11.0 or above, and be stored in a cool place.

5. Sample Preparation

5.1. Decant a sample aliquot for distillation.

5.2. Sulphide is removed by treating the alkaline sample at pH 11.0 with small increments of powdered lead carbonate, $PbCO_3$. Black lead sulphide precipitates in samples containing sulphide. Repeat this operation until no more lead sulphide forms. Filter and rinse the precipitate, add the rinse water to the filtrate, and use an aliquot for analysis. Avoid a large excess of lead

carbonate and a long period of contact in order to minimize complexing or occlusion of the cyanide with the precipitated material.

6. Apparatus

6.1. A 1000-mL three-necked flask fitted with ground-glass joints; to the three necks are fitted a thistle funnel which extends below the liquid level, an air sparging tube drawn to a fine tip, and a Friedrichs condenser (Fig. 1).

6.2. Heating mantle.

6.3. Magnetic stirrer-plate and stirring bar.

6.4. Gas absorption column made from Pyrex tubing, 22 mm I.D. and 450 mm long, filled with glass helices (3 mm I.D.) (Fig. 1).

6.5. Technicon proportioning pump fitted with 8 pumping tubes, 2.8 mm I.D.

6.6. A 100-mL graduated cylinder mounted with clamp on a retort stand so that its position can be adjusted.

6.7. Spectrophotometer for use at 620 nm, providing a light path of 1 cm.

7. Reagents

7.1. Sodium hydroxide solution, 1 N: Dissolve 50 g sodium hydroxide, NaOH, in 1 L distilled water.

7.2. Mercuric chloride solution: Dissolve 34 g mercuric chloride, $HgCl_2$, in 500 mL distilled water. (Caution: Toxic; take care to avoid ingestion.)

7.3. Magnesium chloride solution: Dissolve 51 g magnesium chloride, $MgCl_2 \cdot 6H_2O$, in 100 mL distilled water.

7.4. Sulphuric acid, H_2SO_4, concentrated.

7.5. Sodium hydroxide solution, 0.2 N: Dissolve 8 g sodium hydroxide, NaOH, in 1 L distilled water.

7.6. Acetic acid, CH_3COOH, conc. and 1 + 4.

7.7. Stock cyanide solution: Dissolve 2.51 g potassium cyanide, KCN, in 1 L water. Standardize with 0.0192 N silver nitrate, $AgNO_3$. The solution loses strength gradually and must be rechecked every week. Approximate strength, 1 mL = 1 mg CN. (Caution: Toxic; take care to avoid ingestion.)

7.8. Standard cyanide solution: Dilute 10 mL stock cyanide solution to 1 L with distilled water; mix and make a second dilution of 10 mL to 100 mL. 1.00 mL = 1.0 μg CN. This solution must be prepared daily. (Caution: Toxic; take care to avoid ingestion.)

7.9. Chloramine-T solution: Dissolve 1 g of chloramine-T, $CH_3C_6H_4SO_2NClNa \cdot 3H_2O$, in 100 mL water. Prepare daily.

7.10. 1-Phenyl-3-methyl-5-pyrazolone solution: Prepare a saturated aqueous solution (approximately 0.5 g/100 mL) by adding the pyrazolone, $C_{10}H_{10}N_2O$, to water at approximately 75°C. Agitate occasionally as the solution cools to room temperature. If necessary, the pyrazolone (melting point 127°C to 128°C) can be purified by recrystallization from ethyl alcohol. Usually this is not required.

7.11. Pyridine, C_5H_5N.

7.12. Bis-pyrazolone (3,3'-dimethyl-1,1'-diphenyl-{4,4'-bi-2 pyrazoline}-5,5' dione).

7.13. Mixed pyridine-pyrazolone reagent: Mix 125 mL of the filtered, saturated aqueous solution of pyrazolone with a filtered solution containing 0.025 g bis-pyrazolone dissolved in 25 mL pyridine. Several minutes of mixing is usually necessary to dissolve the bis-pyrazolone in pyridine. The mixed reagent develops a pink colour on standing, but if used within 24 h this does not affect the colour production with cyanide. Prepare daily.

7.14. Standard silver nitrate solution: Dissolve 3.27 g of silver nitrate, $AgNO_3$, in 1 L of distilled water. Store in a dark bottle. One millilitre of this solution is equivalent to 1.00 mg CN.

8. Procedure

8.1. Procedure for distillation.

8.1.1. Close pinch clamp (Fig. 1).

8.1.2. Add about 80 mL of water to the graduated cylinder and adjust the position of the cylinder so that the tube dips near the bottom of the cylinder.

8.1.3. Add 750 mL sample to the flask; insert stirring bar, and start the stirrer.

8.1.4. Add 50 mL 1 N NaOH solution (7.1) to the 250-mL beaker and start the pump.

8.1.5. When the absorption column is wet with NaOH solution, add 20 mL mercuric chloride solution (7.2) and 10 mL magnesium chloride solution (7.3) through the thistle tube.

8.1.6. Slowly add 37 mL concentrated sulphuric acid to the flask through the thistle tube.

8.1.7. Turn on the heating mantle and allow the contents of the flask to boil vigorously (Excess air as the flask heats up will escape from the equipment through the dip tube in the graduated cylinder).

8.1.8. After 1 h of boiling turn off the heating mantle and open pinch clamp.

8.1.9. Remove the tube pumping NaOH from the NaOH solution; rinse the contents of the column into the NaOH beaker by pumping approximately 150 mL distilled water through the absorption column and collect in the NaOH beaker.

8.1.10. Transfer quantitatively to a 250-mL volumetric flask and make up to the mark.

8.2. Procedure for colorimetric measurement.

8.2.1. Transfer 15 mL of distillate to a 50-mL beaker.

8.2.2. To prepare standard solutions for the calibration curve, use cyanide standard 1 mL = 1 μg CN. Pipette 0 (blank), 0.2 mL, 0.5 mL, 0.8 mL and 1.0 mL into 50-mL beakers and make up to 15 mL with NaOH, 0.2 N (7.5). Proceed with 8.2.3, treating samples and standards in the same manner.

8.2.3. Adjust pH to 6-7 with 1 + 4 acetic acid. Transfer to 25-mL volumetric flask.

8.2.4. Add 0.2 mL chloramine-T solution (7.9) and mix. Allow 1-2 min for the reaction.

8.2.5. Add 5.0 mL mixed pyridine-pyrazolone reagent (7.13) and make up to the mark; mix. Allow 20 min for colour development.

8.2.6. Read absorbance at 620 nm in a 1-cm cell.

8.2.7. As a check on the distillation step, periodically process cyanide standard solutions through the complete procedure.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the micrograms of cyanide in the samples by comparing sample peak heights with the calibration graph.

9.3. Calculate the cyanide concentration as follows:

$$\text{mg/L CN} = \frac{F \times D}{C \times E}$$

where E = cyanide determined (μg),
D = diluted absorbing solution (mL),
C = original sample (mL), and
E = aliquot used (mL).

10. Precision and Accuracy

10.1. No data available.

11. References

11.1. Goulden, P.D. Unpublished information on distillation setup. Water Quality Branch, Ottawa.

11.2. American Society for Testing and Materials. 1976. *Book of ASTM Standards.* Part 31. Water, pp. 503-505. Philadelphia.

11.3. American Public Health Association. 1975. *Standard Methods for the Examination of Water and Wastewater.* 14th ed. Washington, D.C.

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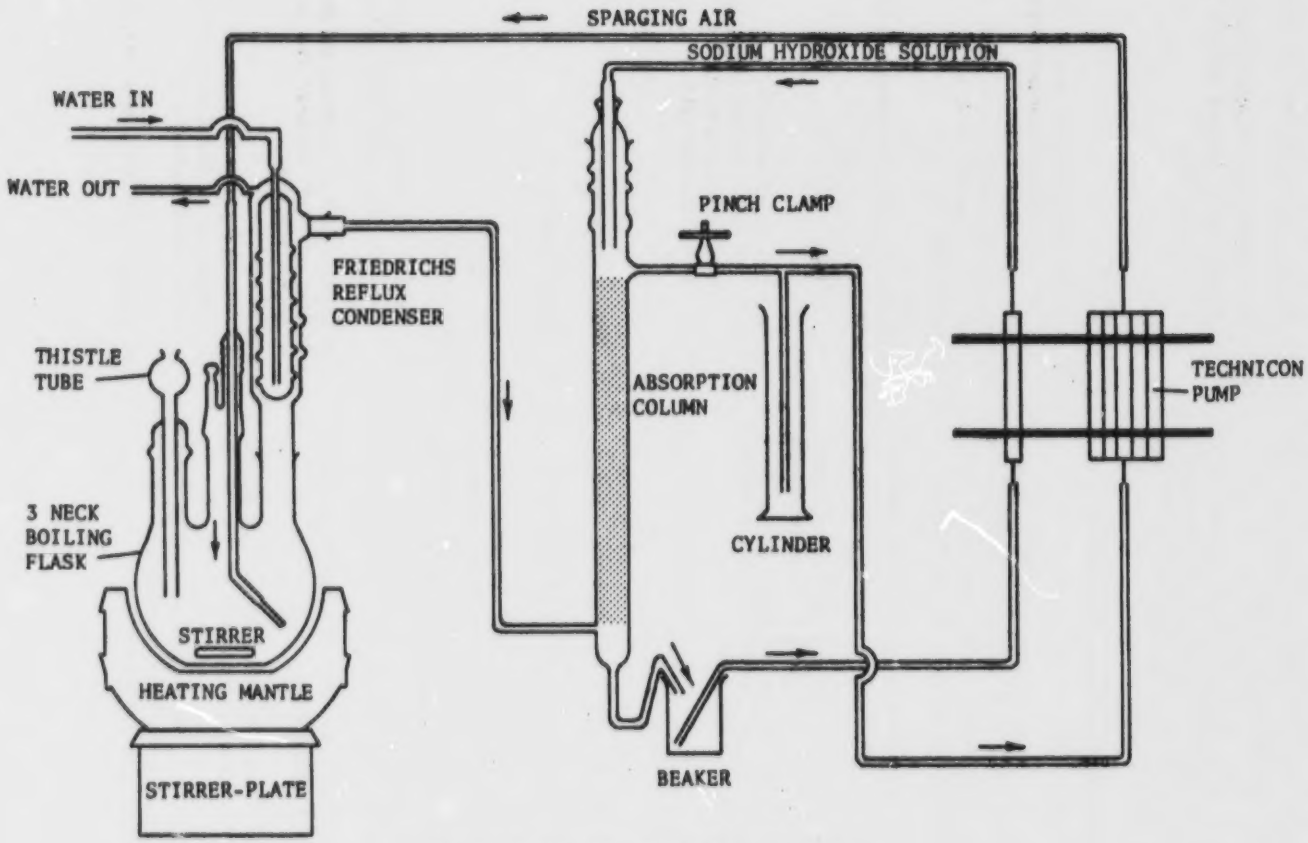


Figure 1. Cyanide distillation apparatus

1. Scope and Application

1.1. This method is applicable to the determination of cyanide in water and wastewaters in the range from 0.001 mg/L to 0.100 mg/L HCN.

1.2. The detection limit for this method is 0.001 mg/L CN^-.

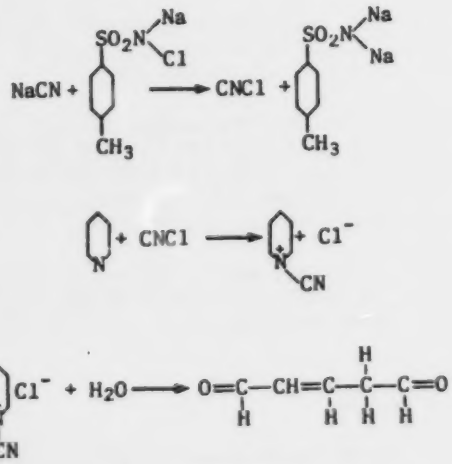
2. Principle and Theory

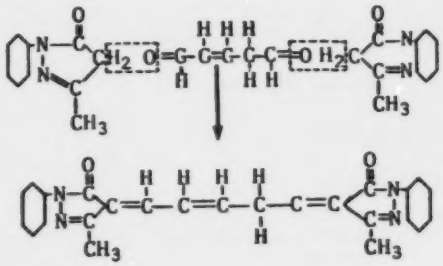
2.1. Complex cyanides are converted to hydrocyanic acid, HCN, by irradiation with ultraviolet light. After irradiation the sample is distilled from phosphoric acid solution into a sodium acetate absorbing solution.

2.2. In the colorimetric measurement, the cyanide in sodium acetate solution is converted to cyanogen chloride, CNCl, by reaction with chloramine-T. The CNCl then forms a blue dye on the addition of pyridine-pyrazolone reagent, and the absorbance is measured at 620 nm.

2.3. Equations:

The reaction may be expressed by the following equations (ref. 11.3):





3. Interferences

3.1. Sulphides interfere and should be removed prior to analysis (see section 5).

3.2. Thiocyanate gives an apparent total cyanide on an equimolar basis.

3.3. Some organic cyanide compounds such as nitriles are decomposed under test conditions.

3.4. Other interfering substances are removed in the distillation step.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a 125-mL plastic bottle and analyzed as soon as possible after collection.

4.2. Samples should be preserved by addition of sufficient NaOH to raise the pH to 11. Usually 1 mL of 10% sodium hydroxide solution per 100-mL sample is adequate.

5. Sample Preparation

5.1. If sulphide is present, decant a 100-mL aliquot of sample and add 0.5 g citric acid and 0.5 g sodium bisulphite, $NaHSO_3$. Stir the solution and allow to stand for 15 min. Decant the supernatant from the precipitated sulphur and neutralize the excess sulphite with hydrogen peroxide (30%), using starch-iodide paper as an indicator. Then immediately treat the sample aliquot with sodium hydroxide solution to raise the pH to above 10.

5.2. Treat samples containing free chlorine with sodium bisulphite using starch-iodide paper as an indicator.

6. Apparatus

6.1. Technicon AutoAnalyzer unit consisting of:

6.1.1. Manifold (Fig. 1).

6.1.2. Recorder.

6.1.3. Sampler.

6.1.4. Colorimeter equipped with 50-mm flow cell and 620-nm filters.

6.2. Proportioning pump, Carlo-Erba model 1512/20.

6.3. UV reactor. The coil consists of quartz tubing, 3 mm I.D. and 12 m long, wound to a diameter of 13 cm. A 400-W mercury lamp is used. For description of the reactor, see the "Nitrogen: Organic" (automated ultraviolet digestion) method.

6.4. Distillation equipment (see Fig. 2). The distillation column consists of borosilicate glass tubing, 12 mm I.D. and 350 mm long, wrapped with 22-gauge heating wire to give a resistance of about 24 ohms. Approximately 65 V ac is applied to the heating wire using a variable transformer.

6.5. Gas absorption column. For details of construction, see Figure 3.

7. Reagents

7.1. Stock cyanide solution, 1000 mg/L as CN: Dissolve 2.51 g potassium cyanide, KCN, in distilled water. Add 10 mL of 10% sodium hydroxide solution (7.2) and make up to 1 L in a volumetric flask. Standardize with 0.0192 N silver nitrate solution using indicator solution (7.4). The solution gradually loses strength and must be rechecked every 2 weeks. (Caution: Toxic; take care to avoid ingestion.)

7.2. Sodium hydroxide solution, 10%: Dissolve 100 g sodium hydroxide, NaOH, in approximately 750 mL distilled water and make up to 1 L.

7.3. Standard silver nitrate solution, 0.0192 N: Dissolve 3.270 g silver nitrate, $AgNO_3$, in distilled water and dilute to 1 L in a volumetric flask (1 mL of this solution is equivalent to 1 mg CN).

7.4. Indicator solution: Dissolve 0.02 g rhodanine (p-dimethylaminobenzylidene) in 100 mL acetone.

7.5. Intermediate cyanide solution, 10 mg/L as CN: Dilute 10 mL stock cyanide solution (7.1) and 10 mL sodium hydroxide solution (7.2) to 1 L with distilled water.

7.6. Standard cyanide solution, 0.1 mg/L as CN: Dilute 10 mL intermediate cyanide solution (7.5) and 10 mL sodium hydroxide solution (7.2) to 1 L with distilled water.

7.7. Working cyanide standards: Prepare a series of standards to cover the required concentration range by appropriate dilutions of the standard cyanide solution (7.6). All standards should be preserved with sodium hydroxide solution at the rate of 1 mL of 10% NaOH per 100 mL solution.

7.8. Phosphoric acid solution: Dilute reagent grade o-phosphoric acid, H_3PO_4, with an equal volume of distilled water.

7.9. Hypophosphorous acid solution: Dilute 50% hypophosphorous acid, $H(H_2PO_2)$, with an equal volume of distilled water.

7.10. Sodium acetate solution, 2%: Dissolve 20 g sodium acetate, CH_3COONa, in distilled water and make up to 1 L. Adjust the pH of this solution to 6.5 with acetic acid (glacial).

7.11. Wash solution, 0.1% sodium hydroxide solution: Dilute 20 mL of 10% sodium hydroxide solution (7.2) to 2 L with distilled water.

7.12. Mixed pyridine-pyrazolone solution: Dissolve 0.75 g 3-methyl-1-phenyl-2-pyrazolin-5-one and 0.05 g 3,3'-dimethyl-1,1'-diphenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione in 50 mL pyridine. Add 250 mL distilled water and mix. Prepare daily.

7.13. Chloramine-T solution: Dissolve 1 g chloramine-T, $CH_3C_6H_4SO_2NClNa \cdot 3H_2O$, in 100 mL distilled water. Prepare daily.

8. Procedure

8.1. Set the system in operation and allow to warm up.

8.2. Determine the rate of distillation by measuring the volume of liquid that overflows from each of the two U-tube traps. Adjust the power to the distillation column heater so that approximately 20% of the liquid is being vaporized in the tube.

8.3. Check to see that the conical joint at the top of the gas absorber column is filled with sodium acetate solution.

8.4. Run sodium hydroxide-treated standards and samples at 20 per hour.

9. Calculations

9.1. Prepare a calibration curve from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of cyanide in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Branch), a natural water sample was analyzed and the coefficient of variation at a level of 0.023 mg/L was ±3.8%. The same sample was spiked with 0.025 mg/L cyanide and the mean concentration found was 0.046 mg/L with a coefficient of variation of ±2.2%. The average percent recovery was 94%.

10.2. The recoveries of standard solutions of complex cyanides were compared with the recoveries of simple cyanide standard solutions (KCN).

Complex cyanide	Recovery (%)
Potassium hexacyanocobaltate	78–80
Potassium tetracyanonickelate	75–80
Potassium ferrocyanide	95–100
Potassium ferricyanide	95–100

11. References

11.1. Goulden, P. D., B. K. Afghan and P. Brooksbank. 1972. Determination of nanogram quantities of simple and complex cyanides in water. *Anal. Chem.* 44:1845-1849.

11.2. American Public Health Association. 1971. *Standard Methods for the Examination of Water and Wastewater.* 13th ed. Washington, D.C.

11.3. Epstein, J. 1947. *Anal. Chem.* 19(4):272-274.

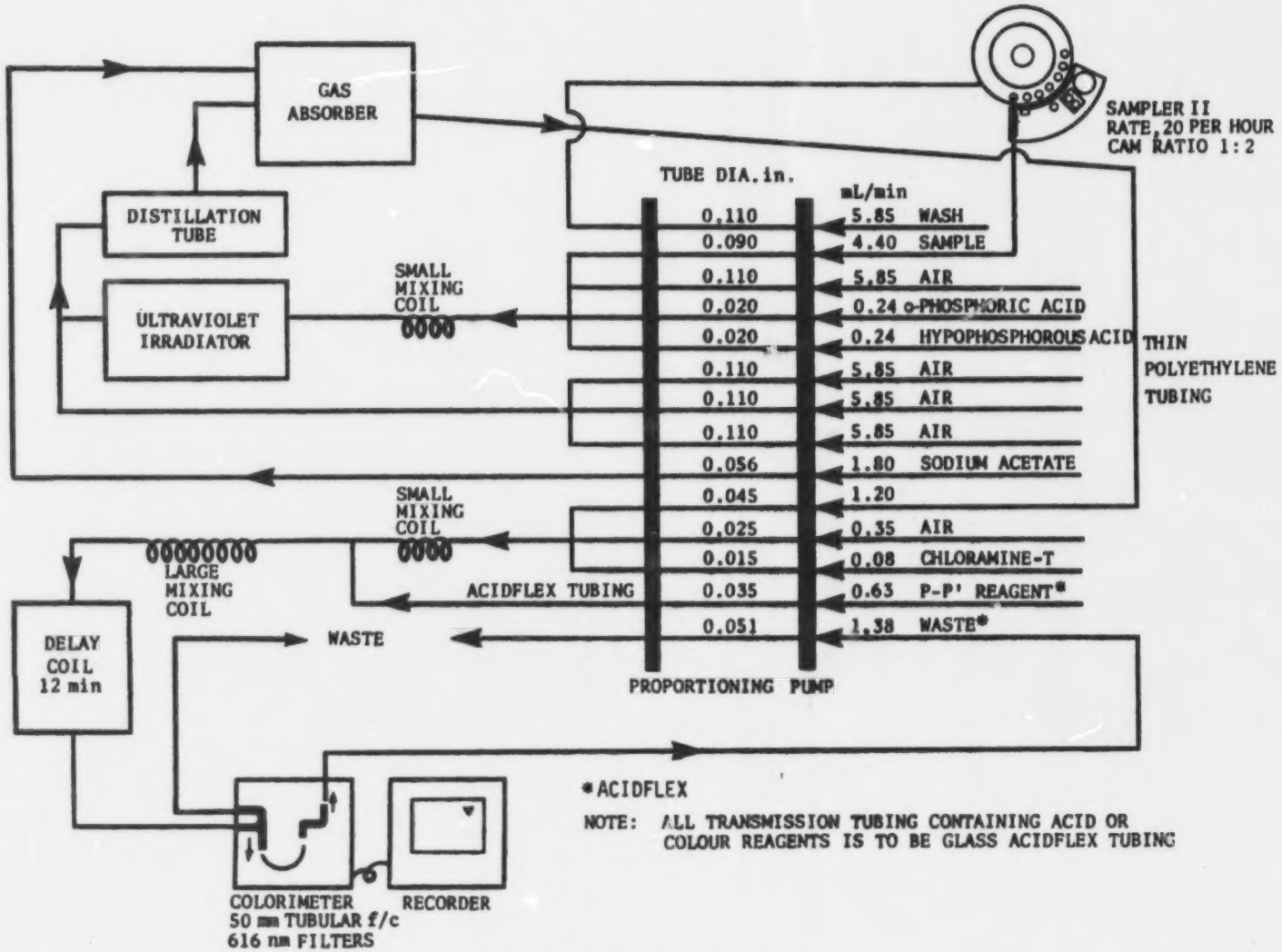


Figure 1. Cyanide manifold

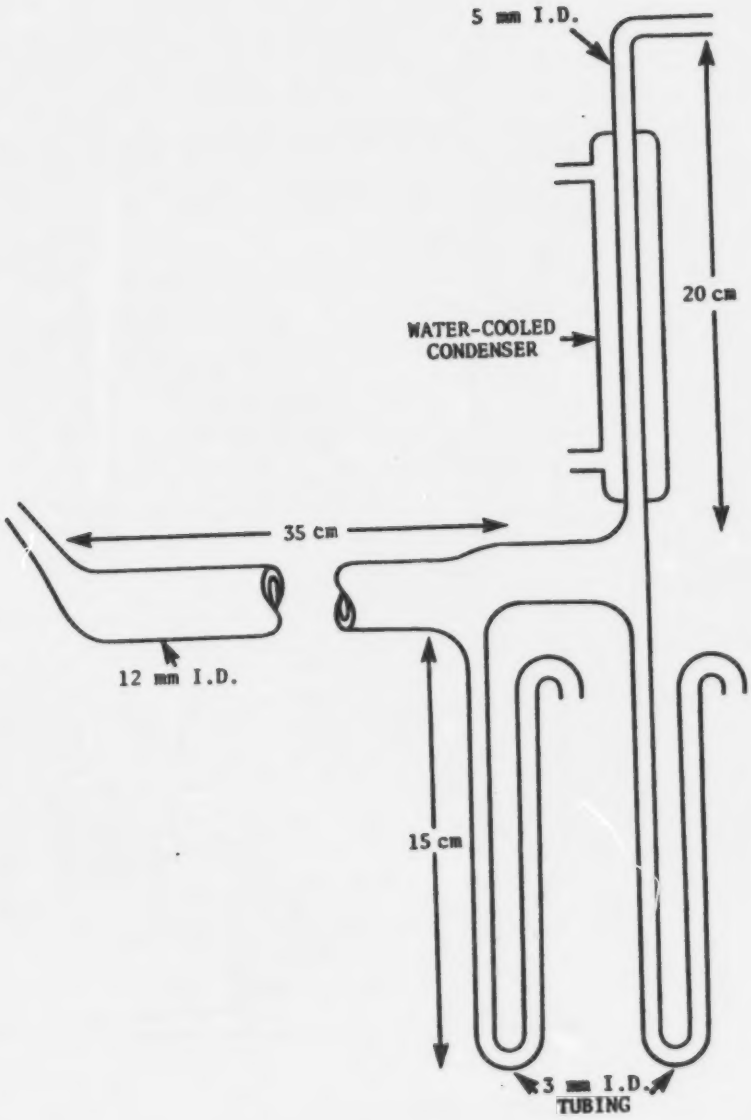


Figure 2. Continuous distillation apparatus

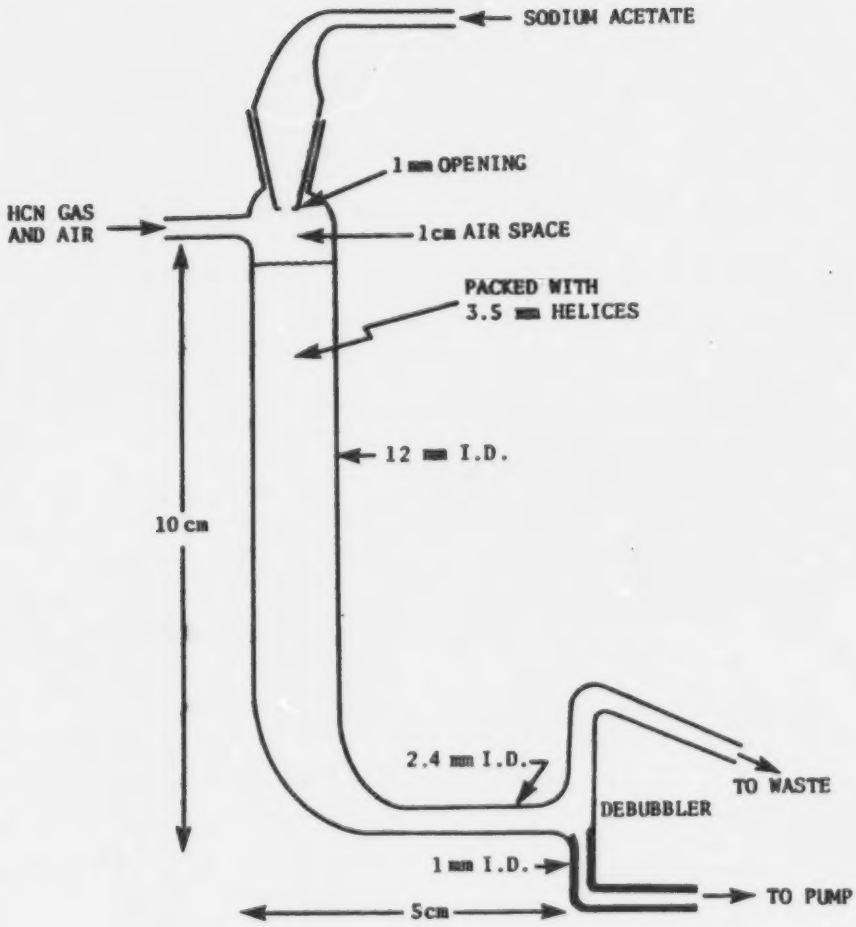


Figure 3. Gas absorption column

CYANIDE ANALYSIS OF MINING EFFLUENTS BY SPECIFIC ION ELECTRODE

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Abstract. The Ag/S specific ion electrode has been evaluated for analysis of both free and total cyanide. Metal cyanide solutions were prepared from reagent grade compounds and by stoichiometric mixture of the metal with a potassium cyanide solution. Solutions containing Cu^{+1}, Ni^{+2}, Fe^{+2}, Fe^{+3}, and Zn^{+2} complexes were analyzed prior to and following EDTA pretreatment. This effort provides an understanding of the effect of each metal cyanide complex on the SIE analysis of free and "total" cyanide.

Background

Efforts to treat mining wastes and effluents to reduce total cyanide levels must be based on both the concentration of cyanide and forms in which cyanide are present. The recognized reflux distillation method with columetric measurement for total cyanide as cited by EPA (1979), ASTM (1977), and Standard Methods (1975) is both time consuming and tedious. It also requires a well-trained and experienced analyst to insure that precise data are obtained. Total cyanide results and their use have been questioned when defining the cyanide toxicity of water streams containing stable complex-metal cyanides. Although metal cyanide complexes are considered inert, questions have been raised concerning their decomposition by UV light in aquatic streams.

The specific ion electrode method for analysis of free cyanide has been previously reported by Frant (1972) and Riseman (1972) and Schluster (1976). An EDTA pretreatment has been presented by Frant to chelate metals from dissociated metal cyanide complexes and therefore allow measurement of their cyanide counterpart as free cyanide. Schluster (1976) evaluated the use of the cyanide specific electrode for determining free and total cyanide of metal cyanide solutions. That effort indicated the CN electrode responds to free cyanide only and not to that complexed to metals. The objective of this study was not to determine stability of complexed metal cyanides, however, the information obtained may be used as a crude comparison.

Study Description

The method used in this study was based on the studies previously performed and published by Frant (1972) and Riseman (1972). The method utilizes the silver/sulfide electrode which is capable of measuring the activity of the silver ion down to a 10^{-20}M concentration. An indicator/buffer containing silver cyanide complex is added to the sample. The complex is in equilibrium with silver and cyanide ions as shown in equation 1:

$$Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^- \qquad (1)$$

As the complex is added to a solution containing cyanide ion, cyanide shifts the equilibrium to the left. For increased cyanide concentrations, the silver ion activity decreases and is observed as a more negative electrode potential. Because the silver cyanide complex requires two cyanide ions for each silver ion, a 118mv decrease will be observed for each tenfold increase in cyanide. This gives twice the slope observed when using a monovalent anion electrode and allows for greater measurement precision.

Riseman noted that the pH of the solutions must be adjusted to at least 11 to convert 98 percent of the cyanide to ionic form. Also, samples and standards should have about the same ionic background. For this study, the ionic background of the standards was adjusted to be consistent with the expected ionic strength of process effluents from the mining industry. This was done by the addition of sodium hydroxide to a 0.5M concentration. This was also more than adequate to raise the pH above 11.

Apparatus

The apparatus used in this study was an Orion Model 701A digital pH/mV meter equipped with an Orion 90-02 double junction reference electrode and an Orion 94-16 silver/sulfide electrode.

Reagents

Electrode Filling Solutions: The Orion filling solutions supplied with the double junction reference electrode were used to fill its inner and outer chambers.

Indicator/Buffer: 17.5g of reagent grade disodium hydrogen phosphate (Na_2HPO_4) were dissolved in approximately 80 mls of deionized water. The solution was stirred for 30 minutes before the addition of 2.2g of sodium hydroxide (NaOH) and 0.1g of silver potassium cyanide ($KAg(CN)_2$). The solution was diluted to a final volume of 100 mls. This solution was checked daily before use and was discarded when any precipitate was noticed.

Stock Cyanide Solution: Two grams of sodium hydroxide (NaOH) was dissolved in about 800 mls of deionized water and 2.51g of potassium cyanide was added before final dilution to one liter. This solution was standardized weekly by potentiometric titration using silver nitrate.

Working Cyanide Solution: The standardized stock cyanide solution was diluted daily as appropriate to give a 100 mg/l working standard.

Silver Nitrate Standard: 3.265g of crushed and dried (40°C) silver nitrate ($AgNO_3$) was dissolved in deionized water and diluted to one liter (1 ml = 1 mg CN^-).

25M Sodium Hydroxide: 200g of sodium hydroxide pellets were dissolved in 200 mls of deionized water.

0.1M EDTA: 3.36 g of the disodium salt of EDTA was dissolved in deionized water and diluted to 100 mls.

Acetic Acid: Reagent grade concentrated glacial acetic acid.

Metal Cyanide Complexes: 100 mg/l solutions (as cyanide) of nickel, zinc, copper, ferric- and

ferro- cyanide complexes were prepared by direct weighing from purchased reagent grades compounds. The composition of each of these compounds is listed in Table 1.

In addition 10 mg/ℓ CN solutions of nickel and zinc cyanide complexes were prepared by the stoichiometric mixture of each metal and potassium cyanide solutions.

Specific Ion Electrode Measurements

The following steps were used for all measurements in this study:

- a 100 ml sample was pipetted into a 150 ml glass beaker,
- 2 ml of 25N sodium hydroxide were added to adjust the pH and ionic background,
- 2 ml of silver cyanide indicator/buffer were added,
- the electrodes were immersed in the sample and the solution was stirred at a low rate on a magnetic stirrer,
- the millivolt reading was observed over a five minute period on the relative millivolt scale before recording the final millivolt reading, and
- the electrodes were rinsed with deionized water and blotted dry prior to the next sample measurement.

Broad Range Standard Calibration Curve

A standard calibration curve was prepared using potassium cyanide solutions over a broad range of concentrations from 50 mg/ℓ down to 0.01 mg/ℓ. The measurements were made in both increasing and decreasing order of concentrations and were repeated on three separate days to determine the reproducibility of the standard curve. At the 95 percent confidence level the standard deviation of all measurements was ± 8mV. Figure 1 presents the broad range calibration curve. Nernstian response is identified from 50.0 to 0.25 ppm cyanide. Readings were reproducible down to 0.01 ppm cyanide, however, the response differential per tenfold change in concentration dramatically dropped at the 0.25 ppm level.

A shorter range standard calibration curve (1.0 to 0.02 mg/ℓ) was also run on a daily basis to determine the concentrations of the metal cyanide complexes.

Determination of Total Cyanide

Total cyanide determinations required that the samples be pretreated to release the cyanide from the metal complexes prior to measurement as the free cyanide ion. This release was accomplished as follows:

- acetic acid was added to lower the pH to 4,
- 1 ml of 0.1M EDTA was added,
- the solution was heated at 50°C for five minutes on a water bath, and
- the solution was cooled to room temperature.

Following pretreatment, the cyanide concentration was determined as described for free cyanide under specific ion electrode measurements.

Determination of Free Cyanide

Free cyanide was determined on each of the metal cyanide complexes by the method previously described. Each complex was diluted to give theoretical cyanide concentrations of 1.0, 0.5, 0.1, 0.05 and 0.02 mg/ℓ. The millivolt reading was used to determine the free cyanide concentration by comparison to the short range standard curve prepared on the day of the determination.

Results and Discussion

The results of the evaluation of the silver/sulfide electrode for the analysis of free and/or total cyanide are given and discussed in the following paragraphs. The results will be given in three parts:

- reproducibility of the method when applied to potassium cyanide standards,
- the measurement of free cyanide in metal cyanide complexes, and
- the measurement of total cyanide in metal cyanide complexes.

Reproducibility of Method

The reproducibility of the silver/sulfide electrode method for the analysis of cyanide was determined by preparing low range free cyanide calibration curves using solutions of potassium cyanide. Table 2 presents the response of the Ag/S electrode to free cyanide. Tests were performed in duplicate on eight days to define the reproducibility of the standard curve. At the 95 percent confidence level mV response is reproducible to ± 9mV. The relative standard deviation is 16 percent at concentrations above 0.25 ppm. The low range calibration curve (Figure 2) again shows linearity down to 0.25 ppm.

Results of Free Cyanide Measurements

The results of the free cyanide determinations are given in Table 3. This table presents the concentration of ionic cyanide (free) for each of the metal cyanide complexes tested. Zinc and nickel results include analysis of the metal cyanide compound and the stoichiometric mixture of free cyanide with the metals. The agreement between both methods of complex generation is fairly good and support one another. Data indicate that at the 1.0 and 0.5 mg/ℓ concentrations the percent free cyanide found by this method varies from less than 10 percent free cyanide for nickel complexes, to 20-30 percent for copper complexes, to 100 percent for zinc

complexes. These data follow anticipated trends since copper and nickel are known to form stable complexes with cyanide while the complex formed with zinc is relatively unstable. The zinc complex appears so loosely bound that the addition of sodium hydroxide for pH/ionic background adjustments breaks up the zinc cyanide complex to form the more stable zinc hydroxide complex. Therefore, this method will not only measure free cyanide but may include along with zinc, other unstable metal cyanide complexes. No detectable free cyanide was observed from either iron complex.

Figure 3 presents the results for free cyanide observed in metal cyanide complex solutions.

Results of the Total Cyanide Measurements

The results of the total cyanide measurements are given in Table 4. The EDTA pretreatment will release part of the cyanide complexed by nickel and copper but will not release that complexed by iron.

A comparison of the diluted compounds indicates greater dissociation for the nickel complex, followed by zinc, and finally copper (Figure 4). Of particular interest is the apparent decrease of cyanide from the zinc complex when subjected to the EDTA treatment when compared with that without treatment.

Discussion

Copper, nickel and zinc results in Figures 5 through 7, provide a visual interpretation of both precision and recovery. Shaded areas on the graphs represent the 95 percent confidence interval of results for free and total cyanide.

The narrow bands for free cyanide for copper and zinc indicate a better reproducibility of results. In comparison wider bands for total cyanide also include greater imprecision due to the added steps in the procedure. Free cyanide for the nickel complex (Figure 6) was quite low and, therefore, a greater band is presented at the detection limit.

To further evaluate loss of cyanide from zinc complexes during the EDTA pretreatment two additional experiments were performed. Both cyanide and metal cyanide complexes were again reanalyzed following EDTA pretreatment. The timing of sodium hydroxide addition after EDTA pretreatment was investigated. Results of this experiment provided additional information concerning recovery. There appears to be no appreciable loss of free cyanide that is related to the EDTA pretreatment itself. An observed loss seems to occur when addition of sodium hydroxide is delayed. When original evaluations were made, solutions were allowed to cool 30-40 minutes prior to sodium hydroxide addition. This delay was consistent in all tests. When additional experiments were performed, approximately 55 percent of free cyanide was lost with a 30 minute delay of NaOH addition. No loss was observed upon immediate addition.

Experimental results of copper, nickel and zinc complexes are tested in Table 5. They do not follow a consistent trend. Both copper and zinc complexes exhibit greater recovery of total cyanide with immediate pH adjustment following the EDTA treatment. However, nickel results are lower with immediate addition. No explanation is made at this time concerning the nickel results. However, no conclusion can be made which is applicable to all metal cyanide complexes concerning cyanide loss.

Conclusions

The results of the evaluation of the silver/sulfide specific ion electrode for the analysis of cyanide have demonstrated the following:

- The method is reproducible and linear in the concentration range from 50.0 to 0.10 mg/l cyanide when using solutions of potassium cyanide.
- For free cyanide analysis, the more unstable metal cyanide complexes such as zinc cyanide decompose to cyanide ion when treated with sodium hydroxide for pH and ionic background adjustment.
- For total cyanide analysis, not all metal cyanide complexes quantitatively decompose to cyanide ion by the EDTA treatment.

Therefore, the specific ion electrode method may be useful for the measurement of the chemically reactive cyanides which include free cyanide plus the easily dissociable complexes such as zinc cyanide. For total cyanide determinations, the method is less useful under the current EPA definition of the parameter since the iron cyanide complexes are not measured by this method.

References

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4. Frant, M. S., J. W. Ross, Jr., and J. H. Riseman, "Electrode Indicator Technique for Measuring Low Levels of Cyanide," Anal. Chem. 44 (8) 2237 (1972).
5. Riseman, J. H., "Electrode Techniques for Measuring Cyanide in Waste Waters," American Laboratory, December, 1972.
6. Schlueter, A., "Application of the Cyanide Electrode for Measuring Free and Total Cyanide," EPA 600/4-76-020, U. S. Environmental Protection Agency, EMSL, Cincinnati, Ohio 45269 (1976).

TABLE 1. CYANIDE COMPOUNDS TESTED

Potassium Cyanide	KCN
Copper Cyanide	$KCu(CN)_2$
Ferric-Cyanide	$K_3Fe(CN)_6$
Ferro-Cyanide	$K_4Fe(CN)_6 \cdot 3H_2O$
Nickel Cyanide	$K_2Ni(CN)_4$
Zinc Cyanide	$K_2Zn(CN)_4$

TABLE 2. RESPONSE FOR CYANIDE CONCENTRATIONS LEVELS
(-mV Response)

concentration:	0.02	0.05	0.10	0.50	1.00
1	182	196	218	289	324
2	171	190	215	294	330
3	169	188	213	291	326
4	168	184	206	287	324
5	175	190	210	286	322
6	168	183	203	279	318
7	175	187	211	289	326
8	175	191	210	285	324
$\bar{X}$	173	189	210	288	326
1.95σ(mV)	9	8	9	9	10
$\bar{X} \pm 1.95\sigma$(ppm)	0.020 ± 0.018	0.050 ± 0.015	0.100 ± 0.025	0.50 ± 0.08	1.00 ± 0.16
rsd(1.95σ)%	90	30	25	16	16

TABLE 3. FREE CYANIDE ANALYSIS OF METAL COMPLEXED CYANIDES

Cyanide Concentration (mg/L)		Iron		Nickel		Iron		Copper
		$K_4[Fe(CN)_6]$ Compound	$Fe(CN)_6^{-4}$ Mixture	$K_2[Ni(CN)_4]$ Compound	$Ni(CN)_4^{-2}$ Mixture	$K_3Fe(CN)_6$ Compound	$K_4Fe(CN)_6 \cdot 3H_2O$ Compound	$KCu(CN)_2$ Compound
1.0	Day 1	1.02	0.94	0.060	0.044	<0.020	<0.020	0.175
	Day 2	1.00	1.05	0.055	0.048	<0.020	<0.020	0.160
	Day 3	1.00	1.04	0.055	0.054	<0.020	<0.020	0.180
	$\bar{X} \pm 1\sigma$	1.01 ± 0.01	1.01 ± 0.04	0.056 ± 0.02	0.050 ± 0.005	<0.020	<0.020	0.173 ± 0.01
0.10	Day 1	0.10	0.15	0.030	0.021	<0.020	<0.020	0.145
	Day 2	0.10	0.10	0.030	0.026	<0.020	<0.020	0.130
	Day 3	0.10	0.10	<0.020	0.041	<0.020	<0.020	0.145
	$\bar{X} \pm 1\sigma$	0.10 ± 0.01	0.10 ± 0.03	<0.022 ± 0.021	0.031 ± 0.000	<0.020	<0.020	0.140 ± 0.009
0.10	Day 1	0.110	0.096	0.020	<0.020	<0.020	<0.020	0.071
	Day 2	0.100	0.100	<0.020	<0.020	<0.020	<0.020	0.070
	Day 3	0.100	0.100	<0.020	0.019	<0.020	<0.020	0.070
	$\bar{X} \pm 1\sigma$	0.103 ± 0.005	0.100 ± 0.006	<0.026 ± 0.011	<0.023 ± 0.005	<0.020	<0.020	0.071 ± 0.002
0.050	Day 1	0.060	0.060	0.031	<0.020	<0.020	<0.020	0.047
	Day 2	0.055	0.053	<0.020	<0.020	<0.020	<0.020	0.047
	Day 3	0.050	0.050	<0.020	<0.020	<0.020	<0.020	0.043
	$\bar{X} \pm 1\sigma$	0.054 ± 0.005	0.054 ± 0.005	<0.024 ± 0.006	<0.020	<0.020	<0.020	0.045 ± 0.002
0.000	Day 1	0.025	0.020	<0.020	<0.020	<0.020	<0.020	0.027
	Day 2	0.027	0.020	<0.020	<0.020	<0.020	<0.020	0.020
	Day 3	<0.020	0.020	<0.020	<0.020	<0.020	<0.020	<0.020
	$\bar{X} \pm 1\sigma$	0.025 ± 0.005	0.022 ± 0.001	<0.020	<0.020	<0.020	<0.020	<0.023 ± 0.005

TABLE 4. TOTAL CYANIDE ANALYSIS OF METAL COMPLEXED CYANIDES

Complexed Cyanide Concentration (mg/l)		Zinc		Nickel		Iron		Copper
		$K_2[Zn(CN)_4]$ Compound	$Zn(CN)_4^{-2}$ Mixture	$K_2[Ni(CN)_4]$ Compound	$Ni(CN)_4^{-2}$ Mixture	$K_4Fe(CN)_6$ Compound	$K_3Fe(CN)_6 \cdot 3H_2O$ Compound	$K_3Cu(CN)_4$ Compound
1.0	Day 1	0.54	0.60	0.54	0.31	<0.000	<0.000	0.30
	Day 2	0.58	0.54	0.56	0.56	0.050	<0.000	0.33
	Day 3	0.38			0.53	0.030	0.000	0.30
	$\bar{X} \pm 1\sigma$	0.47 ± 0.10	0.57 ± 0.04	0.55 ± 0.01	0.46 ± 0.13	<0.023 ± 0.006	<0.000	0.37 ± 0.001
0.50	Day 1	0.26	0.34	0.30	0.37	<0.000	<0.000	0.265
	Day 2	0.35	0.31	0.31	0.30	<0.000	<0.000	0.150
	Day 3	0.20			0.30	<0.000	<0.000	0.180
	$\bar{X} \pm 1\sigma$	0.24 ± 0.03	0.30 ± 0.00	0.30 ± 0.00	0.30 ± 0.03	<0.000	<0.000	0.100 ± 0.000
0.10	Day 1	0.072	0.080	0.070	0.070	<0.000	<0.000	0.061
	Day 2	0.064	0.048	0.080	0.070	<0.000	<0.000	0.000
	Day 3	0.040			0.063	<0.000	<0.000	0.000
	$\bar{X} \pm 1\sigma$	0.052 ± 0.015	0.060 ± 0.000	0.076 ± 0.000	0.070 ± 0.007	<0.000	<0.000	0.057 ± 0.000
0.000	Day 1	0.045	0.030	0.040	0.044	<0.000	<0.000	0.042
	Day 2	0.035	0.000	0.047	0.037	<0.000	<0.000	0.000
	Day 3	0.030			0.030	<0.000	<0.000	0.030
	$\bar{X} \pm 1\sigma$	0.035 ± 0.006	0.033 ± 0.006	0.040 ± 0.005	0.030 ± 0.005	<0.000	<0.000	0.000 ± 0.000
0.000	Day 1	<0.000	0.003	<0.000	0.000	<0.000	<0.000	<0.00
	Day 2	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.00
	Day 3	<0.000		<0.000	<0.000	<0.000	<0.000	<0.00
	$\bar{X} \pm 1\sigma$	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.00

TABLE 5. EFFECT OF NaOH ADDITION TIME ON TOTAL CYANIDE RESULTS*

Delay (Minutes)	Theoretical CN^-	CN^-	$Cu(CN)_2$	$Ni(CN)_4$	$Zn(CN)_4$
0	1.0	1.00	0.52 ± 0.04	0.36 ± 0.04	0.74 ± 0.12
30	1.0	0.49	0.37 ± 0.06	0.55 ± 0.03	0.47 ± 0.19
0	0.5	0.46	NA	0.22 ± 0.03	0.37 ± 0.02
30	0.5	0.33	0.20 ± 0.12	0.30 ± 0.04	0.24 ± 0.06

*Concentration as ppm.

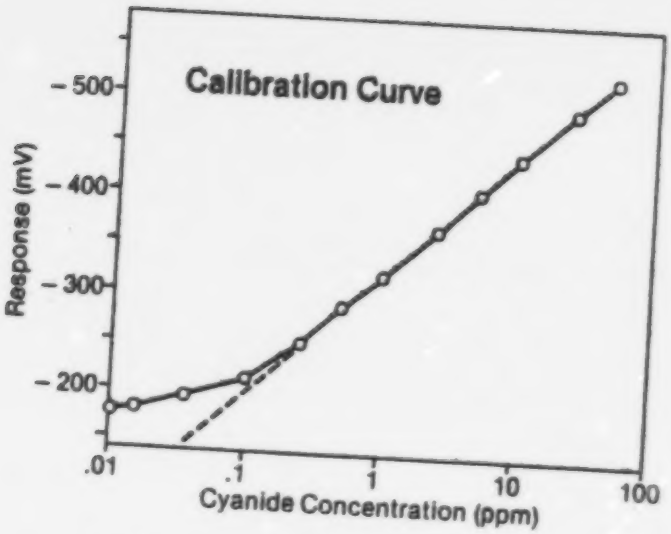

Figure 1. Calibration Curve of Electrode Response versus Cyanide Concentration.

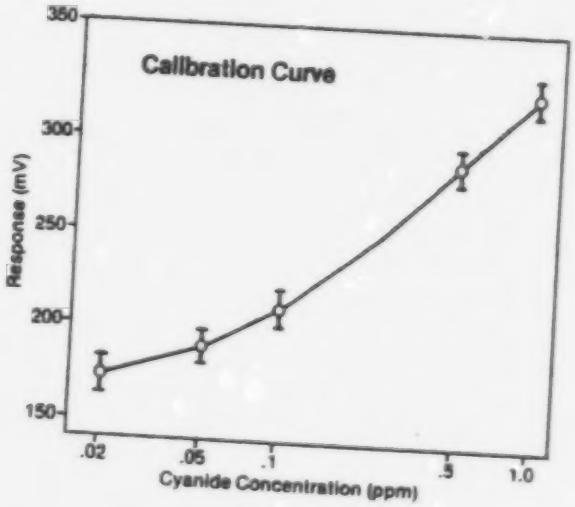

Figure 2. Low Range Calibration Curve.

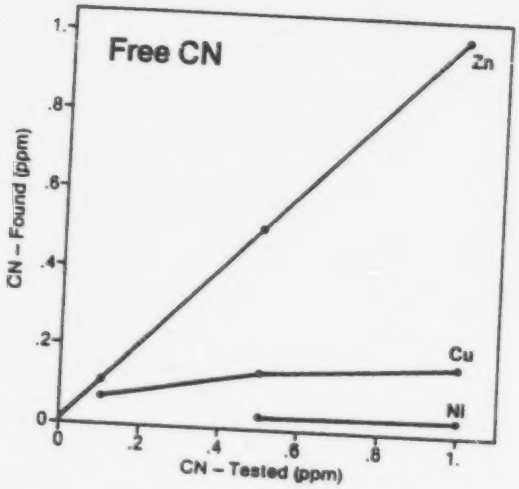

Figure 3. Free Cyanide Analysis Results.

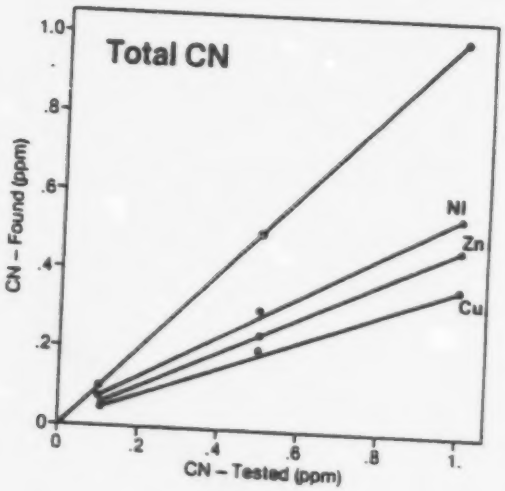

Figure 4. Total Cyanide Analysis Results.

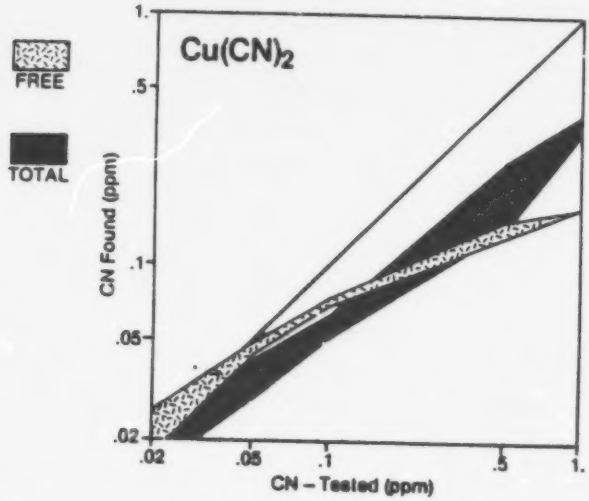

Figure 5. Copper Cyanide Results.

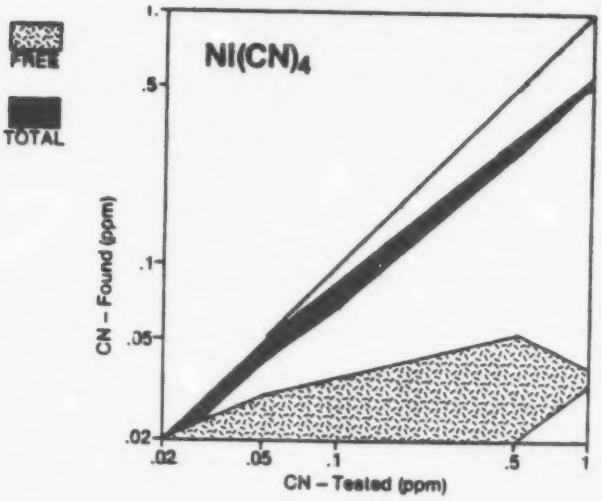

Figure 6. Nickel Cyanide Results.

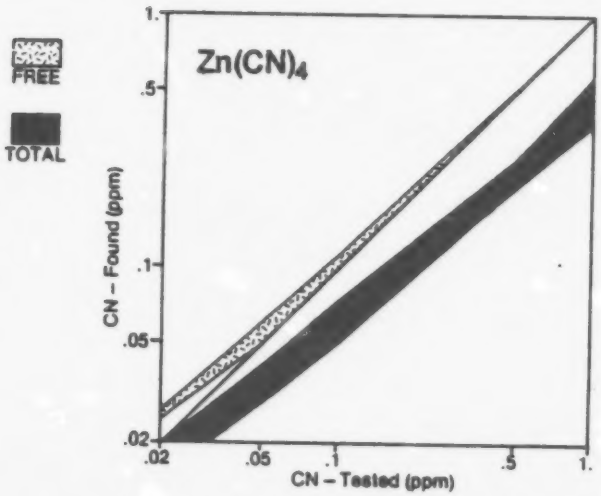

Figure 7. Zinc Cyanide Results.

Cyanide Destruction Plants in Canada

Company	Operation	Year Installed	Process	Flow	Composition (mg/l) Prior to Chlorination	Composition (mg/l) Dec '75 with chlorination	Reagent Consumption	Operating Conditions	Capital Costs	Operating Costs
Western Mines Ltd.	Myra Falls Cu-Pb Flotation CN in thickener overflow	1973/5	Alkaline Chlorination	200,000Igpd 900 m^3/d	pH 7.7 Cu_s 41.9 CN_T 68.3	9.74 0.14 0.13	2000 lb Cl_2/day 3700 lb lime/day	ORP-600mv pH 11-12	1973 $107,000	1973 $96,000/yr
DuPont Exploration Ltd. North Central, BC	Baker Lake Barren Bleed	198	Alkaline Chlorination for tailings detox O_2 replaced by SO_2/Air See below	Barren bleed 3 - 4 gpm	Barren bleed up to 3g/l CN_T		$Ca(OCl)_2$			converted
Carolin Mines Hope, BC	Ladner Creek Mill Mill Recycle Solution		Alkaline Chlorination Barren Bleed Mill solution							
Carolin Mines Hope, BC	Ladner Creed Mill Tailings Decant		Alkaline Chlorination for tailings detox Cl_2 replaced by SO_2/Air then abandoned							

Cyanide Destruction Plants in Canada

Company	Operation	Year Installed	Process	Flow	Composition (mg/l)	Reagent Consumption	Operating Conditions	Capital Costs	Operating Costs
Scottie Gold Mine Stewart, BC	Scottie Gold Mine high pyrrhotite Gold ore Poor washing of pulp		Alkaline Chlorination of tailings Replaced by SO_2/air						
Mosquito Creek	Near Wells, BC		Alkaline Chlorination	Barren bleed					
Campbell Red Lake North Central Ontario	Detour Lake Mill Tailings pulp	1982	Alkaline Chlorination	estimated 4000 m^3d pulp					
Giant Yellowknife Mines Ltd.	Yellowknife, NWT	1981	Alkaline Chlorination	319 million Igpa 8000 m^3/d for 6 mo/v		14 lb Cl_2/lb CN_T			
AMAX Inc.	Climax, CO		Chlorine Dioxide	11,000 m^3/d					

Cyanide Destruction Plants in Canada

Company	Operation	Year Installed	Process	Flow	Composition	Before treatment: Barren Bleed	Before treatment: Tailings	After treatment: Treated Barren Bleed	After treatment: Final Effluent
Dupont Exploration Ltd.	Baker Lake N Central BC	1983 INCO License Now shut down	SO_2/Air Retrofit	100 tpd ore ± 20m³/d barren bleed	CN_T	-	240	-	0.1-0.3
					Cu	-	20	-	1 - 5
					Fe	-	6	-	0.3
					Zn	-	90	-	0.1-0.2
Scottie Gold Mines	near Stewart BC	1982 INCO License	SO_2/Air Retrofit	200 tpd 130 m³/d barrens	CN_T	450	115	0.1-2	0.1-1
					Cu	35	17	1-10	0.2-2
					Fe	1.5	0.7	<0.5	0.02-0.3
					Zn	66	18	0.5-2	<1.0
Carolin Mines	Ladner Creek Mill Retrofit	Now ceased using cyanide	SO_2/Air Retrofit	1300 tpd ore Flotation ion ± 130 tpd Barren Bleed 150 m³/d	CN_T	1500	11-19	3-10	0.3-2
					Cu	350	13-15	5-15	0.5-5
					Fe	75	1.0-3.2	0.1-0.3	0.1-0.3
INCO	McBean Mine Kirkland Lake	now startup	SO_2/Air	about to start up					

CYANIDE DESTRUCTION IN USA

1)	Stibnite, Idaho	-	Superior Minerals Cl_2
2)	Knob Hill, WA	-	Hecla Air Spray
3)	Duval Battle Mtn.	-	Duval Cl_2 NaOH
4)	AMAX Inc.	-	Climax ClO_2
5)	Newmont	-	Carlin Cl_2 standby only
6)	Grey Eagle Mine	-	California I Cl_2 NaOH II
7)	Getty Minerals	-	Mercur, UT NaOCl for recycle solution
8)	Homestake Mining Co.	-	Lead, SD Biological

ZERO DISCHARGE OPERATIONS (No CN detoxification plant)

Pinson Mining	Winnemucca, NV
Tenneco Minerals	Hawthorne, NV
AMOCO Minerals	
Alligator Ridge	
Nerco Metals Inc.	Candalaria Project, Hawthorne, NV
Wharf Resources, Annie Creek	Lead, SD
Chemgold Inc.	Yuma, CA
ASARCO	Waterloo Project, San Bernardino Cty, CA
Freeport Gold Co.	Jarrett Canyon, NV
Carlin Gold	Carlin, NV (Standby Alkaline Chlorination)
American Mining	CA
Tombstone Exploration Inc.	Tombstone, AZ
Pegasus	Zortman/Landusky, Montana
Western States Mining	Elko, NV
Metallgesellschaft Minerals	Margaret Hills Project, Tonopah, NV
Western States Mining	UT

Cyanide Destruction USA

Operation	Location	Flow Rate	Treatment of pulp or solution	CN- destruction Method	CN in Feed ppm	CN in Effluent
Homestake Mining Co (1)	Lead, SD	21,000 m³/d 5,500,000 USgpd 4000 USgpm	S	RBC Bacterial	CN_T 2.1- 15.3 CN_C 1.2- 10.10 CNS 33.7-128.0	0.35 (2) 0.05 1.00

							CYANIDE
Amax Inc.	Climax, CO	11,000 m³d 2000 USgpm	S	Chlorine dioxide	CN_T	0.16- 0.65	0.01-0.38
Noranda Grey Eagle							
Plant I		120 gpm	S	Chlorine	CN_C	150-360	0.2
Plant II		125 gpm 400 gpm max	S		CN_T CNS CN_C	150 120 67	
Hecla Mining	Republic, Washington	Evaporation Pond	S	Spray to Air Solution		5 - 150	?
Getty Mercur Mines	Mercur, UT	Tailings Return Solution to grind	S	NaOCl addition to solution			
Duval Corp. Battle Mountain Op.	Nevada	3450 mtpd 3500-5000 m³/d solution 7000-8500 mt/l pulp	P	CL_2 + NaOH on pulp		300 ppm free CN 845 ppm CNS	?

(1) MUDDER & WHITLOCK (1984)

(2) pilot plant RBC results reported by MUDDER & WHITLOCK

CYANIDE DESTRUCTION - REST OF THE WORLD

OK Tedi	Papua NG	377,000 tpd pulp 0.15 - 0.50 g CN/l		H_2O_2 1.2 K H_2O_2 70% Solution per ton ore
Emperor Gold	Fiji			Roaster gas in splash tower for tailings
ERGO	South Africa	Calcine Circuit		Mixed with lime and raffinate rich in iron
ERGO	South Africa	1,600,000 tpm CIP tails		Last 7 stages of 11 CIL for CN-destruct

TABLE 10

RESULTS FROM HOMESTAKE MINING COMPANY PILOT PLANT INVESTIGATIONS[1]
Source: HUIATT et al

		OZONE		ACIDIFICATION VOLATILIZATION pH 4;4 hrs		ALKALINE CHLORINATION pH 4 4 hrs		ION EXCHANGE A-101-D		PRUSSIAN BLUE PPT		BIODEGRADATION	
		Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction
Total CN	Inf	0.21	33	25	60	10.77	99.5	27	30	7.83	91	5.5	95
	Eff	0.14		10		0.05		19		0.67		0.30	
Free CN	Inf	0.08	62.5	12	98	9.55	99	--	--	5.48	93	3.8	96
	Eff	0.03		0.18		0.02		--		0.37		0.16	
SCN	Inf	3.8	74	--	--	80	99	138	--	89	1	126	92
	Eff	1.0		--		NF		140		88		10	
Cu	Inf	0.03	17	3.4	28	0.67	95	2.95	99	2.22	21	3.2	88
	Eff	0.025		2.45		0.033		NF		1.76		0.36	
Fe	Inf	0.09	--	2.2	36	0.50	--	2.24	99	1.39	71	0.8	94
	Eff	0.10		1.4		0.80		NF		0.41		0.045	
Zn	Inf	NF	--	0.78	99	0.009	11	0.95	99	0.62	98	0.016	--
	Eff	NF		NF		0.008		NF		0.01		0.035	
Ni	Inf	NF	--	0.22	18	0.03	0	0.18	99	0.18	11	0.254	41
	Eff												

[1] Sample units in mg/l Inf = inflow
NF = none found Eff = effluent

TABLE 10 continued

RESULTS FROM HOMESTAKE MINING COMPANY PILOT PLANT INVESTIGATIONS[1]

		HYDROGEN PEROXIDE		HYDROGEN PEROXIDE LIME PPT		HYDROGEN PEROXIDE ION EXCHANGE		HYDROGEN PEROXIDE FERRIC SULFATE		HYDROGEN PEROXIDE FERRIC CHLORIDE	
		Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction	Sample	Percent Reduction
Total CN	Inf	11.5	87	11.5	94	0.28	57	4.7	96	4.7	94
	Eff	1.46		0.70		0.12		0.18		0.26	
Free CN	Inf	8.1	86	8.1	98	0.12	87	3.6	99	3.6	99
	Eff	1.16		1.26		0.034		0.03		0.02	
SCN	Inf	--	--	--	--	89	2	--	--	--	--
	Eff	--		--		87		--		--	
Cu	Inf	2.03	6	2.03	82	0.64	92	1.9	96	1.9	95
	Eff	1.91		0.37		0.054		0.07		0.09	
Fe	Inf	1.31	92	1.31	68	0.017	62	1.0	89	1.0	89
	Eff	0.10		0.42		0.006		0.11		0.11	
Zn	Inf	0.345	98	0.345	97	0.024	79	0.06	67	0.06	83
	Eff	0.008		0.012		0.005		0.02		0.01	
Ni	Inf	0.165	67	0.165	89	0.099	20	0.18	50	0.18	61
	Eff										

[1] Sample units in mg/l Inf = inflow
NF = none found Eff = effluent

EPA Development Document for Effluent Limitations Guidelines and Standards for the Ore Mining Industry and Ore Dressing : Point Source Category. EPA 440/1-82/061 November 1982

TABLE 11[1]. PROFILE OF GOLD MINES

MINE	LOCATION (state)	YEAR OPENED (original facility)	STATUS OF OPERATION	PRODUCT	ANNUAL PRODUCTION (metric tons* of ore mined)	TYPE OF MINE	WASTEWATER TREATMENT TECHNOLOGIES USED	DISCHARGE METHOD	DAILY DISCHARGE VOLUME (m^3 †)
4101	NV	1985	A	Au ore	744,300 (1973)	OP	None	None	0
4102	CO	unk	A	Pb, Zn, Au ore	162,000 (1973)	UG	None	To surface	3,798
4104	WA	1937	A	Au ore	49,610 (1974)	UG	Impoundment	Indirect – seepage and mill makeup	144
4105	SD	1877	A	Au ore	1,418,387 (1973)	UG	None	Mill makeup	11,500
4115	UT	1965	A	Au/Ag ore; some copper	131,060	UG	None	To surface	no
4123	NV	1973	A	Au ore	no	OP	None	None	0
4124	NM	unk	S	Au ore	no	Placer	Impoundment; recycle	None	0
4125	CA	unk	I		no	UG and Placer	unk	unk	no
4126	AK	1924	S		612,000 m^3** (1975)	Placer; dredging; Au recovered by gravity + amalgamation	Settling and partial recycle	Recycle; To surface	minimal
4127	AK	unk	S		~ Same as above	Same as above	Settling and partial recycle	Recycle; To surface	minimal
4130	NV	1973	I		~ 1536m^3/day** (seasonal)	Placer; mechanical excavation	Impoundment; and solar evap.	None	0
4154	NM	unk	UD	Au ore	680,000	OP	None	To surface	unk

*To convert to annual short tons, multiply values shown by 1.10231
†To convert to daily gallons, multiply values shown by 264.172
**Where placer mining is employed, productions are given in cubic meters of ore mined.
Status code: A – active; I – inactive; S – seasonal; UD – under development; EXP – exploration underway

TABLE 11 PROFILE OF GOLD MILLS (Continued)

MILL	LOCATION (state)	YEAR OPENED (original facility)	STATUS OF OPERATION	PRODUCT	ANNUAL PRODUCTION (metric tons* of concentrate)	CONCENTRATION PROCESS USED	WASTEWATER TREATMENT TECHNOLOGIES USED	DISCHARGE METHOD	DAILY DISCHARGE VOLUME (m^3 †)
4119	NV	1975	A	Au/Ag	na	Cyanidation; counter current decantation	Recycle of spent leach sol'n in mill; impoundment of tailings	Small volume discharged from tailings pond to desert floor	~ 10% of total
4120	NV	1977	A	Au/Ag	na	Flotation; cyanidation of flotation concentrate	Impoundment; solar evap and recycle	None	0
4121	NV	1969	I	Au	81,200 troy oz ¶ (1974)	Cyanidation; agitation leach; heap leach and Zn pptn	Impoundment and recycle	None	0
4122	NV	1973	I	Au	23,100 troy oz (1974)	Cyanidation; heap leach; carbon adsorption and electrowinning	Recycle	None	0
4128	NV	1975	A	Au/Ag	na	Cyanidation; heap leach; carbon adsorption; electrowinning	Impoundment and recycle	None	0
4129	CO	1964	UD	Au/Ag	Expect ~ 300,000	Flotation	Settling; partial recycle	To surface	na
4131	NV	1976	A	Au/Ag	Expect 60-80x10^3 troy oz (Au) 30-40x10^3 troy oz (Ag)	Cyanidation; heap leach; carbon adsorption; electrowinning	Impoundment and recycle	None	0
4154	NM	unk	UD	Au	unk	Crushing, cyanide leach, carbon adsorption, electrowinning	Recycle	None	0 (planned)

*To convert to annual short tons, multiply values shown by 1.10231
†To convert to daily gallons, multiply values shown by 264.173
¶To convert to grams, multiply value shown by 31.1
Status code: A – active; I – inactive; S – seasonal; UD – under development; EXP – exploration underway

AN OVERVIEW OF CYANIDE TREATMENT METHODS FOR GOLD MILL EFFLUENTS

by
James S. Scott

INTRODUCTION

Both the technical and patent literature describe a multitude of processes for the destruction or recovery of free cyanide and cyanide-metal complexes from solutions. Included among these are: natural degradation, evaporation, alkaline chlorination, oxidation with sulphur dioxide-air, biodegradation, oxidation with hydrogen peroxide, adsorption on ferrous sulphide, acidification-volatilization, ozonation, ion exchange, chemical precipitation, electrochemical, reverse osmosis, ion flotation, adsorption on activated carbon, electrodialysis, high pressure oxidation, photolysis and polymerization (1,2,3). Even this lengthy list will not include all proposed methods. A number of these methods have been suggested as being applicable to the treatment of gold mill wastewaters.

My purpose today is not to discuss all these methods since in most cases they have been rejected as either technically or economically unacceptable for the treatment of gold mill effluents, particularly in view of the availability more practical processes. Instead, I will limit my remarks to those methods currently in operation at gold mills. These methods are listed in Table 1.

TABLE 1 METHODS IN PRACTICE FOR THE TREATMENT OF GOLD MILL WASTEWATERS

Used at several mills:	Used at one mill:
Natural degradation	Biological
Evaporation	Oxidation with hydrogen peroxide
Alkaline chlorination	Adsorption on ferrous sulphide
Inco SO_2-air	Acidification

Head, Mining and Milling Section
Mining, Minerals and Metallurgical Processes Division
Industrial Programs Branch
Environment Canada

In the further course of this conference a number of speakers will be addressing in depth several of these processes and therefore, I will limit my remarks regarding their subjects. One process on which I will comment in a little more detail is that of alkaline chlorination. I have two reasons for this; one, it is not to be described in a separate paper and two, Environment Canada has completed an extensive evaluation of the full scale performance of this method at four gold mills.

My remarks today stem principally from my experience in Canada since being a Canadian, this is the area in which I have the greatest familiarity. It also appears to be the country in which the greatest variety of chemical methods for the destruction of cyanides is being employed.

GOLD CYANIDATION PROCESS

Before discussing the treatment of gold mill waste effluents I would like to first briefly review the origin and characteristics of these wastewaters.

The common process for the recovery of gold from lode gold deposits is that of cyanidation, in which gold is leached from the ore in a weak cyanide solution, usually NaCN. Although there are a number of variations in gold mill flowsheets, the feed to most cyanidation circuits is finely ground ore.

A simplified flowsheet for the conventional gold milling process is shown in Figure 1. This illustrates the cyanidation process in which the gold is recovered from solution by precipitation with zinc dust, i.e., the Merrill-Crowe process. The overall chemical equation representing the dissolution of gold is:

$$4Au + 8NaCN + O_2 + 2H_2O \longrightarrow 4NaAu(CN)_2 + 4NaOH$$

To recover the gold, the solution is first separated from the leached solids, usually by filtration, then deaerated and the gold precipitated by the addition of zinc dust. The precipitation step is represented by the equation:

$$2NaAu(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Au$$

The gold precipitate is smelted for the production of gold bullion.

A large proportion of the barren (gold free) solution is recirculated to cyanidation to take advantage of its remaining leaching potential for gold. However, it is necessary to bleed off a portion of this solution from the mill to avoid the build-up of deleterious metals, i.e., copper, iron, nickel, zinc, arsenic and antimony which dissolve simultaneously with gold, and would subsequently interfere

with the further dissolution and precipitation of gold. The extent to which barren solution must be discarded is related to the mineralogy of ore.

Some barren solution is used to wash, usually on filters, any gold bearing solution from the leached solids. In some mills the solids are given an additional wash with fresh water to remove the remaining cyanide before the solids are pumped to the tailings impoundment area. The importance of adequate washing with fresh water at this stage to avoid the escape of cyanide cannot be over-emphasized for those mills which practice the treatment of barren bleed directly. The release of cyanide in improperly washed filter cake can be appreciable. Some mill operators claim not to discharge barren solutions but in these cases, although this may not be done directly, barren solution is discarded as moisture with the leached solids filter cake (4).

A relatively recent innovation in gold milling is the carbon-in-pulp (CIP) process by which gold is recovered directly from the leach slurry. In the CIP process gold is recovered by adsorption on activated carbon directly from the cyanidation pulp in agitated tanks following cyanidation. The gold laden carbon is separated from the tailings slurry by screening. The slurry, either treated or untreated for cyanide removal, is then discharged to a tailings impoundment area. Gold is recovered from the carbon, usually by stripping with hot caustic cyanide solution and by electrowinning from the strip solution. Most of the newer gold mills employ the less costly carbon-in-pulp process.

The CIP process introduces two important considerations with regard to cyanide destruction; first, the amount of cyanide discharged from the mill and second, the form of the effluent containing the cyanide. Since there is no recycle of cyanide in this process, a greater amount of cyanide is contained in the mill discharge than with the Merrill-Crowe process. Also the cyanide discharged is contained in a slurry rather than in a clear liquid.

CYANIDE IN GOLD MILL DISCHARGES

In selecting a method for cyanide removal it is important to recognize the forms and stabilities of the cyanides which are present in the waste effluents. Cyanide is not a solvent entirely specific to gold and therefore, depending upon the mineralogical composition of the gold ore, the waste effluents discharged from a mill contain a wide variety of cyanide species. These species have been classified into 5 general categories as indicated in Table 2. In this Table, the cyanide-metal complexes are listed in order of increasing stability from top to bottom. The stabilities of these compounds are important in selecting a cyanide removal method since their stabilities can affect both the kinetics of treatment processes and the applicability of certain methods for removing cyanide.

TABLE 2 RELATIVE STABILITY OF CYANIDE COMPLEXES

TERMS	FORMS OF CYANIDE
1. Free Cyanide	CN^-, HCN
2. Simple Compounds	
a) readily soluble	NaCN, KCN, $Ca(CN)_2$, $Mg(CN)_2$
b) relatively insoluble	$Zn(CN)_2$, $Cd(CN)_2$, CuCN, $Ni(CN)_2$, AgCN
3. Weak Complexes	$Zn(CN)_4^{2-}$, $Cd(CN)_3^-$, $Cd(CN)_4^{2-}$
4. Moderately Strong Complexes	$Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^-$
5. Strong Complexes	$Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$

In addition to the many cyanide complexes, mill solutions often contain appreciable amounts of thiocyanate and thiosalts. These compounds are of particular importance since their presence requires additional reagent in most oxidation type cyanide destruction processes.

Waste barren solutions can be discharged from mills as solutions per se, or as moisture with filtered leached tailings or in tailings slurries from a CIP circuit. The compositions of waste barren solutions vary considerably as shown in Table 3.

TABLE 3 ANALYSES OF TYPICAL WASTE BARREN SOLUTIONS FROM GOLD MILLS (MG/L)

CN_T	*CN_W	CNS	Cu	Fe	Ni	Pb	Zn
74		50	29	0.1	9.0		31.0
86		42	6.1	0.1	0.3	0.1	13.9
220		180	73.0	35.7	2.9	0.1	17.9
300		54	6.7	21.4	10.0	0.1	62.5
310			300.0	0.8	3.1		21.0
310	220	330	10.0	9.4	0.6		93.0
400			130	16.7	5.1		84.6
400		113	35.0	26.0	3.1		71.0
450			35.0	1.5			66.0
610		400	11.0	0.4	1.7	0.1	84.1
890			55.0	80.0	35.0		35.0
1000	710	1900	97.0	100.0	0.9		110.0
2000	1900	1100	290.0	2.4	0.6		740.0

* CN_W - Weak acid dissociable cyanide by ASTM Method-C, i.e., cyanides less stable than iron cyanide.

The underlined figures indicate ranges of concentrations.

Through natural processes and dilution in tailings impoundments the concentrations of pollutants in mill wastewaters are reduced considerably but seldom to desired levels for discharge to the environment. The analyses of effluents discharged from several gold mill tailings ponds are given in Table 4.

TABLE 4 ANALYSES OF TYPICAL TAILING POND EFFLUENTS (MG/L)

CN_T	CN_W	Cu	Fe	Pb	Ni	Zn	Toxicity *LT_{50} (hours)
0.30		0.3		0.05	0.40	0.19	
0.87	0.42	0.1		0.10		0.06	96
1.2		0.5		0.03	0.02	0.13	
2.8	0.34	1.4		0.02		0.05	0.5
3.3	3.1	3.6				3.04	24
4.8	4.5	1.0		0.04		1.32	
6.8		2.3	0.3	0.10	0.10	0.20	
13.0		2.4	0.6	0.10	0.40	0.82	
21.0	16.2	0.3		0.02		2.54	0.2
25.0	18.6	8.2				2.64	0.5
33.0		1.1		0.10	0.60	0.70	
61.0	42.0	16.5		0.04		15.60	0.1

* In this Table LT_{50} refers to the exposure time at which 50% of the test fish died in 100% effluent.

TREATMENT PROCESSES FOR GOLD MILL EFFLUENTS

Until 3 or 4 years ago the treatment of wastewaters from gold mills was limited to natural degradation in tailings ponds. One exception to this was the very limited application of the acidification-volatilization process which will be described briefly later in this presentation.

Natural degradation remains the most common method for cyanide removal. However, over the past 4 years a number of other chemical processes have been applied for the treatment of gold mill wastewaters. These, as mentioned earlier include alkaline chlorination, Inco's SO_2-air process, Homestake Mining's biodegradation system, Degussa's hydrogen peroxide process and the Con Mine's iron sulphide process. The acidification process continues to be used at one gold mill.

I will now say a few words about each of these processes.

Natural Degradation:

Natural degradation involves the removal of cyanide in gold mill wastewaters by natural means while the wastewaters are detained for prolonged periods in tailings or holding ponds. The degradation of cyanide results from a combination of physical, chemical and biological processes, including: volatilization, photodecomposition, chemical oxidation, microbial oxidation, chemical precipitation, hydrolysis and adsorption on solids. Of these mechanisms volatilization is considered to be the most important. Natural degradation is influenced by a number of variables, including: cyanide species and their concentrations in solution, pH, temperature, bacteria present, sunlight, aeration, and pond conditions (area, depth, turbidity, turbulence, ice cover). Few studies have been done to quantify these processes. During the past 3 years Environment Canada has carried out considerable experimental work in order to better understand and mathematically model the natural degradation process. Mrs. L. Simovic will be describing in her paper details of the studies carried out at Environment Canada's Wastewater Technology Centre (5).

Although cyanide removal by natural means may produce acceptable effluents in some cases, one has only to recall the analyses of tailing pond effluents presented in Table 4 to be convinced that this is generally the exception, not the rule. Admittedly, the tailings ponds from which these effluents were released were primarily intended to separate and retain solids and were not designed to take maximum benefit of the natural degradation process. Considerably better understanding of this process is required before it will be possible, if ever, to employ this method in a general and practical manner to consistently meet regulatory standards.

However, it is worth noting that even in cases where natural degradation cannot produce a final effluent of suitable quality it can still be advantageously employed as a valuable intermediate step for the partial, and perhaps considerable, elimination of cyanide prior to chemical treatment. In fact advantage is being taken of this at some gold mills which do treat tailing pond overflows.

Evaporation

At gold mines in arid regions advantage is taken of evaporation to preclude the discharge of wastewaters. This is common practice at gold mines in the south-western United States, Australia and South Africa. In fact the U.S. EPA's effluent limitation for gold mines in areas of net evaporation is one of zero discharge of process wastewaters.

Chemical Treatment Methods

The inability to produce wastewaters of acceptable quality by natural means has led to the wide interest and growing application of chemical treatment methods for this purpose.

Alkaline Chlorination

Although the alkaline chlorination process has been well known and industrially employed for considerable time, it has been applied to the treatment of gold mill effluents only within the past 4 years. I will first describe the results of full scale performance evaluations carried out during the past 3 years at 4 gold mills in Canada and then present additional information obtained from a fifth gold mine operating in California.

The alkaline chlorination process destroys cyanide (except iron cyanide or more stable cyanide-metal complexes) by oxidation with chlorine under alkaline conditions. Chlorine can be provided in the forms of gaseous chlorine or sodium and calcium hypochlorite. Lime is commonly used for pH control.

The complete oxidation of cyanide to nitrogen and bicarbonate requires 2 stages. During the first stage, cyanide is oxidized and hydrolyzed in two steps to cyanate according to the equations:

$$NaCN + Cl_2 \longrightarrow CNCl + NaCl \qquad (1)$$

$$CNCl + 2NaOH \longrightarrow NaCNO + NaCl + H_2O \qquad (2)$$

The oxidation of cyanide-metal complexes is exemplified by the following reaction for the zincocyanide complex:

$$Na_2Zn(CN)_4 + 10NaOH + 4Cl_2 \longrightarrow 4NaCNO + 8NaCl + Zn(OH)_2 + 4H_2O \qquad (3)$$

The second stage of the process, i.e., the further oxidation of cyanate to nitrogen and bicarbonate, can be represented by the overall reaction:

$$3Cl_2 + 2NaCNO + 6NaOH \longrightarrow 2NaHCO_3 + N_2 + 6NaCl + 2H_2O \qquad (4)$$

Reactions (1) - (3) are carried out at pH 10.5 minimum and reaction (4) at about pH 8.5. Considerably greater reagent additions and longer retention times are required in completing both stages. As a consequence of both higher costs and the relatively low toxicity of cyanate (1/1000 the toxicity of free cyanide) regulatory agencies generally require the process to be carried through only the cyanate stage.

During chlorination oxidizable substances other than cyanide, i.e., thiocyanate, thiosalts and metals in low oxidation states consume additional chlorine. A dramatic increase in chlorine demand results when appreciable amounts of thiocyanate are present in gold mill effluents, as unfortunately is often the case.

The first alkaline chlorination systems in Canadian gold mills were installed about 4 years ago. Since that time as many as 6 companies have employed this method and currently 4 mills are operating such systems. During the period from October, 1981 to March, 1983, Environment Canada with the assistance of a consultant, completed a study of the performances of the alkaline chlorination systems at 3 gold mills (Mosquito Creek, Baker and Carolin) in British Columbia. Environment Canada also evaluated the treatment system at a fourth mine (Giant Yellowknife). Detailed reports on these studies have been published (6,7).

Information pertinent to the alkaline chlorination systems is summarized in Table 5. Barren bleed solution were treated at 3 of the mills and tailings pond decant at the fourth. Gaseous chlorine was used as the oxidant in 3 of the mills and solid calcium hypochlorite at one. Except for Giant Yellowknife the treatment systems are located within the mill buildings. Giant Yellowknife has a separate treatment plant located adjacent to the discharge end of its tailings pond. This plant cost $2,000,000.00 to construct in 1981.

This company operates a 2 stage treatment system for the removal of both cyanide and arsenic. A simplified flowsheet of this plant is shown in Figure 2. Cyanide and metals are removed by chlorine addition in stage 1 and arsenic is precipitated in stage 2 by the addition of ferric sulphate. After flocculation the treated effluent from this plant is discharged to a large polishing pond with 15 days retention time. This pond is effective in greatly improving effluent quality. The plant is operated during the ice free period from May to October.

Typical influent and effluent analyses for the 4 alkaline chlorination systems are presented in Table 6.

TABLE 5 PLANT INFORMATION

	Mosquito Creek	Baker	Carolin	Giant Yellowknife
Mill Capacity (tpd)	100	100	1250	1200
Solids Cyanided	Ore	Ore	Concentrate	Roaster calcine
Solids (tpd)	100	100	75	140
Mode of Treatment	Batch	Cont.	Cont.	Cont.
Solution Treated	Barren	Barren	Barren	Tailings pond overflow
Solution rate (igpm)	1-1300 gal. batch/shift	3.5	33	1070
Form of chlorine	Gaseous	Calcium hypochlorite	Gaseous	Gaseous
No. of reactor tanks	1	2	1	1
Retention time (hrs)	6	14	8	0.5
pH	11	11.5	11	11.5
pH control	Manual	Manual	Auto	Auto
Chlorine Control	Manual	Manual	Manual	Manual

TABLE 6 TYPICAL INFLUENT AND EFFLUENT ANALYSES (MG/L)

	Mosquito Creek		Baker		Carolin		Giant Yellowknife		
	Infl.	Effl.	Infl.	Effl.	Infl.	Effl.	Infl.	Effl. (1)	PPO (2)
As							12.1		0.14
CN_T	310	25	2000	8.3	1000	170	7.5	1.3	0.15
CN_W	220	0.49	1900	0.69	710	0.95	7.1	1.2	0.09
CNS	330	int.(3)	1100	int.	1900	int.	6.3	1.0	
Cu	10.0	0.33	290	5.0	97	0.38	6.7	0.09	0.03
Fe	9.4	8.0	2.4	2.8	150	53	<0.1	<0.1	<0.10
Ni							1.2	0.7	
Zn	93	1.4	740	3.9	110	5.8	0.1	0.1	<0.10
% Removal									
CN_T(4)		91.9		99.6		83.0		82.7	98.0
CN_W(5)		98.8		99.9		99.9		85.1	98.7

(1) Cyanide reactor effluent
(2) Polishing pond overflow
(3) Interference during chemical analysis - no analysis
(4) CN_T - Total cyanide by distillation method
(5) CN_W - Weak acid dissociable cyanide by ASTM Method-C

Additional data, 1984 average analyses (mg/l), for the Giant Yellowknife plant are presented below. The Cl_2/CN_T ratio during this period averaged 16.4/1.

	As	CN_T	Cu	Pb	Ni	Zn	NH_3
Plant Influent	13.7	7.8					
Plant Effluent	0.40	0.05					
Polishing Pond Decant	0.38	0.02	0.04	0.02	0.05	0.05	5.5
% Removal	97.2	99.7					

The excellent quality of the tailings pond decant, except for NH_3, is noteworthy.

Wide variations in the compositions of the treated and untreated wastewaters are shown in Table 6. All systems were extremely effective in removing CN_W with % removals ranging from 98.7 to 99.9%. Some plants were less effective in removing CN_T due to the presence of significant levels of iron in solution. This confirms the ineffectiveness of alkaline chlorination for the removal of iron cyanide. The elevated concentrations of thiocyanate (CNS) are significant since on a pound per pound basis the oxidation of CNS requires nearly twice as much chlorine as does CN.

The chlorine consumption at each of these plants is shown in Table 7. The wide variations in chlorine additions are attributed to: the differences in chemical composition of the influents, the process control method employed and the use of manual control of chlorine additions and for lime in some cases.

TABLE 7 CHLORINE CONSUMPTION

Mill	Max. Cl_2 throughput (kg/d)	Estimated Cl_2 Consumption by Titration (kg/m^3)	Actual Chlorine Consumption (kg/m^3)	kg/kg CN_W
Mosquito Creek	136	4.1	4.7	21
Baker	210	7.5	15	8
Carolin	3600	11.3	17	24
Giant Yellowknife	1600	0.13	0.13	18

The estimated chlorine consumptions shown in this Table were based on redox titrations of the influents. In two cases the actual chlorine additions were substantially higher than those estimated by titration. Also shown in Table 7 are the kilograms of chlorine added

per kilogram of CN_W. One must realize that these are rather fictitious ratios in the sense that chlorine reacts with oxidizables in the solutions other than cyanide, notably thiocyanate, thiosalts and metals in low states of oxidation. In fact, in the case of Giant Yellowknife considerable As^{3+} may be oxidized to As^{5+} before removal with ferric sulphate.

The alkaline chlorination process is being used at the 500 tpd Grey Eagle open pit mine near Eureka, California to treat about 400 US gpm tailings pond overflow. As well as receiving mill waste effluents, the tailings pond also receives acidic drainage, containing high iron levels, from an adjacent abandoned underground mine. The treatment plant contains 3 chlorination reactor tanks in series followed by 2 clarifiers in parallel. The clarifier underflows are returned to the tailing pond and the overflows are pumped to a designated land application site. Gaseous chlorine is added to provide a chlorine/total cyanide ratio of about 7.5/1. Retention time in the reactor tanks is 45 minutes at pH 10-11. Table 8 shows typical analyses of water to and from the treatment plant.

TABLE 8 TYPICAL ANALYSES AT GREY EAGLE TREATMENT PLANT (MG/L)

	Tailing Pond Decant	Treated Effluent
CN_T	400	<5
CN_F(1)	250	0.2
Cu	300	0.5
Fe	400	0.3

(1) CN_F is determined using a cyanide specific electrode.

The iron chemistry associated with this plant remains unexplained. Considerable amounts of iron enter the tailings pond in the acidic abandoned mine drainage but this iron does not precipitate at the pond water pH of 8-9. Fortuitously, the iron apparently does not react with the free cyanide in the mill effluent to form stable iron cyanide complexes. This is confirmed by almost complete iron removal during treatment even though it is well known that alkaline chlorination is ineffective in removing iron cyanide.

The alkaline chlorination process is used for treating a slurry at Duval's Battle Mountain, Nevada mining operation. Also, until recently, it was used to treat a slurry at a gold mine in northern Ontario. However, since the chlorine requirements were extremely high this mine has discontinued this practice. Currently chlorination tests on tailings pond decant are being run at pilot plant scale in order to take advantage of some cyanide removal by natural degradation in the tailings pond prior to chlorination.

INCO SO_2- Air Process

In 1982 Inco Metals Company announced the development of a novel method for the destruction of cyanide in gold mill waste streams. The process involves the selective oxidation to cyanate of both free and complexed cyanide species (with the exception of iron cyanide) using a mixture of SO_2 and air at controlled pH (about 9-10) in the presence of copper as a catalyst. Except for iron, metals are precipitated from solution as hydroxides. The process also removes iron cyanide, not by oxidation, but by precipitation as an insoluble copper or zinc ferrocyanide.

The destruction of cyanide by oxidation may be represented by the equation:

$$CN^- + O_2 + SO_2 + H_2O \longrightarrow CNO^- + H_2SO_4$$

This process should not be confused with the older method of acidification-volatilization in which the pH of barren bleed solution is essentially lowered to 2-3 in order to rapidly dissociate metal-cyanide complexes and expel cyanide as hydrogen cyanide gas.

In Canada, the SO_2-air process is receiving wide attention for the treatment of gold mill effluents. Three companies are currently using the process and two others will be doing so next spring. Three companies, previously using alkaline chlorination, have converted to the SO_2-air method due to iron removal problems or high reagent costs. Two of the mills are no longer using the process since one mill has shut down and the second has discontinued gold recovery by cyanidation. Of the three mills currently applying this process, one is treating barren bleed solution and two are treating tailings slurries. The next two users will be treating tailings pond decant.

The SO_2 required for the process may be supplied in a variety of forms, i.e., as gaseous sulphur dioxide, as a soluble sulphite or meta-bisulphite, or as roaster gases containing SO_2. Currently only sodium sulphite and sodium metabisulphite are being used.

I will not describe the process or its application in more detail since Dr. B. Conard of Inco will be doing so later.

However, I would like to add that from what we have learned to date from full scale application, the SO_2-air process appears to offer an effective means to treat gold mill effluents, in either aqueous or slurry forms, to produce effluents containing concentrations much less than 1 ppm for CN_T and for each of the metals commonly found in gold mill effluents, i.e., copper, iron, nickel and zinc.

Due to its recent application further assessment of the process is required, particularly in regard to the toxicity of the treated effluents and the stabilities of the metal-ferrocyanide precipitates produced. Initial investigations by Inco indicate these precipitates to be quite stable ove wide range of pH.

One advantage of the process, from a reagent conservation point of view, i.e., the slow oxidation and removal of thiocyanate, could prove to be a disadvantage in situations in which the removal of thiocyanate may be required. However, thiocyanate may be removed by changing process conditions.

Several reports describing the SO_2-air process have been published (8,9,10,11,12).

Homestake Mining's Biological Process

Until only recently the removal of cyanide from gold mill wastewaters by bacteria has been neither practiced nor received a great deal of attention. The reasons for this in Canada are twofold. First, in the case of barren bleed, these solutions contain both cyanide and metals at sufficiently elevated levels to render them hostile to the support of bacterial activity. In the case of tailings pond water, which contains both cyanide and metals at substantially reduced concentrations due to natural degradation and dilution, biological treatment has been ruled out, at least in Canada, due to low water temperatures during frigid winter conditions.

However, at one gold mine, Homestake Mining Company at Lead, South Dakota, the biological treatment of mill wastewaters has become a reality. Over the past 2-3 years Homestake has developed a biological process to treat their combined mine and tailings impoundment wastewaters. An essential requirement for the successful operation of this process is the ability to blend mine water (70-85°F) with tailings impoundment water (34-70°F) to maintain a year round combined wastewater temperature sufficiently warm (50-65°F) to sustain effective biological process rates. A 3600 US gpm treatment plant was put into operation this past August at a capital cost of approximately $10,000,000.00.

The development of the biodegradation process, which began in 1981, and the design of the full scale treatment facility was described in a 1983 paper authored by Dr. T.I. Mudder and J.L. Whitlock of Homestake Mining (13).

The principal contaminants of concern in Homestake's wastewaters are cyanide, thiocyanate, copper and ammonia. The compositions of the two wastewaters to be treated in the plant are indicated in Table 9.

TABLE 9 COMPOSITION OF WASTEWATERS (MG/L)

PARAMETER	MINE WATER	TAILINGS IMPOUNDMENT WATER
Thiocyanate	1.0-16.0	110.0-240.0
Total Cyanide	0.10-0.50	7.00-30.0
* Method-C Cyanide	0.02-0.10	4.00-20.0
Iron	0.10-10.0	1.50-6.0
Copper	0.07-1.6	1.40-6.0
Nickel	0.01-0.04	0.20-0.40
Zinc	0.01-0.10	0.01-1.5
Ammonia-N	5.0-6.0	less than 1.0
Phosphorus-P	trace	trace
pH	5.0-6.5	7.0-9.5
Temperature (°F)	70-85	34-70

* ASTM Method-C for the analysis of weak acid dissociable cyanide doesn't included cyanide present as iron cyanide.

A simplified flowsheet of the process is shown in Figure 3.

Homestake's biological process is carried out in two stages. The first consists of the bacterial oxidation of cyanide and thiocyanate to carbon dioxide, sulphate and ammonia concurrent with the adsorption of metals by the bacteria. The second stage involves the bacterial nitrification of ammonia to nitrate. Different strains of bacteria are involved in the various stages of the process. Homestake Mining has received two patents for the use and the specific bacteria responsible for the oxidation of cyanide and thiocyanate. Metals associated with cyanide and thiocyanate are removed, once free from cyanide, by adsorption by the bacteria (biofilm) which are attached to slowly rotating vertical disks in tanks (rotating biological contactors). As the biofilm continuously sloughs off the disks the bacteria-metal sludge is removed from the effluent by clarification and dual-media sand filtration and returned to the tailings pond.

Forty-eight rotating biological contactors, with partially submerged disks 12 feet in diameter, are used to contact the bacteria with the wastewater and air. The first 24 contactors are used in the cyanide and thiocyanate removal stage. The contactors are not housed but all are well insulated. The only reagents added are soda ash as an inorganic carbon source to aid nitrification, and phosphorus as a trace nutrient. Following the biological contactors ferric chloride and/or a polymer are added prior to clarification and sand filtration.

The plant is reported to be operating satisfactorily to produce effluents of the quality predicted from the pilot plant tests. The compositions of the influents and effluents typical of both the operation of the pilot plant and the full scale facility are given in Table 10.

TABLE 10 WASTEWATER COMPOSITIONS MG/L)

	PILOT PLANT		FULL SCALE PLANT	
	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
Total Cyanide	6.5	0.35	2.0	0.30
Method-C Cyanide	4.1	0.05		0.02
Thiocyanate	60.0	1.0	50.0	< 0.10
Ammonia	6.0	0.50		0.10
Copper	1.0	0.04	1.0	0.05
Suspended solids				<10.0

The Homestake experience has rekindled considerable interest in the biodegradation of gold mill effluents.

Degussa's Hydrogen Peroxide Process

Although the destruction of cyanide by oxidation with H_2O_2 is well known, the process has only recently been applied to the continuous full scale treatment of a gold mill waste stream. The previous reluctance to apply this process appears to result from its economic unattractiveness.

The destruction of cyanide by H_2O_2 is shown by the reaction:

$$CN^- + H_2O_2 \longrightarrow CNO^- + H_2O$$

In May 1984 OK TEDI Mining Limited in Papua New Guinea brought on stream its 22,500 mt/day gold mill, a giant operation by gold mill standards. Cyanidation and the CIP process are employed for gold recovery. Hydrogen peroxide solution is added directly to the CIP tailings slurry and reacted in an agitated tank to oxidize cyanide to cyanate before discharge. The novelty of the Degussa process is, of course, not the use of hydrogen peroxide for detoxifying gold mill effluents but rather the closely controlled, automated and efficient manner in which the H_2O_2 is utilized.

Without wishing to detract further from Dr. Griffith's later presentation (14) I will only add that the Degussa process is being used effectively at OK TEDI to meet extremely stringent government requirements. Without doubt the continued performance of this process for cyanide destruction will be followed with great interest.

Con Mine's Iron Sulphide Process

Cominco Limited operate a conventional 700 tpd gold mining and milling operation on the shore of Great Slave Lake. Following

the milling process, waste barren bleed solution is treated by the addition of ferrous sulphide to remove both free and complexed cyanides. Finely divided insoluble ferrous sulphide particles are prepared in the mill by reacting ferrous sulphate with sodium sulphide, prior to adding the ferrous sulphide slurry to the waste barren bleed. The removal of cyanide results from the adsorption of cyanide on the ferrous sulphide particles. The reaction which is strongly pH dependent is carried out at pH 7.5 at a flow of about 20 igpm and a retention time of about 15 minutes. The ferrous sulphide to cyanide ratio is maintained near 3 to 1.

The treated effluent from the process is discharged to the mill tailings launder. In the tailings launder ferrous sulphide continues to adsorb cyanide from the water entering with the filtered leach tailings. Ferrous sulphate is also added to the launder to remove arsenic which dissolves from the ore. The cyanide removal step is not intended to produce an effluent of suitable quality to meet the company's effluent discharge limits but relies on further removal of cyanide by natural degradation in the tailings ponds.

Typical analyses of influent to the treatment process and effluent from the tailings pond are presented in Table 11.

TABLE 11 WASTEWATER ANALYSES (MG/L)

	Influent to FeS Process	Tailings Pond Decant	License Conditions
As		0.3	0.50
CN_T	750	0.7	1.5
CN_W		0.35	0.40
Fe	140		
Cu	50	0.3	0.30
Zn	155	0.04	0.30

Acidification

The acidification process is being used at the Emperor Gold Mine in Fiji to remove residual cyanide from cyanided and washed roaster calcine subsequent to a flotation step to recover sulphides. To remove the cyanide the calcine slurry is acidified from pH 9 to 2.5 by being sprayed into a tower counter-currently to SO_2-containing roaster gases. Cyanide is eliminated as HCN gas directly to atmosphere.

The well known Mills-Crowe process of acidification-volatilization-regeneration involves acidifying waste cyanide bearing solutions to pH 2-3 with H_2SO_4 or SO_2, volatilizing the resulting HCN by air flushing and recovering the HCN by absorption in an alkaline solution, i.e., NaOH on $Ca(OH)_2$. The recovered cyanide is the recycled to the cyanidation circuit for reuse. This process is still

in operation at a silver mine in Mexico operated by Compania Beneficiadora de Pachuca. Elemental sulphur is burned to produce SO_2 for acidification of the waste barren solution.

The Mills-Crowe process was used for cyanide recovery by Hudson Bay Mining and Smelting Company at Flin Flon from 1935 to 1978 while the company was cyaniding a base metal tailing for the recovery of gold. Waste barren solution was acidified with a H_2SO_4 solution from their zinc recovery plant. Air was used in towers to sweep HCN from the acidified barren solution and the HCN was absorbed in $Ca(OH)_2$ for reuse in the cyanidation circuit. Ninety-one percent of the "regenerable" cyanide was recovered in this manner. "Regenerable" cyanide was the amount of cyanide which could be released from the waste barren solution in a laboratory acidification test.

The acidification process has been employed principally for cyanide recovery, not for environmental protection and therefore, it is not known what quality of wastewater could be produced by this method if environmental protection was the main goal.

Conclusions

Natural degradation continues to be the most common method employed for the treatment of gold mill wastewaters. However, due to its limitations in producing final effluents of desired quality there has been a growing interest in, and application of, chemical treatment processes. In only a few years the gold mining industry has made considerable progress in demonstrating at full scale a number of effective chemical treatment systems. The two which are used most widely are the alkaline chlorination and the Inco SO_2-air processes.

Some of the processes in commercial operation are capable of removing up to 99.9% weak acid dissociable cyanide and close to that for total cyanide, especially in the absence of iron cyanide.

Since these chemical methods have been in use for only a limited period of time they require further performance evaluation with particular regard to the quality of the treated effluents. A serious shortcoming in the examination of most of the processes has been the lack of sufficient toxicity testing of the resulting effluents. These effluents may contain many substances, e.g., cyanide, metals, chlorine, thiocyanate, cyanate and ammonia which could be present in toxic concentrations. Effluent toxicity must be critically examined to determine that if in attempting to solve the cyanide problem, a new one isn't being created, albeit less severe than the original problem.

However, there are now several commercially demonstrated methods for cyanide removal. The final selection of a method for a specific mill will require careful consideration of the nature of the specific effluents to be treated, the regulatory limits imposed upon the mining company and the alternative treatment costs.

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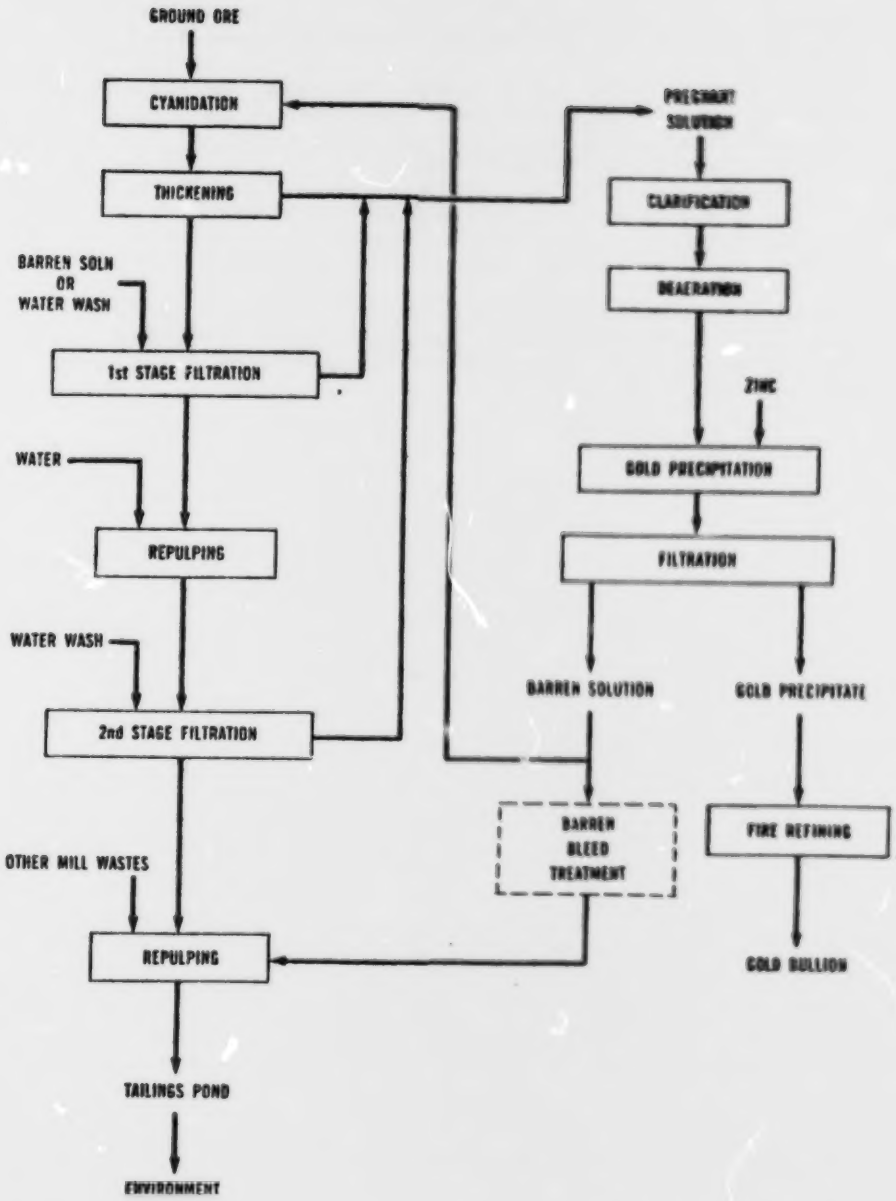


FIGURE 1 CONVENTIONAL GOLD MILLING PROCESS

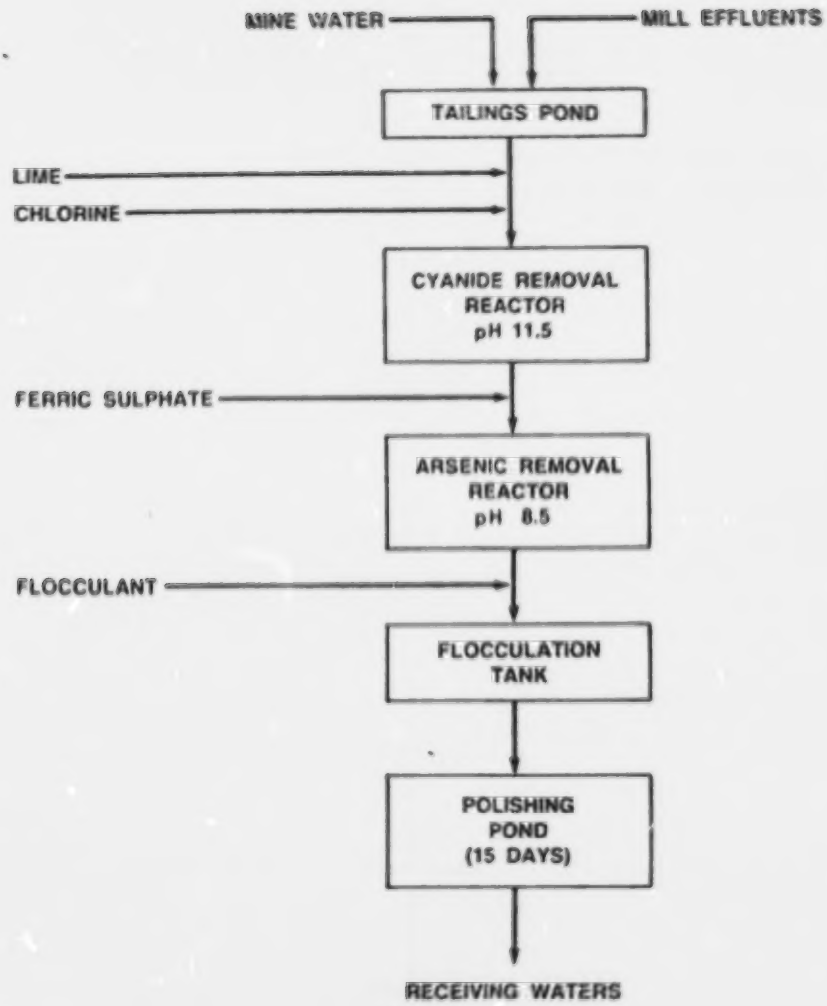


FIGURE 2 ALKALINE CHLORINATION TREATMENT PLANT AT GIANT YELLOWNIFE MINES

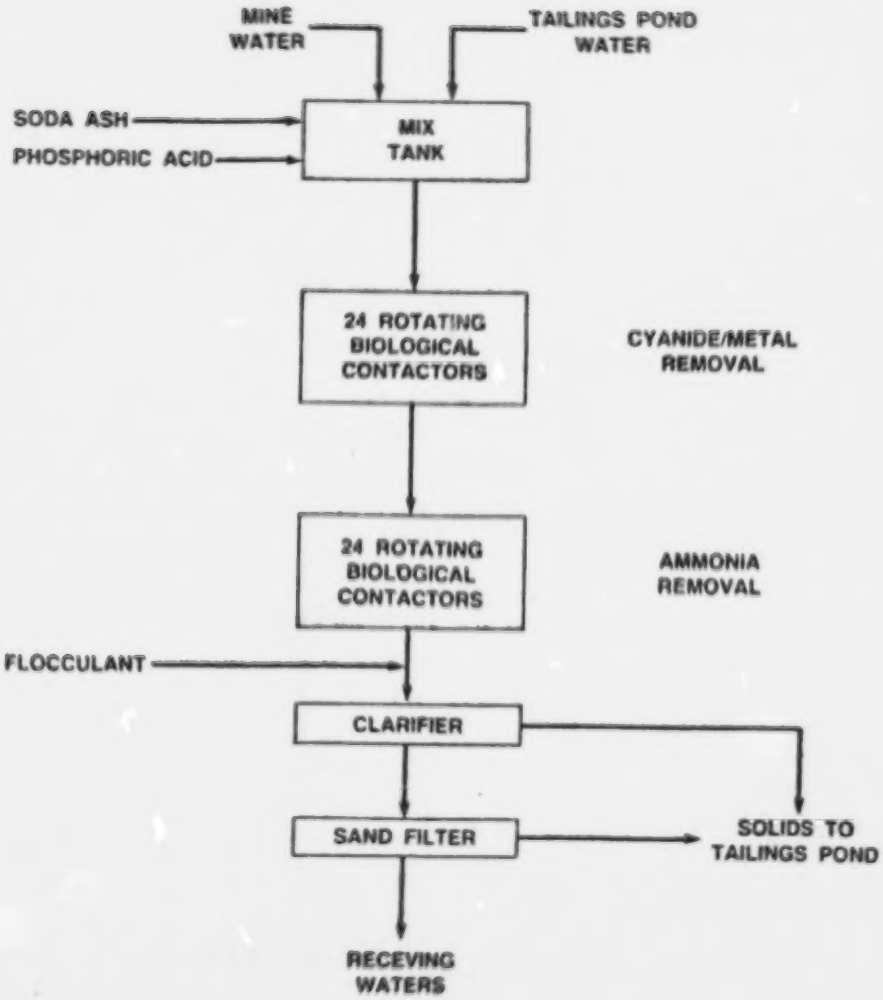


FIGURE 3 BIOLOGICAL TREATMENT PROCESS AT HOMESTAKE MINING COMPANY

OVERVIEW OF CYANIDE TREATMENT COSTS

The direct comparison of cyanide treatment costs from one location to another would be misleading. The cost of reagents varies greatly from site to site. Also, the degree of treatment needed varies from nil to aggressive treatment, depending on performance demanded to meet effluent regulations, whether the site is zero discharge or not, whether natural degradation does all or most of the work requiring minimal additional treatment, whether iron cyanides can be tolerated in effluents, etc., etc.

Some distinction must also be made as to whether the cost parameters are based on real plant experience or on calculated parameter estimates by equipment, chemical, or process vendors.

A few fragmentary items of information on cost parameters gathered in the course of this study are listed below:

ALKALINE CHLORINATION

1. Giant Yellowknife Mines, Northwest Territory, Canada

C/2 Consumption to Achieve 1 ppm CN_T	18 lbs. Cl_2/lb. CN_T 0.3 lbs. Cl_2/ton Ore Solids 14.7 lbs. Cl_2/ton Calcine
Capital Cost (1981)	C$1.9 Million
Operating Cost (1983)	C$780,000/Year
Cost per 1,000 1 Gallons (1983)	C$2.45/1,000 Gal.
Cost per Ton Ore Treated (1983)	C$2.40/t

Performance (mg/l):

	Infl.	Eff.	Polishing Pond Overflow
CN_T	7.5	1.3	0.15
CN_W	7.1	1.2	0.09
CN_S	6.3	1.0	-
Cu	6.7	0.09	0.03
Zn	0.1	0.1	LT 0.10

2. Superior Minerals, Stibnite, Idaho (3,000 tpd HL)

Calcium hypochlorite generated on site.
1.25 lb. $Ca(OH)_2$ added per 1 lb. Cl_2.
4,000 lb. Cl_2/day consumed @ $360/t delivered = $720/day.
12st Cl_2 consumed over 6 days for 30,000t heap = 0.8 lb. Cl_2/ton ore ($0.14/ton ore).
Application rate: 240 U.S. gpm.
Lime cost (pebble lime used) (estimated) = $170/ton $Ca(OH)_2$.
Lime use = 1.25 lbs. $Ca(OH)_2$ per lb. Cl_2 = 1 lb./ton ore ($0.09/ton ore.
Cost of reagents for Superior Mines heap neutralization:

Chlorine - 0.8 lb./ton @ $0.18 =	$0.14/ton ore
Lime - 1.0 lb./ton @ $0.09 =	$0.09/ton ore
	$0.23/ton ore

Comparative cost of $Ca(OCl)_2$ - 60% effective; $Ca(OCl)_2$ - 1.33 lb. @ $1.30 = $1.60/ton ore.

3. Northern California Gold Mine Comparison

Based on Lab Tests:

Alkaline Chlorination	$3-6/lb. CN Neutralized
INCO SO_2-Air	$2-3/lb. CN Neutralized
H_2O_2	$13-14/lb. CN Neutralized
Biological	$1.00/lb. CN Neutralized

Actual Costs for Alkaline Chlorination of Tailings Decant Solution with Relatively High Cu Levels:

$6.34/1,000 U.S. Gallons

Reagent Consumption:

Cl_2 11.1 lb./1,000 U.S. Gal.
NaOH 37.2 lb./1,000 U.S. Gal.

Performance:

Influent:	75 ppm CN_T
Treated:	0.10-0.20 ppm CN_F
	5 ppm Max. CN_T

Operating Costs for SO_2-Air Cyanide Removal

DEVUYST, et al. (1984) gave the following theoretical reagent requirements for a gold mill effluent (barren + tails) containing, for example, in mg/l: 250 CN_T, 250 SCN^-, and 100 $S_2O_3^=$:

Species	Reagent g/g CN_T $Na_2S_2O_5$	Lime
CN^-	3.73	1.42
SCN^-	0.67	0.38
S_2O_3	0.17	1.67
	4.57	3.47

Reagents for SCN^- are based on average oxidation of 10% of SCN^- and complete oxidation of S_2O_3 to S_4O_6. Using empirical reagent efficiencies of 90% for $Na_2S_2O_5$ (10% oxidized by air) and 75% for lime (25% unreacted), the reagent requirements for the above effluent are 5.08g $Na_2S_2O_5$ and 2.23 lime per gram CN_T oxidized.

Based on FOB Vancouver prices reported by DEVUYST, et al. (1984), the cost of the process would be as follows:

Reagent	Price ($/mt)
$Na_2S_2O_5$	550
Lime	180
$CuSO_4.5H_2O$	1,320

Assuming the addition of 25 mg/l Cu^{++}, the cost of treating the hypothetical effluent is C$0.95/m³.

For a typical gold mill treating 1,000 mt of ore per day at 2 lbs. NaCN/ton, the cost per metric ton milled is $1.90, or a yearly cost of $693,000 for reagents.

DEVUYST, et al. (1984) find that at a chlorine cost of C$725/mt, the reagent costs for the same waste treated by alkaline chlorination would be C$2.72/m³ or C$5.44/mt for a yearly reagent cost of C$1,980,000.

	Cost of Reagents per m³ Pulp*	Cost of Reagents per t Ore	Annual Costs for 1,000 tpd
SO_2-Air	C$0.95	C$1.00	C$693,000
Alkaline Chlorination	C$2.72	C$5.44	C$1,980,000

* (250 mg/l CN_T, 250 mg/l SCN^-, 100 mg/l $S_2O_3^=$)

BIOLOGICAL PROCESS - HOMESTAKE MINING CO., LEAD, SOUTH DAKOTA

Capacity: 21,000 m^3/d (3,800 U.S. gpm)

Process: 48 Rotating Biological Contactors
Nutrient Addition
Sludge Disposal

Cost Items: H_3PO_4
Na_2CO_3
Labor
Power
Laboratory

Capital Cost: $10 Million

Operating Cost: No Details Released
Theoretical Optimum Goal - $500/Day

ALKALINE CHLORINATION

Alkaline chlorination has been considered the "standard" method for cyanide decomposition at gold and silver operations. Several plants using this process have been installed in North America.

PERFORMANCE CAPABILITY

Removal by Alkaline Chlorination of

CNS^-	Total Cyanide CN_T	Available Cyanide CN_C	Ammonia	Metals except Fe, Co
Yes	No	Yes	Yes	Yes

TABLE 12

REACTIONS INVOLVED IN THE CHLORINATION OF CYANIDE

1. Hydrolysis - Dissolution of Chlorine Gas

$$Cl_2 + H_2O \longrightarrow H^+ + Cl^- + HOCl$$

2. Formation of Sodium Hypochlorite from Chlorine Gas

$$2\ NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

3. Oxidation of Cyanide by Chlorine Gas: 1st Stage

a) $$NaCN + Cl_2 \xrightarrow[\text{independent of pH}]{\text{instantaneous}} CNCl + NaCl$$

b) $$CNCl + 2NaOH \xrightarrow[\text{pH 8.5 to 9.0; 10-30 min.}]{\text{pH 10-11; 5-7 min.}} NaCNO + NaCl + H_2O$$

2nd Stage with excess Cl_2

c) $$2\ NaCNO + 3\ Cl_2 + 4\ H_2O \xrightarrow{\text{1 to 1.5 hours}} 3\ Cl_2 + (NH_4)_2CO_3 + Na_2\ CO_3$$

d) $$(NH_4)_2CO_3 + 3\ Cl_2 + 6\ NaOH + Na_2CO_3 \xrightarrow{\text{rapid}} 2\ NaHCO_3 + N_2 + 6\ NaCl + 6\ H_2O$$

(White 1972)

4. Oxidation of Zinc Complex Cyanide by Chlorine: 1st Stage

$$Na_2Zn(CN)_4 + NaCN + 12\ NaOH + 5\ Cl_2 \longrightarrow Zn(OH)_2 + 5\ NaCNO + 10\ NaCl + 5H_2O$$

(White 1972)

5. Oxidation of Cyanide by Hypochlorites

$$NaCN + NaOCl + H_2O \longrightarrow CNCl + 2\ NaOH$$

$$2\ NaCN + Ca(OCl)_2 + 2\ H_2O \longrightarrow 2\ CNCl + Ca(OH)_2 + 2NaOH$$

and

$$CNCl + 2\ NaOH \longrightarrow NaCNO + NaCl + H_2O$$

(Liptak 1974)

Source: Adapted from Ingles and Scott 1981, unless otherwise noted.

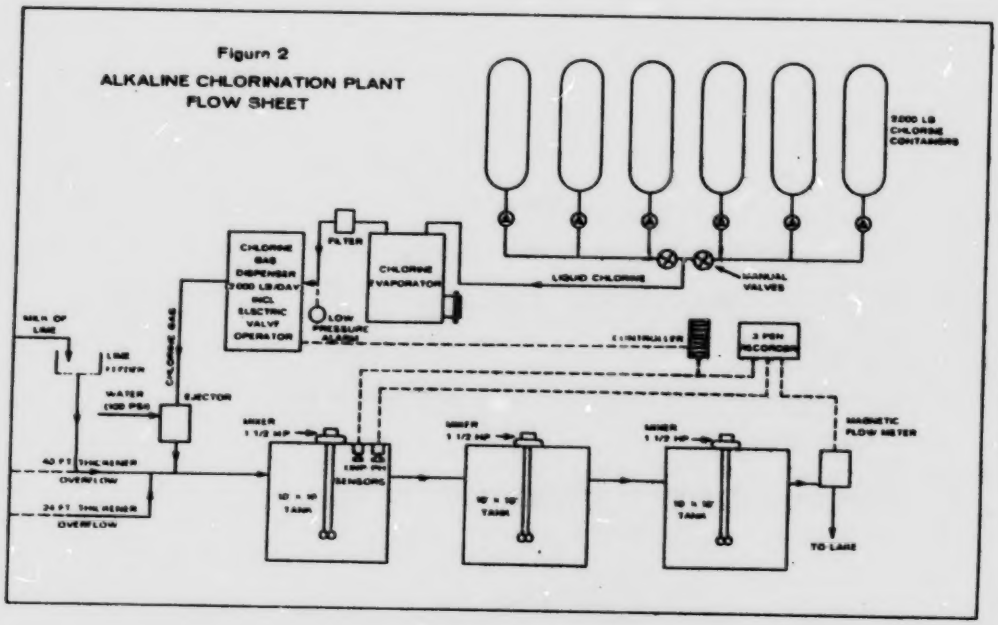
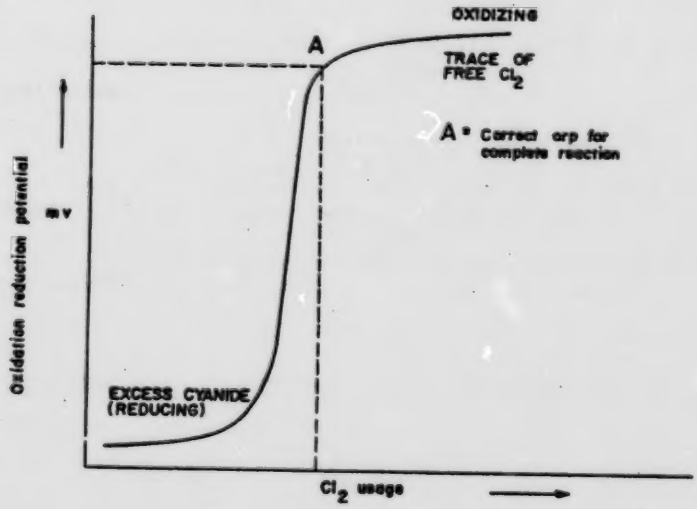


FIGURE 2

ALKALINE CHLORINATION PLANT

FLOW SHEET

CONTROL OF CYANIDE CHLORINATION BY ORP



The reason that total cyanide is not removed by chlorination is that iron cyanide complexes are not decomposed. For flotation tailings where the iron cyanide remains in a solid-liquid pulp which is opaque to sunlight, this is believed unlikely to represent a problem. Where effluents are decanted to shallow exposed streams, photodecomposition of ferrocyanides to cyanide has been reported among others by Environment Canada tests.

CHEMISTRY OF ALKALINE CHLORINATION

The chemical reactions which occur during alkaline chlorination were described by INGLES & SCOTT (1981) and were reproduced on page 1352 of the RANDOL PHASE II report "Innovations in Gold & Silver Recovery," also in HUIATT et al. (1982) and are copied again here for convenience in Table 12.

DESCRIPTION OF ALKALINE CHLORINATION PROCESS

The alkaline chlorination plant is quite simple. It consists of a tank, sized appropriately for the retention time required, equipped with a mixer and baffles to ensure thorough mixing and contact.

The tank is equipped with feed lines and pH as well as ORP probes. A second tank with mixer and baffles is usually placed in series with the main tank and should preferably be equipped with pH and ORP probes. The second tank ensures an adequate retention time for all reactions to be completed and is a safeguard in case the effluent did not get properly contacted in the first tank. (Short circuiting in a one tank mixing system is inevitable.)

Equipment must be corrosion-resistant. Tanks are preferably fiberglass with mixers of coated steel.

Liquid chlorine is supplied in bulk tanks or in one-ton cylinders and is injected into the line by a water jet. Feed rate is measured by flow meters and most desirably controlled by the ORP as discussed below.

For high chlorine demands, say 500 lbs/day or more and for systems in cold climates it may be necessary to use an evaporator which vaporizes liquid chlorine using electric heaters prior to water injection. The gaseous Cl_2 system employing cylinders is arranged in such a way that in the event the pressure drops in the cylinder in use, the system automatically switches over to the next tank. Such systems are employed at Giant Yellowknife and at Noranda Grey Eagle Mines Ltd.

If "solid forms of chlorine" are to be used, this is invariably supplied as calcium hypochlorite $Ca(OCl)_2$ and is added by an adjustable speed dry feeder. Such systems are installed at remote sites which can only be reached by air.

At Battle Mountain Operation of Duval Corp. and at Superior Mineral's Stibnite, ID plant liquid chlorine is first evaporated and then mixed with NaOH or $Ca(OH)_2$ solution to make a solution of NaOCl or $Ca(OCl)_2$ which is injected into the system.

At the Climax Mine of AMAX Inc. it is reported that Chlorine dioxide is used which is generated on site in equipment provided by Olin Corporation but this has not yet been confirmed.

Various ways are used to deal with the precipitates that form depending on the fate of the product solutions or pulps.

1) Climax Mine removes metal precipitates using Lectroclear flotation before alkaline chlorination and follows alkaline chlorination with downflow gravity filtration.

2) Noranda Grey Eagle Mines employs a clarifier to settle flocculated precipitates and then filters the effluent.

3) Superior Minerals at Stibnite, Idaho, uses the hypochlorite solutions to rinse heaps after leaching before moving the heap materials to the tailings dump.

4) Giant Yellowknife follows alkaline chlorination with arsenate precipitation and then settles the precipitates in a settling pond.

5) At Battle Mountain and at Detour Lake the oxidation and precipitation products are contained in tailings pulp which is pumped to the tailings pond.

Although relatively simple in principle it has been found that chlorination systems have been high maintenance items and more operator time intensive than anticipated. Potential users are recommended to investigate the pros and cons experienced in existing systems elsewhere.

ALKALINE CHLORINATION PROCESS CONTROL

The process is controlled by pH and by oxidation-reduction potential ORP.

Alkaline chlorination proceeds in two stages. The first stage to CNO^- proceeds rapidly at pH 10-11, the second stage is slower but goes fastest at pH 8.5 (below 9) to $CO_3^=$, NaCl and N_2. The second stage is not so sharply observed in ORP charge with breakpoint

occurring at 400 mV. Some operators do not recommend the use of ORP control in the presence of NH_3.

Most effluent treatment operations take the process only to completion of the first stage in the plant.

pH is controlled by adjusting the lime solution addition rate to maintain pH 11.

Chlorine is added to maintain redox potential at which it has been determined that all CN_T has been destroyed. Usually this is around -600 mV.

According to JACKSON (date not known) just sufficient chlorine must be added to reach "A" as recorded by the ORP signal from the probe in the first reaction tank and to maintain that level.

Point "A" must be determined experimentally using the actual solution to be treated and verified in the actual operation. This is done with chlorine (hypochlorite is more convenient in the laboratory) to obtain a curve similar to that shown below. ORP is affected to a degree by pH and this must be taken into account when determining point "A". Also, copper, if present in solution, is said to poison platinum ORP electrodes, and some process engineers prefer gold-calumel or silver amalgam electrodes. Reference:

FRED STEVENS
Lancy International
Zelienople, PA

Jim Scott of Environment Canada, Ottawa, referred to a new continuous Cl_2-monitor being developed for plating waste treatment plants which would be useful for controlling alkaline chlorination.

When chlorine is used as a reagent the signal from the ORP probe in the first tank should be used to control the chlorine feed automatically - maintaining level "A" even though effluent flow rates and dissolved cyanide levels may vary. With dry hypochlorite, manual control of the feed rate is usual although presumably the ORP signal could be hooked up to the feeder speed.

A simple field check test for the presence of free chlorine is the instaneous appearance of a blue or purplish blue color when a sample of treated effluent is spotted on a starch-iodide test paper.

A potentially more practical approach for controlling CNaddition for solutions with appreciable levels of copper is to analyze copper which is easy. One northern California operation found that when the copper had been reduced from 300 mg/l to below their

criterion of 0.2 mg/l or so, the free cyanide would always be below 0.2 mg/l in their treated effluent.

REAGENT USAGE

In accordance with the summary equation:

$$2NaCN + 2Cl_2 + 2Ca(OH)_2 = 2\ NaCl + CaCl_2 + Ca(CNO)_2 + H_2O$$

The amount of lime, expressed as CaO needed is 2.2 lbs per lb CN. In practice somewhat more is needed to maintain pH 11 depending on how much other chlorine consumers are present which also consume hydroxyl ions when they react.

The theoretical amount of Cl_2 needed is 2.73 lb Cl_2/lb CN. In practice chlorine demand is also higher than this depending on the concentration of other chlorine consumers - e.g.:

Thiocyanate oxidation
Copper (oxidation from cuprous to cupric)
Ammonia (15 - 20 lb Cl_2 per lb NH_3)
Thiosulfate and thiosalt oxidation

ADVANTAGES AND DISADVANTAGES OF ALKALINE CHLORINATION
(Expanded from HUIATT, et al. (1982)

Advantages:

1) Very widely used method, expertise is available
2) Most feed streams are already alkaline
3) Reactions are complete and fairly rapid
4) Chlorine is readily available in several usable forms
5) Toxic metals are removed
6) Readily adaptable to either continuous or batch operation
7) Capital outlay is relatively low
8) Good fail-safe control
9) Easily controlled to first stage of oxidation if disposal of CNO^- is permitted
10) Can destroy NH_3 if desired
11) Synergistic oxidation of As to As^{+5} is possible ahead of precipitation
12) Chlorination of tailings should result in improved gold loading on carbon columns used to treat decant solution due firstly to incremental Au leach and secondly to remove of base metal cyanides before carbon adsorption.

DISADVANTAGES OF ALKALINE CHLORINATION

1) Reagent costs are high especially if complete oxidation is required. Thiocyanate, thio-salts and ammonia are additional heavy consumers of chlorine.

   1 g CNS^- requires 4.9 g Cl_2

   1 g NH_4 requires 15 - 20 g Cl_2 to breakpoint

2) Requires careful control of pH to prevent formation of cyanogen chloride which is very toxic.
3) Chlorine gas is toxic in the work environment.
4) In cold climates where cyanide destruction is most likely to be required, chlorination plant is installed indoors resulting in an unpleasant work environment. Giant Yellowknife has found a way around this.
5) For locations reachable by air transportation only, solid forms of chlorine are required. These are costly per unit Cl_2 and when used in some solutions result in buildup of metal precipitates in the reactor.
6) Chlorination processes are tricky to control. Complaints of larger than expected volumes of precipitate and scaling problems.
7) For complete removal of CNS a two stage reaction is required. Stage I at pH 11.5 and Stage II below pH 9. This requires complicated plant and process control.
8) Cyanide is not recovered.
9) Hexaferrocyanates are not usually decomposed.
10) Metal values are not recovered.
11) Chloride content of effluent is increased in direct proportion to the chlorine added.
12) Possibility of forming toxic chlorine derivatives e.g., chlorinated organic compounds that require further treatment.
13) Residual excess chlorine can be toxic to aquatic species. It can readily be removed by $S_2O_3^=$ or H_2O_2 addition or activated charcoal columns, but an extra step is needed.
14) Chlorine is very reactive and if tailings pulps are to be chlorinated consumption of Cl_2 may be excessive due to reactions with solids in the pulp.
15) According to vendors of a competing process, cyanide destruction in tailings pulps using Cl_2 has great difficulty achieving most regulatory permit limits.
16) Chlorine is very reactive. Steel components require frequent maintenance and in some cases replacement after 4 - 5 years.

APPLICABILITY OF ALKALINE CHLORINATION

MUDDER & WHITLOCK (1984) report alkaline chlorination as being particularly viable for effluents with low CNS^- and Fe where the chlorine consumption will be lower and a single stage reaction is all that will be required.

Because of the very high consumption of Cl_2 by NH_3 (15 - 20 g Cl_2 per g NH_3) chlorination will be very expensive for solutions containing appreciable levels of NH_3.

Because of reactions between solids in tailings pulp with highly reactive chlorine, use of chlorine for treatment of some pulps may be inapplicable for cost reasons.

Three alkaline chlorination plants were replaced by SO_2-Air treatment in Canada. The reasons that alkaline chlorination was found to be inappropriate at these installations were:

SCOTTIE GOLD, STEWART, B.C.

The cyanided ore contains pyrrhotite which produces high amounts of ferrocyanide in the tailings which decant to a river flowing from British Columbia into a salmon river in Alaska. Cl_2 treatment failed to remove ferrocyanides.

The use of solid hypochlorite in the underground mill at Scottie resulted in operation problems in which the system became congested with solid precipitates. There were safety problems in adding enough hypochlorite into the system.

SO_2-Air treatment resulted in much more comfortable operating conditions.

DUPONT EXPLORATION, BAKER MINE, NORTH CENTRAL B.C.

The alkaline chlorination process was replaced by SO_2-Air for economic reasons when the tailings as well as barrens were to be treated towards the end of the life of the silver mine as ore reserves were depleted.

Alkaline chlorination worked well for the small barren bleed stream of 3 - 4 gpm containing up to 3 g CN^-/l.

This operation experienced no environmental problems and the conversion to SO_2-Air was purely economical because of the lower cost of sodium sulfite requirements than hypochlorite to treat the ore. All supplies to this mine had to be air freighted to the site.

CAROLIN MINES, LADNER CREEK MILL, HOPE, B.C.

After being temporarily shut down on account of effluent and tailings excursions, and being accused by the Provincial and Federal Government of causing fishkills, Carolin Mines had to consider improving their cyanide destruction system.

Even with a second alkaline chlorination treatment facility Carolin's release of tailings decant to the stream was limited because of its ferrocyanide content which was not reduced by alkaline chlorination. As a result of an inadequate bleed from the pond both [Fe] and [CN_T] were building up in the solution resulting in further limitations in release to the stream. A vicious circle was in effect with the potential end result of a third spill when the Provincial and State Government stepped in threatening to close the plant down unless the CN_T was reduced.

Carolin Mines is located on the headwaters of the Fraser River which supports a commercially valuable salmon fishery in southern British Columbia.

After converting the existing chlorination system to SO_2-Air both iron and CN_T levels were reduced. At that time soluble iron levels in the ore increased dramatically and the existing retrofitted reactor was inadequate. An alternative larger system was recommended.

The decision was then made to stop cyanidation and rather to sell a flotation concentrate from the plant thereby eliminating the need for cyanide destruction.

Several operating chlorination plants are discussed briefly below.

GIANT YELLOWKNIFE MINES, YELLOWKNIFE, NWT

Giant Yellowknife is located in an extreme northern climate and experiences a deep freeze for six months of the year. The tailings decant is treated to remove both cyanide and arsenic.

By virtue of the fact that their tailings dam is large enough to accommodate solution that accumulates through the whole winter it is possible to operate an effluent treatment plant for only the summer season. It is sized to treat one year's effluent flow during the six month operating season.

Alkaline chlorination installed in this way avoids the need for indoor reactors. Furthermore in the cyanide decomposition process arsenic is oxidized which is an important first step in Giant's subsequent arsenic removal step with ferric sulfate. Although Giant uses cyanide to leach calcines and is therefore likely to introduce

ferrocyanide into their commingled tailings which will not be removed by alkaline chlorination, this must make up a relatively small part of the overall tailings flow considering the results achieved. Alternatively, in the arsenic removal step using ferric sulfate addition possible ferrocyanide is removed by precipitation of Prussian blue.

Giant's alkaline chlorination plant is said to be one of the very best in concept and is appropriate to their needs. It is discussed in detail in a separate trip report as well as by several authors including PRICE (1981).

Giant's chlorine consumption works out to 13.5 lbs Cl_2 per lb CN_T to achieve levels below 1.0 ppm. This compares with a target Cl/CN_T ratio of 8:1 based on bench scale work and 9:1 on pilot testwork. Theoretical consumption in the absence of other chlorine consumers is 2.7 lbs Cl_2 per lb CN.

Typical Analyses of Giant Yellowknife Effluents (mg/l)

	Flow	pH	As	CN_T	TSS	Fe	Cu	Zn	Ni
Tailings Pond decant before treatment	5000 m^3/d	8.8	12.1	8.6	-	-	6.87	0.10	1.23
Treated Decant Solution	5000 m^3/d	7.7	0.14	0.20	1.20	-	0.08	0.05	0.11

Chlorine and lime consumption make up the major cost of operating this plant. Due to its remote location shipping costs are very high which exaggerates the cost of reagents.

Data for 1983 work out as follows:

Volume of Water Treated:	1,207,000 m^3/yr, 319 mm igpa
Chlorine Consumption:	191 tons
Lime Consumption:	573 tons
Tons Ore Treated:	325,000 tons
Tons Calcine Cyanided:	28,600 tons
Chlorine Consumption=	0.34 lbs Cl_2/ton ore
	14.7 lbs Cl_2 /ton calcine cyanided
	18 lbs Cl_2/lb CN_T
Capital Costs were	C$1,900,000 (1981)
Operating Costs	C$ 780,520 (1983)

Costs per 1000 gallons =	C$2.45/1000 I gallons(1983)
Cost per ton ore treated =	C$2.40/ton ore (1983)

WESTMIN RESOURCES LTD., MYRA FALLS OPERATION

The following account of the installation of an alkaline chlorination plant to treat 200,000 Igpd (757 m^3/d) water containing 4.7 ppm CN_T and 2.85 ppm Cu is of interest.

Firstly, it illustrates some of the operating and maintenance-replacement problems that were encountered. Secondly, it illustrates just how much excess Cl_2 may sometimes be required.

200,000 Igpd solution	= 747 m^3/d	
@ 4.87 ppm CN_T	= 3.63 Kg CN_T^-/d.	= 8.0 lb/d CN
This required 2000 lbs Cl_2	= 250 lb Cl_2/lb CN	

True the excess Cl_2 was carried over with the treated solution to the tailings line where any CN^- in the pulp would also be oxidized by the excess Cl_2, but it appears likely that instead of discharging 8.0 lbs CN^-/day plus some copper, Western Mines may now be adding Cl_2 to the water.

Pollution Control At Western Mines' Myra Falls Operations

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Abstract

Western Mines' milling circuit produces three concentrates (copper, lead and zinc), with the tailings being disposed of at the bottom of Buttle Lake. In view of the mine's location and the method of tailing disposal, a comprehensive pollution control program has been in effect since start-up.

Changes in the ore over the past few years have required the use of increasing quantities of sodium cyanide in order to effect a good copper-lead separation. This led to the use of alkaline chlorination for destruction of residual cyanide and precipitation of dissolved copper contained in the tailing effluent. The development of Western Mines' alkaline chlorination plant is discussed in detail, including initial test work and the evolution of procedures leading to the present operation. The current monitoring program is also reviewed.

Introduction

THE WESTERN MINES LIMITED copper-lead-zinc operations are located in Strathcona Provincial Park, near the geographic center of Vancouver Island. This park includes Buttle Lake, which feeds the Campbell River water system. The latter is the source of domestic water for the town of Campbell River, approximately 58 miles from the mine site.

Operation of the concentrator commenced in December 1966, at which time the tailings were discharged into a small pond near the plant. On May 8, 1967, Permit No. 185 was granted to the company, allowing discharge of the tailings, through a submerged outfall, to the bottom of Buttle Lake.

The concept of operating a mine within a park, and the discharge of tailings into Buttle Lake, generated considerable controversy. However, this has all but been eliminated over the years by the proven effectiveness of Western Mines pollution control program. In 1973, this program was further upgraded by the introduction of alkaline chlorination. Effluent treatment by this method became necessary as a result of process modifications, and has been effective in maintaining the effluent characteristics of the tailings within the ever-increasing pollution control requirements imposed on the industry.

A. G. Eccles was born in Rossland, British Columbia, and received his early schooling in Victoria. He graduated from the University of British Columbia in 1962 with a B.A.Sc. in metallurgical engineering. Following graduation, he was employed in various industries, including steel rolling, lead and zinc smelting, light manufacturing and mineral processing. He joined Western Mines Limited in 1972, where he holds the position of Mill Superintendent.

Mr. Eccles is a member of the C.I.M., the A.S.M. and the British Columbia Association of Professional Engineers.

Keywords: Environmental control, Pollution control, Western Mines Limited, Myra Falls, Tailings disposal, Chlorination, Alkaline chlorination, Effluents.

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TABLE 1 — Typical Mill Feed and Concentrate Grades

	Oz/T Au	Oz/T Ag	% Cu	% Pb	% Zn
Mill Feed	0.08	4.4	1.1	1.3	7.5
Copper Concentrate	1.4	68.0	27.5	3.0	10.0
Lead Concentrate	0.7	65.0	3.5	42.5	20.5
Zinc Concentrate	0.1	5.0	0.6	0.8	52.5

Plant Operation and Tailing Disposal

COMPLEXITY OF THE ORE

Western Mines is currently mining and milling some of the most complex polymetallic ores in B.C. Compared to most operations containing one major metal, and perhaps a by-product, Western Mines' ores contain recoverable quantities of copper, lead, zinc, gold, silver, and cadmium. In order for the operation to be viable, these metals must be recovered as completely as possible in the form of marketable concentrates.

Separation of the three base-metal sulphides is difficult due to close interlocking, and levels of impurities in the concentrates are high. These impurities are in some cases subject to penalties, and if above specified levels could be grounds for rejection. Table 1 illustrates typical mill feed and concentrate grades.

The three-way selective flotation of these metals presents one of the most complex milling problems, and requires close control of grind, pulp density, pH and reagents in order to achieve the best metallurgical results. These, in turn, must be balanced against the stringent limitations on quality of the tailing discharge.

PRESENT MILLING PRACTICE

The milling circuit consists of conventional crushing and grinding followed by differential flotation to produce separate copper, lead and zinc concentrates. A simplified flowsheet showing the milling and tailing disposal circuits is given in Figure 1.

The first flotation stage produces a copper-lead rougher concentrate, which contains as much as 35 per cent of the zinc. Tailing from this circuit, includ-

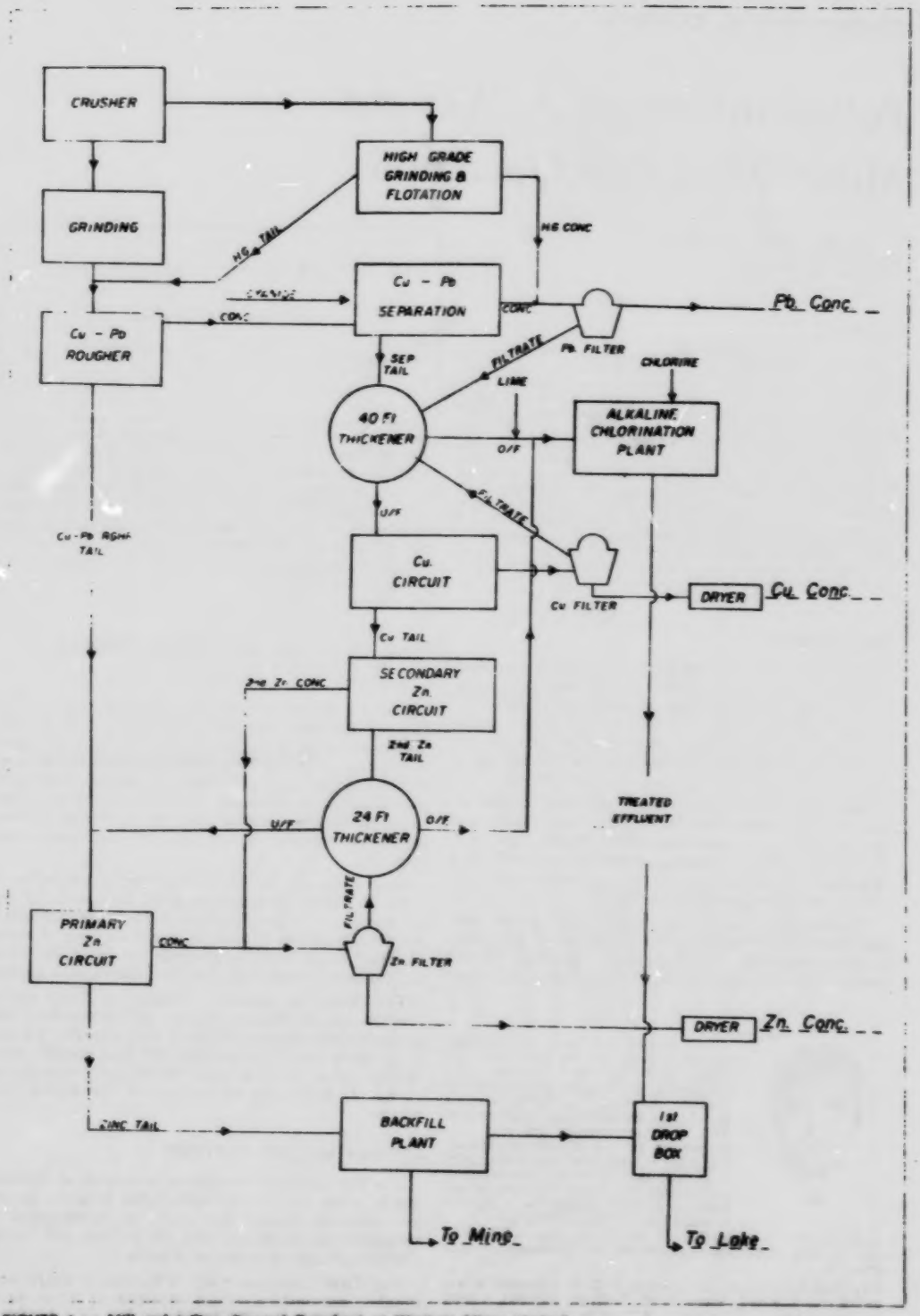

FIGURE 1 — Mill and tailing disposal flowsheet at Western Mines Limited.

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ing the remaining 65 per cent of the zinc, feeds the primary zinc circuit.

Sodium cyanide is added to the copper-lead concentrate in the separation circuit, depressing the copper and producing a lead concentrate. As this depends on complexing of copper by the cyanide ion, significant levels of soluble copper cyanide complexes are present in the separation circuit tail. This is pumped to a 40-ft double tray thickener, which serves to separate the effluent containing cyanide and dissolved copper for subsequent treatment.

Underflow from the 40-ft thickener is reground and treated by flotation for recovery of copper concentrate. Copper circuit tailing reports to the secondary zinc circuit.

Zinc flotation consists of a primary circuit which handles the copper-lead rougher tail and a secondary circuit which treats the copper tailing. Secondary zinc tailing reports to the primary zinc circuit through a 24-ft thickener. The thickener overflow, containing cyanide and dissolved copper carried over from the copper circuit, is treated with the 40-ft copper thickener overflow prior to disposal. Primary zinc circuit tailing reports to the mine backfill cyclones for recovery of solids prior to disposal.

In addition to the main copper-lead-zinc circuits discussed above, a separate circuit is operated to process a small high-grade orebody containing high gold and silver values. The high-grade lead concentrate produced is blended with the regular lead concentrate prior to filtration. High-grade tailing reports to the main circuit for recovery of copper and zinc.

All concentrates are filtered, but only the copper and zinc products are dried. Copper and lead filtrates are pumped to the 40-ft copper thickener; the zinc filtrate reports to the 24-ft secondary zinc thickener.

TAILING DISPOSAL

The zinc circuit tailing, representing approximately 70 per cent of the total tailings volume, contains all of the solid waste. Approximately 50 per cent of these solids are removed by three 12-inch cyclones for use as mine backfill. The cyclone overflow, containing 7 to 10 per cent solids, flows by gravity through approximately 3 miles of 10-inch plastic pipe and a series of seven vertical drop boxes to a tailing raft located on Buttle Lake.

Waste effluents from the thickeners, containing significant amounts of dissolved copper and cyanide, report to the alkaline chlorination plant, details of which are discussed later. The treated effluent flows approximately 2 miles through a separate pipe line to the first drop box, where it mixes with the backfill overflow.

The combined tailings flow to a raft anchored several hundred feet offshore in the south basin of Buttle Lake. The tailings are discharged through a 32-inch submerged outfall, which extends vertically from the raft to approximately 80 feet below the surface (i.e., below the thermocline). Solids, with the aid of flocculant addition, settle to the bottom of the lake, which is from 100 to 150 feet deep at this point.

The tailing line is equipped with a flow alarm located at the lake. Thus, any interruption in flow due to line breakage can be acted upon immediately. A small emergency tailing pond is located near the plant for dealing with material discharged during breakdowns or maintenance of the tailing line.

EFFLUENT QUALITY

During the first six years of operation, pollution control procedures at Western Mines were adequate to meet the requirements of Permit No. 185. Emphasis at that time was placed on effective disposal of the solid material. Dissolution of heavy metals was not a problem, due to both the extremely low solubility of metal sulphides and the high pH of the circuit. Lead production commenced in June, 1970, but was very limited for the following 2½ years. Consequently, the presence of dissolved copper cyanide complexes was not significant until early 1973, at which time milling of ore from the Myra Falls mine had commenced. The high lead content of this orebody, plus more severe limitations on the lead content of the copper concentrate, necessitated full-time operation of the copper-lead separation circuit. The essential usage of cyanide increased substantially the levels of cyanide and dissolved copper in the effluent, because copper will complex with cyanide even under strongly alkaline conditions.

Investigations indicated that the most efficient and economical method of removing these contaminants from the effluent would be by alkaline chlorination. Construction of a plant for this purpose commenced in August, 1973, but numerous start-up problems prevented satisfactory operation until mid 1975.

Alkaline Chlorination

CHEMISTRY

The process of alkaline chlorination, whereby cyanide is oxidized to cyanate, is well documented. The most frequent application has been in metal finishing operations, such as heat treating, dipping, stripping, flashing and electroplating, all of which produce cyanide wastes. However, the volume of wastes in the above are considerably smaller than the 200,000 to 300,000 IGPD of effluent requiring treatment at Western Mines. Consequently, the scale had to be expanded considerably from operations discussed in the literature.

Two basic chemical reactions are involved, the first being the formation of cyanogen chloride, which is not pH dependent:

$$NaCN + Cl_2 \rightarrow CNCl + NaCl$$

At a pH of 10.5 or higher, obtained with lime addition (or caustic soda), the cyanogen chloride decomposes to cyanate:

$$2\,CNCl + 2\,Ca(OH)_2 \rightarrow Ca(CNO)_2 + CaCl_2 + 2H_2O$$

The above oxidation of a simple sodium cyanide solution requires a residence time of 15 to 30 minutes using 3.4 pounds of chlorine per pound of cyanide. However, the effluent originating from the copper-lead separation circuit contains 30 to 100 mg/l of dissolved copper, which, at the prevailing high pH, must be retained in solution as a cyanide complex, with copper being part of the anion. The anion may be cupricyanide $[Cu\ (CN)_3]^-$ or cuprocyanide $[Cu\ (CN)_2]^-$, although the latter tends to be more stable. Zinc will complex with cyanide in a similar manner, but this does not present a problem in the subject operation. Alkaline chlorination decomposes these complexes in an analogous manner to the simple cyanide, precipitating the metal cation as a hydroxide. However, the residence time for such reactions is much longer, possibly up to 1½ hours.

TESTWORK

Sampling throughout the plant confirmed that the overflow from the 40-ft thickener represented the primary source of cyanide and dissolved copper in the tailing effluent. This overflow contains 50 to 150 mg/l of cyanide and 30 to 100 mg/l of dissolved copper, depending on the rate of cyanide addition to the circuit. The latter varies with the copper and lead content of the ore, which can change considerably from day to day. The thickener underflow obviously contains similar concentrations of these pollutants, which are carried to some extent through the circuits to the zinc tailing. Sampling of the latter showed copper and cyanide levels of approximately 1 mg/l, which at the time were well below the permit requirements. This, plus the fact that chlorination of the entire tailing stream would be unfeasible, directed the program toward treatment of the 40-ft thickener overflow only.

Preliminary lab tests were conducted using calcium hypochlorite as a chlorinating agent. Although residual levels of cyanide and dissolved copper contained in samples of 40-ft-thickener overflow were reduced to acceptable values in these tests, the use of hypochlorite in a full-scale operation was deemed both inefficient and uneconomic.

A second series of tests was run on 500-gal. batches of 40-ft-thickener overflow. Chlorine gas was supplied from a 150-lb cylinder by means of a 100-lb-per-day chlorinator. It was assumed at this stage of the testing that the pH of the thickener overflow, at 10 to 11, would be sufficient to complete the reaction. Although cyanide was almost completely eliminated from the effluent by this procedure, the pH had dropped to approximately 3 at the end of each test cycle. Thus, lime addition to pH 12 was required to precipitate the dissolved copper.

The batch tests established tentative parameters for chlorine addition rate and retention time upon which a full scale treatment plant could be developed. However, it was decided to run a pilot-scale test concurrent with the design of permanent treatment facilities. In addition to evaluating the effects of a continuous operation on the entire effluent stream, the pilot operation served to maintain the cyanide and dissolved copper levels within acceptable limits in the interim.

Chlorine for the pilot-scale operation was supplied through two 500-lb-per-day chlorinators, each connected to a 1-ton chlorine cylinder. These were set up to feed chlorine directly into the 40-ft-thickener overflow line. The high pH of the effluent was again relied upon for alkalinity, and the time of travel down the 3-mile length of trailing line was assumed to be sufficient retention time. The high pH of the backfill plant overflow was deemed sufficient to precipitate the copper following destruction of the cyanide. The above operation ran for a 7-week period, during which a comprehensive 24-hour sampling program was conducted. Data collected indicated that 800 to 1000 lb per day of chlorine was required in order to maintain the cyanide and dissolved copper content of the tailings below the 1967 permit levels.

CHLORINATION PLANT

Construction of the chlorination plant commenced in mid August 1973. Following a continuing series of delays related to construction problems, slow equipment deliveries, etc., the plant was sufficiently complete to operate on a manual basis by December 1973.

Chlorination of the effluent takes place in three 10- by 10-ft fibreglass tanks, arranged in series to obtain a retention time of approximately 1½ hours for flow rates of 200,000 IGPD. Chlorine is delivered in 1-ton cylinders, which are connected to a manifold six at a time. Valving is such as to have three cylinders on stream and three on standby. The initial set-up included a 1000-lb-per-day chlorinator which drew chlorine gas directly from the cylinders. Controls included pH and ORP recorders, a magnetic flowmeter and an automatic chlorine changeover system. The latter, activated by a pressure switch, automatically switched to the standby set of cylinders when the operating set ran empty. As in the case of the pilot tests, it was assumed that the pH of the thickener overflow was sufficient for complete reaction, with copper precipitation taking place when the treated effluent mixed with the backfill overflow at the first drop box.

Operation of the chlorination plant over the first four months following start-up was less than satisfactory. Although levels of cyanide and dissolved copper ran marginally within the requirements of the 1967 permit, numerous operating problems were en-

TABLE 2 — Comparison of Western Mines' Permit Specifications and Monitoring Results

	MAXIMUM PERMIT LEVELS		AVERAGE RESULTS ON MONTHLY COMPOSITE TAILING EFFLUENT SAMPLES	
	Original 1967	Amended 1975	Jan.-June 1973 No Chlorination Plant	July-Dec. 1975 Chlorination Plant in Full Operation
Total Solids	135,000 mg/l	135,000 mg/l	*	70,517 mg/l
pH	6.5 - 8.5	6.0 - 10.0	7.7	9.74
Dissolved Copper	10.0 mg/l	0.3 mg/l	2.85 mg/l	0.08 mg/l
Dissolved Lead	—	0.1 mg/l	0.17 mg/l	0.06 mg/l
Dissolved Zinc	5.0 mg/l	5.0 mg/l	3.27 mg/l	0.43 mg/l
Dissolved Cyanide	5.0 mg/l	—	*	*
Total Cyanide	—	0.5 mg/l	4.72 mg/l	0.18 mg/l
Dissolved Hexavalent Chromium	10.0 mg/l	—	*	*
Dissolved Sulphate	—	1000 mg/l	*	300 mg/l
Total Chlorine	—	—	*	>0.1 mg/l

*Not recorded

ountered. Concurrent with the above, the Pollution Control Branch notified Western Mines in April 1974 hat Permit No. 185 was to be amended. The limits f the amended permit are compared to those of the riginal in Table 2. Although the discharge at that ime was meeting most of the new requirements, the evels of cyanide and dissolved copper presented a roblem.

In light of these developments, a thorough study of he chlorination plant was made by both Western Mines and an outside consultant. As a result of the nvestigations, several modifications were made to he process. These are discussed below and are illustrated in Figure 2, which depicts the present plant ayout.

1. The assumption that the 40-ft-thickener overflow was sufficiently alkaline for the process was found to be incorrect. Apparently it is essential that the pH be maintained at 10.5 or higher, not only to ensure complete cyanide oxidation, but also to adequately precipitate the copper and eliminate any possibility of toxic cyanogen chloride emission. This had not been the case during the initial months of operation. Addition of chlorine to the effluent lowered the pH to approximately 3, thus contributing significantly to the inefficient operation encountered during this period. In addition, the acidity of the solution created corrosion problems, and the presence of cyanogen chloride gas was detected throughout the area.

   Provisions were made at the end of April 1974 to supply lime directly to the 40-ft-thickener overflow upstream from the chlorine addition point. It is added in excess to maintain the pH between 11 and 12. Manual control of the feed rate by means of a simple slotted weir box has proved both effective and trouble-free.

2. Under the terms of the amended permit, a substantial increase in the degree of cyanide and dissolved copper elimination was necessary. This required a 25 to 50 per cent increase in the chlorine addition rate. The capacity of the 1000-lb-per-day chlorinator was readily increased to 2000 lb per day by minor changes to the flow valve assembly. Operating data following this change indicated that complete cyanide destruction was effected at chlorine flow rates of 1200 to 1500 lb per day (assuming other operating parameters are correct). However, withdrawal of the compressed chlorine at these rates produced considerable heat loss due to the gas expansion. This in turn chilled the chlorine cylinders and contents, often to the point where the vapour pressure would drop sufficiently to substantially reduce the flow of chlorine. The situation was compounded when the ambient temperature fell below 50°F.

   The solution to the refrigeration effect noted above was a chlorine evaporator. This unit draws liquid chlorine from the cylinders and vapourizes it in a heated chamber, thus ensuring a continued supply of chlorine at the large flow rates required. An evaporator was ordered in May 1974 and, following a long series of unwarranted delays, delivery finally took place in March 1975. Operation continued in the interim on a less than satisfactory basis. Installation of the evaporator resulted in a substantial improvement in plant operation. The 8000-lb-per-day capacity of the unit is more than adequate to ensure a steady chlorine flow within the capacity of the chlorinator.

   Withdrawal of liquid chlorine and the necessary procedures involved in emptying cylinders, lines, etc., during tank changes precluded the use of the automatic changeover system. Therefore, the system was replaced with manually operated valves and a low-pressure alarm.

3. As noted previously, the original concept of effluent treatment was directed to the 40-ft-thickener overflow, which contains approximately 90 per cent of the residual cyanide and dissolved copper discharged from the separation circuit. Under the terms of the original permit, levels of these contaminants in the backfill plant overflow, carried over from the 40-ft-thickener underflow via the copper, secondary and primary zinc circuits, were not significant. However, with the advent of the permit amendments, steps were required to upgrade the quality of this stream. This was accomplished by diverting the secondary zinc circuit tail to a 24-ft thickener for decantation prior to treatment in the primary zinc circuit. The overflow from this thickener reports to the chlorination plant. This procedure has reduced the residual cyanide and dissolved copper in the backfill plant overflow to acceptable levels.

4. The availability of a sufficient and steady supply of chlorine made it possible to install an automatic control system, whereby the chlorine flow can be governed by the oxidation reduction potential (ORP) of the effluent. As ORP is based on the change from a reducing system (alkaline cyanide) to an oxidizing system (hypochlorite analogous to free chlorine), the proper millivolt setting for the ORP on the controller will ensure a sufficient supply of chlorine, within the capacity of the plant, to completely convert all cyanide to cyanate. Empirical determinations have indicated that optimum operating conditions are attained at an ORP setting of -600 mv at the prevailing pH of 11 to 12. The plant has operated on this basis since August 1975.

Current operation of the alkaline chlorination plant is fairly satisfactory, although problems have been encountered due to impurities in the chlorine supply. This has resulted in frequent plugging of lines, orifices, etc., in the gas dispensing system. A chlorine filter, installed in July 1976, appears to have alleviated the situation. Typical results attained by the plant following completion are given in Table 3.

Capital costs, including installation labour, totalled $107,000. Chlorine and lime addition, at 1.5 and 2.75 lb. per ton of ore milled respectively, account for most of the operating costs, which average $8,000 per month.

TABLE 3 — Elimination of Cyanide and Dissolved Copper - Average of Daily Samples Taken During September 1975

	Total Cyanide (mg/l)	Dissolved Copper (mg/l)
Chlorination Plant Feed	68.3	41.9
Chlorination Plant Discharge	0.13	0.14
Backfill Overflow	0.06	< 0.01
Total Tailings	0.07	0.02

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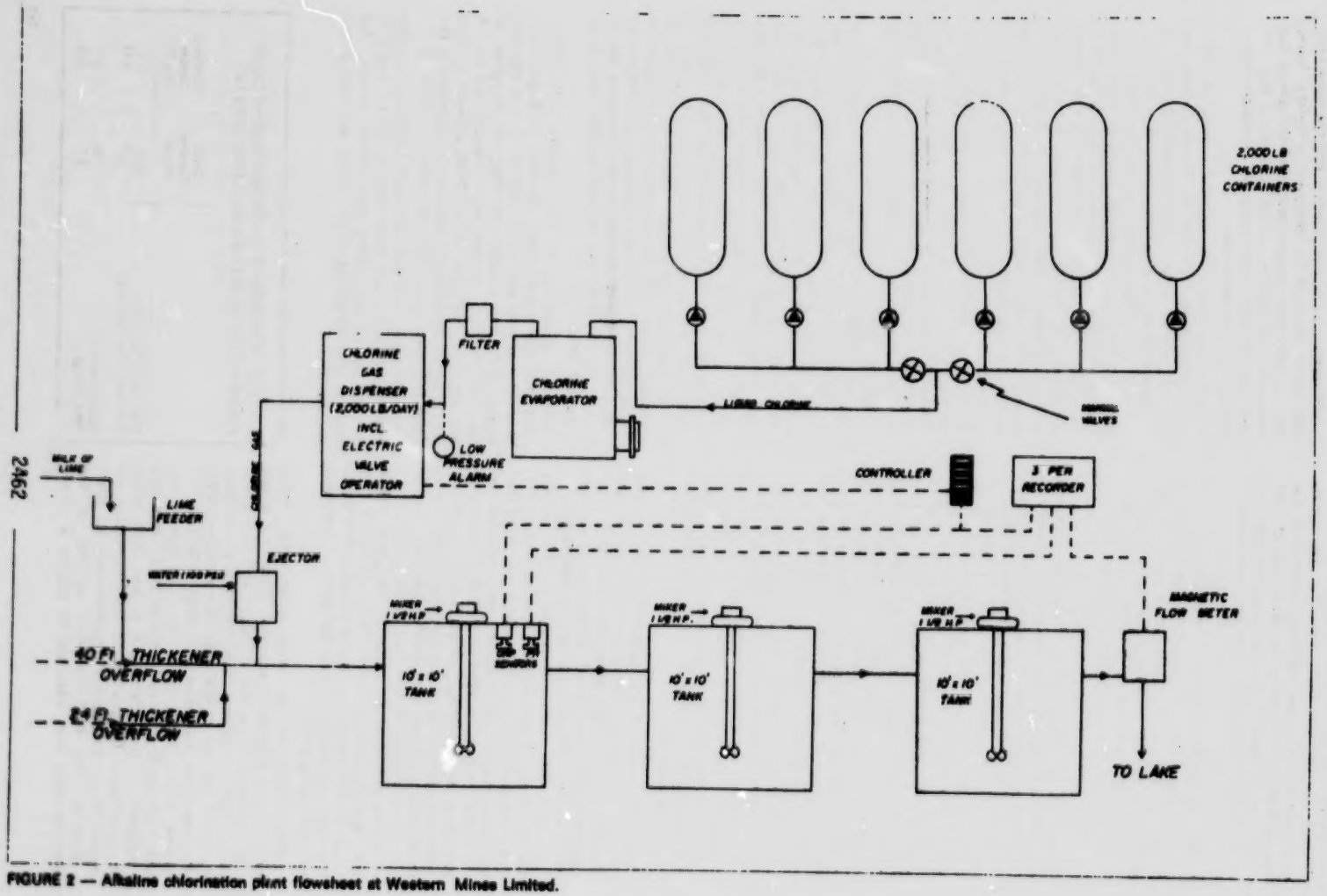

FIGURE 2 — Alkaline chlorination plant flowsheet at Western Mines Limited.

Monitoring Program

MONITORING OF THE TAILING EFFLUENT

Chlorination plant feed and discharge, backfill overflow and total tailings are sampled and assayed daily. This is done primarily as a control function, and is supplemented with monthly samples of the total tailings, which are sent to an independent laboratory for more comprehensive analyses. The results of the latter are submitted to the Pollution Control Branch, who in turn perform independent sampling of the discharge several times per year. The improvement in tailing effluent quality following installation of the alkaline chlorination plant is illustrated in Table 2, which compares average monitoring results during the first half of 1975 to those of the last half of 1975.

Although the monitoring results have been generally acceptable, in many cases assays on identical samples, run at different laboratories, have differed markedly, often by as much as 1000 per cent. This cast considerable doubt on the validity of the entire program. Subsequent investigations indicated that lack of proper sample preservation prior to shipment to the assay lab was a significant cause of the discrepancies. Standardization of sampling, preservation and assaying procedures has resulted in a substantial improvement in the agreement of all results, except those of cyanide. The latter is still under investigation.

The sampling and assaying procedures described above are supplemented by 96-hour LC 50 static bioassays, performed on the tailing effluent twice per year. However, these were only initiated in August 1975, and the data are too limited to be conclusive.

MONITORING OF BUTTLE LAKE

The long-term effects of discharging tailings into Buttle Lake is assessed by routine sampling of both the lake water and fish. A comprehensive set of analyses is performed annually on the former and results are compared with those obtained concurrently on all creeks entering the south basin of the lake. Fish specimens are collected three times per year near Western Mines' tailing raft and both flesh and liver are analysed for copper, lead, zinc and mercury. The data collected over the years does not indicate any increasing trend in levels of the pollutants tested.

Conclusions

The implementation of alkaline chlorination at Western Mines Limited has been successful in reducing cyanide and dissolved copper controls in the mill tailings to acceptable levels. Further, the extensive data collected over the past ten years by both the company and various regulatory bodies indicate that the discharge of tailings into Buttle Lake has not had any adverse effect on the quality of the water, either for aquatic life or domestic purposes.

Acknowledgment

The author wishes to acknowledge the substantial contribution made by H. E. Jackson, senior research chemist, Cominco Ltd., who acted as a consultant to Western Mines Limited during the development of the alkaline chlorination plant .

SUPPLEMENT TO "POLLUTION CONTROL AT WESTERN MINES' MYRA FALL OPERATION"

INTRODUCTION

The following is an update of the earlier paper published September 1977 in the Canadian Mining & Metallurgical Bulletin. The purpose is to review the operation of Western Mines' alkaline chlorination over the past five years with regard to maintenance, operating effectiveness, cyanide levels and costs.

OPERATION AND MAINTENANCE

Overall operation of the alkaline chlorination plant over the past five years can be considered generally satisfactory. The only operating problem of any significance has been frequent plugging of lines, orifices, etc., in the gas dispensing system. As noted in the previous paper, the situation is caused by impurities in the chlorine supply. Although samples have been submitted to the supplier, the source of impurities has not been identified other than the fact that they are organic in nature. However, installation of a chlorine filter in 1976 alleviated the situation considerably. Disassembly and complete cleaning of the chlorinator is now required once per year, rather than once per month as was necessary prior to filter installation.

During the first years of operation, chlorine addition rates of 1200 to 1500 lbs. per day were adequate to reduce cyanide in the effluent to satisfactory levels. However, ore changes over the past twelve to eighteen months have necessitated increases in cyanide addition rates of up to 30%. This, in turn, has increased the chlroine requirements to 1800/2000 lbs. per day (and higher on occasion). In addition to continuously taxing the chlorinator to its limit, these rates have considerably shortened the life of the unit. Thus, at the time of writing, a complete rebuild or replacement of the chlroinator will be necessary within six months. The latter is the logical choice in view of the increased loading, and a 4000 lb./day unit has been budgeted for 1981.

The chlorine evaporator, with a capacity of 8000 lbs./day, has presented very few problems. Other than minor electrical repairs and replacement of one or two gauges, this unit continues to operate trouble-free. The evaporator and all related piping was completely disassembled, cleaned and inspected in October 1980 and no evidence of corrosion or deterioration of any kind was observed.

CYANIDE LEVELS

The alkaline chlorination plant, given sufficient quantities of chlorine and lime, is capable of reducing both dissolved cyanide and dissolved copper to "trace" levels . The effluent from this plant is further diluted upon mixing with the remainder of the tailing from the backfill plant (essentially Cu and CN free). This ensures that the final tailing discharged to the lake, under normal operating conditions, is capable of meeting the permit requirements.

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SUPPLEMENT TO "POLLUTION CONTROL AT WESTERN MINES' MYRA FALLS OPERATION"

Although the alkaline chlorination process will effectively eliminate dissolved cyanide, problems have been encountered from time to time with fairly high "total" cyanide levels in the chlorination plant discharge. The explanation for this would appear to be the formation of insoluble ferrocyanides due to the presence of ferrous iron in the ore. These ferrocyanides are highly stable and are not amenable to treatment by alkaline chlorination. However, due to the extreme stability and very limited occurrence of these compounds, it is recognized that they do not pose a threat to the environment.

As noted in the original paper, assaying for cyanide continues to be unreliable. The problem is due both to the difficulty in obtaining uniform, representative samples of a slurry and the fact that subsequent assays are unreliable as a result of interference from a number of constituents present in the effluent. To date, this problem has not been resolved.

COSTS

Operating costs by the end of 1980 were averaging $13,000.00 per month, and increase of roughly 65% over the 1976 costs noted in the original paper. Chlorine, at approximately 1.8 lbs. per ore ton accounts for 80% of the above, with lime at 2.7 lbs. per ore ton making up the balance.

Maintenance costs to date have averaged under $3,000.00 per year, although as noted earlier extensive costs will be incurred in 1981 for replacement of the chlorinator.

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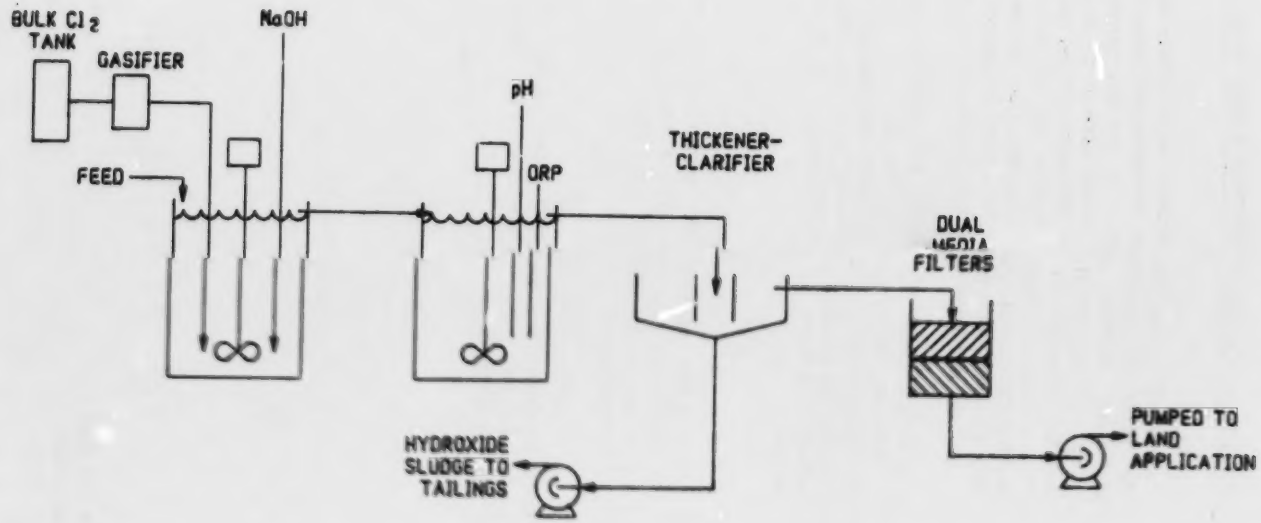
December 1980

NORANDA GREY EAGLE MINES ALKALINE CHLORINATION



NORANDA GREY EAGLE MINES, INC.

Noranda Grey Eagle Mines, Inc. at Happycamp, California, operates a 120 USgpm alkaline chlorination plant to treat excess tailings solution from a 500 stpd gold cyanidation plant.

According to a report to the California Regional Water Quality Control Board dated September 1983 the existing alkaline chlorination plant treats decant solution containing:

200 - 450 mg/l Cu
150 - 360 mg/l CN (free).

A second, larger cyanide treatment plant was under consideration to treat seepage below the dam wall. For this application both alkaline chlorination and SO_2-Air treatment were considered. However, for the purposes of this report, only the existing plant is discussed from the point of view of some of the difficulties that were encountered which appear similar to those reported elsewhere - (notably at Scottie Gold Mining and Carolin Mines).

This plant uses chlorine and caustic as reagents. After metal cyanide complexes are decomposed the metals precipitate as hydroxides and are settled in a clarification step. For final polishing a filtration step is used before pumping treated effluent to a land application site.

"Problems with plant operation have resulted from scale buildup in pumps, from ferric chloride plugging the chlorine system, from clarifier carryover and from filter mechanical problems."

Cyanide and metals loading in tailings decant have been higher than anticipated. Copper in the ore has been high and correspondingly higher cyanide dosages in the mill have been used. As a result, caustic and chlorine demand have been high and solids production, primarily a copper precipitate have been greater than that for which the original clarification and filtering plant were designed.

The plant supply pump (on a barge in the tailings pond), chlorine injector pumps and filter supply pumps require periodic cleaning of a scale buildup. The scale is believed to be a copper compound, likely a hydroxide. The scale is tenacious, requiring scraping or power wire brushing for removal, and at times builds up in sufficient thickness to stop pumps or reduce pump output. An anti-scaling agent was being investigated and preventative maintenance upgraded.

The chlorine system uses liquid chlorine drawn from a steel bulk storage tank. Chlorine forms ferric chloride in the presence of steel and moisture and causes a buildup in the chlorine evaporators and chlorinator components. Manufacturers recommend cleaning

components twice annually. With the very high chlorine throughput, however, monthly maintenance was necessary. Moisture inputs to the system and problems with impurities were investigated as sources of maintenance problems.

Controls have been made more responsive by moving oxidation-reduction-potential (ORP) probes to the chlorine reaction tanks. Initially the probes were remote from the tanks for safety reasons. However, the pH control system maintains pH consistently at proper levels, and the new location should not introduce safety risks. Scaling of the pumps supplying sample water to the remote probe location was the root of the problem.

The clarification facility has been overloaded with solids from the high levels of metal hydroxide sludge. As a result, the flocculation basin used to become plugged by settled sludge.

The clarifier portion experiences some carryover of small precipitate sludge particles. It was believed that the clarifier capacity might have been too small for the quantity of precipitate and clarifier expansion was under investigation.

Scaling of small orifices in the clarifier has resulted in periodic maintenance. Enlarging the orifices has been recommended.

Filtration was provided to polish the effluent. At times the filters were not needed and copper levels could be reduced sufficiently in the clarifiers. Clarifier modifications were to be made to increase the efficiency and reduce the need for filtration. Valve scaling and backwash on the filter system had aso presented maintenance problems. The manufacturer-supplier was investigating system modifications to improve reliability.

A Noranda internal report dated 3 June 1983 appeared in the compilation of data presented to the California Regional Water Quality Control Board showing that test data indicated that available cyanide and metals are equally well removed from the slurry by alkaline chlorination as by the SO_2-Air process at comparable reagent consumptions. However, the SO_2-Air process was more successful at reducing CN_T results due to ferrocyanide removal as discussed below.

Since the above status was established in 1983, the cyanide detoxification plant problems at NGEM have been successfully sorted out, but details were not pursued.

NORANDA RESEARCH CENTRE

INFORMATION MEMORANDUM 3 June 1983

cc:

FROM: M. Wasserlauf

SUBJECT: NORANDA GREY EAGLE MINE - PROJECT N-8321-3B - DESTRUCTION OF CN IN TAILINGS SLURRY

SUMMARY

Bench-scale tests conducted at the Noranda Research Centre indicate that Grey Eagle tailings can be detoxified with CN levels of <3 mg/L in the treated effluent. While SO_2 treatment removes the CN almost completely, alkaline chlorination resulted in a total CN residual of approximately 30 mg/L, due probably to iron cyanide complexes which are not removed by chlorine. Free cyanide levels in both cases were <1 mg/L CN in the effluent.

Treatment alternatives evaluated included detoxification of existing tailings (40% solids), as well as dewatering to 60-65% solids using thickeners or filters, then detoxifying. Due to the lower CN loading, the latter alternatives would lower operating costs by a half.

Additional work is on-going to evaluate stability of metals (Cu, Zn, Fe) in the detoxified tailings under varying pH conditions, and this work will be reported later.

1. INTRODUCTION

Noranda's Grey Eagle Mine discharges 500 TPD of tailings solids in a slurry containing 40% solids. Results of CN destruction tests conducted at the Noranda Research Centre with tailings made from the Grey Eagle ore were reported previously([1]). This memorandum presents results of tests conducted with actual mill tailings.

2. TAILINGS CHARACTERIZATION

Samples of Grey Eagle tailings were received at the Noranda Research Centre on May 24, 1983. Tests on the tailings yielded the following characterization:

RECEIVED JUN 7 1983

pH = 10.6
% solids = 39.2 W/w
Pulp density = 1.33
Cyanide in decant :
= 1700 mg/l Total CN (Picric acid)
= 1125 mg/L Total CN (distillation & CN electrode)
= 750 mg/L Free CN (CN electrode)

Cyanide in pulp = 1171 mg/L Total CN (distillation & CN electrode)
Thiocyanate = 365 mg/L CNS
Thiosalts = Not detected

3. CYANIDE BALANCE

Based on the above values, a cyanide balance can be computed as follows:

- Water in Tails = $\frac{500 \text{ T solids/day}}{60.8 \text{ \% water content}}$ = 822 T/day

- CN content: Due to CN: = 1125 mg/L
  Due to CNS: 365 mg/L X $\frac{26 \text{ (M.W. of CN)}}{58 \text{ (M.W. of CNS)}}$ = 163.6 mg/l
  1289 mg/L

CN in tails = 1289 mg/L X 822 T water/day
= 1.06 T CN/day (both CN & CNS)

This can be expressed as 2.0 t NaCN/day
or 8.0 lb NaCN/ton ore treated

This appears to agree with current NaCN useage in the mill.

4. CN TREATMENT TESTS

4.1 Methodology

Tests for CN destruction were carried out on 500 ml samples of magnetically stirred Grey Eagle tailings. Two methods were tested:

- SO_2 destruction: solutions of 20% Na_2SO_3 were added to the tailings pulp samples under variable test parameters, including SO_2:CN ratio, pH, added Cu concentration. A constant aeration rate of 1L/min was maintained.

- Alkaline chlorination: solutions of NaOCl (5.9% Cl_2) were added to the tailings pulp samples. Main test parameter was Cl_2:CN ratio, with pH maintained at 9 to 9.5.

Samples were taken at 0.5, 1, 2 h, with some also taken 24 h later. Total CN was analyzed by the picric acid, and distillation methods, with free CN analyzed by the specific ion electrode. Thiocyanate analysis was as per APHA Standard Methods.

4.2 SO_2 Results

Results of the SO_2 tests are presented in Table I. Based on the data, the following conclusions can be drawn:

TABLE I

NORANDA GREY EAGLE MINE

Results of SO_2 Tests

Time (h)	Parameter	Control (No SO_2, No Cu)	SO_2:CN ratio (without Cu added)				SO_2:CN ratio (with 100 mg/L Cu added)		
			3.75	7.5	11.25	11.25	11.25	11.25	15.0
0.5	pH	8.5	11.0	11.1	11.0	8.5	10.9	8.5	8.5
	Total Cn (P) (mg/L)	1650	790	290	195	121	95	26	23
	Free CN (mg/L)		150	88	60	37	22	13	13
	CNS (mg/L)								
1.0	pH	8.5	11.0	11.0	11.1	8.5	10.9	8.5	8.5
	Total CN (P) (mg/L)	1625	605	255	180	125	99	23	23
	Free CN (mg/L)		125	86	60	17	25	1.5	12
	CNS (mg/L)								
2.0	pH	9.5	10.8	10.8	11.0	8.5	10.9	8.5	8.5
	Total CN (P) (mg/L)	1388	450	80	80	<1 mg/L	30	3.0	2.5
	Free CN (mg/L)		94	23	34	<1 mg/L	12	1.1	1.2
								305	115
20.0	Total CN (P) (mg/L)							<1.0	<1.0
	(D) (mg/L)								0.25

P = picric acid
D = distilled

4.2.1 Reagent requirements: Reagent requirements are about 11 lb SO_2/lb CN.

4.2.2 Reaction pH: A pH of 8.5 is required. Tests at pH of 11 (the pH of tails and Na_2SO_3) resulted in excessively high CN residuals (>80 mg/L).

4.2.3 Copper additions: There appears to be no advantage to the use of supplemental copper.

4.2.4 Reaction time: The CN destruction reaction with SO_2 were found to proceed quite rapidly initially, with a removal of roughly 1000 mg/L at optimal conditions in the first 30 min. The removal of the remaining CN was, however, much slower. Thus, it appears that a reaction time of 2 h is necessary.

4.2.5 Aeration: Air addition to the control sample (1L/min) resulted in a 16% decrease in CN levels after 2 h.

4.3 Cl_2 Results

Results of alkaline chlorination tests are presented in Table II. These data provide the following conclusions:

4.3.1 Reagent Requirements

Alkaline chlorination provides total removal of CN amenable to chlorination with a residual of <1 mg/L CN (by picric acid method) at a CL_2/CN ratio of between 12 and 15.

4.3.2 CN Removals

Analysis by distillation indicates a residual of about 30 mg/L CN, probably due to iron cyanide complexes, which are not destroyed by chlorination.

4.3.3 Reaction Time

Test results indicate rapid reaction kinetics, with no changes in parameters monitored after 30 min.

5. FORMS OF CN

CN analysis were conducted by distillation on both tailings pulp, and decant samples both before and after treatment. In all cases, results of these tests (below) indicated similar values, suggesting that CN is present entirely in the liquid phase.

TABLE II - NORANDA GREY EAGLE MINE

RESULTS OF ALKALINE CHLORINATION TESTS

Time (h)	Parameter	Cl_2:CN Ratio			
		3.75	7.5	11.25	15
0.5	pH	9.7	9.6	9.1	8.6
	Total CN (P) (mg/L)	950	210	7.5	<1.0
	(D) (mg/L)				29.6
	Free CN (mg/L)	300	100	2.5	<1.0
	CNS (mg/L)				<1.0
1.0	pH	9.8	9.7	9.3	
	Total CN (P) (mg/L)	950	270	7.0	
	Free CN (mg/L)	300	120	1.9	

(P) = picric acid

(D) = distilled

Sample	Total CN (mg/L) Pulp	Decant
Tailings before treatment	1171	1125
SO_2 Tests (SO_2:CN = 15:1)	0.25	<0.25
Cl_2 Tests (Cl_2:CN = 10:1)	30.0	29.6

6. TREATMENT SCHEMES

Three principal treatment schemes can be considered:

Scheme No. 1 - End of pipe treatment of tailings (40% solids w/w) - Figure 1.

Scheme No. 2 - Thickening of tailings to 60% solids (as indicated by Noranda Research settling tests), treatment of thickener underflow for CN, recycle of thickener overflow to mill - Figure 2.

Scheme No. 3 - Filtering of tailings to 65% solids (as indicated by SRK tests), reslurring of coke; and treatment for CN, recycle of filtrate to mill - Figure 3.

Based on the most recent data, the approximate mass balances are as follows:

Scheme 1	Scheme 2	Scheme 3
166 gal/min mill tailings pulp @ 40% solids = 822 T/day water @ 1125 mg/L Total CN	Thickener underflow @ 60% solids = 333 T/day water @ 1125 mg/L total CN	Filter coke @ 65% solids = 270 T/day water @ 1125 mg/L Total CN
= 1850 lbs/day CN	= 750 lbs/day CN	= 607 lbs/day CN

For each scheme, CN destruction by alkaline chlorination, and SO_2 treatment can be considered.

REFERENCES

1. Wasserlauf, M., Noranda Research Centre, Destruction of CN in Tailings Slurry, Noranda Research Centre Memorandum, 17 May 1983.

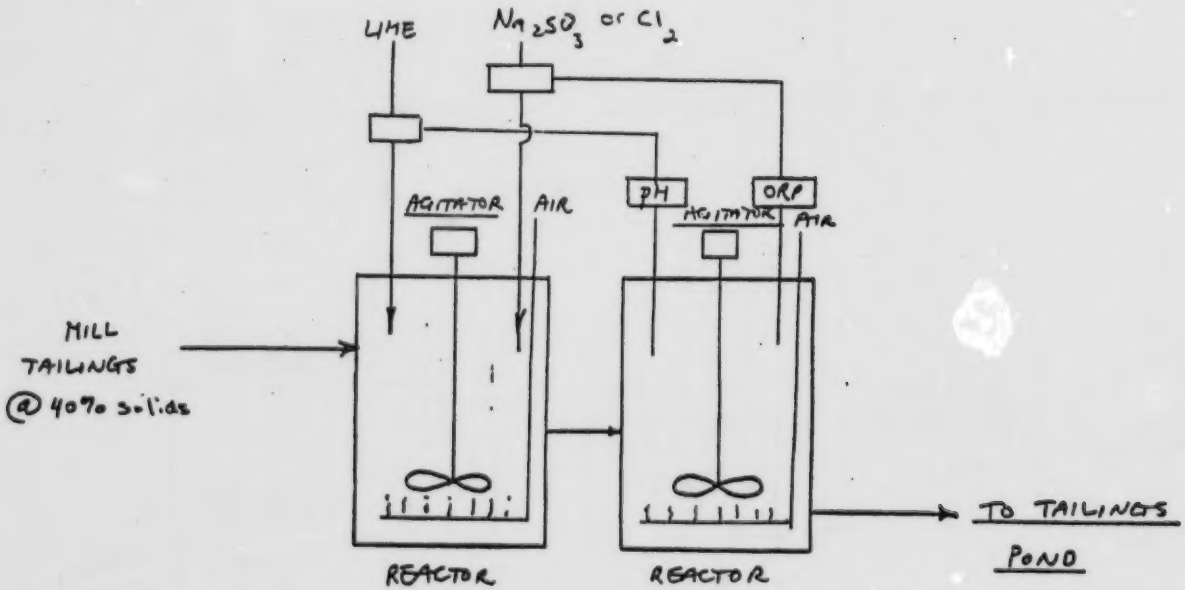


FIGURE 1 : SCHEME No. 1 - END OF PIPE TREATMENT

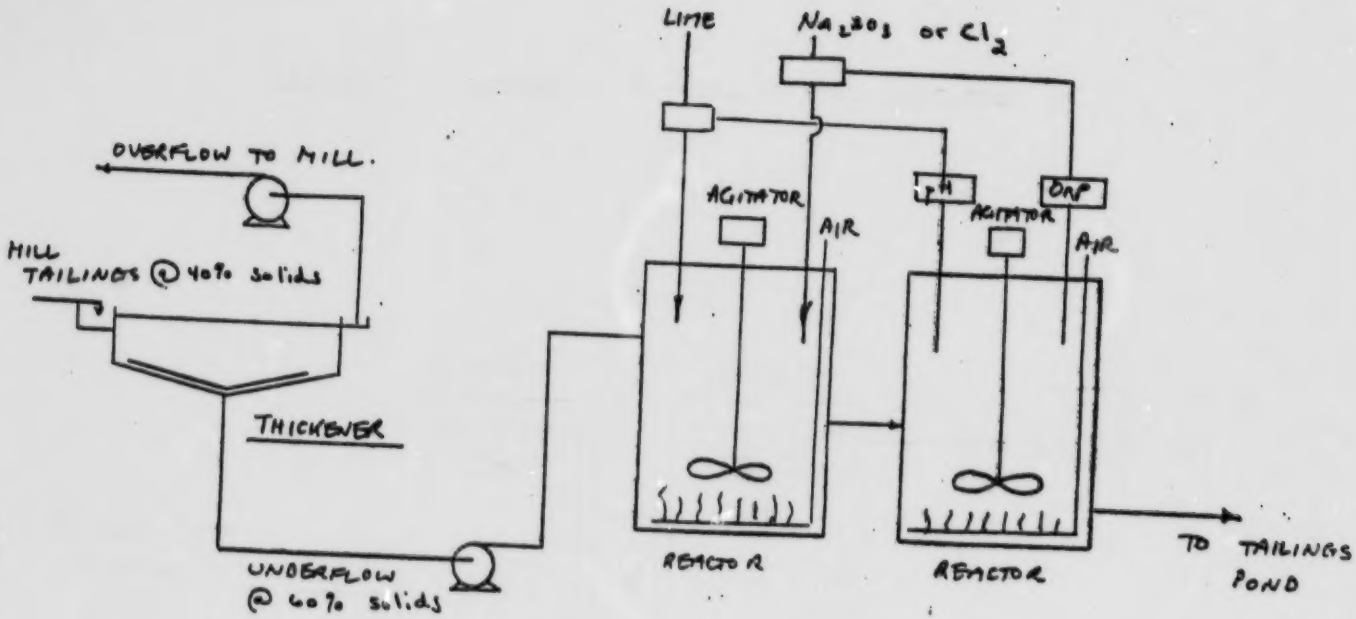


FIGURE 2 : SCHEME NO. 2 - THICKENING, FOLLOWED BY CN DESTRUCTION

TABLE 13

LABORATORY ANALYSES(1)
CDM LABORATORIES
SAMPLED MARCH 31, 1983

PARAMETER	UNITS	TAILINGS POND	D-1	D-2	D-4	WELL NO. 1
Date Sampled		3/31/83	3/31/83	3/31/83	3/31/83	3/31/83
Flow	gpm	—	37.5	7.0	—	—
pH	S.U.	6.9	7.8	5.8	4.5	6.0
TDS	mg/l at 180°C	2,400	1,900	1,500	790	180
TSS	mg/l at 105°C	8	<5	54	14	9
Major Cations:						
Calcium	mg/l	260	190	160	91	12
Magnesium	mg/l	18	82	78	39	14
Potassium	mg/l	31	4.3	3.1	1.1	0.1
Sodium	mg/l	350	130	110	4.0	9.7
Major Anions:						
Carbonate	mg/l	0	0	0	0	0
Bicarbonate	mg/l	200	230	92	0	20
Chloride	mg/l	550	290	190	<5	<5
Nitrate	mg/l as N	0.11	0.23	0.18	0.10	<0.05
Sulfate	mg/l	850	760	720	510	84
Metals:(2)						
Aluminum	mg/l	0.4	<0.5	4.6	6.6	1.8
Arsenic	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005
Cadmium	mg/l	0.010	0.008	0.013	0.015	0.007
Copper	mg/l	51	120	89	9.5	0.079
Iron	mg/l	0.26	0.015	16	26	2.6
Lead	mg/l	0.005	<0.005	0.007	0.012	0.008
Manganese	mg/l	0.55	11	9.3	5.9	0.22
Zinc	mg/l	0.68	0.12	2.8	4.4	0.18
Cyanide:						
Total	mg/l	260	160	100	0.021	0.010
Total Amenable to Chlorination	mg/l	260	150	97	<0.005	<0.005
Total Amenable to Chlorination Without Distillation	mg/l	110	71	39	0.014	0.007
Weak Acid Dissociable	mg/l	240	150	100	0.033	0.013
Free	mg/l	68	67	32	0.008	<0.005
Thiocyanate	mg/l	110	120	72	<0.5	<0.5

NOTES:

(1) Samples collected by SRK on March 31, 1983. Analyses performed by CDM Laboratories, Inc., Wheatridge, Colorado.

(2) Total metals.

"—" = Not measured.

DISCUSSION

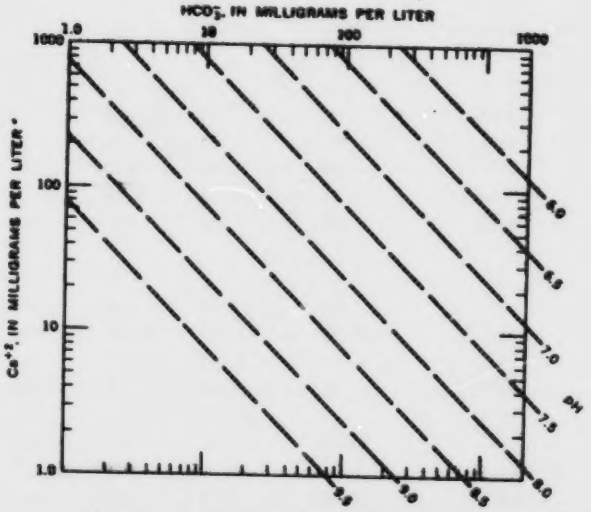
Based on the water chemistry shown in the following table it is concluded that a large part of the scale and precipitate is likely to be a $CaCO_3$ precipitate which results when the pH is raised over 7.3.

$$HCO_3^- + OH^- \rightleftharpoons CO_3^= + H_2O$$

$$Ca^{+2} + CO_3^= \rightleftharpoons CaCO_3$$

CALCIUM AND BICARBONATE SOLUBILITY VS pH

Source: HEM (1970)



–Equilibrium pH in relation to calcium and bicarbonate activities in solutions in contact with calcite. Total pressure 1 atmosphere; temperature 25°C.

200 mg/l $CO_3^=$ is already present in solution as bicarbonate, but additional carbonate may be generated if excess chlorine is applied with a long enough residence time for Stage 2 reactions to take place. Each 1 g CN^- could theoretically generate just over 2 g $CO_3^=$. Consequently 260 gm/l CN^- could generate 520 gm/l $CO_3^=$ making a total of 720 gm $CO_3^=$/l assuming all cyanide is reacted to completion through Stage II reactions.

Even with the 200 ppm HCO_3^- already in solution, at pH 6.9 this solution is already saturated with Calcium at 260 mg/l. According to the diagram shown on page 134 of HEM (1983) at pH 9.5 Calcium concentrations as low as 1 ppm would be saturated, and about 400 mg $CaCO_3$ per l or more could be expected to precipitate. No doubt the copper released by CN decomposition coprecipitates as $Cu(OH)_3$.

There are two possible solutions to the scaling problem. First is to employ a $CaCO_3$ scale inhibiting reagent. The second is to remove CO_2 from solution ahead of addition of the NaOH and chlorine which would involve an additional step but would also reduce NaOH consumption.

CYANIDE DETOXIFICATION AT SUPERIOR MINERALS, STIBNITE, IDAHO

At Superior Mines Yellowknife Idaho heap leaching operation, cyanide must be rinsed from the leached heaps and the heaps then detoxified. Also the leached heaps are moved to a tailings area and detoxified again using a $Ca(OCl)_2$ solution prepared on the site from pebble lime and liquid chlorine.

The 3000 stpd heap leaching operation is located at a high altitude in steep mountainous terrain alongside the Salmon River that is the headwaters for an important salmon fishery downstream.

The main environmental aspects of concern are to prevent cyanide and heavy metals from getting into the stream. The second concern is to prevent suspended solids from getting into the creek.

HEAP LEACHING

The 10 feet high heaps of ore crushed to 1½" X 0 are 1.5 lbs lime added per ton ore during stacking. The 10' heaps are subjected to 50 day leach cycles made up of:

10 days to build the heap
20 days to leach
10 days to wash the heap
10 days to remove the heap.

CYANIDE DESTRUCTION

The 10 day wash phase is broken down further as follows:

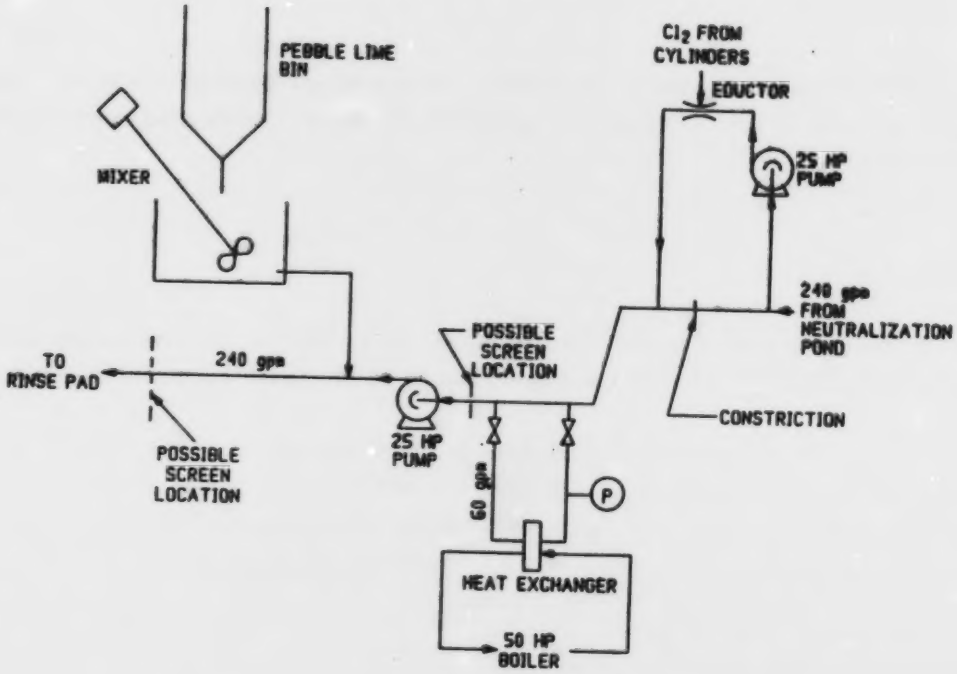
2 days drain after leach
6 days wash with $Ca(OCl)_2$ solution
2 days drain after washing.

By raising the pH to pH 12-13 it is possible to greatly speed up the detoxification step to 6 days. When the solution is applied at pH 10, it took 22 days to get "off" solution down to 0.2 ppm CN.

Solution is applied to the 200' X 250' heaps at a rate of 0.3 gph/ft^2 (0.005 gpm/ft^2) i.e., 2500 lb per minute per heap.

CN destruction if found to proceed faster at pH 12-13. Solution from the special reservoir of cyanide neutralization solution at pH 12-13 is applied by spraying it through the same distribution system as was used to spray leach solution onto the heaps.

One problem is that grit in the pebble lime used to make $Ca(OCl)_2$ sometimes clogs the sprinklers. This could possibly be avoided by installing Bateman Filtomat units into the line. Operating staff turn off the line supply temporarily allowing Cl_2 to reduce the solution pH which, more often than not, unclogs the sprinklers.



CALCIUM HYPOCHLORITE ADDITION PARAMETERS

1.25 lb $Ca(OH)_2$ is added per lb of Cl_2
4000 lb Cl_2/day are added @ 240 USgpm
i.e., 12 st Cl_2 over 6 days per 30,000 t heap = 0.8 lb Cl_2/t heap
@ a price of \$360/t Cl_2 delivered this works out to US \$0.14t ore.

CHLORINE PRICE

\$360/t Cl_2 = \$0.18/lb Cl_2

This compares very favorably with the quoted cost of \$1.30/lb $Ca(OCl)_2$ @ 60% effective Cl_2 strength.

At all times 3.5t $Ca(OCl)_2$ are on standby in case the $Ca(OCl)_2$ manufacturing system shown in the sketch above should fail.

Cl_2 is supplied by Pennwalt in 1 ton cylinders. Ten cylinders were hooked to the Cl_2 gasifier for automatic changeover should any one become empty. Pennwalt also supplied a Cl_2 metering device.

MONITORING

CN^- levels are monitored at regular intervals in the "off" solution during chlorination.

CN^- is also monitored at ppb levels in solutions drawn from monitor wells and analysed using a HACHMETER model DR100 colorimeter Model 41100.

HACH CO.
Box 389
Loveland, CO

FREEZE PROTECTION

The heaps are detoxified before the leached material is placed on the tailings dump. It is also deemed necessary to detoxify any heap that may be in the process of being leached when a sudden freeze occurs. If the frozen heap were to be left through the winter with CN^- still in it, this could leak during the spring runoff.

In case of such a freeze, the detoxification system is fitted with a 50 HP Boiler and heat exchanger to heat the solution which is pumped to the heap at 240 gpm.

PEBBLE LIME

By converting from NaOH to $Ca(OH)_2$ for pH control on the heap it was found that NaCN consumption dropped from 1.5 lb/t ore to 0.2 lb NaCN/t ore. The reason for this is suspected to be that NaOH solubilizes iron or other base metals which consume CN^-.

Pebble lime is used for the $Ca(OCl)_2$ manufacturing in preference to slaked lime which would blow around.

Because pebble lime introduces grit into the circuit which clogs sprinkler orifices, some sort of grit screen would be appropriate in the line.

DETOXIFICATION Pond

A 1 mm gallon pond is used to contain the neutralization (detoxifying) solution.

CYANIDE

So sensitive is the stream considered to be to cyanide that from August 1 to September 15 no chemical reagents are hauled along the roadway to the plant to avoid any possibility of an accidental spill into the stream.

More information on the CN^- destruction system can be requested from:

MR. WILLIAM STOTT
Manager
Canadian Superior Mining US Ltd.
Mining Division
Post Office Box 385
Spokane, WA 99210

DUVAL CORPORATION, BATTLE MOUNTAIN OPERATIONS

Alkaline chlorination of cyanide tailings pulps is known to be practiced at Duval Corporation's Battle Mountain Operations where 3450 mt/d ore in a 35-50% solids slurry is detoxified. After treatment the pulp flows via several drop boxes to the valley below where the tailings pulp are discharged to the desert floor. Because of the high copper content it is unlikely that this solution could be recycled to a great extent without causing metallurgical headaches.

A description of the tailings treatment plant is included in the Randol Phase I report "Innovations in Gold and Silver Recovery" which was written before expansion of the Battle Mountain CIP plant. The data therefore refers to a 2720 mt/d operation. In June 1984 management declined to discuss their tailings treatment and mention of the subject is not made by TODD & ANDERSON(1984) in their paper describing the operation although they did indicate that the free cyanide residual after leaching ranges from 200-500 mg CN/l with high copper cyanide levels.

TAILINGS DISPOSAL

After CIP, BATTLE MOUNTAIN tailings are treated in a final contactor known as their Tank #7 in which chlorine and lime are added to destroy residual cyanide.

Tailings then flow down a high density polyethylene pipe to a tailings dam at the base of the mountain. There are about twenty drop boxes enroute.

Cyanide addition in the leaching circuit was adjusted to maintain 1 lb free NaCN per ton solids in the final pachuca, i.e., 500 PPM NaCN. Because of copper and iron in the ore, considerable quantities, cyanide complexes of these metals will also be present. In the CIP effluent pulp, about 10 PPM soluble copper is measured which will be present as the complex $[Ca(CN)_3]^{=}$.

Oxidation with chlorine is designed to destroy all free cyanides according to the following reactions:

$$NaCN + NaOCl = NaCNO + NaCl \quad (1)$$

$$Cl_2 + 2NaOH = NaOCl + NaCl + H_2O \quad (2)$$

$$2NaCNO + 3NaOCl + H_2O = CO_2 + N_2 + 3NaCl + 2NaOH \quad (3)$$

Reaction (1) is accelerated by increasing pH being completed within minutes at pH 10 or above.

Reaction (3) is accelerated by reducing pH being extremely slow at pH 10, but only 10 minutes at pH 8. Below pH 7, the cyanate (CNO) converts to ammonia.

BATTLE MOUNTAIN generate OCl^- using lime and chlorine rather than soldium hydroxide.

A suitable effluent treatment plant controlling pH and redox conditions has been designed by:

POLLUTION CONTROL SYSTEMS
1295 West 78th Street
Cleveland, Ohio 44102
(216) 651-7703 or (216) 251-3430

Chlorine consumption for cyanide destruction in tailings amounts to 3700 US gallons per day (20 st) and costs $5,000/day. An additional 40 lbs of lime per ton of ore is consumed in the OCl^- generating system. Another source of data showed chlorine consumption at 16 to 22 lbs per ton ore.

3700 US gal./d 40,000 lb Cl_2/day$5000/d
132 tons/d lime @ $65/st $8500/d

12.12 lbs Cl_2 per ton ore @ 12.54/lb Cl_2 $1.52/ton ore
40.0 lbs lime per ton ore @ 3.34/lb Cl_2 $1.32/ton ore

Cost of Reagents for Tailings Treatment $2.84/st ore

A small EIMCO filter has been installed to test recovery of cyanide solution from CIP tailings. This would reduce the amount of chlorine required to destroy cyanide, and might hopefully recover reagent values for recycling.

One aim of the belt filter is to reduce the soluble copper levels in the tailings since copper ties cyanide up, which reports as free cyanide in the silver nitrate titration.

Virtually nothing is known about the belt filter test work or how it was applied, since this was installed too late for review in the Phase II Report. The belt filtration test work for cyanide tailings treatment is an aspect of definite interest for further followup.

RANDOL INTERNATIONAL LTD believes that the BATTLE MOUNTAIN plant may be an ideal location to test other cyanide destruction techniques identified as part of this investigation and discussed in the secton of this report dealing with effluents and tailings disposal.

DETOUR LAKE, ONTARIO

This new mine, mill and CIP gold recovery plant operates currently at 2500 mt/d ore throughput with announced plans to expand to 4400 mt/d by 1987.

It is believed that after CIP the tailings pulp is treated by alkaline chlorination before pumping to the pond.

It is not yet known what the cyanide levels are before or after treatment.

SUPPLIERS OF CHLORINE DOSING SYSTEMS

Installation	Cl_2 System Supplier
Superior Minerals - Stibnite, ID	Pennwalt Corp.
Giant Yellowknife Mines, Ltd.	Pennwalt Wallace & Tiernan Div. 925 Warden Avenue Scarborough, Ontario Canada M1L 4CS
Getty Mercur	Not determined
Duval - Battle Mountain	Not determined
Noranda Grey Eagle Mine	Not determined
	Fischer & Porter (Canada) Ltd. #4, 1485 Rupert Street North Vancouver, BC V7J 1G1 Telephone: (604) 986-4145 H. N. (Harry) Hill

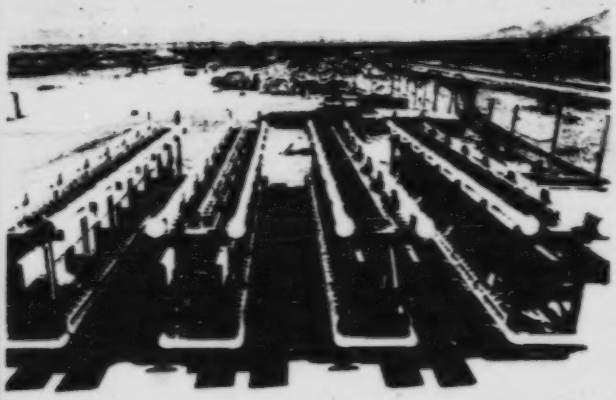
COST OF CHLORINE

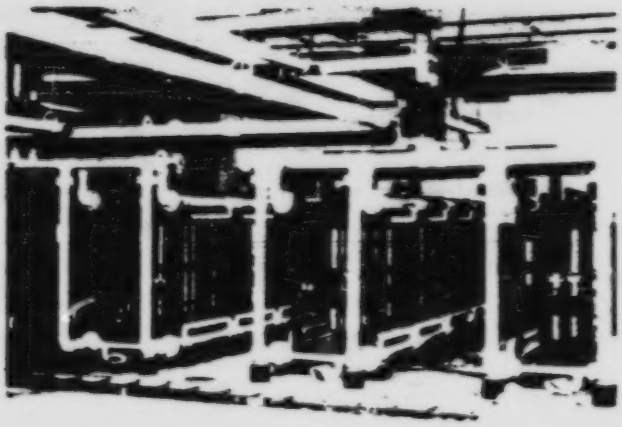
Mid 1983	Stibnite, Idaho	\$360/t Cl_2 liquid

Produce Sodium Hypochlorite (NaOCl) on-site with the PEPCON TYPE PF System

Chlorination, Disinfection, Odor Elimination, Slime and Marine Organism Control for • Municipal Water and Wastewater Treatment Plants • Industrial Plants • Chemical Manufacturers • Food Processors • Power Plant Circulating and Service Water Systems • Cooling Towers • Offshore Platforms

Type PF parallel flow vertically-mounted cells for sea water and special brine (purchased salt) applications





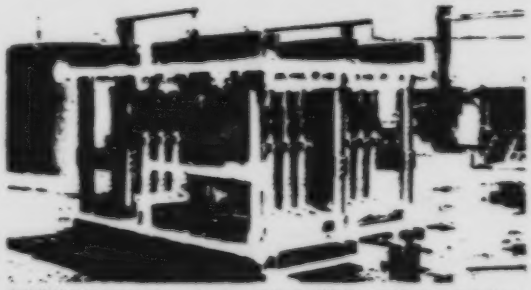
PEPCON 280-cell system for producing 5,600 lbs. per day of sodium hypochlorite for final effluent disinfection at the Waterloo, Iowa Water Pollution Control Plant (Average plant flow—20 MGD; peak flow—35 MGD). Left—Cell modules pre-assembled in convenient rows for easy installation, ready for shipment. Right—Cells installed at Waterloo, Iowa.

A safe and dependable alternative to liquid chlorine (Cl^2) or commercial hypochlorite

The advanced PEPCON System is economical to operate and simple to maintain. As pictured above, it is built around an efficient electrolytic system, the heart of which is the inexpensive, long life, PEPCON cell with its special anode, operating at low D.C. voltage. Simply supply inexpensive salt, or seawater, to the PEPCON unit to produce the amount of NaOCl you require.

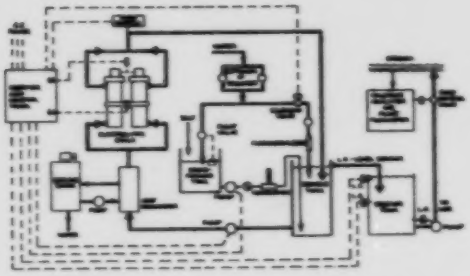
Conversion of chlorides to a safe, dilute NaOCl solution takes place entirely within the unique PEPCON cell. The hazards and the expense of transporting, storing and handling chlorine are eliminated.

Safety, reliability, and economy of the PEPCON electrolytic cell have been proven by more than fifteen years of operating experience.

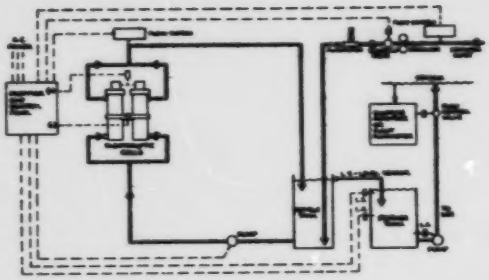


PEPCON 32 cell seawater system for producing 800 lbs. per day of sodium hypochlorite for control of marine organisms for an overseas waterflood project.

Sodium hypochlorite generation—
From 10 pounds per day to any required amount



Typical Flow Diagram for PEPCON NaOCl-from-Brine System with Recycle, Cooling and Product Storage.



Typical Flow Diagram for NaOCl-from-Seawater System with Recycle and Product Storage

How the PEPCON system functions

Prepared brine or seawater passes through the PEPCON cells where it is electrochemically transformed into sodium hypochlorite (NaOCl). The hypochlorite solution produced is either discharged directly into the receiving stream or to storage.

The maximum concentration of NaOCl generated can be varied by selection of a system designed to operate on a once-through, recycle, or recycle with cooling basis.

Economics of PEPCON method of sodium hypochlorite production

For brine systems the system design can be varied to take best advantage of the relative costs of salt and electric power at the specific jobsite. Safe hypochlorite is usually produced at a cost competitive with liquid chlorine delivered in tank cars or ton cylinders.

For "once-through" seawater systems the power required for the electrolytic cells typically ranges from 2.00 to 2.75 kilowatt-hours per lb. of NaOCl generated, depending on the salt content and temperature of the seawater. If recycle or solution cooling is incorporated in the system design an additional small amount of power is required.

Production cost for PEPCON hypochlorite, generated on-site, is well below that for hypochlorite purchased from outside sources.

Other PEPCON electrolytic systems

- Type SF Hypochlorite Generators for most brine (purchased salt) applications.
- Direct "flow-through" treatment for deodorization of digester supernatants, centrates, and filtrates, and for disinfection and odor control of industrial and municipal effluents.
- OdorMaster single stage and multiple stage gas odor control systems.

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U.S. and Foreign Patents and Patents Pending

Features:

- Modular design permits sizing for any required NaOCl production.
- Designed for trouble-free operation. Changing a cell is like changing a fuse. It is never necessary to return a PEPCON cell to the factory for replating. When required an inexpensive replacement anode is simply inserted in the reusable cathode by operating personnel at the jobsite.
- Cells are factory mounted to corrosion resistant fiberglass structural supports, for easy field installation.
- Operation is at a safe 5-7 volts D.C. per module. Rectifiers are equipped with polarizers to prevent cell damage from galvanic action during routine "system-off" periods.
- Choice of system control and injection methods.
  (1) Produce NaOCl at varying concentrations, paced by a plant flowmeter or residual chlorine analyzer, and inject directly into the stream to be treated.
  (2) Produce and store NaOCl at a constant concentration, with injection from storage controlled by a timer, flowmeter, or residual chlorine analyzer. Automatic on-off generation system operation in response to level sensors in the storage tank.

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OPTIMIZATION OF CYANIDE DESTRUCTION
by
THE ALKALINE CHLORINATION PROCESS
as related to
TREATMENT OF GOLD MILL EFFLUENTS

EXECUTIVE SUMMARY

by

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for

Supply and Services Canada
and
Environmental Protection Service
Environment Canada

DSS File No. 02SE.KE405-3-6267
KPA File No. 25021.02
September, 1983

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1 INTRODUCTION

1.1 General

Following submission of an unsolicited proposal to Supply and Services Canada in August, 1981, Ker, Priestman & Associates Ltd. (KPA) of Victoria, B. C. were awarded Contract No. 43SS.KE145-1-0497 in January, 1982.

The unsolicited proposal was formulated in response to a recognized need by both industry and the regulatory authorities for a better understanding of the capabilities and limitations of the alkaline chlorination process, which was coming into common usage in the Canadian gold milling industry, as a treatment method for cyanide-bearing effluents.

The program was sponsored by the Environmental Protection Service of Environment Canada; the scientific authority assigned to the project was:

Mr. A. Zaidi, P. Eng. - Process Development Engineer,
Wastewater Technology Centre,
Environmental Protection Service,
Environment Canada,
Burlington, Ontario.

The main Ker, Priestman & Associates Ltd. personnel involved in this study were:

J. B. Brodie, P. Eng.- Manager, Environmental Division
R. Wilkes - Senior Technician

Also involved, during the later stages of the program was:

L. Whittle - Senior Process Development Technologist,
Wastewater Technology Centre,
Environmental Protection Service,
Environment Canada,
Burlington, Ontario.

1.2 Objectives

The objectives of the program were to:

(a) determine the optimum conditions for the destruction of cyanide and other contaminants, by the alkaline chlorination process

(b) establish a valid data base relative to the effluent quality which can be routinely achieved by alkaline chlorination under optimum conditions

(c) make recommendations regarding operating controls, procedures and equipment.

1.3 Scope

The program was divided into four phases:

Phase 1 was a preliminary review of the mechanical and chemical operation of the systems to ensure that they were functioning properly. This phase was carried out by Harry Jackson, an independent consultant, under separate contract. Mr. Jackson's conclusions and recommendations are not included in this report.

Phase 2 involved a series of tests under different process conditions to determine the optimum conditions for alkaline chlorination.

Phase 3 was the routine collection of data, with each system operating under previously-established optimum conditions.

Phase 4 was the interpretation of data and report preparation.

The mines studied were identified, for the purpose of anonymity, as Mines A, B, and C. The study of Mines A and B took place between February and October, 1982, followed by the study of Mine C between December, 1982 and February, 1983.

2 CHEMISTRY

2.1 Process

A simplified block diagram outlining the main steps in the process for the recovery of gold from its ores, shown in Fig. 1, consists of the following operations:

a) crushing and grinding the ore
b) flotation of a sulfide concentrate containing the gold (Mine C only)
c) leaching the ground ore or flotation concentrate with an alkaline solution of sodium cyanide to dissolve gold from the gangue
d) filtering and washing the leached residue to separate the pregnant solution from the solids
e) recovering gold from pregnant solution by the Merrill Crowe process
f) treatment of effluents by alkaline chlorination
g) discharge of effluents to a tailings pond.

Cyanide-bearing wastes originate in gold mills from a variety of sources including, most commonly, the barren bleed solution and the cyanide leach residue. The latter is generally not treated because the presence of solids interferes with chlorination. Free cyanide, metal-cyanide complexes, thiocyanate and dissolved metals represent the major contaminants.

The following terms and symbols are pertinent:

CN_T total cyanide
CN_W weak-acid dissociable cyanide*

---

* The term "weak-acid dissociable cyanide" refers to an analytical method similar to that used for total cyanide, except that the conditions in the distilling flask are such as to encourage breakdown of nearly all cyanide complexes except the most stable, viz. those of iron and cobalt. See Section 3.1.

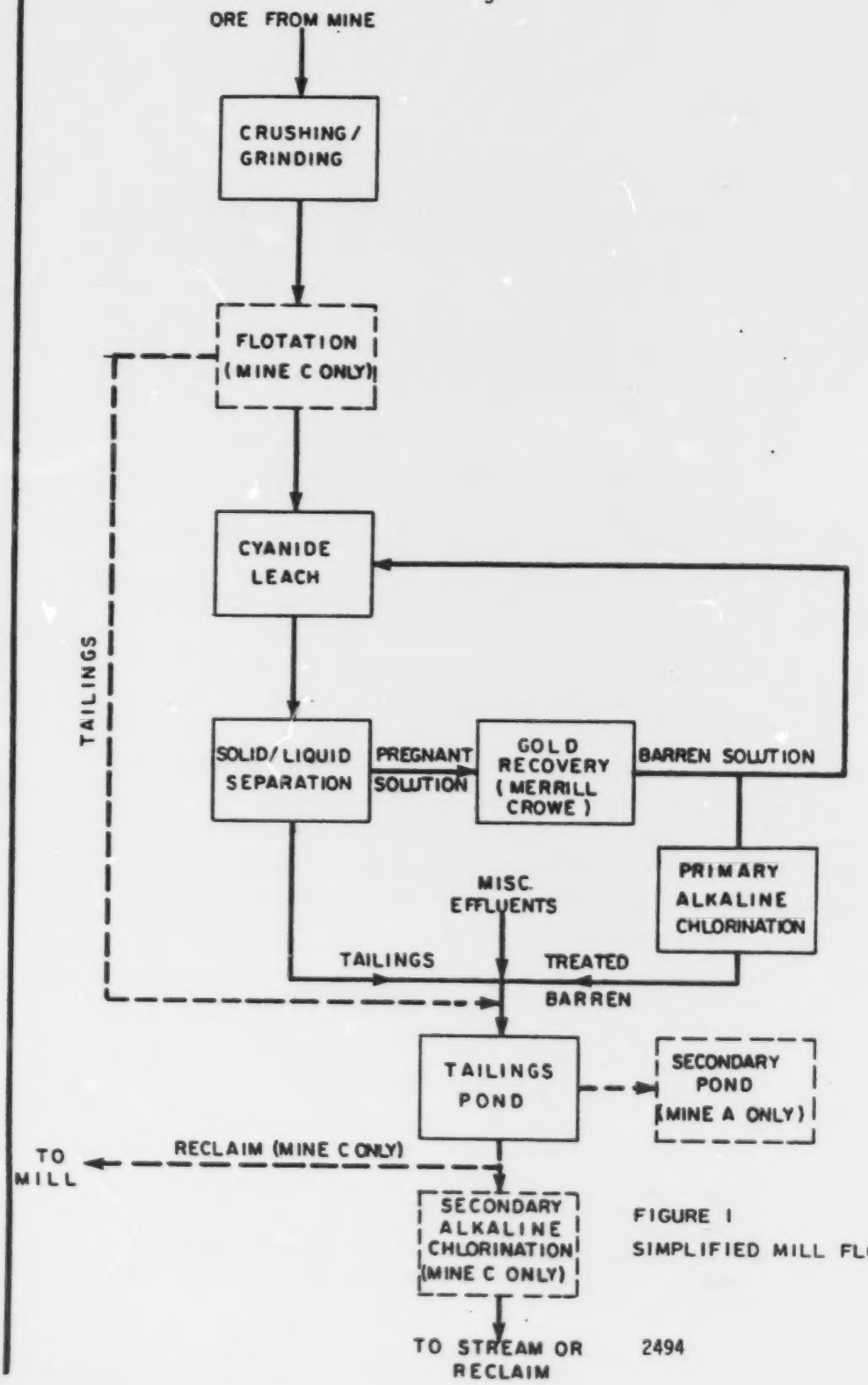

FIGURE I
SIMPLIFIED MILL FLOWSHEET

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CN_{Fe}	CN_T minus CN_W
CNS	thiocyanate
CNO	cyanate
TCR	total chlorine residual
FCR	free chlorine residual
redox	oxidation-reduction potential (relative to the saturated calomel electrode).

2.2 Alkaline Chlorination

Alkaline chlorination refers to the controlled addition of chlorine or hypochlorite at a high pH (10 - 12) for the oxidation of free cyanide and metal-cyanide complexes to the cyanate form or further to bicarbonate and nitrogen, by the following reactions:

$$CN^- + Cl_2 + 2OH^- \rightarrow CNO^- + 2Cl^- + H_2O$$
$$2CN^- + 5Cl_2 + 10(OH)^- \rightarrow 2HCO_3^- + N_2 + 10Cl^- + 4H_2O$$

A number of ancillary reactions are known to occur including the oxidation of thiocyanate to cyanate, the oxidation of metal ions and precipitation of metal hydroxides. Cyanate may hydrolyze to some extent to form ammonia and bicarbonate. The ammonia, in turn, may form chloramines or be further oxidized to nitrogen.

A knowledge of the chemistry of the solution to be treated enables an estimate to be made of its chlorine demand. According to the stoichiometry of the main reactions, chlorine consumption can almost entirely be assigned to weak-acid dissociable cyanide (CN_W) in a ratio of 2.7 parts chlorine to 1 part CN_W, and thiocyanate (CNS) in a ratio of 4.9 parts chlorine to 1 part CNS. The chlorine demand can also be determined by titrating solution samples with chlorine or hypochlorite, while monitoring the redox potential of the solution. The dosage of chlorinating agent at which the redox suddenly rises (called "saturation") corresponds with the chlorine demand. If analyses of the chlorinated sample for total chlorine residual (TCR) are obtained during preparation of redox curves, an approximately linear relationship is obtained between TCR and chlorine dosage, beyond the saturation point.

3 METHODS

The program objectives were achieved by collection and interpretation of operating data and field measurements such as pH, redox, chlorine residual and flowrates together with analysis of samples by a commerical laboratory (CAN TEST LTD.) for total cyanide, weak acid dissociable cyanide, cyanate, thiocyanate, dissolved and total metals, and several other parameters. Attention was focussed on the cyanide bearing waste streams and final effluents.

Sampling and analysis methods are summarized below:

3.1 Total Cyanide (CN_T) and Weak Acid Dissociable Cyanide (CN_W)

Because of the reported adsorption of cyanide by solids(2), all samples collected for CN_T, CN_W, CNS and CNO were first filtered on a glass-fibre filter; the pH was then raised to 12 with NaOH and the sample dechlorinated, if necessary, with sodium arsenite ($NaAsO_2$). The $NaAsO_2$ was added until the total chlorine residual (TCR) of the sample was below detection. A heavy precipitate which formed upon $NaAsO_2$ and NaOH addition was not removed prior to analysis, except during special quality assurance checks.

The analytical procedure for CN_T is a modification of the standard acid reflux/distillation using hydrochloric acid and hydroxylamine hydrochloride, followed by colourimetric determination of CN(2). The method for CN_W is the same except that the reflux/distillation is carried out at pH 4.5 using an acetic acid-sodium acetate buffered solution, with zinc acetate to prevent decomposition of iron-cyanide (2).

3.2 Thiocyanate (CNS)

The sample preparation is the same as described for CN_T and CN_W. Thiocyanate was determined colourimetrically using ferric nitrate (1).

3.3 Cyanate (CNO)

The sample preparation is the same as described for CN_T and CN_W. Cyanate was determined by conversion to ammonia which was then measured by ammonia selective electrode (1).

3.4 Dissolved and Total Metals

Samples for analysis of dissolved metals were field-filtered on a 0.45 micron membrane filter and acidified with nitric acid. Total metals samples were not filtered. Problems were occasionally encountered with precipitates which formed upon acidification, and in such cases the analytical laboratory was then required to further digest the samples before metal analysis. Analysis was mainly by plasma spectrograph, but sometimes direct atomic absorption was used for cobalt, and hydride generation atomic absorption used for arsenic (1).

3.5 Field Analysis

Field analyses were performed for pH, redox, temperature, total chlorine residual (TCR) and free chlorine residual (FCR).

All redox measurements were made with respect to the saturated calomel electrode (SCE).

Total chlorine residual was measured by titrating a sample aliquot plus potassium iodide and acetic acid, with sodium thiosulfate using starch as endpoint indicator - i.e. Iodometric Method I (1).

Starch/iodide test paper was used as an indicator of the presence of free chlorine residual (FCR), although the method is not actually specific to FCR. During the testwork at Mine C, a DPD colourimetric test kit was used to determine FCR.

4 PROCESS DESCRIPTION

4.1 Mine A

The process used at Mine A follows the basic circuit shown on Fig. 1. The ore is ground and leached directly and subjected to conventional gold recovery techniques. Tailings consisting of leached and washed filter residue plus treated barren bleed (batch discharge) are conveyed to a tailings pond. Pond supernatant is periodically pumped to a secondary pond for natural degradation and exfiltration.

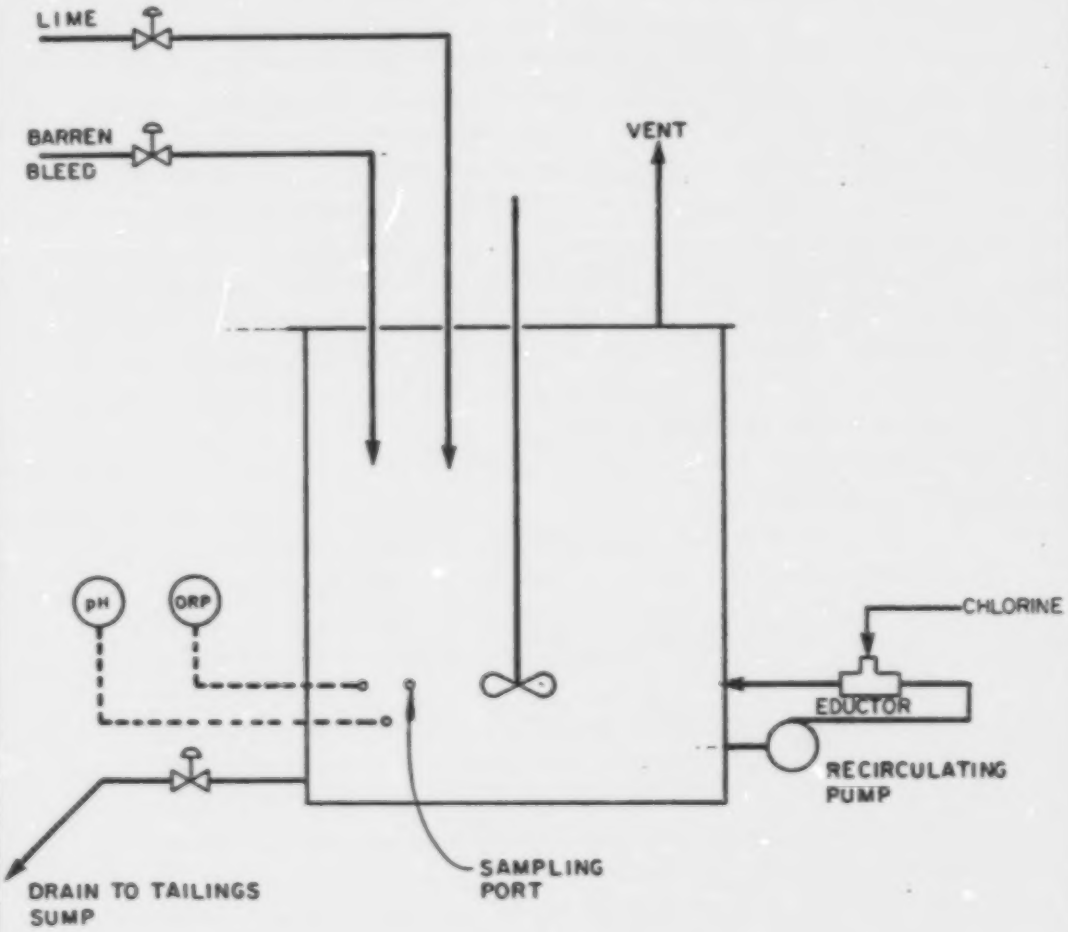
A batch alkaline chlorination process (Fig. 2) is utilized for treatment of barren bleed solution, with gaseous chlorine supplied from 900 kg (1 ton) cylinders. Dissolution of chlorine occurs in an eductor supplied with recirculated treated barren from the tank. Control of pH is maintained by lime slurry addition. Instrumentation consists only of pH and redox sensors and all controls are manual. Treatment of three batches per day generally is in balance with the need to release barren bleed as dictated by water balance. Each batch takes 6 - 8 hours at the maximum chlorination rate, given the throughput of the chlorinator. A rise in redox signals the completion of reaction to the operator, who then confirms it by checking for the presence of chlorine residual in the tank contents using starch/iodide test paper; the batch is then dumped and a new batch is commenced.

4.2 Mine B

The milling operation of Mine B also follows the simple circuit configuration of Fig. 1. The tailings and barren solution contain higher levels of cyanide than Mine A for two reasons:

a) the cyanide consumption is higher due to the high ore silver content, which results in more concentrated cyanide solutions,

b) use of a belt filter for secondary filtration, which has experienced poor washing efficiency and, in addition, required a belt-cleaning spray cycle which introduces an additional cyanide-laden effluent to the waste.



NOTE

ORP = REDOX

FIGURE 2 - ALKALINE CHLORINATION PLANT - MINE A

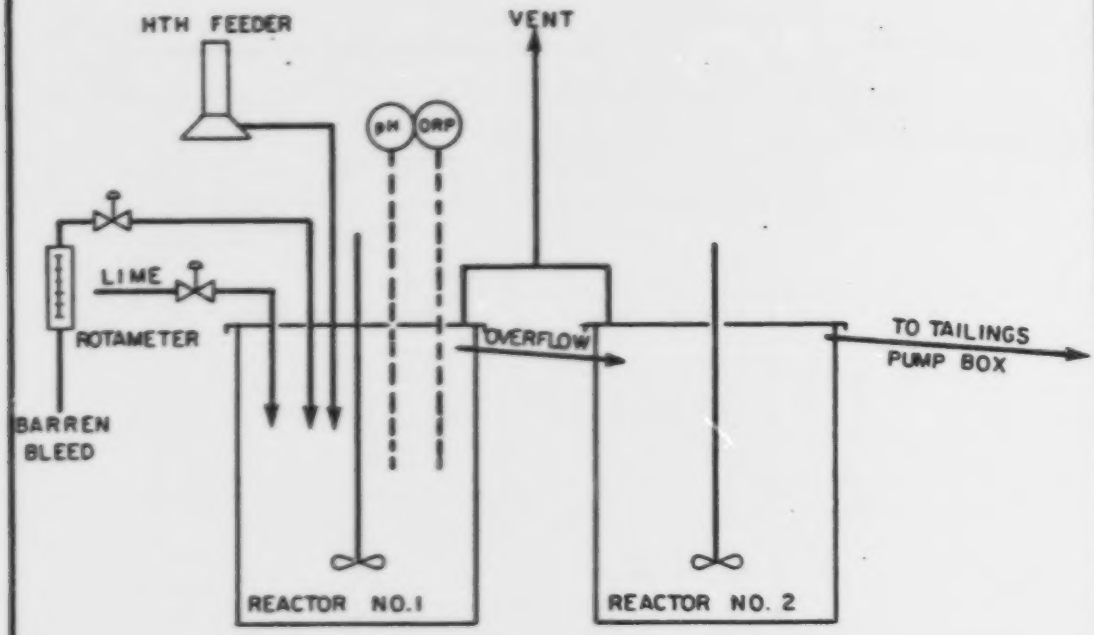
The tailings pond supernatant exfiltrates. No secondary pond is provided.

The alkaline chlorination circuits are also different. Mine B utilizes a continuous treatment system, feeding solid calcium hypochlorite (HTH) to the first of two tanks in series (Fig. 3). Redox and pH sensors are immersed in the first tank and connected to indicator/recorders. HTH is fed into the system at a rate which is known to result in the presence of a chlorine residual at the outlet, and also on the basis of long-term trends in the level of cyanide in the tailings pond. Barren bleed, lime, and HTH feed rates are controlled manually. The final effluent discharged to the tailings pond consists of leached and washed filter residue, treated barren bleed and miscellaneous streams.

4.3 Mine C

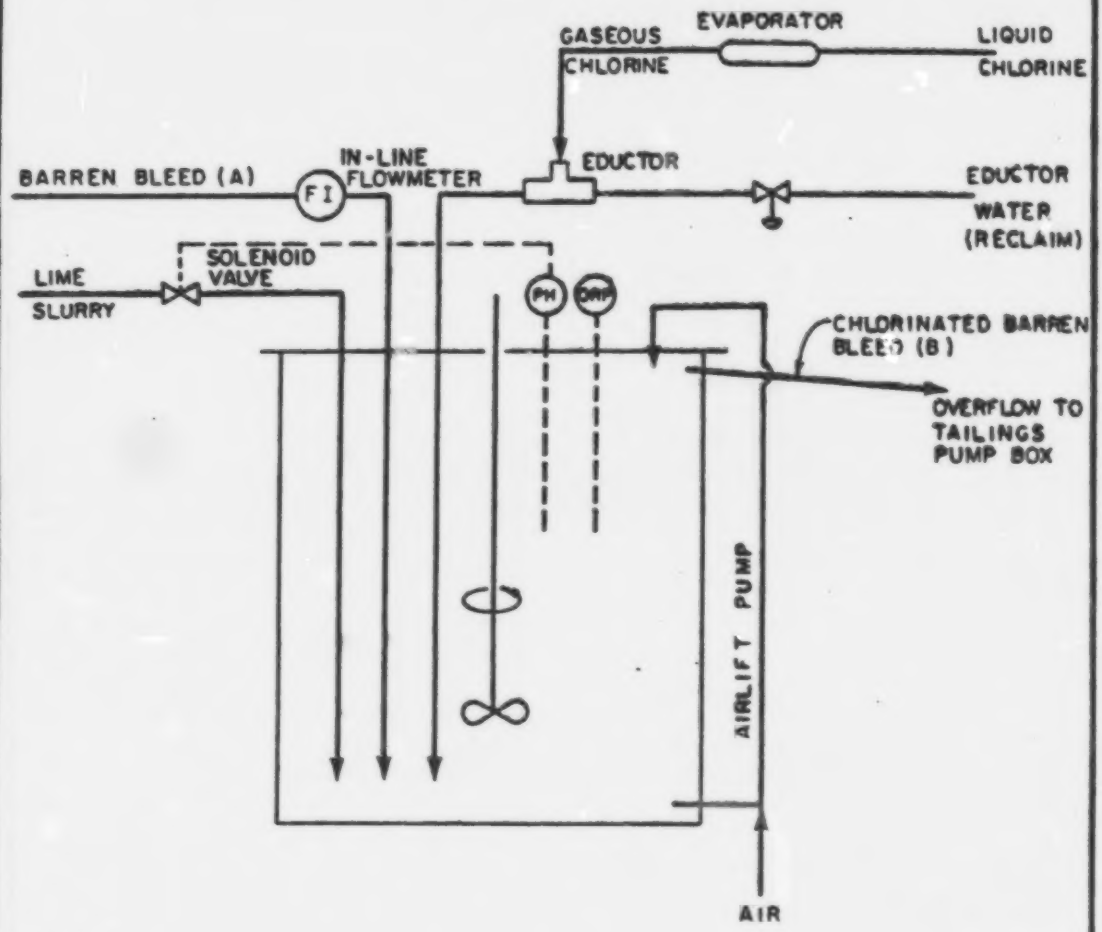
The Mine C mill and treatment systems are the most complex of the three operations studied. The feed to the leaching circuit consists of a sulfide concentrate prepared from the ore by primary flotation. After leaching and filtering, the residue is re-floated to recover graphite which is then re-leached to recover gold. Almost all process water needs are met by reclaiming water from the tailings pond. Barren bleed is treated in a primary alkaline chlorination plant prior to joining the tailings. A secondary alkaline chlorination plant is employed to treat a portion of pond reclaim water which must be discharged from the system in order to maintain water balance. The leaching of gold from a pyrrhotite concentrate gives rise to high iron and thiocyanate levels in mill solutions and effluents. In an effort to resolve metallurgical and environmental problems the mill and effluent treatment systems have been subject to almost continuous modification prior to, during, and after the testwork period.

Primary alkaline chlorination of barren bleed is carried out continuously in a disused leaching tank which provides about 8 hours of detention time (Fig. 4). Gaseous chlorine is supplied through an



NOTE
ORP = REDOX

FIGURE 3 - ALKALINE CHLORINATION PLANT - MINE B



LEGEND

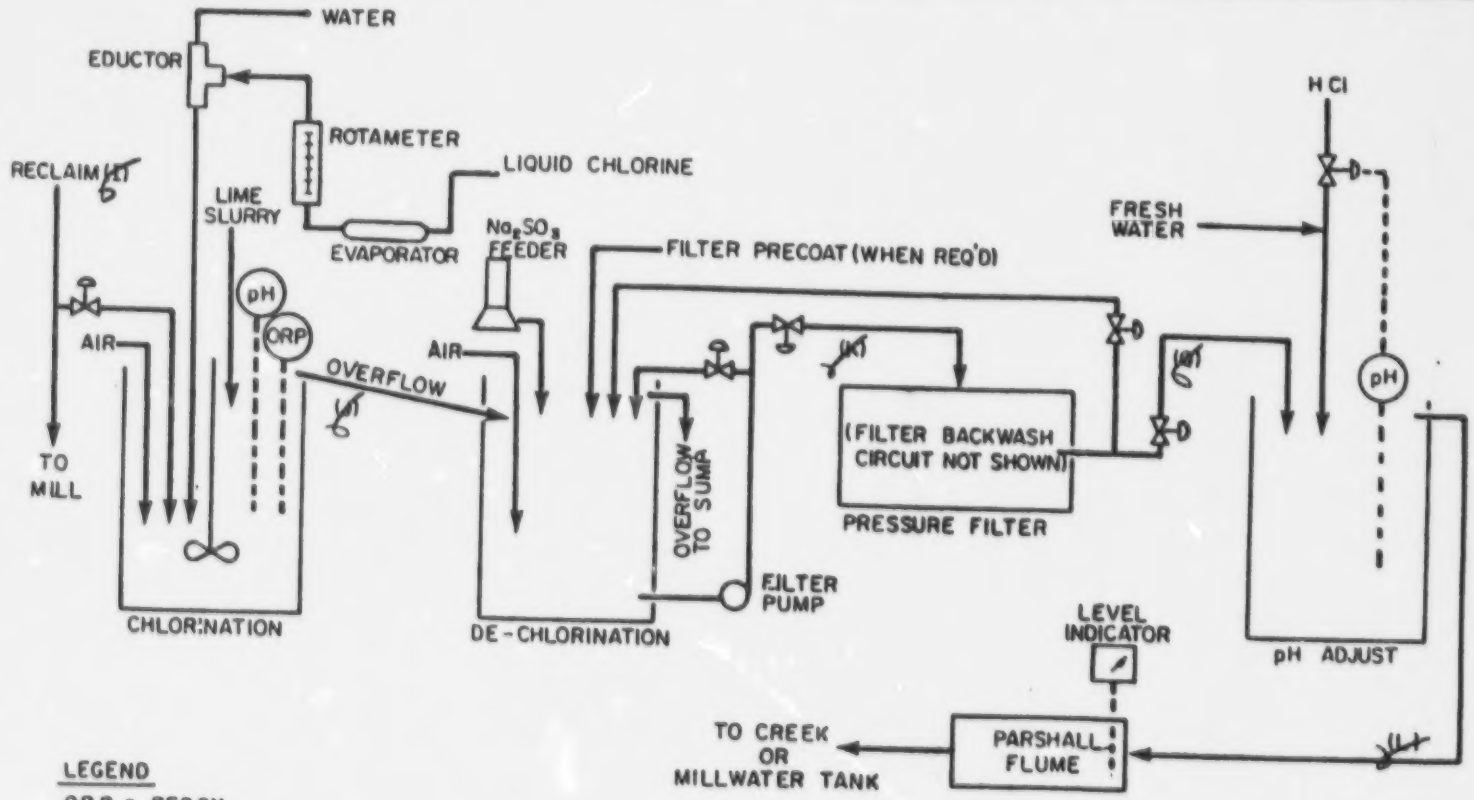
SAMPLE IDENTIFICATION IN PARENTHESES

ORP = REDOX

FIGURE 4 - MINE C - PRIMARY ALKALINE CHLORINATION

evaporator from three 900 kg (1 ton) cylinders in parallel. Control of pH is automatic, using lime slurry. Redox control was manual during the testwork period but is now automatic.

The secondary treatment plant (Fig. 5) provides continuous chlorination, dechlorination, filtration and pH adjustment of pond reclaim water prior to release to a stream. Automatic controls are gradually being installed although most functions were manual at the time of the testwork. Gaseous chlorine is supplied from 900 kg (1 ton) cylinders (now by way of an evaporator). A feeder supplies dry sodium sulfite for dechlorination. A pressurized pre-coat disc filter with backwash capability removes suspended solids, and final pH reduction is accomplished with hydrochloric acid. Measurement of redox provides a control signal for chlorination. Mill personnel indicated their intention to also utilize redox for control of dechlorination, subsequent to the testwork period. The detention time in the chlorination tank varies depending on the influent flowrate, but averages 45 minutes.



LEGEND

ORP = REDOX

SAMPLE IDENTIFICATION IN PARENTHESES.

NOTE: MODIFICATIONS MADE TO PLANT AFTER TESTWORK PERIOD NOT SHOWN

FIGURE 5 - MINE C - SECONDARY ALKALINE CHLORINATION

5 RESULTS - PRIMARY ALKALINE CHLORINATION

A summary of the results obtained, including percent removal, for primary alkaline chlorination is shown in Table 1. The quality of the barren being treated varied considerably between the three mines. The barren solution at Mine A contained the lowest levels of CN_T, CN_W and CNS and, consequently, had the lowest titration chlorine demand (3.2 g/L). Mine B barren solution had the highest strength solution in terms of CN_W and, coupled with a high CNS, displayed an elevated chlorine demand (9.2 g/L); however, diss. Fe was the lowest at Mine B. At Mine C, both CN_W and CNS were high, resulting in the highest chlorine demand of the three mines (12.5 g/L).

Removal of CN_T during alkaline chlorination was inversely related to iron levels, and mean removal varied between 83 and 99.6%. Percent removals were not determined for CN_{Fe} because of the poor confidence in these values, obtained by subtraction of CN_W from CN_T. However, the low removal of iron (max. 15%) for Mines A and B is consistent with the belief that alkaline chlorination is not effective in destroying iron-cyanide complexes; the higher apparent removal of iron at Mine C is due mainly to dilution from reclaim water added to the system along with barren.

Based on mean values, removal of CN_W was 99.8% or greater in all cases, corresponding with residual levels of 0.5 - 1.0 mg/L in the treated barren. Dissolved zinc and copper were 95 - 99.6% removed.

Table 1

Primary Alkaline Chlorination

Parameter	Barren Solution Initial Level (mg/L) mean	Barren Solution Initial Level (mg/L) std.dev.	Treated Effluent Final Level (mg/L) mean	Treated Effluent Final Level (mg/L) std.dev.	Mean % Removal
MINE A					
Chlorine demand	3200				
CN_T	310	120	25	15	92
CN_W	220	63	0.49	0.55	99.8
CN_{Fe}	86	90	24	14	
CNS	330	58	int.		
CNO	130	94	330	240	
Cu D	10	4.2	0.33	0.40	97
Fe D	9.4	5.4	8.0	4.5	15
Zn D	93	13	1.4	0.93	98
TCR			320	520	
MINE B					
Chlorine demand	9200				
CN_T	2000	670	8.3	5.3	99.6
CN_W	1900	630	0.69	1.1	99.96
CN_{Fe}	100	79	7.6	5.4	
CNS	1100	320	int.		
CNO	320	460	2200	2200	
Cu D	290	150	5.0	2.8	98
Fe D	2.4	2.1	2.8	1.9	0*
Zn D	740	190	3.9	1.1	99.5
TCR			2800	2300	
MINE C					
Chlorine demand	12,500				
CN_T	1000	250	170	48	83
CN_W	710	180	0.95	1.4	99.9
CN_{Fe}	320	150	170	47	
CNS	1900	270	int.		
CNO	52	8.2	230	64	
Cu D	97	59	0.38	0.70	99.6
Fe D	100	36	53	20	47
Zn D	110	43	5.8	3.1	95
TCR			190	150	

int. = interference

6 RESULTS - SECONDARY ALKALINE CHLORINATION

Table 2 displays a summary of test results for the secondary alkaline chlorination plant, which only existed at Mine C. Because of the low strength of the pond reclaim water being treated, the chlorine demand was also low (mean value 0.80 g/L).

As was the case for the primary plant, the final CN_{Fe} (and thus CN_T) level was dependent upon the iron concentration and found to be present in approximately the predicted weight ratio of 2.8 parts CN to 1 part Fe, which confirms its existence as the ferro- or ferricyanide complex $[Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}]$.

Although the final mean CN_W concentration (0.30 mg/L) was lower than that obtained for any of the primary plants, the percent removal was only 97% due to the lower initial concentration.

An apparent 27% removal of iron is believed to be partially due to known (6%) dilution from fresh water added with HCl for pH adjustment but otherwise the result is inconsistent with the CN_{Fe} data (which actually showed a concentration increase, or a negative removal). Removal of Cu averaged 98.5% and zinc was below detection in the effluent. Treatment appears to have been somewhat effective in removal of ammonia (70%) although known sample preservation problems suggest caution with respect to this conclusion.

Table 2

Secondary Alkaline Chlorination

MINE C ONLY

Parameter	Reclaim Water[1] Initial Level (mg/L)		Treated Effluent[2] Final Level (mg/L)		Mean % Removal[3]
	mean	std.dev.	mean	std.dev.	
Chlorine demand	800				
CN_T	21	4.5	12	0.91	33
CN_W	11	2.9	0.30	0.39	97
CN_{Fe}	10	4.3	11	0.88	0 [4]
CNS	99	31	int.		
CNO	43	7.9	40	18	
Cu D	9.1	1.8	0.12	0.16	98.5
Fe D	5.4	0.57	3.8	0.73	27
Zn D	0.033	0.018	<0.015		
TCR			0.2	0.6	
NH_3/NH_4	5.8	0.61	1.5	1.5	70

int. = interference

Notes:

(1) Data for reclaim water pertains to Campaigns 1, 2 and 3.
(2) Data for treated effluent pertains to Campaign 3 only.
(3) Mean % removal calculated on basis of influent and effluent for Campaign 3.
(4) a CN_{Fe} concentration increase was obtained - removal deemed to be 0%.

7 RESULTS - OTHER EFFLUENTS

Because a gold milling operation, its tailings discharge, and effluent treatment plants are interrelated portions of a total system, it is relevant to consider the contaminant levels of other effluents.

The data in Table 3 illustrate that the discharges to the tailings ponds of all three mines contained significant levels of all relevant chemical parameters, in spite of treatment of barren bleed to low levels by alkaline chlorination. Monitoring data show that the additional contaminants mainly originate with leach residues discharged from the filters. A specific case of a sump discharge which contained water from the spray cleaning of a belt filter cloth was another major source at Mine B. Total chlorine residual was measurable in the tailings discharge, originating from the treated barren.

The quality of the tailings pond supernatant (Table 4), for most parameters, was superior to the tailings discharged, and likely reflects the effect of natural processes. Sampling of pond supernatants at Mines A and B took place in the late spring or summer; compared with the tailings discharged, lower Fe, CN_T and CN_{Fe} levels in pond supernatant are indicative of the breakdown of iron-cyanide complexes. By comparison Mine C was sampled during the winter when ice cover and cold would prevent natural breakdown, and only a small difference was noted between tailings and pond supernatant (reclaim) concentrations.

The use of a secondary pond for final effluent polishing and exfiltration is unique to Mine A. Results, presented in Table 5, demonstrate the effectiveness of the natural treatment of effluent in a shallow pond, isolated from the influence of new tailings input. In this case, essentially all parameters were reduced in comparison to the tailings pond supernatant.

Table 3

Quality of Discharge to Tailings Pond

Parameter	Mine A *(mg/L)		Mine B (mg/L)		Mine C (mg/L)	
	mean	std.dev.	mean	std.dev.	mean	std.dev
CN_T	22	8.6	190	140	25	12
CN_W	4.3	6.5	170	130	13	4.8
CN_{Fe}	18	11	20	16	12	8.4
CNS	int.		int.		98	26
CNO	300	180	N.D.		71	22
Cu D	0.92	1.3	55	31	10	3.9
Fe D	6.0	2.8	1.0	0.77	7.3	4.5
Zn D	0.59	0.46	31	20	0.074**	
TCR	16	15	89	83	N.D.	

* during release of treated batch

** max. value recorded; several values <0.015 mg/L

int. = interference

N.D. = not determined

Table 4

Quality of Tailings Pond Supernatant

Parameter	Mine A (mg/L)		Mine B (mg/L)		Mine C* (mg/L)	
	mean	std.dev.	mean	std.dev.	mean	std.dev
CN_T	14	6.3	31	22	21	4.5
CN_W	11	5.0	29	22	11	2.9
CN_{Fe}	3.2	2.2	2.1	1.5	10	4.3
CNS	30	3.5	11	3.6	99	31
CNO	37	24	200	52	43	7.9
Cu D	1.6	0.32	9.4	8.6	9.1	1.8
Fe D	0.14	0.10	0.17	0.11	5.4	0.57
Zn D	2.8	1.4	9.8	6.9	0.033	0.018
TCR	0.0		72	16	N.D.	
NH_3/NH_4	N.D.		N.D.		5.8	0.61

* reclaim water quality

N.D. = not determined

Table 5

Quality of Secondary Pond Supernatant

MINE A CNLY

Parameter	mean	std.dev
CN_T	1.3	1.3
CN_W	1.0	1.1
CN_{Fe}	0.38	0.55
CNS	6.9	1.7
CNO	41	11
Cu D	0.76	0.49
Fe D	0.34*	
Zn D	1.2	1.7
TCR	0.0	

* max value recorded; several values < 0.03

8 QUALITY ASSURANCE

A quality assurance (QA) program was integrated into the testwork. It consisted of the routine preparation of unspiked and spiked replicate samples, and special sample preparations and analyses where problems were identified. The results of this program are presented in a separate volume.

The program demonstrated the difficulty of obtaining reliable analyses of total and weak acid dissociable cyanide. Selected QA data which are believed to represent most typically the statistics pertaining to each of the sample types are shown in Table 6.

In this table, data which were grossly erroneous, pertained to unsuitable spike levels, resulted from double-filtered samples, or to samples known to have been excessively exposed to light have been excluded.

It was concluded from the QA program that:

(1) Precision (relative standard deviation) and accuracy (spike recovery) both generally improved at higher CN_T and CN_W concentrations. At the levels encountered, both precision and accuracy were generally better for CN_T than for CN_W.

(2) CN_W, and to a lesser extent CN_T, are affected by exposure to light. Consistent differences were found during one QA series between otherwise identical replicate samples known to have been shipped in translucent containers and those shipped inside coolers:

Shipped in Coolers		vs.	Shipped in Translucent Containers	
CN_T	CN_W		CN_T	CN_W
48.5	0.11		51.5	4.26
44.0	0.17		45.7	4.01
5.27	5.10		5.77	5.29
1.49	1.37		2.08	1.40
258	0.40		260	3.39
260	0.55		252	6.79

In these examples, the samples having the highest CN_T concentrations were observed to release the most CN_W.

In further support of this theory, a sample spiked with 25 mg/L CN_T as $K_3Fe(CN)_6$ was found to release 17 mg/L CN_W over a period of 36 hours, if the sample was exposed to normal daylight.

These results demonstrate the need to isolate samples from the light during sample preparation, shipping, storage and analysis.

(3) Long sample storage times (up to 6 weeks) prior to analysis were believed to be a factor which contributed to erratic CN_T and CN_W results during the QA program. However, the effect of sample storage time could not be isolated from the effect of variable sample exposure to light as laboratory records do not provide this information.

(4) A series of tests which was carried out to evaluate the effect of final filtering of dechlorinated samples (see Section 3.1) indicated that the precision and accuracy of CN_T and CN_W analyses were not improved in any consistent way by final filtration. At a low level of CN_T (5 mg/L) the loss

Table 6

Quality Assurance Data

		CN_T			CN_W		
Mine	Type	Level (mg/L)	Precision S'(%)	Spike Recovery (%)	Level (mg/L)	Precision S'(%)	Spike Recovery (%)
A	Barren	230	-	101 - 110	212	-	108 - 114
B	Barren	1410	-	98 - 101	1325	-	98 - 100
C	Barren	1065	-	94 - 98	893	-	84 - 87
A	Chlor.barren	48.5	1.8	96 - 97	0.11	20	67 - 113
B	Chlor.barren	5.27	4.7	79 - 133	5.10	4.7	85 - 111
B	Chlor.barren				0.12	42	84 - 96
C	Chlor.barren	258	4.1	76 - 88			
C	Chlor.barren				3.39	21	83 - 91
C	Chlor.barren				0.51	4.0	94 - 104
C	Tr.Reclaim	16.0	1.4	94 - 98	0.54	28	83 - 118
B	Tailings Supernatant	17.4	3.8	94 - 97	14.8	10	101 - 108
C	Tailings Supernatant	25.6	6.2	83 - 96	13.5	2.6	86 - 96
A	Pond No.2	0.41	50	68 - 130	0.21	91	25 - 185

due to final filtration was substantial (up to 75% recorded). The results were inconsistent with respect to CN_W. Due to the loss of CN_T, final filtration is not recommended.

On this basis, it might be suspected that lack of care in thoroughly shaking the sample bottle prior to obtaining the aliquot for analysis might considerably affect the CN_T results.

(5) An evaluation of the effect of variable amounts of sodium arsenite used for sample dechlorination within the range of one-to-two-times the stoichiometric requirement for dechlorination, was inconclusive. The larger dosage appeared to decrease the CN_T concentration and increase the CN_W concentration. However, precision and accuracy were not affected in any consistent way. Further testwork is required over a greater range of sodium arsenite additions.

9 CONCLUSIONS

1. Treatment of gold mill barren solution (primary process) by alkaline chlorination was found to be capable of removing >99% of weak acid dissociable cyanide from influents having a wide variation in composition. Residual CN_W concentrations were:

	Mean (mg/L)	Std.Dev. (mg/L)
Mine A	0.49	0.55
Mine B	0.69	1.1
Mine C	0.95	1.4

2. Alkaline chlorination of tailings pond reclaim (secondary process), practiced only at Mine C, achieved 97% removal of weak-acid dissociable cyanide, producing a final effluent containing a mean CN_W of 0.30 mg/L with a standard deviation of 0.39 mg/L.

3. Primary and secondary alkaline chlorination were able to achieve up to an apparent 47% dissolved iron removal only where considerable dilution of influent streams existed; calculation on a mass basis gave a removal close to 0%. In other cases, the iron removal was, at most, 27%.

4. Final values of CN_{Fe} (i.e. CN_T - CN_W) in treated effluents were dependent upon dissolved iron levels; the ratio of CN:Fe was approximately 2.8:1, which is consistent with the stoichiometry of ferro- and ferri- cyanide complexes. Because of the low CN_W concentrations in treated effluents, the final CN_T and CN_{Fe} levels were very similar, and thus it can be concluded that alkaline chlorination is not capable of treating effluents containing high iron levels, to low CN_T concentrations.

5. Removal of dissolved copper and zinc exceeded 97% and 95%, respectively. Residual concentrations were:

	diss. Cu (mg/L)		diss. Zn (mg/L)	
	mean	std.dev.	mean	std.dev.
Mine A (Primary)	0.33	0.40	1.4	0.93
Mine B (Primary)	5.0	2.8	3.9	1.1
Mine C (Primary)	0.38	0.70	5.8	3.1
Mine C (Secondary)	0.12	0.16	<0.015	-

6. Both chlorine residuals and ammonia were found to be present in effluents treated by alkaline chlorination. Ammonia was apparently reduced by alkaline chlorination and subsequent processes in use at Mine C for treating tailings pond reclaim water.

7. Only at Mine B was any evidence found for an optimum redox potential (above saturation) which maximized the removal of cyanide and dissolved metals. However, this was not deemed to be a practical operating value, because of the steepness of the curve at this redox; in other cases the results appeared to be unaffected by the amount of excess chlorine present (as reflected by redox).

8. Total chlorine residual (TCR) concentrations in treated effluents were a reflection of any excess used during treatment. The continuous process used at Mine C produced the lowest TCR (190 mg/L, mean) in treated effluent and the continuous process at Mine B which intentionally used excess calcium hypochlorite resulted in the highest TCR (2800 mg/L, mean). However, although it was evident that downstream reactions are effective in reducing TCR levels considerably, TCR may be detectable in tailings pond supernatant, as was the case at Mine B.

2518 9. Both batch and continuous systems were found to be suitable for alkaline chlorination of gold mill effluents, with little

evidence to recommend one system over the other from the viewpoint of effluent quality. The batch system has the advantages of simplicity and more precise control of final conditions; it would therefore appear to be most economical in usage of chlorine. The continuous process requires less operator attention, which should then be supplemented with more sophisticated instrumentation (i.e. automatic control of redox). If automatic control of redox is not employed, the system must generally be operated with a surplus of chlorine in order to ensure complete oxidation under varying influent conditions, at the expense of higher chlorine consumption.

10. The final redox (in the case of batch systems) or the control redox (in the case of continuous systems) was not generally found to be critical to effluent quality provided that a chlorine residual is present in the treated effluent (exception noted in 7 above). The preparation of redox titration curves provides relevant information on the redox response to increasing chlorine dosages, but actual redox control targets are better determined by recording of corresponding redox and chlorine residuals in full-scale operating systems.

11. Carbon balances prepared for primary and secondary alkaline chlorination plants consistently showed an unaccounted loss of carbon in the treated effluents, i.e. the cyanate level was never high enough to account for the destruction of oxidizable species. There is insufficient data to indicate whether this unaccounted loss is due to conversion of cyanate to ammonia (or nitrogen) and bicarbonate, or to analytical problems.

12. Washed filter residues were determined to be the largest contributors of cyanide to tailings ponds. Additional sources were flotation tailings and other effluents containing pond reclaim water, and belt filter cleaning spray waters, in specific instances.

13. Although not within the scope of the study, there was some evidence, on the basis of total cyanide, weak-acid dissociable cyanide and dissolved iron relationships in discharges and pond supernatants to suggest the natural degradation of iron cyanides, under summer/fall conditions. No evidence was found for this phenomenon during winter sampling.

14. A secondary alkaline chlorination plant treating tailings pond supernatant appears to be at least a partial answer to the problem of untreated cyanide-bearing effluents discharged to tailings ponds. The use of a secondary pond system for polishing of tailings pond supernatant was also demonstrated to have a positive effect upon effluent quality.

15. Problems were encountered with the analyses of total and weak-acid dissociable cyanide, cyanate, thiocyanate, and ammonia. Isolation of samples from the light prior to analysis appears to be a critical factor, particularly with weak-acid dissociable cyanide.

10 RECOMMENDATIONS

(1) Ammonia, free chlorine residual, and combined chlorine residual are products of the chemical reactions in alkaline chlorination of gold mill effluents; the presence of these constituents in addition to cyanide and dissolved metals should be considered during design of future treatment systems and monitoring programs.

(2) Future operations should consider the following measures to minimize cyanide discharges to the environment:

- improved washing of tailings solids
- routing of all contaminated streams not containing solids, to alkaline chlorination
- alkaline chlorination treatment of tailings pond supernatant in addition to, or in place of, barren bleed
- the use of secondary treatment ponds for final effluent polishing
- if removal of iron cyanide is required in order to meet quality obectives for total cyanide, then an alternative process to alkaline chlorination should be considered.

(3) The various design recommendations for alkaline chlorination plants may be summarized as follows:

- properly designed and installed, both batch and continuous systems have advantages, and should be considered for use; no significant effluent quality advantages can be ascribed to one system or the other.
- the importance of pH control, in order to ensure the completion of reactions and to prevent toxic gas release, suggests that pH control be automatic for both batch and continuous systems. Audible alarms are required to warn of low pH conditions.
- whereas none of the systems studied employed redox-based automatic chlorine control (at the time of the testwork)

balancing of chlorine demand/supply. The use of automatic control of chlorine based on redox is therefore recommended for continuous systems.

- automatic control of chlorine supply in a batch system would not be appropriate, except possibly for chlorine supply shut-off in response to a minimum pH condition or batch completion. However, the one batch system observed was found to function easily with manual controls, and therefore automatic control is not recommended.
- control valves and other equipment which may have to be serviced during system operation, should be installed in such a location that exposure to toxic gases produced during the chlorination reaction, is avoided.
- reaction tanks should be covered and adequate ventilation provided.
- the need for frequent inspection, calibration, and cleaning of pH and redox sensors, suggests that they be easily accessible.
- proper feeding and metering equipment for reagents is imperative. Dry feeders should be designed to deliver, without dusting or plugging, the material being fed. They should be capable of fast, repeatable rate adjustment and be easily calibrated.
- of the oxidants studied, gaseous chlorine or liquid chlorine plus evaporators (for chlorine consumption exceeding 900 kg/d) supplied from cylinders constitutes the most convenient form.
- dissolution in water using an eductor is the conventional means of introducing gaseous chlorine into the effluent. Fresh water economies were successfully gained in two cases by use in the eductor of recycled, partially-treated effluent, ~~for the batch system studied,~~ and by use of tailings pond reclaim water in two of the continuous systems studied. Provided the eductor is located physically close to the point of application, there appears to be no reason why such effluents cannot

be used as a carrier for chlorine. Direct sparging of chlorine was not in use, and therefore cannot be commented upon.

- suitable equipment for removal of solids must be employed if the metal hydroxides precipitated during alkaline chlorination are of concern. One possible treatment option is flocculation and settling followed by filtration.

(4) Operational recommendations are as follows:

- provision of on-site technical assistance during start-up of alkaline chlorination systems.
- provision of competent analytical services for process tune-up and routine quality control.
- routine process supervision and monitoring of operating data.
- operator education regarding process chemistry, control targets and potential hazards should be provided. The importance of maintaining pH above 10.5 during alkaline chlorination so as to prevent toxic gas release should be emphasized. These and other pertinent matters may be outlined in an Operation Manual.
- redox and pH sensors must be regularly cleaned of scale and checked for breakage. This frequency should be once/day until experiences proves otherwise.
- redox and pH indicating and control instruments require regular calibration. Procedures recommended by the manufacturer should be followed in this regard.
- redox curves should be prepared for effluents on a regular basis (say, twice per week) in order to provide guidance as to relative chlorine dosages.
- the final redox (in the case of batch systems) or operating redox (in the case of continuous systems) is not critical to system performance, provided that a chlorine residual is present in the treated effluent. Provision for checking chlorine residual by the

its use. Use of starch/iodide test paper is the simplest method but will likely result in an over-usage of chlorine due to its insensitivity at the proper pH for alkaline chlorination. The final residual chlorine levels may then be related, by experience, to redox readings which would be used on a routine basis for control purposes.

(5) Because serious problems were encountered, more work needs to be done, under controlled laboratory conditions, to evaluate sampling and analysis methods for

- total cyanide
- weak-acid dissociable cyanide
- cyanate
- thiocyanate
- ammonia

relative to gold milling effluents.

REFERENCES

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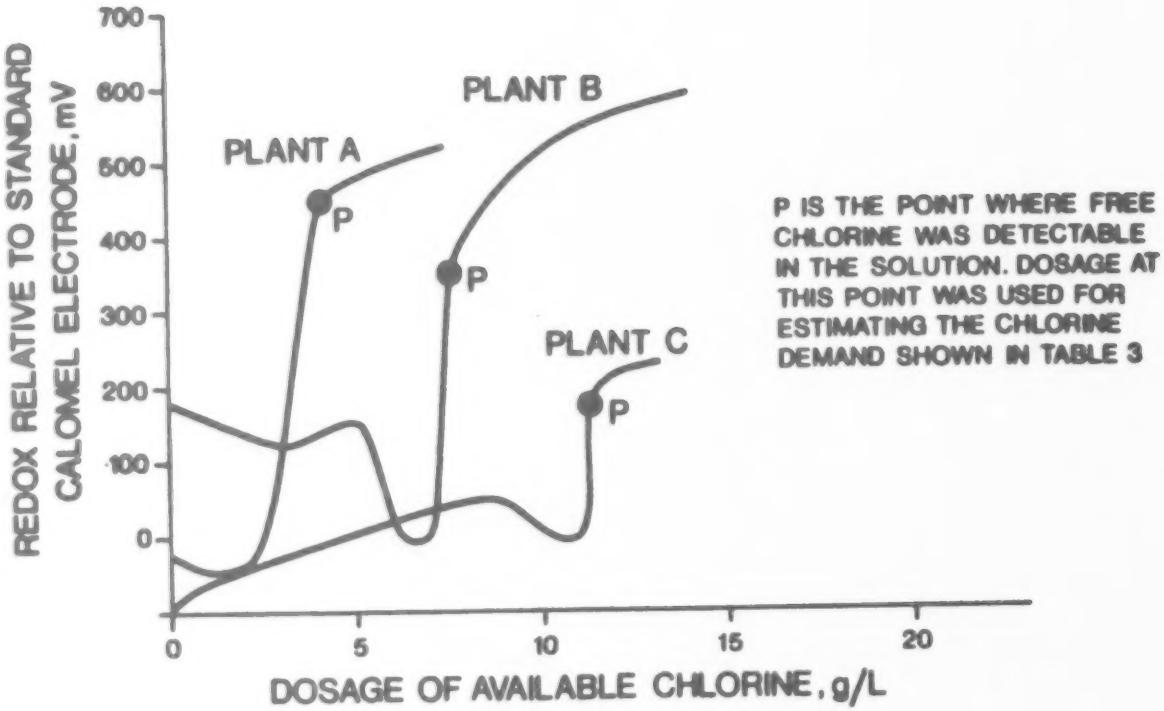

FIGURE 7. TYPICAL REDOX CURVES FOR THE INFLUENTS TO PLANTS A, B AND C

CYANIDE DETOXIFICATION BY SO_2-AIR

Cyanide has been removed from flotation pulps since the 1940's at Emperor Gold Mine, Fiji RANDOL (1982), COLBERT (date?) and at Lake Shore Mines Ltd. in Ontario BLOMFIELD et al. (1941) and WILLIAMSON et al. (1947) to improve flotation performance. In these cases copper was present in the pulps.

Since 1982 INCO Ltd. have been marketing, demonstrating and expounding on the merits of an SO_2-Air copper catalyzed cyanide destruction process which has been installed in at least four small gold mining operations to date and tested successfully on a host of other pulps. SO_2-Air when compared with alkaline chlorination purely on technical ground appears to offer several advantages.

SO_2-Air Removal of					
CNS^-	Total Cyanide CN_T	Available Cyanide CN_s	Ammonia	Metals	Suitable for Slurry Treatment
No	Yes	Yes	No	Yes	Yes

MUDDER & WHITLOCK (1984) dismissed the SO_2-Air process out of hand because "estimates of chemical usage rendered this process cost prohibitive for this application (Homestake, Lead, SD.)" The basis for MUDDER & WHITLOCK's cost rejection has not been elaborated on to date. Certainly, however, SO_2-Air does not remove CNS^- or NH_3 and it also does not reach the extremely low levels of CN_T required to meet the Homestake permit.

CHEMISTRY OF SO_2-AIR CYANIDE REMOVAL

The chemistry of SO_2-Air removal of cyanide is described by DEVUYST et al. (1984) and DEVUYST et al. (1982) which are inserted below. The main features are:

$$CN_T + SO_2 + O_2 + H_2O = CNO + H_2SO_4 \text{ (fast)}$$

$$SCN^- + 4SO_2 + 4O_2 + 5H_2O = CNO^- + 5H_2SO_4 \text{ (very slow)}$$

$$2Me(CN)_n + (2x-6)SO_2 + (2x-6)O_2 + Fe + (2x-6)H_2O = Me_2Fe(CN)_6yH_2O + (2x-6)CNO + (2x-6)H_2SO_4$$

(Me=Cu,Ni,Zn)

The reactions are catalyzed by dissolved Cu which is essential to achieve low CN_T results. Also the reaction is very pH dependent and works best between pH 8.5 - 9.5. The process has commercial potential for removal of cyanide, complexed cyanide and metals including iron, but not ammonia or thiocyanate.

RESULTS OF SO_2-AIR CYANIDE REMOVAL

The results on experimental and commercial scale installations are set out clearly in the above two papers by DEVUYST et al. In general CN_T can be reduced to 0.1-0.3 mg/l in solutions and slurries and DEVUYST (1984b) indicates that copper levels of below 0.50 mg/l can be achieved in a properly designed plant.

In the data presented by DEVUYST et al. (1984) for Carolin Mines' Ladner Creek tailings it is noted that Table IV reports copper values of 5-15 ppm in the treated barren bleed and 0.5-5 mg Cu/l in the final tailings pond. These results require some explanation as they may not properly reflect the ability of the process to remove copper.

In this case some copper is left in the treated barren bleed deliberately to provide adequate catalysis in the next step where treated barren bleed and tailings are combined for further SO_2-Air treatment.

At Carolin Mines the SO_2-Air process was retrofitted in an alkaline-chlorination system and it was not ideal for the job. Consequently because the existing equipment was not ideal the SO_2-Air process was not optimised and final results of 0.5-5 mg/l Cu were obtained. With appropriate tanks designed from scratch DEVUYST (1984b) has indicated that 0.50 mg Cu/l can be achieved in this pulp.

Achieving very low metal and CN_T levels in liquid effluents requires that the reaction be carried out in a two step process settling out the $Me_2Fe(CN)_6.nH_2O$ (Me=Cu,Ni,Zn) precipitates between reactor 1 and reactor 2.

OPERATING COSTS FOR SO_2-AIR CYANIDE REMOVAL

DEVUYST et al. (1984) gave the following theoretical reagent requirements for a gold mill effluent (barren + tails) containing, for example, in mg/l: 250 CN_T, 250 SCN^- and 100 $S_2O_3^=$:

Species	Reagent g/gCN_T	
	$Na_2S_2O_5$	Lime
CN^-	3.73	1.42
SCN^-	0.67	0.38
S_2O_3	0.17	1.67
	4.57	3.47

Reagents for SCN^- and $S_2O_3^=$ are based on average oxidation of 10% of SCN^- and complete oxidation of S_2O_3 to S_4O_6. Using empirical reagent efficiencies of 90% for $Na_2S_2O_5$ (10% oxidized by air) and 75% for lime (25% unreacted), the reagent requirements for the above effluent are 5.08g $Na_2S_2O_5$ and 2.23 lime per gram CN_T oxidized.

Based on FOB Vancouver prices reported by DEVUYST et al. (1984) the cost of the process would be as follows:

Reagent	Price ($/mt)
$Na_2S_2O_5$	550
Lime	180
$CuSO_4.5H_2O$	1320

Assuming the addition of 25 mg/l Cu^{++}, the cost of treating the hypothetical effluent is C$0.95/m³.

For a typical gold mill treating 1,000 mt of ore per day at 2 lbs NaCN/ton the cost per metric ton milled is $1.90, or a yearly cost of $693,000 for reagents.

DEVUYST et al. (1984) find that at a chlorine cost of C$725/mt the reagent costs for the same waste treated by alkaline chlorination would be C$2.72/m³ or C$5.44/mt for a yearly reagent cost of C$1,980,000.

	Cost of Reagents per m³ pulp*	Cost of Reagents per t ore	Annual Costs for 1000 tpd
SO_2-Air	C$0.95	C$1.00	C$693,000
Alkaline chlorination	C$2.72	C$5.44	C$1,980,000

* (250 mg/l CN_T, 250 mg/l SCN^-, 100 mg/l $S_2O_3^=$)

ADVANTAGES AND DISADVANTAGES OF SO_2-AIR CYANIDE REMOVAL

Advantages

1) Process has been tested on numerous pulps and effluents with success, and successfully demonstrated on a commercial scale.

2) Most feed streams are already alkaline.

3) Reactions with CN_T are complete and fairly rapid.

4) SO_2 may be available as roaster gas, if not it is readily available in cylinders or in solid form as sodium sulfite Na_2SO_3, or sodium bisulfite $NaHSO_3$ or sodium metabisulfite $Na_2S_2O_5$.

5) Toxic metals are removed.

6) The process is suitable as a batch or continuous process.

7) Since SCN^- is virtually not affected, SO_2 reagent consumption is less than Cl_2 consumption which attacks SCN^-.

8) SO_2-Air removes ferrocyanides and hence achieves a much lower CN_T if iron is present in pulps or solutions than alkaline chlorination.

9) Capital outlay is relatively small.

10) The process works very well on pulps as well as solutions.

11) The SO_2 process can be retrofitted into many alkaline chlorination systems.

12) Good fail safe control.

13) SO_2-Air process is claimed to make a more comfortable work environment than alkaline chlorination if installed indoors.

14) The effluent after treatment is non-toxic, i.e., no residual Cl_2.

15) Based on comparisons of cost by INCO Ltd. the reagent consumption for SO_2-Air is much lower than alkaline chlorination for a typical gold effluent. See DEVUYST (1984).

16) Experienced technical help is available from INCO Ltd.

DISADVANTAGES OF SO_2-AIR

1) SO_2-Air does not remove ammonia or thiocyanate under normal conditions.

2) The process does not recover cyanide.

3) Metal values are not recovered except as a precipitate sludge.

4) Royalty payments may be high (if they have to be paid).

5) The toxicity of SO_2-Air treated effluents has not yet been firmly established. There is some concern about long term toxicity of CNS^- on fish, for example.

THE INCO ROLE

Various levels of royalty payments have been referred to for INCO's SO_2-Air process. A royalty of 0.75% of the gold produced by the facility using the INCO SO_2-Air process with no front end payments has been one reference. Additional charges would apply if INCO Tech Ltd. were to test the pulp, design, install and/or start up and optimize a treatment facility.

INCO Tech Ltd. have made a very significant contribution in demonstrating and optimizing the SO_2-Air process for cyanide destruction. There can be no question that the experience and knowhow of INCO Tech Ltd. technical staff in making SO_2-Air work would be valuable in the plant design or startup phase.

It is expected that there will be several more SO_2-Air cyanide removal installations to treat both pulps and solution over the next few years.

INDUSTRIAL APPLICATION OF THE INCO SO_2-AIR CYANIDE REMOVAL PROCESS

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ABSTRACT

The Inco process for continuous cyanide removal from industrial waste effluents was recently invented by G.J. Borbely, et.al. The process uses SO_2-air mixtures as an oxidant and lime for pH control and requires copper in solution as a catalyst. Iron cyanide is removed as a sparingly soluble metal ferrocyanide and other metals are removed as hydroxides. The process has been successfully tested in the laboratory on a wide variety of industrial effluents, both liquors and slurries, typically achieving less than 1 mg/L CN_T and as low as 0.05 mg/L CN_T.

The purpose of the present paper is to discuss results achieved during industrial application of this new technology. In early 1982, pilot plant tests were carried out at Campbell Red Lake Mines on barren solution with good agreement with laboratory results with respect to reagent consumptions, retention time requirements and final effluent quality achievable.

The process has been implemented at three gold mills in British Columbia that had been practicing alkaline chlorination without being able to meet effluent discharge regulations.

The first full commercial operation was at Scottie Gold Mines in October, 1982. Reactors already available on site, modified for air sparging, are being used. Barren solution and tailings slurry are treated separately with treated barren solution joining the untreated tailings slurry. During 1983, the total Scottie mill effluent discharge typically contained (in ppm): CN_T 0.2, Cu 0.2, Fe <0.03 and Zn <0.2.

The process was implemented in October, 1983, at Carolin and Du Pont of Canada Exploration's Baker mine in British Columbia. At Carolin barren solution is treated in a single existing reactor modified for air sparging and the total tailings are treated in another type of reactor. Promising results were obtained in the early stages operation with total tailings discharge analyzing CN_T 0.3-15 mg/L. At Baker, total tailings slurry was treated in two existing reactors in series, also modified for air sparging, and CN_T as low as 0.1 mg/L was achieved.

The McBean gold operation in Ontario, due to start up in 1984, is expected to use the process to treat barren solution. Also, the process has been successfully tested for treatment of various cyanide containing effluents and rinsewaters from a major electroplating shop in Ontario.

The form of SO_2 reagent used in the commercial operations is selected based on location, availability and reagent cost. At Campbell Red Lake, liquid SO_2 and roaster gases were successfully used in pilot plant treatment of barren solution.

Source: DEVUYST et al (1984)

In the B.C. locations, sodium sulfite and/or metabisulfite are currently the preferred SO_2 reagents. At McBean's gold operation the use of sodium metabisulfite is planned. The use of sulfurous acid, using SO_2 from a sulfur burner, is also possible and would be advantageous for large operations.

INTRODUCTION

The Inco process for continuous cyanide removal from industrial waste effluents was recently invented by G.J. Borbely, et.al. (1). The process is based on the use of SO_2 (gas or sulfite salt or solution) in combination with air as an oxidant and lime for pH control. Copper in solution is essential as a catalyst for cyanide oxidation. The importance of the Inco process is based on the fact that it has significant advantages over other commercial or patented processes in the completeness of cyanide removal (iron cyanide is removed), operational simplicity, better safety, and lower reagent requirements and costs.

Cyanide removal technologies, which have been reported for gold and silver mill effluents include the Prussian Blue process (2), the Cominco iron sulfide process (3), acidification - volatilization - reneutralization (4), biodegradation (5), ion-exchange (6), electro-chemical oxidation (7), the Dupont-Kastone H_2O_2 process (8), ozonation (9) and alkaline chlorination (10).

These processes cannot be judged on common criteria. Some processes, such as acidification - volatilization - reneutralization, have the objective of recovering cyanide for recycle and therefore may be cost effective if such recovery is imperative. Other processes, such as electrochemical oxidation, may be able to recover base metals as a cathodic deposit, which may be significant in the electroplating industry, or may be able to partially convert effluent SCN^- to CN^- for recycle (11). The prevalent operational philosophy at gold and silver mills, however, is to treat barren solution bleed or tailings water without concern for base metal recovery or cyanide recycle. Toward this end it is clear that successful processes must be highly reliable as far as environmental impact is concerned, and must be safe, efficient and economical to use.

Until 1982, the most acceptable process for cyanide effluent treatment was alkaline chlorination. However, it has serious shortcomings. First, safety is a concern, not only because of handling Cl_2, but also because CNCl, a very toxic gas, is known to form during treatment and must be hydrolyzed as quickly as possible by maintaining a pH of at least 10.5. Second, the process can be extremely reagent intensive and thereby very expensive. Particularly unfortunate in this regard is the preferential chlorination of less toxic SCN^- over the more toxic free CN^-. Chlorination of $S_2O_3^=$ also consumes considerable reagent. Moreover, Cl_2 is highly reactive with sulfidic minerals usually present in the mill tailings and this fact usually prohibits for cost reasons the removal of cyanide contained in tailing slurries. Third, strong oxidants such as Cl_2, do not remove cyanide complexed with iron. This results in treated effluents containing unacceptable concentrations of CN_T*, which, despite being strongly complexed, can be decomposed by ultraviolet radiation to release free CN at some later time, perhaps after discharge to the environment.

With the advent of the Inco SO_2/air process in 1981, economical, safe and reliable treatment of cyanide containing solutions or slurries is possible and achieves low CN_T concentrations (including Fe complexes). The purpose of this paper is to report the commercial results of this technology at three gold mills in Canada.

* CN_T = total cyanide, including free CN^-, HCN and complexes of cyanide, SCN^- is not included.

PROCESS CHEMISTRY

The SO_2/air process has been extensively described in several recent Inco publications (12-16).

The oxidation of cyanide (free and complexed with transition metals other than iron and cobalt) closely follows the stoichiometry of the following overall reaction to form CNO^-:

$$CN^- + SO_2 + O_2 + H_2O \rightarrow CNO^- + H_2SO_4 \qquad (1)$$

Based on this reaction, the SO_2 requirement is 2.47g SO_2 per g CN. The cyanide oxidation reaction is catalyzed by the presence of copper ions in solution. Often the necessary copper ion concentration is already present in the effluent to be treated. When the copper concentration is insufficient, it is usually added as a copper sulfate solution. The optimum operating pH is in the range 8 to 10. Temperature has no significant effect on the cyanide oxidation rate in the range 5 to 60°C. The preferred volume percent SO_2 (or equivalent SO_2 volume percent if a sulfite solution is used) in air is at or below 2, but SO_2 of up to 10 vol.% in air can be successfully employed.

The kinetics of oxidation of thiocyanate with SO_2/air are slow under normal process conditions and usually less than 10% of the thiocyanate is oxidized during treatment.

During cyanide oxidation, iron cyanide is removed from solution by precipitation of insoluble metal ferrocyanide compounds of the form $Me_2Fe(CN)_6$ (where, for example, Me = Cu, Zn and Ni). Excess copper, zinc and nickel are removed by precipitation of metal hydroxides at the reaction pH. Metals forming weak cyanide complexes, such as arsenic and antimony, can also be removed by oxidation - precipitation in the presence of iron.

PROCESS APPLICABILITY

Details of successful laboratory treatment of a wide variety of Canadian gold and/or silver mill effluents, both barren solutions and tailings slurries, were reported in previous publications (13-15). Miscellaneous effluents such as flotation tailings and coke oven and blast furnace scrubber waters were also successfully treated (14). To date, Inco has successfully tested over fifty effluents without failure, but treatment conditions and control strategy vary considerably. Recently Canviro Consultants has reported results on the application of the Inco SO_2/air process to a variety of Canadian gold mill barren solutions and effluents from metal finishing operations (17).

PILOT PLANT

Starting in February, 1982, piloting of the Inco SO_2/air process was carried out on barren bleed solution at a facility constructed at Campbell Red Lake Mines Ltd. (in Ontario) and was operated by Inco personnel for a total of five weeks (the last three weeks running continuously).

The circuit comprised two reactors operated in series with the option of solids removal between stages. Air or roaster gases (about 1 vol.% SO_2) were supplied to the reactors by a blower. When running without roaster gases, SO_2 (liquid) from one ton cylinders was metered into the air stream. A pH electrode in each cell was used to control lime addition to maintain the pH set-point. Monitoring the ORP was successfully used as a guide for both SO_2 and copper

catalyst addition rates. Hoods were installed over the reactors and were connected to a ventilation duct. An hydrogen cyanide monitor installed in the duct with an alarm setting at 5 ppm HCN was not triggered at any time during the campaign.

Typical results achieved in the laboratory and at Campbell Red Lake for the flowsheet shown in Figure 1 are summarized in Table I. Detailed results of the campaign are available in a separate Inco publication (15). Results show cyanide removal from 890 mg/L in the feed to <0.7 mg/L in the second stage effluent when SO_2 was supplied at >3.0 g/g CN_T. Both laboratory and pilot plant results showed the process improved when Ni/Fe-containing solids were removed between treatment stages. Roaster gases were shown to also be acceptable as an SO_2 and air source. There was generally very good agreement between pilot plant and laboratory results when operating under the same conditions.

COMMERCIAL INSTALLATIONS

Due both to the failure of alkaline chlorination plants to achieve required effluent quality and high operating costs, three gold mills have licensed the Inco SO_2/air process for their cyanide destruction. At each of these sites chlorination facilities existed. To avoid further capital expenditures, each site requested that the implementation of the SO_2/air process use the existing equipment wherever possible. Thus, none of these commercial installations may be considered the most appropriate way to carry out or control the process, but the good results achieved to date show the flexibility the process has for accommodation to various design concepts and local conditions.

Scottie Gold Mines

Scottie Gold Mines, near the town of Stewart, British Columbia, was the first licensee in October, 1982. Scottie mines a pyrrhotitic ore at 200 t/d with a grade of about 0.50 oz/t. The ore is leached with cyanide following grinding in a mill located underground. Leached tails are washed and discarded. Gold recovery from pregnant is by Zn precipitation. Barren solution bleed may average 130 m^3/d. Prior to SO_2/air at Scottie two stirred tanks in series were in use for alkaline chlorination on barren solution bleed. Washed tailings solids were discarded directly to a pond and at times contained up to 10% of the total cyanide bleed.

Two tanks previously used at the site for alkaline chlorination and a third tank that was available were equipped with air spargers and agitators. Although liquid SO_2 could have been used, the transportation problems due to the remote location of the mine and safety considerations due to Scottie's underground mill caused other forms of SO_2 to be investigated. Two solid forms of SO_2, namely, sodium sulfite (Na_2SO_3) and sodium metabisulfite ($Na_2S_2O_5$) were selected. These reagents were dissolved in water in small make-up tanks and were added at the desired rates.

A schematic of the circuit at Scottie Gold is shown in Figure 2. Barren solution bleed is treated in one reactor with Na_2SO_3 and $Na_2S_2O_5$. The addition of Na_2SO_3 is made in proportion to the total weight of CN in the barren bleed. The addition of $Na_2S_2O_5$ is only made if the pH in the reactor rises above 9. Copper sulfate solution is added to the barren bleed from a small holding tank by means of a Clarkson feeder. The treated barren is mixed together with the washed mill tails from the tailings repulper in reactor II where they are treated with Na_2SO_3 and $Na_2S_2O_5$ solutions in the presence of air. Reactor II overflows into

reactor III where the reaction is continued. Typical results achieved in the laboratory and in the plant are summarized in Table II.

The most significant fact about Scottie's effluent treatment is that during all of 1983 Scottie was able to keep the CN_T in their treated effluent below 1 mg/L on monthly averaged analyses.

Du Pont of Canada Exploration's Baker Mine

The Baker Mine, owned and operated by Du Pont of Canada Exploration, is located near Smithers, British Columbia. It is completely serviced by air. This mine operated at 100 t/d on a combined gold-silver ore graded at about 1.1 oz/t (gold equivalent). Leaching was carried out using NaCN. Filtered tailings generally had about 20% of the total cyanide bled from the system. Barren bleed and sump water accounted for the remaining 80% of the cyanide.

Prior to licensing the Inco process, Baker had treated barren bleed in two reactors in series using $Ca(OCl)_2$ and $Ca(OH)_2$ in the first reactor. The treated barren overflowed into a tailings reactor, which also received sump water. Details of this operation were reported by W.W. Muir (18). One of the concerns at the Baker mill was that the washed tailings and sump water were left untreated by chlorination and, due to their small holding pond, insufficient natural degradation was obtained.

The Inco process was licensed in October, 1983. After modifying three existing reactors for air sparging, a similar approach for effluent treatment as used at Scottie Gold was initially tested. Barren bleed solution was treated with Na_2SO_3 in the first reactor, overflowing into a second reactor where only air was added. Since the third reactor receiving the tailings solids could not be moved, the tailings solids, sump water and treated barren solution were combined in the third reactor and treated with $Na_2S_2O_5$.

Due to limited compressed air availability the system only worked at low barren bleed flows. Also, due to the excessive basicity of the tailings solids, a large excess of $Na_2S_2O_5$ was required in the third reactor simply to keep the pH in the desired range.

Based on the results of further laboratory studies an improved circuit was installed in which total tailings slurry was treated in two reactors in series with addition of $Na_2S_2O_5$ to the first reactor as shown conceptually in Figure 3. A dedicated compressor was used with the two reactors. Washing the tailings solids with barren solution instead of fresh water eliminated the need of taking a separate barren bleed, since sufficient barren bleed was obtained in the form of tailings cake moisture.

Typical results achieved in the laboratory and in the plant are summarized in Table III. Both achieved CN_T from 0.1 to 0.3 mg/L in the final slurry.

Carolin's Ladner Creek Operation

Carolin Mines' Ladner Creek mill is the most complex of the mills in which the SO_2/air process has been employed. Mill capacity is about 1300 t/d with an ore grade of about 0.1 oz/t. Flotation is used to upgrade the gold into a sulfide concentrate which is then leached with cyanide. The tails are sent to scavenger flotation cells where a graphite concentrate is further recovered.

Barren bleed is typically about 150 m^3/d. Process water is obtained by recycling tailings pond supernatant. Considerable efforts were made by Carolin to optimize effluent treatment by alkaline chlorination. In that prior work, a large agitated tank was used to treat barren bleed with chlorine and lime. Washed tailings solids, containing 5 to 10% of the cyanide bled, were discarded to the tailings pond without treatment. Pond supernatant was treated in a secondary alkaline chlorination circuit and then dechlorinated and pH adjusted prior to discharge to Ladner Creek. However, the rate of discharge from the pond was limited by the presence of iron cyanide in the pond. The iron cyanide was found to increase during the winter months and this created serious problems for Carolin during periods of spring run off.

The Inco process was licensed in October, 1983. Since more than 90% of the iron in the pond originated from the barren bleed, implementation of the Inco SO_2/air on barren solution was carried out first.

The schematic flowsheet of the Inco SO_2/air process at Carolin is shown in Figure 4. Barren bleed is treated in the same tank as was used for chlorination, but two aeration agitators were positioned on a bridge support on each side of an existing central aerator. Addition of $Na_2S_2O_5$ is in proportion to the barren flowrate and cyanide content. No copper sulfate addition is required. Lime is added on pH demand by means of a titrator-pH controller.

In the current practice, tailings solids are also treated at Carolin. This is done by adding excess $Na_2S_2O_5$ to the treated barren overflow which joins the tailings box. Some $Na_2S_2O_5$ is also added to flotation scavenger cells, which provide good aeration.

Typical laboratory and plant results achieved on treatment of barren solution are shown in Table IV. Treated barren with (in mg/L): 10 CN_T, 5-15 Cu and 0.1-0.3 Fe was obtained. These results are not as good as in the laboratory where the effluent analyzed (in mg/L): 1.4 CN_T, 1.4 Cu and 0.4 Fe, but inadequate mixing and poor air dispersion in the plant reactor are likely responsible. While this could be catastrophic for another location, achieving low cyanide in the treated barren at Carolin is not critical, since further cyanide removal can be obtained by addition of $Na_2S_2O_5$ to the treated barren overflow which joins the tailings box. Typical total tailings treatment obtained is summarized in Table IV. With no addition of excess $Na_2S_2O_5$, the typical CN_T in the total tailings discharge to the pond was 15 mg/L (with 90% of the cyanide being contributed by the tailings input). With addition of $Na_2S_2O_5$, cyanide was removed to the range 0.3 to 2 mg/L in the tailings discharge to the pond. An estimated 12 mg/L of cyanide is removed in the tailings pipe for this operation. Based on these results, $Na_2S_2O_5$ addition to the scavenger cells is now also being made to take advantage of the aeration present in these cells and hopefully to further improve CN_T in the tailings discharge.

General Comments

Reactor Selection. In the presence of sufficient copper catalyst, the rate-limiting step in the oxidation of cyanide in the SO_2/air process is determined by the rate of oxygen transfer to the solution. Therefore, reactors providing maximum air dispersion and good agitation are preferred. Flotation cells are considered to be excellent reactors for applications of this process. Flotation cells were used by Inco at Campbell Red Lake and excellent agreement was obtained between laboratory and pilot plant operation with respect to retention time, reagent requirements and effluent quality achieved. The Inco process is, however, not limited to the use of flotation cells. Simple agitated tanks, modified for air

sparging, can be considered. Such reactors, depending on size, could be fitted with flotation-type agitators for air dispersion.

In general, air dispersion efficiency per unit volume of reactor decreases with increasing reactor size and it may be preferable to use two or more smaller reactors instead of one reactor of equal total volume.

Reagent Selection. The choice of SO_2 reagent is dependent on mine location, reagent cost and process control strategy. The cheapest primary reagent for SO_2 is elemental sulfur. Conversion of the sulfur to SO_2, however, requires a sulfur burner and this may not be economically justified for small operations. Liquid SO_2 has a relatively low cost if it can be brought to the site by rail. Liquid SO_2 in one ton cylinders has a unit cost similar to solid sulfites such as Na_2SO_3 and $Na_2S_2O_5$. The use of liquid SO_2 requires a reliable lime delivery system for pH control. Sodium sulfite compounds,on the other hand, are quite soluble in water (up to 250 g/L), and are safer and more convenient reagents for both SO_2 supply and neutralization (containing equivalent or half of the base required to neutralize the acid generated).

Treatment Options. If a mine recovers gold by carbon in pulp, total tailing slurry treatment is required. The Inco SO_2/air process is quite suited for this treatment. The number of reaction tanks required, and whether in sequence or in parallel, should be determined by empirical studies.

Gold mines recovering gold by zinc cementation produce two effluents, namely, barren solution bleed and repulped tailing solids. The optimum effluent treatment scheme for such a mill is dependent on the particular mill operation, retention time available, SO_2 reagent usage, effluent composition, solids composition and process control strategy. Inco has wide experience in designing systems for these variables and should be consulted during the testing and design stages of any plant.

Process Control. Process control strategy for optimum performance and most economical use of reagents is quite site specific. Numerous options are available and have to be evaluated under laboratory conditions. Inco has a continuous bench-scale apparatus for this kind of testwork.

OPERATING COSTS

Theoretical reagent requirements for the oxidation of cyanide contained in a gold mill effluent (barren + tails) containing, for example, in (mg/L): 250 CN_T^-, 250 SCN- and 100 $S_2O_3^=$, are as shown below:

Species	Reagent(g/g CN_T) $Na_2S_2O_5$	Lime
CN^-	3.73	1.42
SCN^-	0.67	0.38
$S_2O_3^=$	0.17	1.67
	4.57	1.67

Reagents for SCN^- and $S_2O_3^=$ are based on average oxidation of 10% of SCN^- and complete oxidation of $S_2O_3^=$ to $S_4O_6^=$. Using empirical reagent efficiencies of 90% for $Na_2S_2O_5$(10% oxidized by air) and 75% for lime (25% unreacted), the reagent requirements for the above effluent are 5.08g $Na_2S_2O_5$ and 2.23g lime per gram CN_T oxidized.

Prices FOB Vancouver (all currency expressed in Cdn $) for reagents are:

Reagent	Cost ($/MT)
$Na_2S_2O_5$	550
Lime	180
$CuSO_4.5H_2O$	1320

Based on these costs and using the above reagent requirements, also taking into account an average addition of 25 mg/L of Cu^{++}, the cost of effluent treatment per m^3 is $0.95. For a typical gold mill treating 1,000 MT of ore per day at 2 lbs NaCN per MT, the cost per MT milled is $1.90. This corresponds to a yearly reagent cost of $693,500.

Alkaline chlorination, on the other hand, using an empirical reagent efficiency of 75% for both Cl_2 and lime, has reagent costs for treatment of the same effluent of $2.72/$m^3$ or $5.44/MT (Price FOB Vancouver for Cl_2 is $725/MT). The corresponding yearly reagent cost is about $1,980,000. Consequently, for this typical effluent, the savings achieved with the SO_2/air process is $1.77/$m^3$ effluent or $3.54/MT milled or $1,290,000 per year. This calculation considers a "good" case for chlorination since most tailings slurries would be more highly reactive to chlorine and would consequently have a considerably higher chlorine reagent cost. Moreover, if the SCN^- concentration is increased over 250 mg/L (used in the example), which is often found to be the case, then the chlorine consumption and cost is significantly higher, but the SO_2/air reagent cost only marginally increases due to only 10% of the SCN^- being oxidized by the latter process compared to 100% by chlorination. Finally, any iron present in the effluent cannot be removed by chlorination and therefore, despite its high cost,chlorination is unable to produce an effluent of equal quality to that produced by the lower cost SO_2/air process.

Licensing of the SO_2/air technology is handled through IncoTech, a Division of Inco, Ltd. Licensing fees are a fraction of the savings the process offers.

ACKNOWLEDGEMENTS

The authors would like to thank many Inco personnel for their discussions and assistance during the course of this work: Inventors G. Borbely, K. Schitka, V. Ettel and A. Mosoiu, who maintain an active interest; B. Tandi, who has skillfully conducted all the laboratory work reported; analytical services and advice from V. Zatka and P. Iamarino; plant operational assistance from R. Agius, B. Wilson, E. Lostracco and F. Daley, and Inco Tech assistance from D. Lowney. In addition, successful testing and implementation could not have been done without the cooperation of S. Roberts at Campbell Red Lake, Wayne Ash at Scottie, T. Law and W. Muir at Baker, and G. Robbins and R. Samuels at Carolin.

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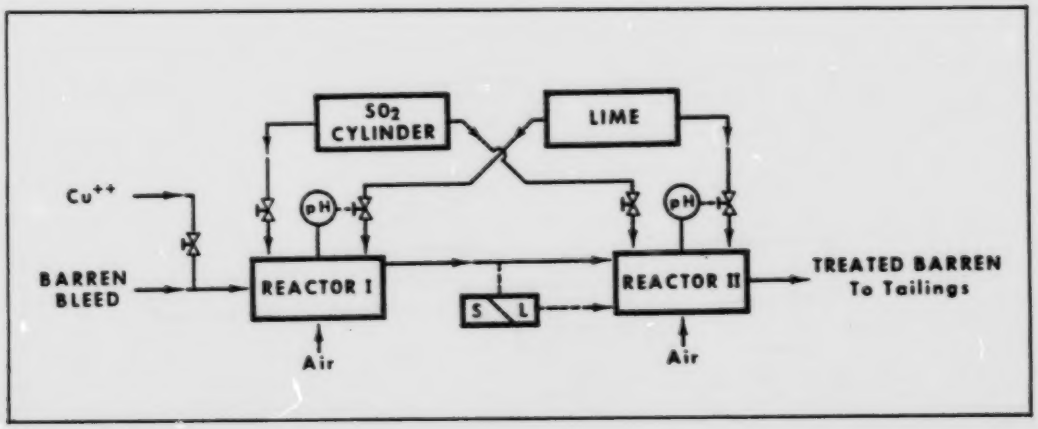
Table No. I
Campbell Red Lake Results

Site	Stream	pH	Assays (mg/L) CN_T	Cu	Fe	Ni	Zn	Reagents (g/g CN_T) Cu^{++}	SO_2	Lime
Plant	Barren Bleed	9.5	890	55	80	35	35			
	Stage II Effluent	9.5	1.6	0.4	0.4	1.6	<.2	0.11	2.2*	3.4
Plant	Barren Bleed	10.5	665	62	35	50	78			
	Stage II Effluent	9.8	0.7	0.5	0.2	0.2	0.2	0.07	3.6	5.4
Lab	Barren Bleed	11.1	940	39	118	20	63			
	Stage II Effluent	10.0	0.7	0.6	0.2	0.4	<.2	0.15	3.0	5.1

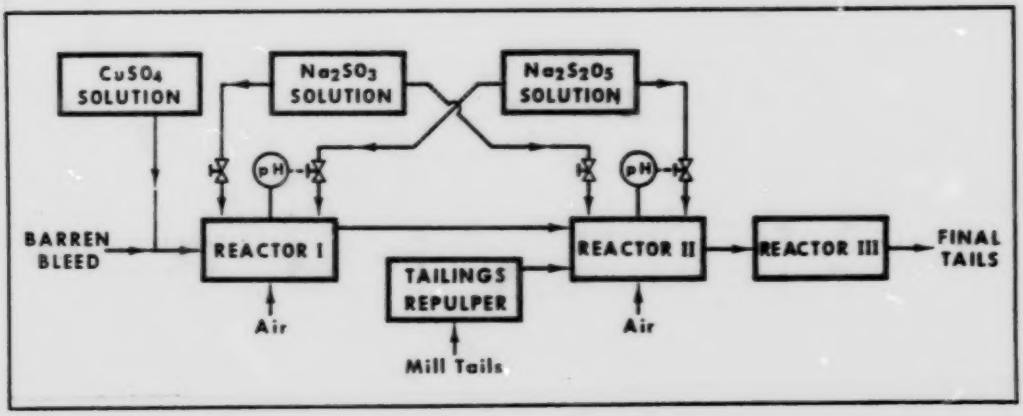
* Roaster gases as SO_2 source.



Conceptual Inco SO_2/Air Process at Campbell Red Lake Mine Figure 1.

Table No. II
Scottie Gold Results

Site	Stream	pH	Assays (mg/L) CN_T	Cu	Fe	Zn	Cyanide Distribution (%)
Plant	Barren Bleed		450	35	1.5	66	75
	Treated Barren Bleed	9.0	0.1-2	1-10	<.5	0.5-2	0.4
	Mill Tails (55% solids)		115	17	0.7	18	25
	Final Effluent (35% solids)	8.0	0.1-1	0.2-2	0.02-0.3	<.1	<.5
Lab	Barren Bleed		340	44	1.0	71	75
	Treated Barren Bleed	8.9	0.2	2	0.2	2	0.04
	Mill Tails (40% Solids)		48	12	1.4	10	25
	Final Effluent(32% Solids)	8.0	0.3	0.2	0.2	<.1	0.2

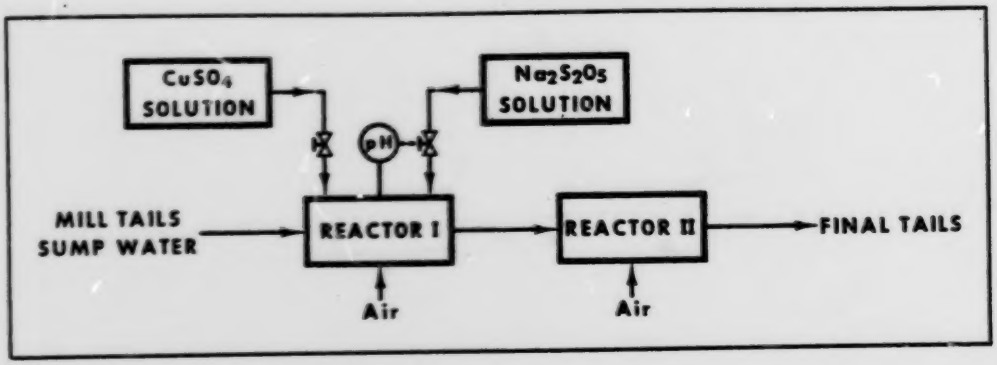


Conceptual Inco SO_2/Air Process at Scottie Gold

Figure 2.

TABLE No. III
Du Pont of Canada Exploration Baker Mill Results

Site	Stream	pH	Assays (mg/L) CN_T	Cu	Fe	Zn	Cyanide Distribution (%)
Plant	Sump + Mill Tails	11.0	240	20	6	90	100
	Final Tails	8.0	0.1-0.3	1-5	0.3	0.1-0.2	0.2
Lab	Sump + Mill Tails	10.8	230	46	6.2	57	100
	Final Tails	8.2	0.3	0.9	0.1	<.1	0.12

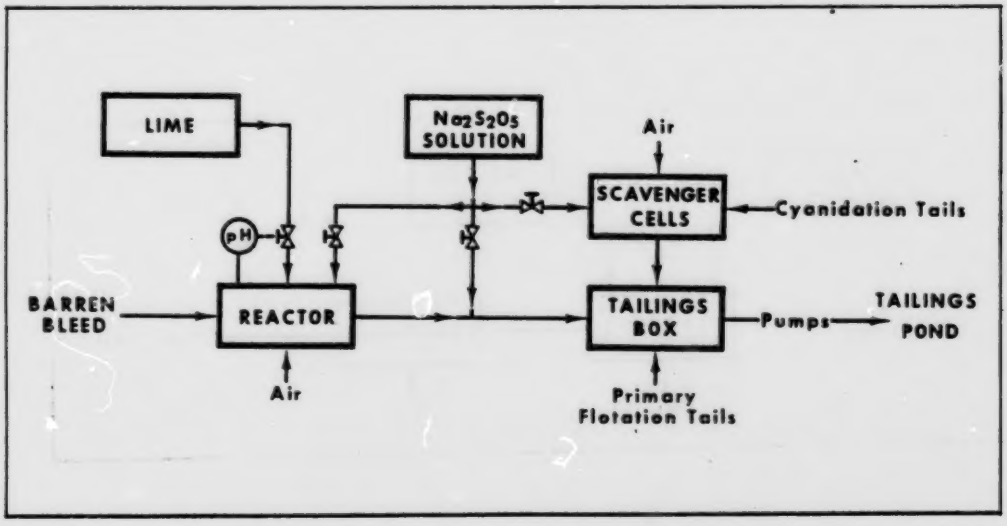


Conceptual Inco SO_2/Air Process at Du Pont of Canada Exploration Baker Mine

Figure 3.

Table No. IV
Carolin's Ladner Creek Mill Results

Site	Stream	pH	Assays (mg/L) CN_T	Cu	Fe	Cyanide Distribution (%)
Plant	Barren Bleed	11.0	1500	350	75	91-84
	Treated Barren Bleed	9.6	3-10	5-15	0.1-0.3	1
	Mill Tails + Treated Barren	9.0	11-19	13-15	1.0-3.2	9-16
	Final Tailings to Pond	8.7	0.3-2	0.5-5	0.1-0.3	<2
Lab	Barren Bleed	11.8	2100	230	310	100
	Treated Barren Bleed	9.0	1.4	1.4	0.4	0.07



Conceptual Inco SO_2/Air Process at Carolin's Ladner Creek Operation Figure 4

INCO TECH

2060 Flavelle Boulevard, Sheridan Park
Mississauga, Ontario L5K 1Z9

September 24, 1982

Dear Sir or Madam,

Thank you for your inquiry about the Inco SO_2/air process for cyanide removal from industrial effluents.

Enclosed please find several recent papers on this subject, the most recent one being given in September, 1982, reporting pilot plant and initial full-scale plant trials on gold mill barren and tailings slurries.

We will continue to keep you informed about the process developments as they occur. Technical questions can be addressed to:

Dr. Bruce R. Conard
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Sheridan Park
Mississauga, Ontario. L5K 1Z9
Tel: (416) 822-3322

Licensing information should be requested from:

Mr. Donald Lowney
Manager - Administration
Inco Tech - Inco Ltd.
Mississauga, Ontario. L5K 1Z9
Tel: (416) 822-7265

Again, thank you for your interest.

Sincerely yours,

BRConard.

A UNIT OF INCO LIMITED

A NEW PROCESS FOR THE TREATMENT OF WASTEWATERS CONTAINING CYANIDE AND RELATED SPECIES

by

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TO BE PRESENTED AT THE 21st ANNUAL
CONFERENCE OF METALLURGISTS,
TORONTO, ONTARIO
AUGUST 29-SEPT. 1, 1982

ABSTRACT

A new process for the removal of free and complexed cyanide in wastewaters has been developed by Inco laboratories using sulfur dioxide (either as gas or as sulfite solutions), air and lime. High reaction rates are obtained at room temperature at pH = 7-10 in the presence of dissolved copper, which acts as a catalyst. Cyanide in the treated effluents can be reduced to <1 mg/L CN_T, including cyanide complexed with iron.

Examples of laboratory continuous treatment of gold mill effluents, plating rinse waters and flotation liquors are given.

Pilot plant experience treating barren solution at the Campbell Red Lake operation is discussed, as well as promising results from a plant trial at Scottie Gold Mines.

INTRODUCTION

A number of important industrial processes produce waste effluents containing high levels of cyanide either as a free ion or complexed with heavy metals. Before being discharged into receiving waters such effluents need to be treated to achieve acceptably low levels of cyanide.

Various techniques for oxidizing cyanide to less toxic species using strong oxidants are reported in the literature (1-8). Other reported methods use ion-exchange(9), iron sulfide(10), ferric hydroxide(11), polysulfides(12), aeration at low pH(13) and ferrous sulfite(14). Excellent reviews of the field have also recently appeared(15,16).

Of the methods known, alkaline chlorination is the most widely used in commercial practice. This method, however, has several serious shortcomings, namely, high reagents costs due to thiocyanate being oxidized prior to cyanide, formation of highly toxic cyanogen chloride as a reaction intermediate, contamination of the effluent by chlorine, and incomplete oxidation of the cyanide complexed with the iron, which remains in solution as $Fe(CN)_6^{-3}$ and has the potential for release of free cyanide at a later time. Recently the $FeSO_4$ + sulfite process has received some attention. However, possible serious shortcomings may be relatively high reagent costs ($FeSO_4$ and Na_2SO_3 or $NaHSO_3$ and NaOH or Na_2CO_3), difficult solid-liquid separation operation(solids containing possibly ferric hydroxide), and multi-step operation(addition of sulfite and $FeSO_4$, neutralization, filtration).

Inco Limited has reported a new method for removing cyanide in solution involving SO_2/air as an oxidant and small amounts of dissolved copper as a catalyst(17). The potential advantages of the process are:

- removal of both free and complexed cyanide, especially complexed with iron, to achieve effluents containing total cyanide(CN_T) of <1 mg/L;
- very rapid kinetics at room temperature;
- low reagent consumption because thiocyanate(SCN^-) is only slowly oxidized under the preferred conditions;
- possible low reagent cost because roaster gas can be used as oxidant where available or elemental sulfur can be burned to provide SO_2.

Details of successful laboratory treatment of a wide variety of Canadian gold mill barren solutions and pulps, as well as a number of other industrial waste waters, and pilot plant treatment of barren solution at the Campbell Red Lake gold mill, were reported in three previous publications(18,19,20). The objective of the present paper is to summarize and update the data on the SO_2/air process. The process is shown to be applicable to cyanide removal from flotation tailings liquors and slurries, plating rinse waters, coke oven and blast furnace scrub waters, silver and gold milling barren solutions and slurries. Laboratory, pilot plant and plant results are presented.

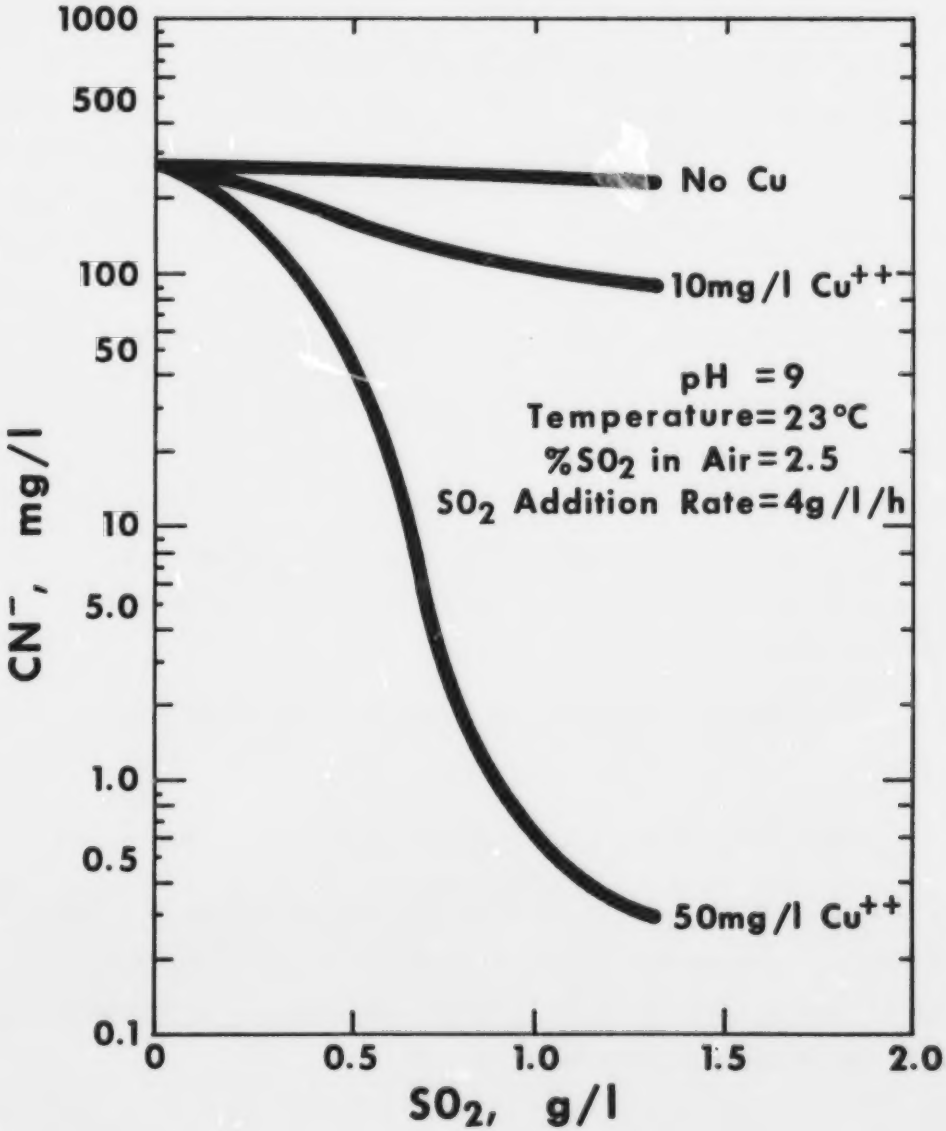
PROCESS CHEMISTRY AND VARIABLES

The overall reaction for cyanide oxidation with SO_2/air is postulated to be

$$CN_T^- + SO_2 + O_2 + H_2O \rightarrow CNO^- + H_2SO_4$$

The reaction is catalyzed by copper approximately in proportion to the amount of copper present in the range 0 to 50 mg/L as shown in Figure 1. The amount of copper catalyst necessary is somewhat variable depending on the specific effluent being treated.

Figure 1
EFFECT OF COPPER



In the presence of 50 mg/L copper, the effect of varying the treatment pH in the range 6 to 11, at room temperature, is shown in Figure 2. The preferred range of pH is 9-10. Again, depending on the specific effluent being treated, or the type of sulfite-air mixture used, another operating pH may be preferred.

Studies previously reported(18,19) have shown that temperature variation in the range 4-60°C has no significant effect on the process. Sulfur dioxide concentrations between 0.5 to 10 vol.% can be used, but for optimum oxidation efficiency a range of 1-3 vol.% SO_2 in air is preferred.

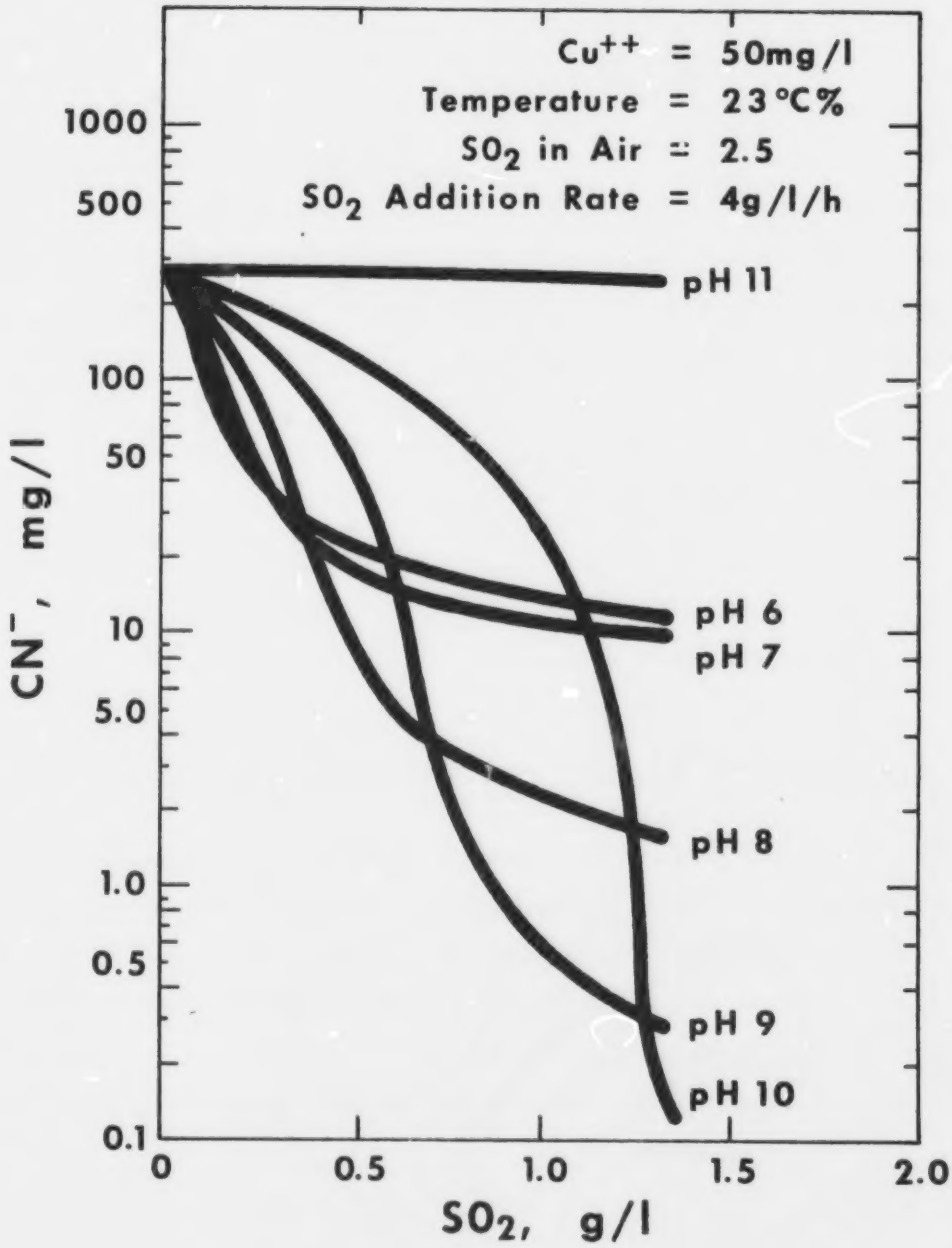
The order of metal cyanide removal in the SO_2/air process is Zn>Fe>Ni>Cu. The Fe cyanide complexes are reduced to the Fe^{++} state by SO_2/air and the insoluble salts $Me_2Fe(CN)_6.xH_2O$(Me = Zn, Cu, Ni) precipitate during treatment. Following the removal of Fe in this way, the remaining Cu, Zn and Ni ultimately report to the solids as hydroxides as the cyanide is oxidized to cyanate.

The oxidation of thiocyanate according to the postulated overall reaction:

$$SCN^- + 4\ SO_2 + 4\ O_2 + 5\ H_2O \rightarrow CNO^- + 5\ H_2SO_4$$

is very slow, but SCN^- can quickly react with other species that may be present, such as $Ni(OH)_2$, to release free cyanide which, of course, is not desirable. This type of reaction can be minimized by removing the solids in an intermediate step or in some instances by operating at lower pH.

Figure 2
EFFECT OF pH



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LABORATORY EXPERIMENTAL PROCEDURE

Laboratory tests were carried out either batchwise in a 1 liter capacity reaction vessel or continuously using one or two 0.5-1.5 liter capacity vessels placed in series(Figure 3). Sulfur dioxide was added into each vessel as a mixture in air(0.6 - 3 vol.% SO_2). In some cases a sodium sulfite or sodium meta-bisulfite solution was used instead of SO_2. The experiments were conducted at room temperature keeping a pH 9 or in some cases 6.5 to 10, using a lime-water suspension(38 g/L lime). When feed composition dictated, copper was added as a cupric sulfate solution to the feed. The reduction-oxidation potential(Redox) versus the standard calomel electrode (S.C.E.) was monitored in each reaction vessel.

In all of the testwork carried out more reliable data was obtained from continuous processing than from batch tests. Batch tests were only conducted to scope the SO_2/air process on a particular effluent.

LABORATORY RESULTS ON INDUSTRIAL EFFLUENTS

The SO_2/air process was tested on a wide variety of industrial waste liquors and pulps which originate from the following typical operations:

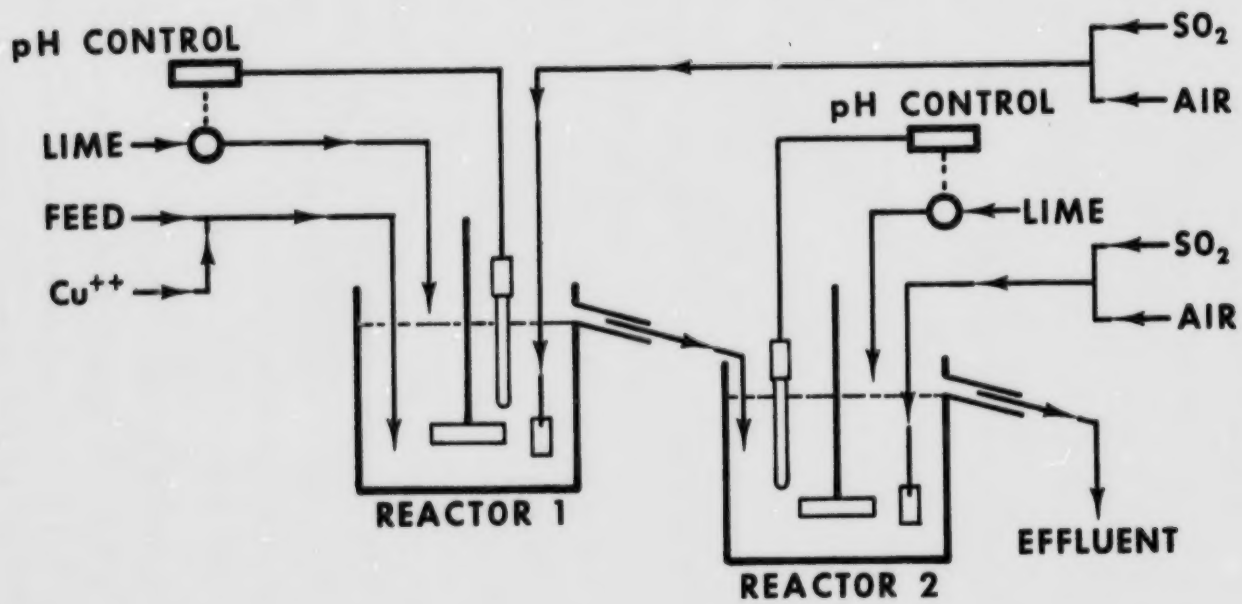
(a) precious metals extraction(silver and gold milling)

(b) mineral dressing(pyrrhotite and base metal flotation)

(c) electro-plating(rinse waters)

(d) steel manufacturing(coke oven and blast furnace scrub waters)

Figure 3
LABORATORY CONTINUOUS SET UP



The above effluents contain, in addition to cyanide(free and complexed with heavy metals), variable amounts of thiocyanate, flotation agents, ammonia and organics. The principal metals present at various concentrations are copper, nickel, iron, zinc, arsenic and cadmium.

Treatment of effluents from flotation tailings

Examples of continuous treatment of flotation tailings liquors are shown in Table 1.

For liquors from pyrrhotite flotation, for example, in which synthetic stack gas(air + 0.6 vol.% SO_2 + 1 vol.% CO_2) was used, the pH in each of the two stages was kept at 6.5 instead of the preferred pH of 9, to avoid excessive lime consumption by reaction with CO_2 in the gases. A total residual cyanide(CN_T) of 0.6 mg/L was obtained with a total retention time of 7.4 minutes. None of the thiocyanate was removed at this pH. A high grade precipitate at ~20 wt.% Ni + Cu was recovered.

For liquors resulting from flotation of copper and copper-zinc ores, very low residual cyanide levels(CN_T <0.1 mg/L) were obtained by treating the effluents with SO_2/air at pH 9. The exceptionally low CN_T in this case is attributed to a low Ni and Fe content of the feed. Such effluents can be treated in one stage continuous to achieve CN_T <1 mg/L as shown in Table 1.

Examples of batch treatment of pyrrhotite tailings slurries are shown in Table 2. The tailings, containing 62% by weight solids, were reacted with SO_2/air at pH 8. No cyanide was removed in the absence of copper addition. With addition of copper at 160 mg/L(on a continuous basis as $CuSO_4$) virtually all of the cyanide was removed.

TABLE 1

CONTINUOUS CYANIDE REMOVAL FROM SELECTED INDUSTRIAL EFFLUENT LIQUORS

Type of Effluent	Stream	Retention Time (min)	pH	Redox (S.C.E.) (mV)	Analyses (mg/L) or (wt.%)* CN_T^-	SCN^-	CNO^-	NH_3	Cu	Ni	Fe	Zn	Cd	Reagents Added (g/g CN_T) SO_2	Lime
Pyrrhotite Flotation Liquor	Feed	-	9.5	-	116	117	-	-	36	47	0	0	0	-	-
	R1	4.6	6.5	-	9.9	117	-	-	13	0.2	-	-	-	6.10	3.90
	R2	2.8	6.5	-	0.6	115	-	-	0.2	0.2	-	-	-	3.70	2.70
	Residue*	-	-	-	-	-	-	-	7.9	10.5	-	-	-	-	-
Base Metal Flotation Liquor	Feed	-	9.6	+125	69	30	-	-	37	<.2	<.2	<.2	0	-	-
	R1	9.75	9.0	+ 20	<.1	-	-	-	0.7	<.2	<2	<2	-	3.73	5.60
	Feed	-	7.1	+280	80	42	-	-	41	<.2	<.2	19	0	-	-
	R1	4.9	9.0	+ 40	0.77	-	-	-	1.8	<.2	<.2	<.2	-	4.02	6.00
	R2	4.9	9.0	- 10	<.05	-	-	-	1.8	<.2	<.2	<.2	-	1.34	2.00
Plating Rinse Water	Feed	-	-	-	142	-	-	-	47.3	0	18.0	14.3	10.0	-	-
	R1	7.2	9.0	+100	<.4	-	-	-	6.0	-	<.1	<.05	<.1	4.69	6.40
	R2	7.2	9.0	+120	<.4	-	-	-	2.6	-	0.2	<.05	<.1	2.35	3.21
	Effluent	36	10.0	-	0.88	-	-	-	0.8	-	0.4	<.05	<.1	0	0.10
	Residue*	-	-	-	-	-	-	-	2.37	-	0.84	0.72	0.52	-	-
Silver Mill	Feed	-	11.6	+100	56	31	5	4	11.6	0	0	36.3	0	-	-
	R1	5.6	9.0	+ 85	0.13	-	-	-	7.6	-	-	0.6	-	3.80	5.33
	R2	5.6	9.0	+ 15	0.04	25	60	6	0.6	-	-	1.0	-	1.90	2.66
	Residue*	-	-	-	0.89	-	-	-	9.9	-	-	38	-	-	-

Treatment of plating rinse waters

An example of two stage continuous treatment of mixed cadmium and zinc plating rinse waters is shown in Table 1. Although the total cyanide was removed to below 0.5 mg/L in the first reaction stage, a residual copper concentration of 6 mg/L remained in solution. This copper is presumably present as a Cu^{+} complex with inorganic or organic species present in the effluent and gradually hydrolyses out of solution by oxidation of Cu^{+} to Cu^{++}. The final effluent, after standing for 36 minutes at pH 10, analyzed 0.8 mg/L Cu.

Treatment of silver mill barren solution

Results of a two stage continuous treatment of silver mill barren solution with SO_2/air at pH 9 is shown in Table 1. Very low residual CN_T of 0.04 mg/L was attained, which is typical of the results achieved in the absence of Ni and Fe. Analyses of the various streams for CNO^{-}, SCN^{-} and NH_3 indicate that most of the cyanide was oxidized to CNO^{-} with some of the CNO^{-} hydrolyzing to CO_2 and NH_3 and a very minor amount of the cyanide(less than 2% of CN_T) reporting with the residue.

Treatment of coke oven and blast furnace effluents

Unlike most other effluents, coke oven and blast furnace effluents from gas scrubbing mostly contain free cyanide and traces of iron. The effluents also contain ammonia and variable amounts of phenol.

Results of batch treatment of such effluents with SO_2/air at pH 9 are given in Table 2. Copper catalyst addition was required to achieve total cyanide removal. Only part of the phenol was removed and none of the ammonia.

Treatment of gold mill barren solutions

Results of two stage continuous cyanide removal from several gold mill barren solutions using SO_2/air are given in Table 3. These results show that:

- CN_T in the treated effluents was <.5 mg/L for effluents containing no or small amounts of nickel; the weak acid dissociable cyanide(CN_W) was in some cases below 0.1 mg/L.
- reagent consumptions were in the range 3 to 7 g SO_2 and 6 to 10 g lime per g CN_T. When Na_2SO_3 was used(effluent A), no lime was required.
- metal impurities, including As(when present), were usually removed to well below 1 mg/L. In some cases, however, 1-2 mg/L of Cu, Ni and/or Zn remained in solution at the time of sampling, even though the CN_T was below 0.1 mg/L. It would appear that hydrolysis of these metals is retarded by the presence of complexing ions in solution. These effluents always showed much lower metal concentrations when refiltered at a later time.

TABLE 2

BATCH CYANIDE REMOVAL FROM SELECTED INDUSTRIAL EFFLUENT LIQUORS AND SLURRIES

Type of Effluent	Stream	% Solids in Pulp	pH	Time (min)	Redox (S.C.E.) (mV)	Analyses (mg/L) CN_T^-	SCN^-	Cu	Ni	Fe	NH_3	Phenol	Reagents Added (g/g CN_T) Cu^{++}	SO_2	Lime
Pyrrhotite Tailings Slurry	Feed	62	8	0	-	113	350	17	33	13	-	0	-	-	-
	Effluent	62	8	60	-	113	436	0.9	47	0.4	-	-	0	18.6	-
	Feed	62	8	0	-	152	452	12	30	11	-	0	-	-	-
	Effluent	62	8	60	-	0.8	372	0.8	2.3	0.5	-	-	1.07	13.8	-
Coke Oven	Feed	0	9	0	-	55	-	0	0	1.1	300	8.9	0.18	0	0
	Effluent	-	9	60	+145	<5	-	2	-	-	300	-	-	76	-
	"	-	9	180	+120	<.5	-	0.5	-	0.2	300	2.4	-	228	-
Blast Furnace	Feed	0	9	0	-	6	-	0	0	0	18	-	0.93	0	0
	Effluent	-	9	5	+160	<.02	-	0.06	-	-	18	-	-	58	-

TABLE 3

CONTINUOUS TWO STAGE TREATMENT OF GOLD MILL BARREN SOLUTIONS

Stream	Retention Time (min)	pH	Redox (S.C.E.) (mV)	Analyses (mg/L) or (Wt.%)*										Reagents Added (g/g CN_T)	
				CN_T^-	CN_W^-	SCN^-	CNO^-	NH_3	Cu	Ni	Fe	Zn	As	SO_2	Lime
Feed A	-	0		1680	1600	820	75	13	210	0.6	2.0	758	0	-	-
R1	97	9.3	+110	0.13	<.10	767	2467	38	0.54	<.1	<.1	3.2	-	3.20	0
Feed B	-	12.6	- 80	420	-	1584	-	-	137	1.6	19	71	0	-	-
R1	26	9.0	+ 55	-	-	-	-	-	13	0.2	5.2	0.4	-	5.44	8.16
R2	26	9.0	+120	0.11	0.09	1408	-	-	1.4	0.2	0.2	0.2	-	1.36	2.04
Feed C	-	9.5	-	500	-	270	27	12	55	53	66	53	0	-	-
R1	22	9.0	+ 85	3.0	-	220	-	-	13	3.2	0.2	-	-	3.40	4.39
R2	22	9.5	+110	1.2	-	216	496	19	0.4	0.8	0.2	0.4	-	0.85	2.19
Residue*	-	-	-	27	-	-	-	-	0.66	6.15	8.53	5.99	-	-	-
Feed D	-	11.4	-120	220	-	230	-	-	64	13	8	21	1.0	-	-
R1	9	9.0	+ 95	6.5	-	192	-	-	17.4	1.6	0.2	0.4	-	3.05	4.30
R2	9	9.0	+115	.5	-	205	-	-	1.0	1.2	0.2	0.4	0.008	1.50	2.14
Residue*	-	-	-	-	-	-	-	-	18.0	3.45	2.23	6.47	0.39	-	-

- very little SCN^- was oxidized, resulting in low SO_2 consumptions.
- the bulk of the cyanide was oxidized to cyanate (CNO^-) with some of the CNO^- hydrolyzing to NH_3 and CO_2. When iron was present, some of the cyanide was precipitated with iron as $Me_2Fe(CN)_6.x\ H_2O$(Me = Ni, Cu, Zn).

Total removal of cyanide from effluents containing high nickel and iron concentrations was difficult to attain(see Table 4), because of the back-reaction of precipitated solids with solution species. A substantial improvement in residual CN_T in a second treatment stage was obtained by removing the solids between stages: effluent C(Tables 3 and 4) yielded a final treated effluent with 0.3 mg/L instead of 1.2 mg/L CN_T and effluent E gave a treated solution with 0.7 mg/L instead of 6 mg/L CN_T. Copper addition was required in effluent E because of the very high Fe content of this feed.

Solids precipitated from iron containing effluents are stable towards cyanide redissolution in the pH range 4 to 9 as shown in Table 5. Treated effluents were acidified to pH 6 and 4 in the presence of the cyanide containing solids and reanalyzed after 4 and 7 days. Only acid soluble hydroxides were redissolved.

TABLE 4

CONTINUOUS TWO STAGE TREATMENT OF GOLD MILL BARREN SOLUTIONS; EFFECT OF INTERMEDIATE SOLIDS REMOVAL

Intermediate Solids Removal	Stream	pH	Redox (S.C.E.) (mV)	Analyses (mg/L) CN_T^-	SCN^-	Cu	Ni	Fe	Zn	Reagents Added (g/g CN_T) Cu^{++}	SO_2	Lime
Yes	Feed C	9.5	-230	500	270	55	53	66	53	-	-	-
	R1	9.0	+ 50	20	190	24	14	0.6	<.2	-	2.28	3.24
	R2	10.0	+ 50	0.3	178	0.2	0.6	0.2	<.2	-	0.85	1.63
No	Feed E	11.1	- 50	940	230	39	20	118	63	0.13	-	-
	R1	9.0	+120	12	-	1.8	6.8	1.0	<.2	-	2.71	3.79
	R2	9.5	+140	6.4	170	0.2	1.2	1.6	<.2	-	0.90	1.26
Yes	Feed E	11.1	- 50	940	230	39	20	118	63	0.15	-	-
	R1	9.0	+145	10	175	11	3	<2	<.2	-	2.71	3.86
	R2	10.0	+ 80	0.7	176	0.6	0.4	0.2	<.2	-	0.27	1.27

TABLE 5

STABILITY OF PRECIPITATED FERRO-CYANIDE SALTS

Stream	Time of Sample	Analyses (mg/L) or (Wt.%)				
		CN^-_{TOT}	Cu	Ni	Fe	Zn
Residue	0	10.5	15.1	1.10	3.58	10.5
Effluent (pH 9)	0	<0.2	1.2	0.6	<0.2	1.4
Effluent (pH 6)	4 days	0.23	32.8	25.2	<0.2	63
Effluent (pH 6)	7 days	0.14	30.0	22.0	<0.2	56
Residue	0	3.6	1.43	1.21	2.04	1.54
Effluent (pH 8.3)	0	0.50	0.8	1.0	0.4	0.4
Effluent (pH 7.0)	7 days	0.20	0.2	1.6	<0.2	0.4
Effluent (pH 4.0)	7 days	0.45	1.4	55.0	<0.2	37.0

TABLE 6

CONTINUOUS REMOVAL OF CYANIDE FROM GOLD MILL BARREN PULPS

Stream*	% Solids	Retention Time (min)	pH	Redox (S.C.E.) (mV)	Analyses (mg/L) CN_T^-	CN_W^-	SCN	Cu	Ni	Fe	Zn	Reagents Added (g/g CN_T) Cu^{++}	SO_2	Lime
Feed F	38	-	-	- 30	420	-	466	178	1.7	40.2	0.1	0	-	-
R1	38	30	8.0	+ 90	0.8	-	364	1.3	-	0.2	<.1	-	5.6	-
Feed G	36	-	11.3	-120	149	-	-	53	0	7.6	72	0	-	-
R1	36	26	8.1	+ 80	0.09	0.07	-	<.5	-	<.5	<.5	-	5.0	0
Feed H	50	-	10.1	- 70	100	-	227	11.8	1.4	<.5	37.5	0.35	-	-
R1	50	30	9.0	+140	2.1	0.77	-	<.2	<.2	1.4	<.05	-	8.5	-

* Feed F: carbon in pulp gold extraction; 4 Vol.% SO_2 in air; sulphidic solids.
Feed E: gold cementation with Zn powder; 134 g/L Na_2SO_3 solution; sulphidic solids.
Feed H: carbon in pulp gold extraction; 1 vol.% SO_2 in air; roasted solids.

Treatment of gold mill barren slurries

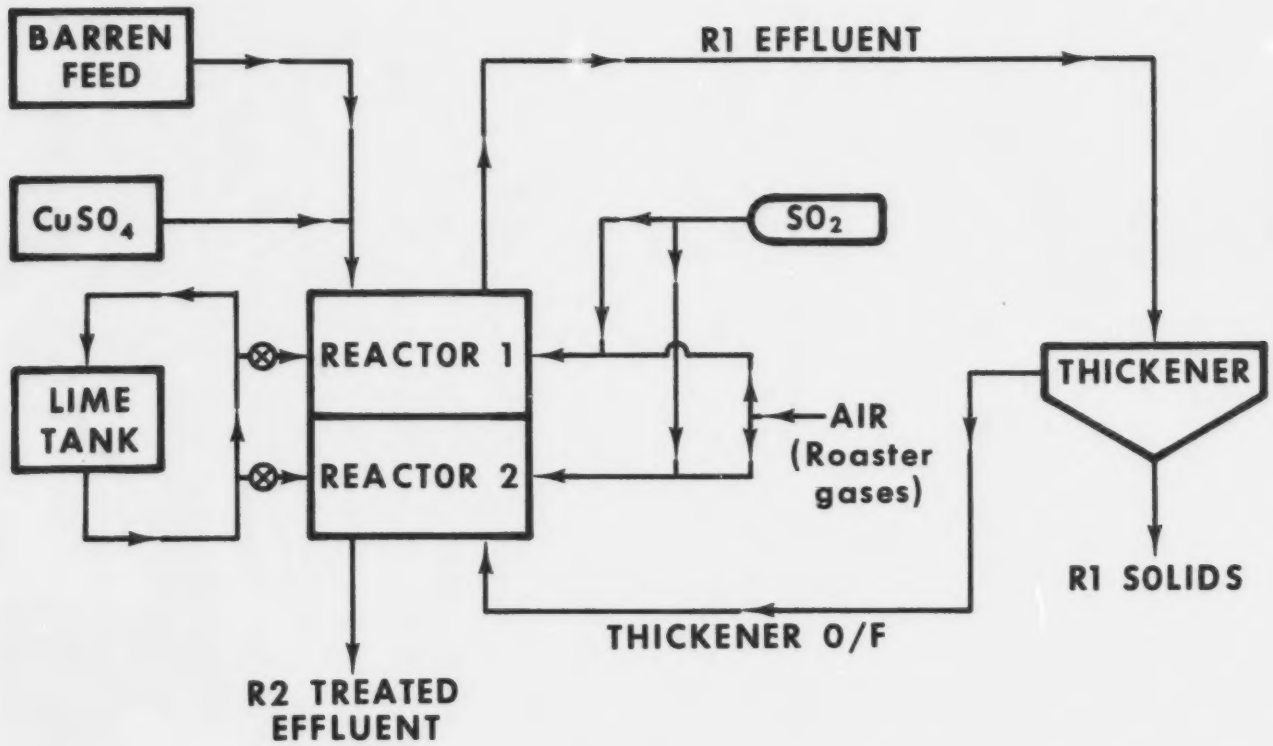
Results of successful continuous cyanide removal tests from various gold mill barren slurries using SO_2/air are given in Table 6. Feeds F and H result from carbon in pulp treatments and feed G from zinc cementation treatment of pregnant solution. Feeds F and G contain sulfidic solids and feed H roasted solids, mainly hematite.

The results show that:

- the residual total cyanide in the treated effluents was in the range 0.1 to 2 mg/L and the weak acid dissociable cyanide(CN_W) in the range 0.07 to 0.8 mg/L.
- the cyanide was removed in a single stage continuously with typically ~30 minutes retention time.
- reagent consumptions were in the range 5 to 8.5g SO_2/g CN_T. Feed G was treated with sodium metabisulfite and required no base.
- the preferred treatment pH with slurries is 8. Higher pH may result in incomplete iron removal(feed H).

Slurries containing more highly reactive solids towards SO_2 and air may require more intensive treatment conditions.

Figure 4
PILOT PLANT FLOWSHEET



PILOT PLANT RESULTS

Detailed results on a five week pilot plant trial at the Campbell Red Lake gold mill were given in a previous publication(20). The pilot plant circuit comprised two 2 m^3 flotation tanks(Figure 4), and one 50 m^3 thickener.

Use of Roaster Gases

The use of roaster gases as the oxidizing reagent, instead of liquid SO_2 in air, was tested without intermediate solids removal. Excellent results were obtained, as summarized in Table 7, with the second stage effluent reporting at 1.6 mg/L CN_T. Roaster gas SO_2 strength was not measured during the test, but we calculate that it was about 0.6 vol.% SO_2.

Optimum results

Roaster gases were not used for process optimization because precise SO_2 addition rates were required. Results from both laboratory and pilot plant treatment of Campbell effluent showed the necessity of removing Ni/Fe-containing solids and minimizing CN_T in reactor 1 to achieve the lowest residual CN_T in the treated effluent. When CN_T is plotted versus redox for reactor 1(see Figure 5) using all data obtained from the pilot plant and laboratory tests, a clear CN_T minimum is found between +90 mV to +130 mV (S.C.E.). Optimum results were obtained by controlling the SO_2 addition rate to reactor 1 to maintain +110 mV redox. Under the optimum conditions, the residual CN_T achieved in the treated effluent was <0.7 mg/L and the weak acid dissociable cyanide(CN_W) was <0.2 mg/L(Table 7).

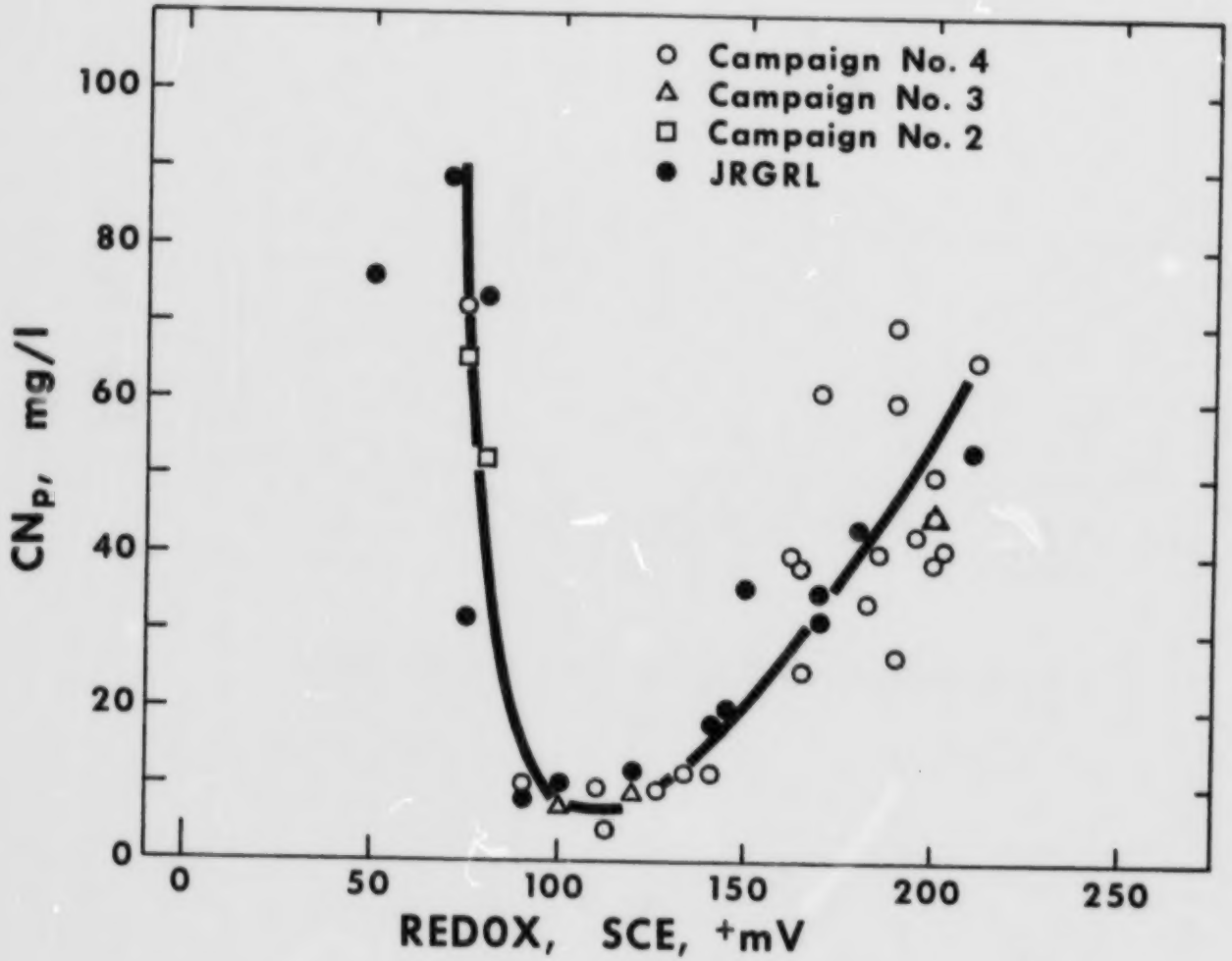
TABLE 7

TYPICAL PILOT PLANT RESULTS ON CAMPBELL RED LAKE BARREN SOLUTION

Stream	pH	Redox (S.C.E.) (mV)	Analyses (mg/L) CN_T^-	CN_W^-	Cu	Ni	Fe	Zn	Reagents Added (g/g CN_T) Cu^{++}	SO_2	Lime
Feed	9.5	-	890	-	55	35	80	35	0	0	0
R1	9.0	-	10	-	8.0	7.4	0.2	<.2	0.09	(1.5)	2.3
R2	9.5	-	1.6	-	0.4	1.6	0.4	<.2	0.02	(0.7)	1.1
Feed	9.5	-	665	-	62	50	35	78	0.07	-	-
R1	9.0	+110	4	-	11	7	<.2	1	-	2.5	3.8
R2	9.8	-	0.7	0.2	<.5	<.2	<.2	<.2	-	1.1	1.6

Figure 5

CAMPAIGN No. 4, 3, 2 & LABORATORY, REACTOR 1



PLANT RESULTS

The Inco SO_2/air cyanide removal process on both barren solution and tailings slurries is currently being tested on a plant scale at Scottie Gold in B.C. Initial results are promising. The tests on barren bleed were carried out continuously at 100-400 L/min effluent feed rate to a 6 m^3 stirred reactor using air and sodium sulfite solution as the oxidizing reagents. Typical results are shown in Table 8.

It was not possible to analyze for CN_T at the plant site, and therefore the picric acid method for cyanide analysis was used. Since the CN_P gives the free cyanide and cyanide complexed with Cu, Ni and Zn, and was measured to be <.1 mg/L in the treated effluent, the only cyanide present was due to cyanide complexed with iron. The maximum cyanide complexed with 0.2 mg/L Fe is 0.6 mg/L as $Fe(CN)_6^{3-}$ and therefore the CN_T in the treated effluent was below 0.7 mg/L.

Plant tests on tailings slurry at this site are continuing.

SUMMARY

A new and comparatively inexpensive process for removing cyanide in waste waters has been developed and successfully tested on a wide variety of effluents. Reagents required are SO_2(gas, sulfite, roaster gases), air and neutralizing agent(eg. lime) and process consumptions are low, typically ~5 lb SO_2 and 8 lb $Ca(OH)_2$ per lb CN_T in the feed. The cyanide is removed by both oxidation to cyanate and by precipitation as insoluble ferrocyanide salts.

TABLE 8

PLANT CONTINUOUS TREATMENT OF GOLD MILL BARREN SOLUTION

Stream	pH	Analyses (mg/L) CN_p^-	Cu	Fe	Zn	SO_2 Added (g/g CN_T) (as Na_2SO_3 soln)
Feed	11.0	240	50	20	25	-
Treated Effl.	9.6	<.1	<.5	0.2	<.2	10

Feedrate: 35 US Gal/min

Retention: 170 min.

CN_p = CN by picric acid method which excludes iron complexes.

The oxidation of cyanide is catalyzed by soluble copper, which can be present in the feed or can be added to the process as Cu^{++}. Little SCN^- oxidation is experienced. Metal values in the feed report as hydroxides or as metal-ferrocyanide salts.

Excellent laboratory results have been achieved in a continuous operation using waste waters and pulps produced in gold milling, pyrrhotite and base metal flotation, plating shop rinse waters and metallurgical coke oven and blast furnace operations.

A successful five week pilot plant operation of the process was demonstrated at Campbell Red Lake on their barren solution. Roaster gases were shown to be an effective source of SO_2 and process control using redox potential worked well.

Full-scale plant trials at Scottie Gold Mines were carried out with successful results on barren bleed using a stirred tank reactor and Na_2SO_3, the use of which obviated the need for lime.

The new technology is available for licensing through INCO TECH, a business unit of Inco, Ltd.

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Gold ore treatment at Emperor Gold Mining Co. Ltd., Vatukoula, Fiji

P. Colbert[1]

INTRODUCTION

Emperor Gold Mining Co. Ltd. operates a 1000 t/day gold ore treatment plant (Fig. 1) at Vatukoula, Fiji. Ore comes from underground and open cut mines (Table 1) and typically averages 5.5 g/t gold. Gold and silver occur mainly as tellurides associated with sulphides, but there is a minor amount of native gold present.

Treatment involves

1. crushing, removal of primary slime, and grinding,
2. flotation of a separate gold-telluride concentrate and a sulphide-gold concentrate from the main ore, and flotation of a concentrate from primary slime,
3. treatment of gold-telluride concentrate for recovery of gold and tellurium as described in Chapter 13, and
4. recovery of gold from sulphide-gold concentrate by roasting and cyanidation.

CRUSHING AND GRINDING

Fig. 2 is a simplified version of the crushing and grinding circuit. Primary crushing is done in a 900 mm by 600 mm Kue Ken crusher. Primary slime is liberated in a 2.1 m by 3.6 m blade mill and removed by screening and rake classification for separate treatment. Plus 35 mm oversize from the Allis Chalmers screen is crushed minus 16 mm by a 1300 mm Symons Short Head cone crusher in closed circuit with a Mogensen sizer. Minus 16 mm screen undersize and rake classifier sand are conveyed to a 2000 t fine ore bin.

TABLE 1

Typical metallurgical figures at Emperor Gold Mining Co. Ltd.

Feed grade*	
Open cut ore	4.1 g/t Au
Underground ore	7.7 g/t Au
Flotation concentrate grade	
Telluride concentrate	2500 g/t Au
Sulphide concentrate	85 g/t Au
Tailing assay	
Final tailing	1.1 g/t Au
Recoveries	
Gold	75%
Silver	20%

* Plant feed comprises 60 per cent open cut ore and 40 per cent underground ore.

[1] Research Metallurgist, Emperor Gold Mining Co. Ltd., Vatukoula, Fiji.

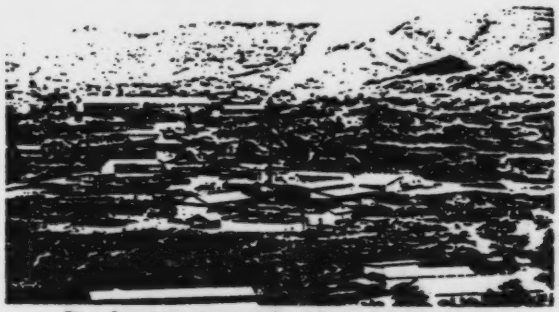


Fig. 1 – General view of treatment plant of Emperor Gold Mining Co. Ltd.

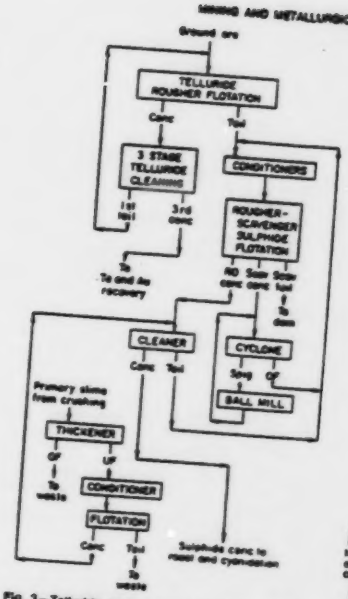


Fig. 3—Telluride, main sulphide, and primary slime flotation circuits of Emperor Gold Mining Co. Ltd.

as shown in Fig. 4. Concentrate is thickened, filtered on a 4-disc Otsuka filter, and then dead roasted in two Edwards 60-rabble roasters. Treatment rate is 26-40 t/day. Roasting is normally autogenous, but oil burners are sometimes needed.

Calcine is given a water wash in a thickener and pumped to a precyanidation agitator where lime is added to give 0.15 per cent CaO in solution; Cyquest is also added. Calcine is then cyanided in three 4.5 m by 3.8 m agitators at 0.05 per cent NaCN.

Cyanided calcine is washed in a thickener and filtered. Thickener overflow and filtrate from the Moore filters is clarified and pumped to a standard Merrill-Crowe circuit for gold recovery. Pregnant solution assay about 1.5 g/t Au and barren solution 0.03 g/t.

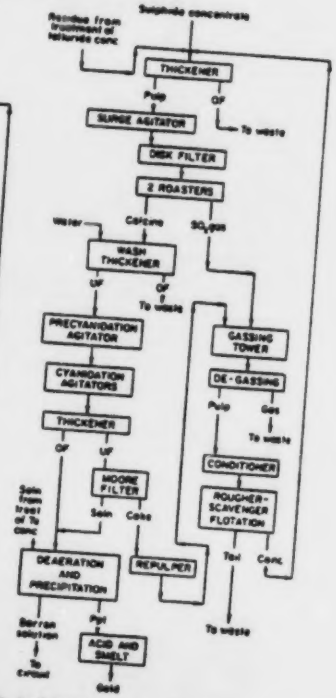


Fig. 4—Sulphide concentrate treatment circuit at Emperor Gold Mining Co. Ltd.

Washed calcine is gassed with SO_2 from the roasters to destroy cyanide and to activate unroasted sulphides. The pulp is then aerated and floated as shown in Fig. 4 to recover the sulphides. Flotation is conducted at natural pH (about 6) using copper sulphate, xanthates, and a frother (Table 2). Rougher concentrate joins the main sulphide concentrate and tailing is pumped to the tailing dam.

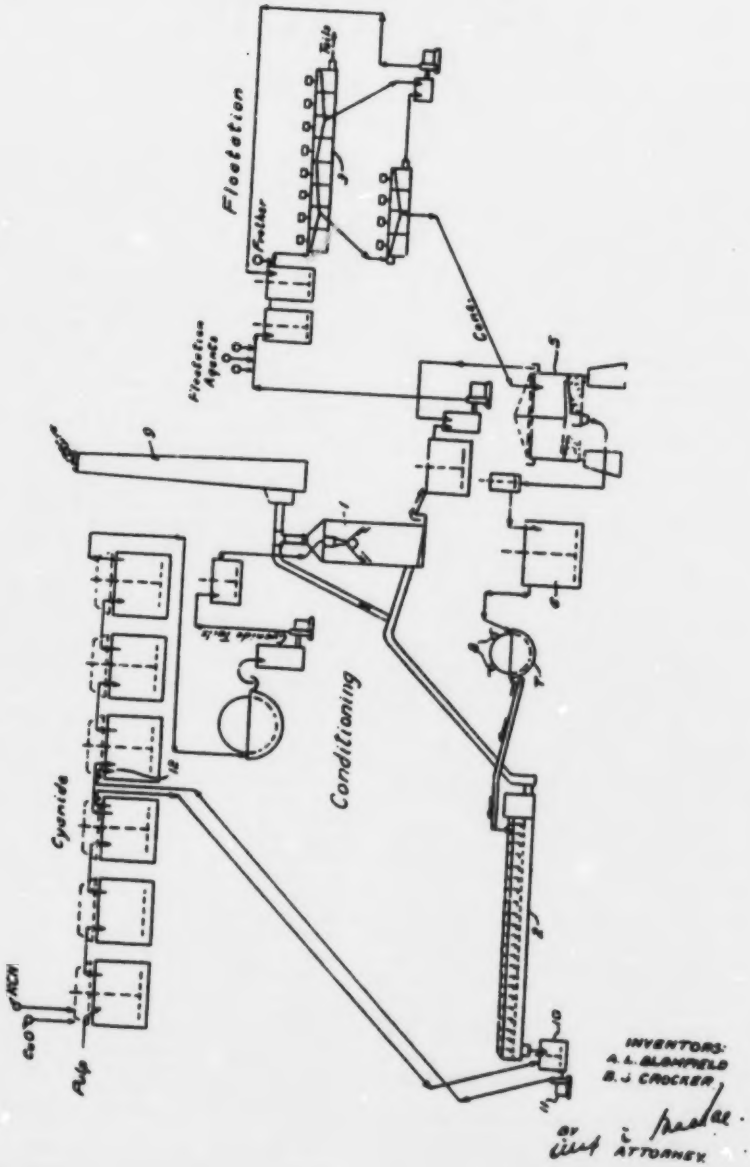
May 6, 1941.

A. L. BLOMFIELD ET AL

2,240,976

FLOTATION SEPARATION OF MINERALS

Filed Nov. 8, 1940



Patented May 6, 1941 2,240,976

UNITED STATES PATENT OFFICE

2,240,976

FLOTATION SEPARATION OF MINERALS

Alfred Leslie Bloomfield and Bunting Snowball Crocker, Kirkland Lake, Ontario, Canada, assignors to Lake Shore Mines Limited, Kirkland Lake, Ontario, Canada

Application November 8, 1940, Serial No. 364,789
In Canada November 28, 1938

6 Claims. (Cl. 75—2)

This invention relates to the flotation method for the separation of minerals and is more particularly directed to the conditioning of the mineral pulp to be subjected to flotation in order to overcome the effect of constituents of the pulp which hinder flotation.

Broadly the invention comprises the step of treating the mineral pulp with a roaster gas, preferably formed by the roasting of the concentrates produced by flotation, with a view to overcoming the depressing effect upon flotation of undesirable materials in the pulp.

The invention will be described in relation to the treatment of cyanide tails and with reference to the accompanying drawing which illustrates a flow sheet of a combined flotation and roasting process.

It will be observed that the tailings from the cyanide treatment are conditioned with roaster gases, floated, roasted and returned to be incorporated in the pulp undergoing cyanide treatment for extraction therefrom of gold, or other recoverable values, along with at least a portion of the extraction from the ore itself. A portion of the ore pulp is preferably withdrawn from the cyanide unit and incorporated with the roaster calcines, as indicated, and the mixture is returned to the cyanide unit at a point to allow sufficient cyanide contact to recover the values from the calcines.

In operation the cyanide tailings, as indicated in the flow sheet, or such other ore product as is to be treated, in pulp form is passed through one or more splash or absorption towers 1, preferably in counter-current to the flow of gases from a roaster 2. Various types of splash or absorption towers may be used. In that illustrated the pulp enters at or near the top and is sprayed through a nozzle, or caused to impinge upon a ball or the like located within the tower chamber to disperse the pulp. The pulp spray should contact the walls of the chamber to insure passage of the roaster gases, which are shown as entering adjacent the bottom of the tower, through the pulp and in sufficiently intimate contact therewith to permit the desired pulp conditioning reactions. The pulp preferably flows from the bottom of the tower providing a gas seal as shown.

The pulp may be further conditioned and subjected to agitation, as required, with the addition of desired flotation or frothing agents such as, copper sulphate, xanthates, pine oil or the like, and then passed, by means of a pump or the like, through flotation cells 3 as in usual practice. The flotation tails are discarded as indicated and the concentrates are thickened 5, agitated 6, and passed through a filter 7, preferably equipped with so-called flappers 8 adapted to beat the filter cake to decrease its moisture content. The thus dried concentrate passes to the roaster 2 from which a controlled portion of the roast gases is conveyed through the reaction tower 1, the balance going directly to the stack 9 for discharge to the atmosphere as indicated.

The roasted flotation concentrate is cooled, preferably in the roaster 2, mixed 10 with a portion of the partially treated cyanide pulp and pumped 11 back to the cyanide unit at a point 12, approaching the end of the cyanide treatment, say eight hours before the end of a forty-eight hour treatment. Thus the gold or other value remaining in the calcines is recovered during the final period of the ore treatment.

It will be apparent that cyanide tailings contain lime and cyanide. It is known that these reagents interfere with efficient flotation. The adverse effect of such constituents of the pulp is overcome by the treatment with roaster gas, which changes them to a form which is not deleterious to flotation. The lime is perhaps changed to sulphites or sulphates by the sulphur dioxide in the roaster gas and the cyanide is rendered harmless.

The method is applicable to all cyanide tailings and may be applied to any pulp to be treated by flotation. The cost of treating low grade ores, or the retreatment of tailings and the like, is the determining factor in the commercial possibilities of such mineral products. The present method is particularly economical, effecting a substantial saving in reagent costs and provides an improved more or less cyclical procedure wherein flotation concentrates are used to provide conditioning reagents for the pulp and the roasted concentrates are returned for further cyanide treatment to recover remaining values.

We claim:

1. A method of recovering values from ore products which includes successively cyanide treatment, concentration of the cyanide tailings by flotation, and roasting of the concentrates, characterized in that the pulp formed from the cyanide tailings for flotation is treated with the gases formed by roasting the flotation concentrates.

2. A method as defined in claim 1, wherein the roasted concentrates are returned to the cyanide circuit for retreatment.

3. A method of recovering metals from cyanide

tailings which comprises forming a pulp therefrom, treating the pulp with roaster gases, subjecting the so-treated pulp to flotation and roasting the flotation concentrates to provide the gases for conditioning said pulp.

4. A cyclic method of recovering metals from ore which comprises treating the ore with cyanide, subjecting the cyanide tailings to the action of roaster gases, treating the so-conditioned tailings to concentration by flotation, roasting the flotation concentrates to provide said roaster gases and returning the calcined concentrates to the cyanide circuit.

5. A method as defined in claim 3, wherein the pulp is passed through an absorption tower in counter-current flow to said roaster gases to provide intimate contact between the pulp and the gases.

6. In the cyanide treatment of metal ores, the method which comprises subjecting the cyanide tailings in the form of a pulp to the action of gases formed by roasting at least a portion of the ore to condition the pulp for flotation treatment and thereafter subjecting the so conditioned pulp to froth flotation treatment to recover metal values from said tailings.

BUNTING SNOWBALL CROCKER.
ALFRED LESLIE FOMFIELD.

Environment Canada | Environnement Canada
Environmental Protection | Protection de l'environnement

Your file Votre référence

Our file Notre référence

Ottawa, Ontario
K1A 1C8

October 10, 1984

Dr. H. Von Michaelis
Randol International Ltd.
21578 Mountsfield Drive
Golden, Colorado
80401

Dear Dr. Michaelis:

RE: DESTRUCTION OF CYANIDE IN GOLD MILL EFFLUENTS

Thank you for the information from you report on the Emperor Gold Mine which you sent to me recently.

After reading the description of the gasification process used for the destruction of cyanide, there is no doubt in my mind that cyanide is being destroyed by the well known acidification-volatilization method and not by the newer Inco SO_2-air process. In fact on page 86, your report indicates that SO_2 is used to acidify the pulp and this is confirmed on page 87 where the slurry pH is shown to drop from 9.5 - 2. As you are aware, it is essential in the Inco process to operate at an alkaline pH and maintain that pH by adding lime.

I am making these comments, not with the purpose of protecting Inco's patent claims but rather with the purpose of providing objective comment on how I view the cyanide destruction process being used at the Emperor mine.

.../2

As promised in a recent telephone conversation, I am pleased to send you the summary report of the performance evaluation of the alkaline chlorination process used at three gold mines in British Columbia, carried out by Ker, Priestman and Associates. I am also attaching a paper by J.B. Brodie (Ker, Priestman) and S.A. Zaidi (Environment Canada) based on this study. Should you have any questions regarding this work feel free to contact me again.

Best regards,

James S Scott

J.S. Scott
Section Head
Mining, Mineral & Metallurgical
Processes Division
Industrial Programs Branch

NATURAL DEGRADATION AND BACTERIAL PROCESSES FOR CYANIDE REMOVAL

Introduction

Natural degradation of cyanide has been relied upon for years to decompose cyanides and thiocyanate in gold and silver cyanidation effluents. It works well in climates that are warm throughout the year.

SCHMIDT et al. (1981) reviewed these natural degradation processes with particular emphasis on a study conducted on cyanide containing effluent from the DOME Mines at Timmins, Ontario, showing how during summer months cyanide in the barren bleed holding pond at the Dome Mine falls from around 100 mg CN_T/l to less than 0.1 mg CN_T/l due to natural degradation. Several parameters were reported such as temperature in the shallow pond, pH, iron and copper concentrations, etc. This work was continued by SIMOVIC, et al. (1984) who conclude that volatilization of free cyanide and metalls-cyanide decay are the mechanisms that explain cyanide removal during natural degradation. Their paper is inserted below.

EPA Report No. EPA 600/2-78-158 entitled "Investigation of Landfill Leachate Pollution Attenuation by Soils" provides some EPA observations on the attack on cyanide by organic matter which are probably bacterial in nature.

ECHO BAY MINES - LUPIN PROJECT

Several mining companies including several in the far north of Canada rely on natural degradation to destroy cyanide. Echo Bay Mines' Lupen project, for example, employs a huge shallow effluent lagoon for the purpose of impounding effluent during the winter months when little or no degradation is possible and only after degradation of cyanide in summer, releases an effluent. In the northern reaches of Canada with its myriad of lakes and vast open spaces, land is available for such huge impoundments.

The Lupin tailings pond is frozen for much of the year but, in summer, there is a steady wind and 24 hours of sunshine--ideal conditions for natural degradation in a shallow pond. The Lupin tailings decant composition has been the subject of an intense study. Cyanide levels increase noticably from ice break-up until around mid-August when there is a dramatic drop in cyanide levels. North West Territory water effluent limits for cyanide can easily be met and two stages of ponding are likely to be used at the Lupin tailings site. The first pond will allow arsenic removal by $FeSO_4$ addition as well as natural degradation of cyanide. The second will be a polishing pond.

More information can be requested from:

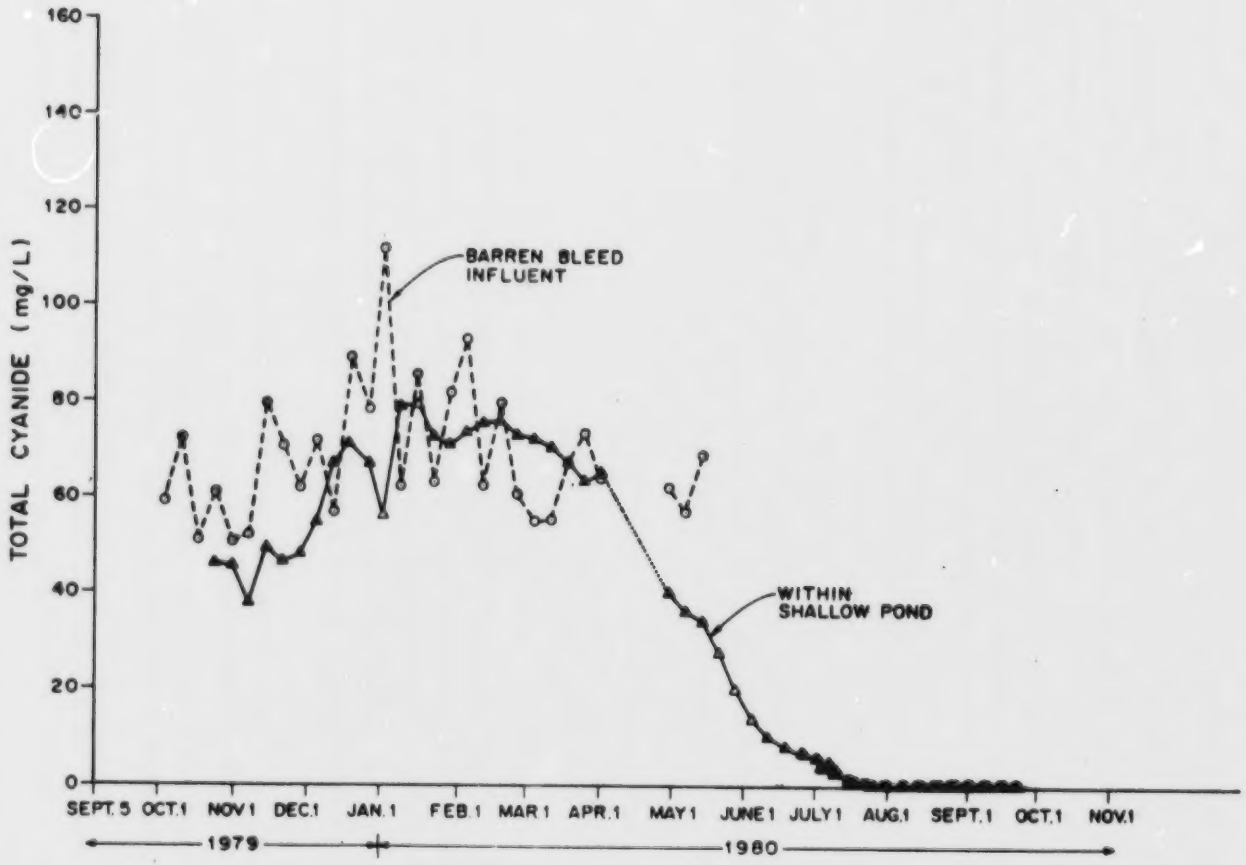


FIGURE 8 – TOTAL CYANIDE IN BARREN BLEED HOLDING POND

Source: SCHMIDT et al (1981)

ECHO BAY MINES LTD.
10180-101 Street
Edmonton, Alberta T5J 3F4
(403) 429-5885
Hugh Wilson
Manager of Environmental Services

This operation is likely to be the first really well-defined test case of the effectiveness of natural degradation of cyanide in a climate with frozen winters. It looks extremely promising.

However, in some parts of the world there is inadequate land for long term ponding and with the tighter limits that have been imposed on effluents and the given climatic constraints and volumes of water generated from both underground and tailings, there would in numerous cases be no possible way to meet them through natural degradation. One of these is Homestake Mining Company's operation at Lead, South Dakota.

RANDOL CONCEPT FOR ENHANCED NATURAL DEGRADATION OF CYANIDE IN CANADIAN MILL EFFLUENTS

Considering the frequent case where natural degradation is shown to partially remove cyanide from Canadian gold mill effluents in summer. the following concept is proposed as one potential way to ehance the process.

The process may be suitable where:

1) Water is available in abundant supply.

2) Sewage and other nutrients such as phosphates are available at a reasonable cost.

3) Land is available and a natural site is available on which to engineer a bog.

Concept

1) Barren bleed to be stored separately through the winter months in a shallow pond.

2) Tailings pond to be large enough to contain tailings all winter and precipitation without effluent discharge.

3) In Spring raw sewage from a winter accumulation pond, or from local residential area to be pumped into the barren bleed holding pond which should be fitted with an aeration mechanism such as used in municipal water treatment.

4) After aeration of the nutrient enriched barren bleed pond, effluent is pumped to a settling pond where the densest sludges are settled.

5) Solution is next decanted to a large engineered bog of cattails and associated plants with a large surface area designed so that solution passes through a system of trenches in which the plants are grown in a managed fashion.

Aims of Concept

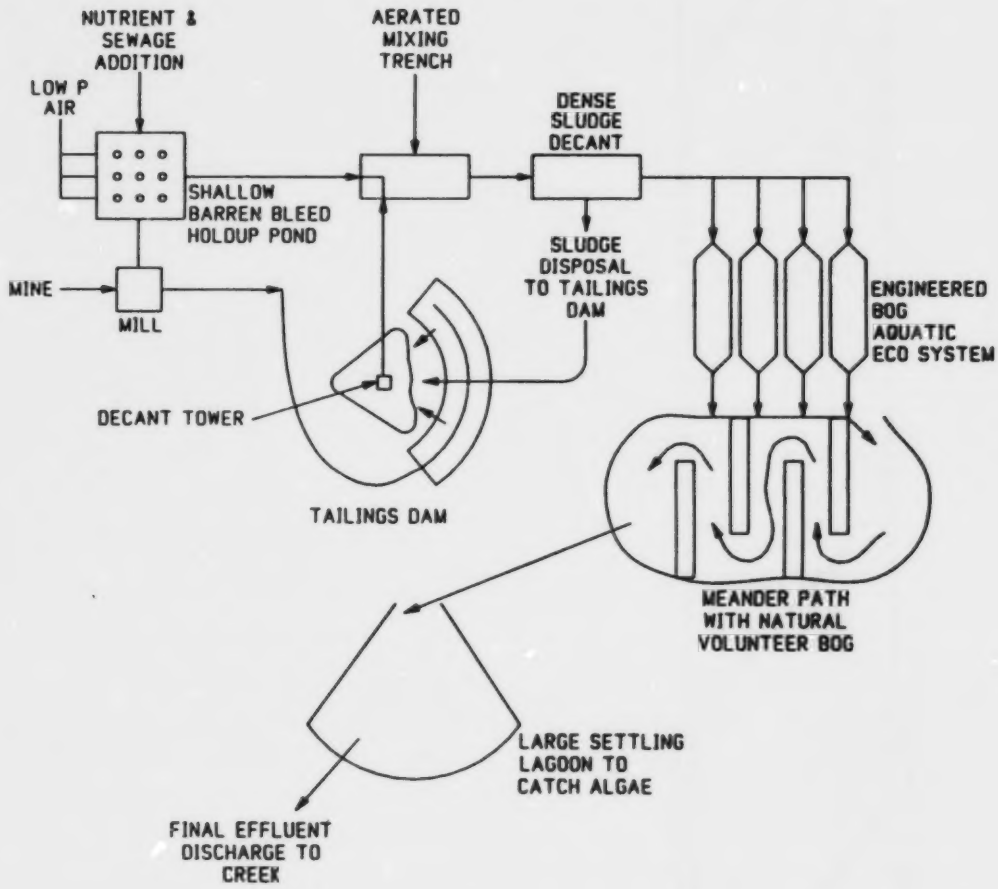
1. To provide a process that will enhance natural degradation of cyanide and metallocyanide complexes.

2. To add a minimum of expensive reagents to the process.

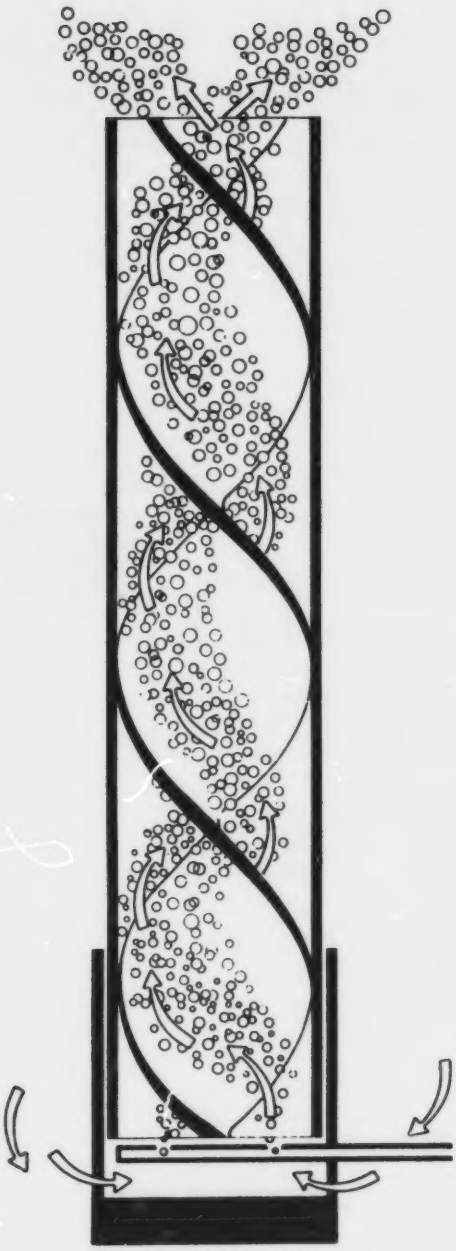
3. To remove total cyanide, metals, and ammonia.

4. To use natural polishing ability of plants if the bog is properly engineered.

ENHANCED NATURAL CYANIDE DETOXIFICATION CONCEPT



Note: The above is a RANDOL INTERNATIONAL LTD. concept that has yet to be tested.



Oxygen transfer efficiency	12.3	%
Oxygen supply/Helixor	2.82	kg/h
Air supply/Helixor-minimum	40.0	m^3/h
Air supply/Helixor-maximum	77.0	m^3/h

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AERATORS

Frings Aeration & Mixing Co., Inc.

2591

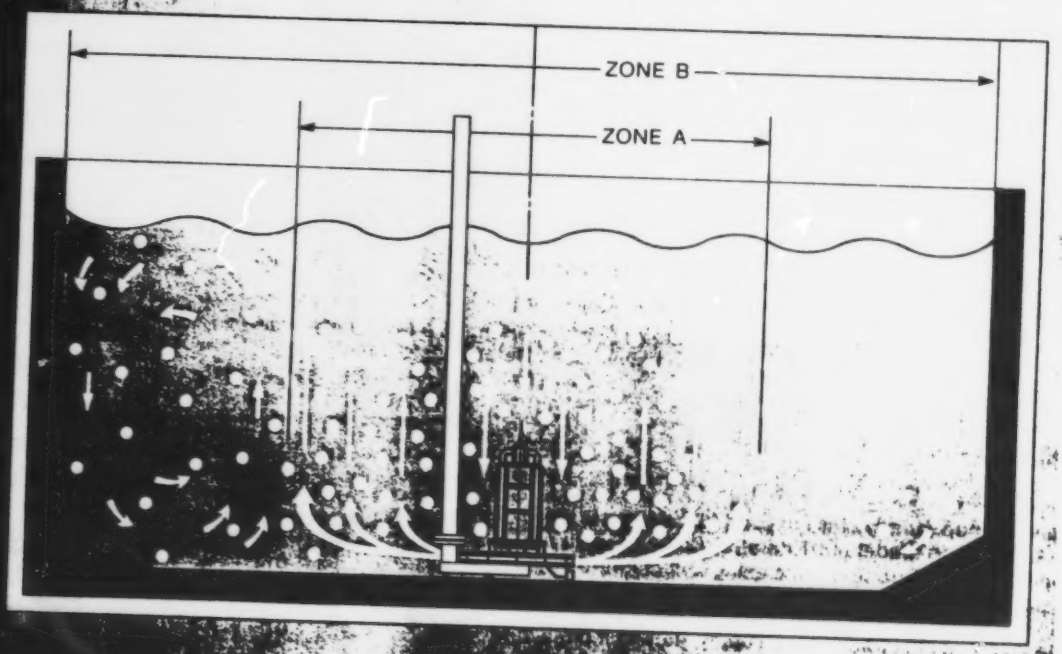
OPERATION

The turbine turns inside the stator creating a vacuum at the [illegible] of the turbine. This vacuum is filled with air that enters the [illegible]bine through the standpipe open to the atmosphere. The [illegible]er enters the turbine through openings between the turbine [illegible] the motor. The air and water are mixed in the turbine. The [illegible]ture is discharged into the diffuser channels of the stator. The [illegible]h circumferential speed of the turbine within the stator and [illegible] stator design itself create a fine bubble dispersion of the gas-[illegible]ter mixture with excellent oxygen transfer efficiency and good [illegible]ing. The aerator has two zones of influence:

ZONE A Within this area there is intimate contact of the gas-water mixture with the surrounding waters. This zone would be applicable for sizing air floatation or high BOD loading wastewater treatment processes.

ZONE B There is a complete suspension zone within this area created by the air lift effect of the gas-water mixture. This zone would be applicable for sizing stream oxidation, activated sludge or other normal BOD loading wastewater treatment processes.

Model	DIAMETER IN FEET A Zone Mixing	B Zone Suspension	Aeration Zone
075T	18	30	150
150T	25	40	175
300T	35	65	225
600T	45	75	300
900T	50	90	350
1200T	65	125	375
1800T	70	130	450
2400T	80	140	525



[illegible] influence can be increased by utilization [illegible]ped unit attached to a cable guide. The [illegible] along the cable extending the area [illegible] to a rectangle of approximately 500 feet [illegible] solids and BOD loading [illegible]

TYPICAL SPECIFICATION

Aerator(s) will be submerged, self-aspirating type. The guide blade rim will be of stainless steel construction with a 304 stainless steel turbine.

The motor(s) will have cast iron housing, stainless steel motor shaft, oil filled chamber, double mechanical seal with a seal minder and heat protections. All motors will have 25 feet of electrical cable for hook-up to a 230/460 volt, 3 phase, 60 Hertz electrical system.

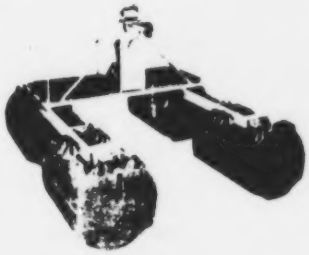
The aerator system when put into operation, will provide _____ pounds per hour of oxygen (CWTR) at _____ cfm and _____ foot depth when measured at standard conditions of zero dissolved oxygen, twenty degrees centigrade, and one atmosphere pressure. The design brake horsepower shall not exceed the motor rating horsepower of _____%. The oxygen transfer efficiency at standard conditions at the design depth and air flow will be _____%.

Installation will be made in accordance with manufacturer's specifications. The aeration equipment manufacturer will provide start-up services of a qualified technician or engineer.

The manufacturer guarantees that the aeration equipment will operate as specified above. The manufacturer will be responsible for equipment design, material and workmanship for a period of one year from date of start-up, not to exceed 18 months from date of shipment. The manufacturer will not be liable for contingent damages caused by malfunction of the equipment.

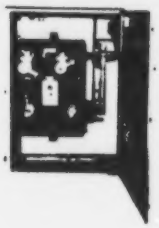
ACCESSORIES

SERVICE FLOAT



The float consists of 17 or 26 inch gull wing floats filled with a closed cell polyurethane. The urethane filler makes this rugged assembly virtually unsinkable. The service float has non-skid grating and a hand winch for lift.

MOTOR CONTROLS



Control centers are engineered specifically for use with Framco aerators. Each control center contains visual or audible indicators for the safety devices. Every control center is designed to meet the requirements of the specifying engineer or controlling agencies. All control centers are available with standard outdoor enclosures.

AIR INLET PIPE

Carbon steel or PVC pipe is available with or without an air throttling valve. A hooded wire mesh screen or air filter, can also be provided.

SUPPORT LEGS

Three or four legs, depending on the model, can be provided, to clear bottom objects. The legs are steel pipe with stainless steel hardware.

ADDITIONAL ACCESSORIES

Suction Strainer — Semi-Bridge
Suction Silencer — Lifting Device Including Hoist
Guide Brackets — Steel Lifting Lugs Including Clamp and Bolts

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DEVELOPMENT OF A MODEL TO DESCRIBE THE NATURAL DEGRADATION OF CYANIDE IN GOLD MILL EFFLUENTS

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ABSTRACT

Natural degradation is the oldest treatment method used by Canadian gold mines to remove cyanide from their effluents. This paper presents the results of a study carried out to determine the main mechanisms which control the natural degradation of cyanide, and to develop a mathematical model for predicting cyanide degradation in gold mill effluents.

The most important mechanism in the natural degradation of cyanide was recognized as being volatilization. Among the variables affecting the degradation process, the three identified as most important were selected for study, namely: temperature, UV light and aeration. Temperature had the largest effect upon reaction kinetics and ultraviolet irradiation had a significant effect upon the decay rate of the iron cyanide complex.

Synthetic solutions of simple cyanide (NaCN) and metallo-cyanide complexes of Cu, Zn, Ni and Fe were used in bench-scale tests to generate the data for estimating kinetic parameters for the model. In addition, tests were carried out on synthetic solutions and actual gold mill effluents, to calibrate the model and evaluate its effectiveness in predicting cyanide degradation in a variety of aqueous solutions.

The mathematical model, developed during this study, fitted the experimental data at the 95% confidence level for five of the eight tests on synthetic wastewaters. Using coefficients derived from the synthetic solutions, the model was applied to actual gold mill effluents. It predicted the degradation of cyanide from tailings pond water very closely, but for the barren solutions it required further recalibration. The use of the model as a design tool is illustrated.

BACKGROUND

In most Canadian gold mills, gold is extracted from the ore by the process of cyanidation. The waste streams from the process contain, among other impurities, a high concentration of cyanide and heavy metals making treatment essential prior to discharge to the environment.

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The oldest treatment practised by Canadian gold mines for destruction of cyanide is natural degradation. In this method, cyanide-bearing waste streams are impounded, usually in a tailings pond, for a period of a few days to several months, while the process of natural degradation of cyanide occurs (Scott and Ingles, 1981). Although natural degradation has been practiced for many years, the process chemistry has not been well documented. In 1979, Environment Canada's Wastewater Technology Centre in Burlington, Ontario, carried out an extensive sampling program at one Canadian gold mine (Schmidt et al, 1981). The results of this study indicated that the main mechanisms of cyanide removal were volatilization of free cyanide (90%) and chemical oxidation (10%). To better delineate the main factors and mechanisms affecting the process for design purposes, a bench scale study was recommended.

In this study, the removal of total cyanide from synthetic metallo-cyanide complex solutions was evaluated experimentally at the Wastewater Technology Centre in Burlington. This evaluation utilized (i) an experimental design to determine the main factors controlling cyanide removal; (ii) the development of a mathematical model to describe cyanide removal and (iii) the application of this model to synthetic solutions containing a mixture of metallo-cyanide complexes. Finally, this model was applied to actual gold mill wastewaters, barren solution and tailings pond water. For illustrative purposes, the model was used in a hypothetical design.

EXPERIMENTAL DESIGN

The literature generally indicates that the mechanisms of volatilization, hydrolysis, dissociation, photodegradation, chemical and bacteriological oxidation and precipitation-dissolution may have important influences on the process of natural degradation of cyanide in ponds depending on the cyanide species present and physicochemical conditions (Leduc et al, 1982).

Palaty and Horokova-Jakubu (1959) examined several factors that affect HCN removal from unbuffered, synthetic simple cyanide solutions(KCN) at relatively low concentrations (10-50 mg CN^-/L) over a period of 11 days. They were pH, temperature, solution depth, presence or absence of aeration and the rate of aeration. Their general conclusions were: the HCN removal rate increases with decreasing pH down to 5; an order of magnitude difference in the rates of HCN removal exists between aerated and nonaerated solutions; the HCN removal rate is indirectly proportional to the solution depth and almost directly proportional to the rate of aeration; a temperature increase of 10°C (from 0.8 to 11°C) causes the HCN removal rate to increase by >40% (from 0.112 to 0.216 h^{-1}).

Based on a review of the literature and a set of screening experiments, the three most important variables influencing cyanide removal were incorporated into a factorial experimental design; temperature, UV light and aeration. The high and low levels were chosen as reasonable approximations of what might be expected under actual conditions.

A full 2^3 factorial design (Box et al, 1978) was used (Table 1) to determine which variable had the greatest effect on the rate of cyanide degradation. In total, 56 runs were made for up to 13 days in duration.

TABLE 1. DESIGN MATRIX

	Variables		
Run No.	UV Light (mW/cm^2) A	Air (cm^3/min) B	Temp. (°C) C
8	-	-	-
6	+	-	-
7	-	+	-
5	+	+	-
4	-	-	+
2	+	-	+
3	-	+	+
1	+	+	+
	UV light	Air	Temp.
Experimental	- +	- +	- +
Settings	0 2	0 100	4 20

METHODS AND MATERIALS

Seven synthetic cyanide solutions were used in one set of laboratory tests. These consisted of a simple cyanide solution (NaCN), four solutions containing a single metallo-cyanide complex (Cu, Zn, Ni and Fe) and two mixtures. The "low mix" contained a low concentration of metals relative to the concentration of total cyanide, i.e. a metal cyanide (MCN) to total cyanide (TCN) weight ratio of 0.17, while the "high mix" was saturated with metals (MCN/TCN = 1.17). The initial total cyanide concentration in all the solutions was about 200 mg/L. The experiments were carried out in 2000 mL graduated cylinders at two different temperatures (4°C and 20°C). The experimental pH chosen was 7.0; a phosphate buffer was used to maintain a constant pH.

Barren solution was also tested in the laboratory with a similar experimental setup (20°C, AIR, UV). For the tailings pond water, a field experiment was conducted using a large tank located outdoors.

Total cyanide was analyzed by the methods described by Conn (1981). Heavy metals were analyzed by atomic absorption spectroscopy (AAS).

RESULTS AND DISCUSSION OF EXPERIMENTS ON SYNTHETIC CYANIDE SOLUTIONS

Upon completion of the experiments, plots of temporal changes in total cyanide concentrations in the single metallo-cyanide solutions were prepared and examined visually. Specific examples of these plots with the general trends are given in Figure 1. In several tests the residual total cyanide concentration attained was <1 mg/L (see the NaCN and Cu-CN examples); in most tests it was <10 mg/L (see the Fe-CN example) but in some cases the concentration seemed to plateau between 30 to 40 mg/L; (see the Ni-CN example).

The initial rapid decrease in cyanide concentration (first part of the curve), was observed to be complete after 48 to 72 hours under all experimental conditions. This was assumed to be controlled by the volatilization of free cyanide from the solutions.

The slope of the second part of the curves varied among the different metals and experimental conditions. This was assumed to result from the different rates of dissociation or decay of these metallo-cyanide complexes. Thus, the graphs suggest that volatilization controls the cyanide removal rate during the first part of the curve but metallo-cyanide dissociation controls the removal rate during the latter part of the curve.

To interpret the data, first-order reaction kinetics were applied to each of the two parts of the curve. By using linear regression, the volatilization mass transfer coefficient, k_v, was determined for the first part of the curve and the metallo-cyanide decay coefficient, k_1, for the second part of the curve. These coefficients were used as the response variables in the factorial design. The main effects and the two and three factor interactions were determined. Since no replicate runs were conducted, the three factor interaction was used as the estimate of error variance. Temperature was found to have a significant effect (5% level of significance) on the rate of volatilization of free cyanide from all metallo-cyanide solutions and together with aeration a high effect on volatilization of free cyanide from NaCN solution. In addition, temperature had a significant effect on the metallo-cyanide decay process in all metallo-cyanide solutions except iron cyanide and the "low mix", where UV light had the largest main effect (Simovic, 1984).

MODEL DEVELOPMENT

The second objective of the study was to develop a mathematical model with predictive capabilities. Because the measurements of cyanate made during the experimental runs showed that there was no CNO^- present, it was decided that chemical oxidation of cyanide to cyanate was not an important mechanism.

The concentration of total cyanide in the aqueous solution was the only parameter that was measured in the experiments. Total cyanide is the summation of all the different cyanides (metal and free) that exist in solution (TCN = MCN + FCN).

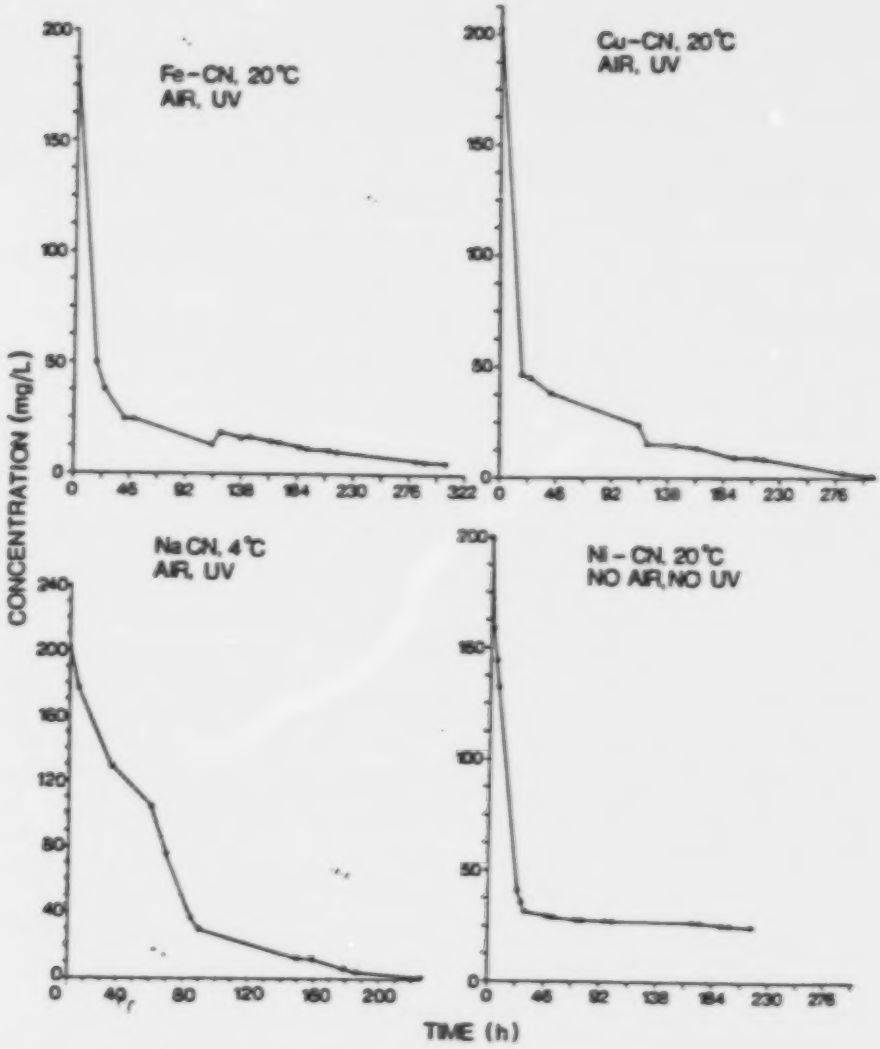

FIGURE 1. TYPICAL RESULTS OF TOTAL CYANIDE DEGRADATION IN Fe, Cu, Na AND Ni CYANIDE SOLUTIONS

The initial study results coupled with the available literature suggested that a mathematical model should be based upon the following:

1 - Metal cyanide complexes dissociate into metallic and cyanide ions ($MCN \rightarrow M^+ + CN^-$).
2 - Cyanide ions, in a reaction with hydrogen from water, produce HCN. The equilibrium developed between CN^- and HCN is pH dependent ($CN^- + H^+ \rightleftharpoons HCN$).
3 - The dominant form of free cyanide at pH 7.0 is molecular HCN. Molecular HCN is the species that volatilizes.
4 - Temperature influences the rate of decay of most metallo-cyanides. UV light affects the dissociation of iron-cyanide complexes.

To develop a model for a single metallo-cyanide complex solution, each chemical species containing cyanide was considered to be a separate component. A schematic of the various forms of cyanide that are included in the total cyanide (TCN) measurement and the proposed transformations is given in Figure 2.

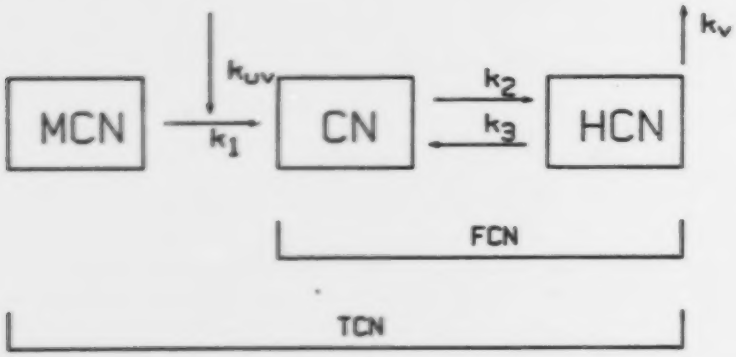

FIGURE 2. CYANIDE DEGRADATION MODEL

The first component in Figure 2 is the metallo-cyanide complex (MCN), the second is the cyanide ion (CN^-) and the third is molecular hydrocyanic acid (HCN). If the second and third are taken together they represent free cyanide (FCN). Each arrow between the components represents a transformation of mass. It has been assumed that one metallo-cyanide complex (rather than two or more complexes) and free cyanide can explain the observed characteristics of cyanide loss from solution in the single metallo-cyanide solutions. The coefficients k_1, k_2, k_3 are the rate constants (h^{-1}) of transformation between the

different forms; k_v is the volatilization mass transfer coefficient (cm/h), while k_{uv} represents the additional effect upon k_1 due to ultraviolet irradiation (h^{-1}).

Evaluation of the model schematic (Figure 2) shows that there are three potential steps (i.e. parameters) which can control the rate of removal of cyanide from solution. They are the rate of dissociation of MCN, the rate of formation of free cyanide (HCN and CN^-) and the rate of volatilization of HCN. Since the kinetics of HCN formation from CN^- and its dissociation to CN^- are extremely rapid (Caruso, 1975):

$$[HCN] \rightleftarrows [H^+] + [CN^-] \quad K_a = 4.36 \times 10^{-10} \text{ (at 20°C)}$$

the formation of HCN is not rate limiting. This allows one to treat HCN and CN^- as being constantly in equilibrium relative to other processes. Hence, there are two potential rate controlling steps, and the model to be derived can be represented by a two compartment reaction-in-series model.

For a batch reactor, the mass balance equations are:

- for metal cyanide

$$\frac{d[MCN]}{dt} = -k_1 [MCN] - k_{uv} [MCN] \qquad (1)$$

- for free cyanide (sum of CN^- and HCN)

$$\frac{d[FCN]}{dt} = k_1 [MCN] + k_{uv} [MCN] - \frac{k_v}{Z_h} [HCN] \qquad (2)$$

where $Z_h = V/A_s$. Here A_s (cm^2) is the area of the air-water interface across which volatilization occurs, and V is the reactor volume (cm^3). If the UV light effect is insignificant, k_{uv} becomes zero.

Summing these two equations produces one for total cyanide:

$$\frac{d[TCN]}{dt} = -\frac{k_v}{Z_h} [HCN] \qquad (3)$$

These three equations represent the derived model.

PARAMETER ESTIMATION

To solve the differential equations (1 to 3) a numerical integration routine was applied using the Runge-Kutta-Verner fifth and sixth order method (DVERK) available from the International Mathematical and Statistical Libraries Inc. for CYBER systems. This method requires that the initial conditions be known, then calculates simultaneously the change of concentration over time for total, metallo- and free cyanides using in this case, ten-hour time increments.

The initial value for TCN was set equal to the measured TCN concentration. Three parameters were estimated: initial metal cyanide concentration $[MCN]_o$, metallo-cyanide decay coefficient (k_1), and the volatilization coefficient (k_v). In order to determine the initial value for the volatilization rate, linear regression analysis was applied on the first part of the degradation curve and the 95% confidence interval (C.I.) was then calculated. The rate of volatilization of HCN from single metallo-cyanide solutions was found to be within the 95% C.I. of the volatilization rate of HCN from NaCN solution. Therefore, the value calculated as the volatilization rate of free cyanide from NaCN solution was used in parameter estimation and modelling work. The metallo-cyanide decay coefficient, k_1, previously determined, was used as an initial value.

To obtain the best estimates of the parameters for the model, an iterative, nonlinear least squares parameter estimation subroutine was used (GAUSHAUS*).[2] It is based on Marquardt's method which combines the Gauss method (Taylor series) and the method of steepest descent (Meeter and Wolfe, 1965).

From the estimated parameters the ratios of initial concentration of metal cyanide (MCN_o) to the initial total cyanide concentration (TCN_o) were calculated under all experimental conditions and compared to the theoretical value of MCN/TCN = 0.17. The results are presented in Table 2. Despite the range of MCN_o/TCN_o values from

TABLE 2. THREE PARAMETER ESTIMATION MODEL (MCN_o, k_1, k_v)

Cu - CN	$\frac{MCN_o}{TCN_o}$ = 0.07 to 0.69 R^2 (%) = 97 to 99
Zn - CN	$\frac{MCN_o}{TCN_o}$ = 0.12 to 0.74 R^2 (%) = 98 to 99
Ni - CN	$\frac{MCN_o}{TCN_o}$ = 0.11 to 0.53 R^2 (%) = 96 to 99
Fe - CN	$\frac{MCN_o}{TCN_o}$ = 0.12 to 0.41 R^2 (%) = 98 to 99

* GAUSHAUS now called UWHAUS

0.07 to 0.74, the calculated multiple correlation coefficient, R^2, indicated that 96 to 99% of the total variability in the data was explained by the model.

To determine whether these estimated values were statistically different from the theoretical ratio for MCN/TCN of 0.17, the model was fitted using different MCN/TCN ratios (0.0425, 0.085, 0.17, 0.34, and 0.68). The initial metallo-cyanide concentration, $[MCN]_o$, k_v, and k_1 were estimated for each ratio for all experimental conditions. Analysis of the residual sum of squares (RSS plotted versus ratio) using an F test, showed that the model fit obtained in 27 out of 32 conditions (4 metals and 8 conditions) in the first analyses was not significantly different (5% level of significance) from the fit obtained for the stipulated ratio MCN/TCN of 0.17. It was concluded that the theoretical MCN/TCN weight ratio of 0.17 could be used for the initial ratio in the laboratory solutions of single metallo-cyanides.

The estimated metallo-cyanide decay coefficients were averaged for experiments at 4°C and 20°C (Table 3). This was justified because the temperature had a significant effect on metallo-cyanide decay rates, aeration had no effect, and ultraviolet light had a significant effect only on the Fe-CN and "low mix" solutions.

TABLE 3. AVERAGE METALLO-CYANIDE DECAY COEFFICIENTS (h^{-1})

	$k_1 \times 10^2$ (4°C)	$k_1 \times 10^2$ (20°C)
Zn-CN	1.78	4.49
Cu-CN	0.29	0.75
Fe-CN	0.14	0.47
Ni-CN	0.04	0.09

The Zn-CN decay rate was the fastest (an order of magnitude more rapid than Cu-CN); decay of Cu-CN was double that of Fe-CN, while Ni-CN was an order of magnitude slower than Cu-CN and Fe-CN.

VERIFICATION STUDY - LOW MIX

The averaged metallo-cyanide decay coefficients (Table 3) were used in the simulations for the "low mix" solutions. The "low mix" solutions should theoretically contain 17% of the total cyanide complexed with the four metals present.

A typical comparison of model predictions and observations is presented in Figure 3. There was good agreement between the model and observations during the volatilization of free cyanide (first 70 h of the curve) and during the degradation of metallo-cyanides in the latter part of the curve. Overall, the model predictions agreed with the observations at the 5% level of significance for five out of the eight sets of experiments performed on the "low mix", however, for the other three, agreement was not as good.

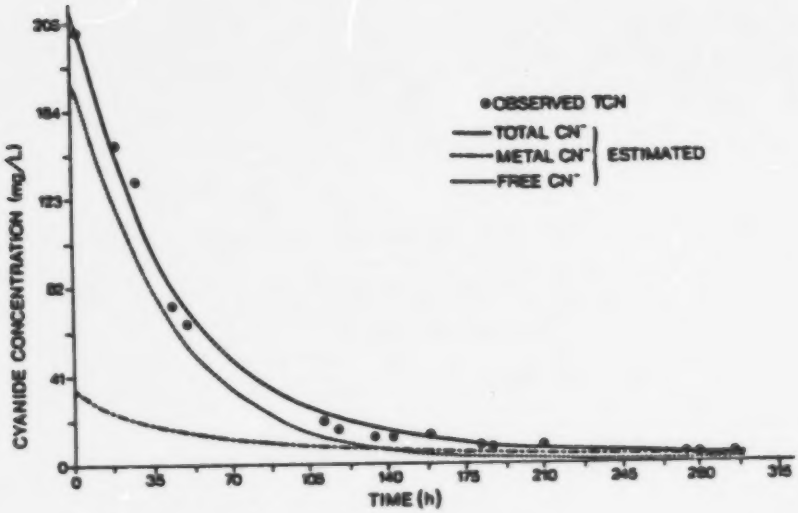

FIGURE 3. LOW MIX SIMULATION - 20°C, NO AIR, UV

EVALUATION OF THE MODEL WITH GOLD MILL EFFLUENTS

The model derived from synthetic solutions was tested on data on effluents from two Canadian gold mines (batch systems). One effluent was a barren solution (bench scale experiment), and the second was tailings pond water (field experiment). Data describing the characteristics of these solutions at the beginning and at the end of the experimental period are given in Table 4.

TABLE 4. CHARACTERISTICS OF GOLD MILL EFFLUENTS (BEFORE AND AFTER TREATMENT)

Gold Mill Effluent Type	TCN (mg/L)		pH		Cu_T (mg/L)		Zn_T (mg/L)		Ni_T (mg/L)		Fe_T (mg/L)		RT (d)
	I	F	I	F	I	F	I	F	I	F	I	F	
Barren Sol'n.	145	2.3	11.5	8.2	7.1	7.1	31	21	1.5	1.3	0.1	<0.1	55
Tailings Pond Water	4.3	0.2	8.2	8.1	0.7	0.3	0.1	<0.1	0.2	<0.1	1.0	0.6	65

RT - Retention time; I - Initial value; F - Final value

The apparatus used for the barren solution was the same as the one used for the synthetic solutions (2000 mL graduated cylinder). The experiment was conducted in the laboratory under the best conditionsfor the natural degradation of cyanide, i.e. 20°C, AIR and UV. During the retention time of 55 d, the concentration of total cyanide in this solution decreased 98%, from 145 to 2.3 mg/L (Table 4). The pH changed from 11.5 to 8.2 during the same time period.

The apparatus used for the tailings pond water was an open circular tank with a diameter of 7.3 m and a depth of 1.6 m. It was exposed to natural environmental conditions from July to October of 1983. The effluent was aerated with compressed air, at an air flow rate of 0.3 m^3/min. The initial concentration of total cyanide in this effluent was significantly lower than in the barren solution. During 65 d, the total cyanide decreased 95% from 4.3 to 0.2 mg/L (Table 4).

The only differences that existed between these gold mill effluents and synthetic solutions were the initial cyanide and metal concentrations, the pH of the solutions, and the depth of the experimental vessel used for the tailings pond water. To model these effluents it was assumed that the actual gold mill effluents contained the same metallo-cyanide complexes as the synthetic solutions (i.e., $Cu(CN)_3^{2-}$ $Zn(CN)_4^{2-}$ $Ni(CN)_4^{2-}$ $Fe(CN)_6^{3-}$). An adjustment to the model was required because of the difference in pH values. Since the model equations were derived for synthetic solutions at pH 7.0, corrections for volatilization rate were required to account for the pH dependent speciation of HCN (i.e. $HCN \rightleftharpoons H^+ + CN^-$). A second adjustment involved the effect of solution depth on the volatilization coefficient in equation (2).

The results of the model simulation on cyanide degradation in barren solution are presented in Figure 4a. Considering the initial cyanide value (145 mg/L), the model predictions fitted the data well particularly during the volatilization process (first part of the curve). However, as inspection of the latter part of the curve shows, the model predicted a more rapid decay of the metallo-cyanides than actually occurred. There are three possible reasons for this discrepancy. Firstly, it was originally assumed that the effect of pH on the metallo-cyanide decay rate was insignificant and that the main effect of pH was upon HCN and CN^- speciation. In fact, the pH may affect the decay rate. Secondly, the barren solution may contain different metallo-cyanide complexes than the ones assumed. Thirdly, at the high pH values (i.e. 11.5 and 8.2), the cyanide ion released upon metallo-cyanide dissociation could not form HCN, therefore, it could complex with another metal or even form thiocyanate and precipitate. The metal would be more successful in competing for CN^- at high pH than the H^+ form. The model would not account for these conditions.

The final value calculated by the model for TCN was compared to the experimental value observed for TCN in Table 5. The predicted TCN

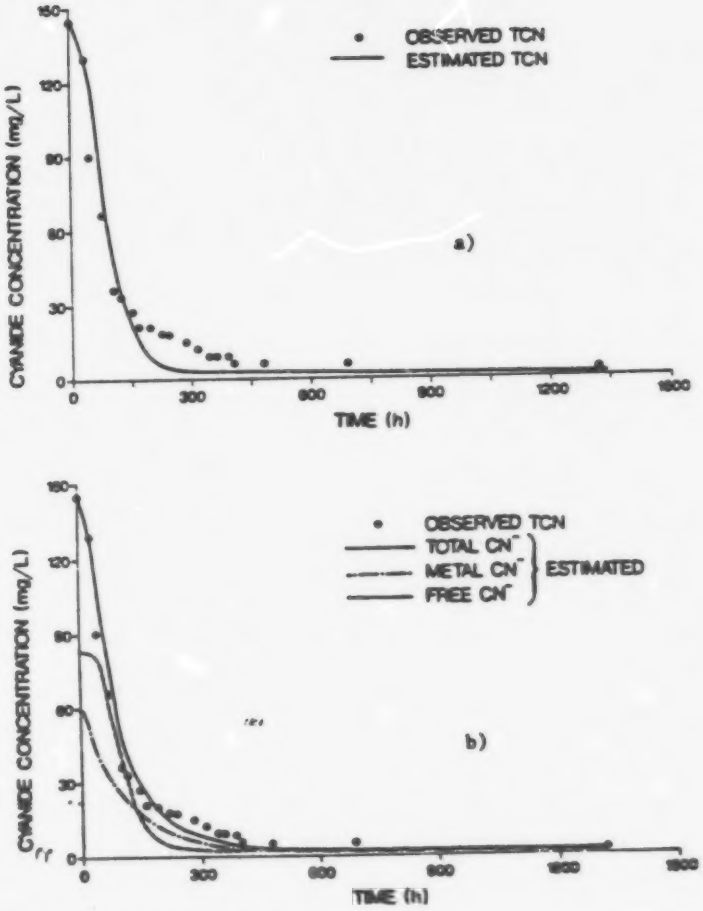

FIGURE 4. SIMULATIONS ON BARREN SOLUTION -
a) ORIGINAL b) RECALIBRATED k_{Zn} AND k_{Ni}

for the barren solution was lower than the value obtained in the experiment. Similarly, the predicted break-point between volatilization and metallo-cyanide decay occurred earlier than observed from the barren solution experiment (see Figure 4a: deviation from curve at about 225 h).

TABLE 5. RESULTS OF THE SIMULATIONS ON ACTUAL GOLD MILL EFFLUENTS

Gold Mill Effluent Type	Time (h)	TCN (mg/L)	
		Expt.	Predicted
Barren Solution	1320	2.3	0.75
Tailings Pond Water	1560	0.1	0.05

In the experiments on single metallo-cyanide solutions there was variability in the volatilization rates, and in the metallo-cyanide decay rates for the same experimental conditions. A similar degree of variability can be expected in model predictions involving actual effluent data. Hence, to obtain a better fit for the barren solution data, some model recalibration from the mean parameter values of the single metallo-cyanide solutions can be expected to be required.

Inspection of the characteristics of these two effluents (Table 4) showed that the barren solution contains a higher concentration of nickel. Nickel was found to be the slowest degrading metallo-cyanide complex (Table 3). When the reaction rate constant for Ni was recalibrated (from 0.00095 to 0.00024 h^{-1}, obtained from an examination of the curve) the predicted metallo-cyanide decay part of the curve improved considerably (predicted TCN = 1.9 mg/L). However, there was no significant change in the location of the volatilization-metallo-cyanide decay break-point on the curve.

It was also noted (Table 4) that for the barren solution, the concentration of Zn was the highest of all the metals. It also has the fastest degradation rate (Table 3). Accordingly, it was hypothesized that the Zn-CN in the barren solution controls the location of the break-point. When the reaction rate constant for Zn was recalibrated (from 0.045 to 0.009 h^{-1}, obtained from an examination of the curve) the agreement of the model predictions with the data improved considerably (Figure 4b: better fit at about 225 h).

The model prediction for the tailings pond water (Figure 5) was considerably better than for the barren solution. Because the total cyanide concentration was very close to the calculated metallo-cyanide concentration, cyanide degradation was controlled by the metallo-cyanide decay stage. Therefore, model calculations for volatilization had little effect upon the shape of the curve.

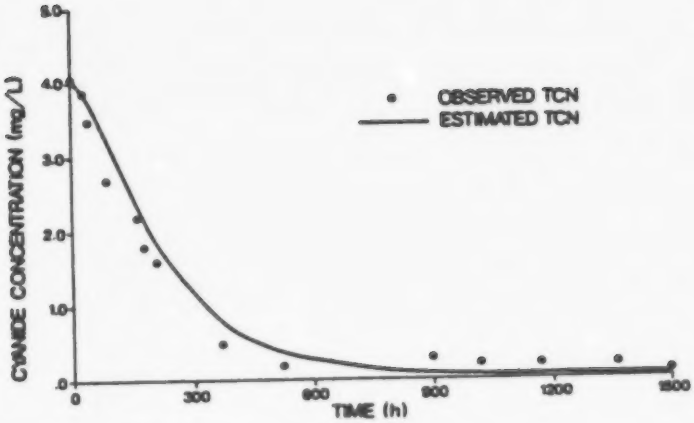

FIGURE 5. SIMULATIONS ON TAILINGS POND WATER

The results obtained from modelling actual gold mill effluents validate the original idea, that the rate of volatilization and the rate of metal decay, control the process of degradation. Recalibration of the reaction rate constants, for particular barren solutions, appears to be necessary to achieve good agreement with observations, owing to the complexity and variability of different natural solutions. An assessment of the frequency and degree of recalibration to be expected must await further model testing.

MODEL APPLICATION

The purpose in producing the model was to develop a design tool for natural degradation systems. To illustrate its use, it was assumed that two systems could exist: (i) a batch system, representative of a holding pond filled with barren solution and allowed to sit over summer to degrade naturally; and (ii) a continuous stirred tank reactor (CSTR) system, representative of a tailings pond, having a continuous inflow and discharge with a retention time (RT) of 3 days. The total cyanide concentration in the influent to the tailings pond is low in the winter time, because the barren solution is stored in a separate pond. However, in the summer time the influent cyanide concentration is higher because the barren solution is also fed into the tailings pond.

For the batch system, an effluent objective of 0.05 mg/L total cyanide was required. From the estimated rate constants of the metallo-cyanides (Table 3), nickel-cyanide is the complex that degrades the slowest. Therefore, the required retention time was calculated, applying the derived model equations to a batch reactor, for the worst conditions, i.e. decay of nickel-cyanide complex. The retention time necessary to achieve this effluent objective was calculated to be 5.8 months in the summer (20°C). This value agrees well with the actual results attained at a Canadian gold mine (barren solution holding pond volume V = 6000 m^3) where a concentration of 0.05 mg/L was reached after 5.5 months (Schmidt et al, 1981).

For winter conditions (at 4°C) and the same effluent objective, the retention time calculated was 12.5 months. The approximate CN degradation during this time would be 97% of Ni-CN, and 100% of the other three metallo-cyanide complexes (Cu, Zn and Fe), and the free cyanide. This result cannot be compared to any existing system in Canada, because no pond in Canada would remain at 4°C for one year. Further, most ponds are either filled during the winter, thus preventing them from being considered as a spiked, batch system, or are frozen solid during winter months and thus no data on TCN is available.

For the tailings pond (CSTR), two time periods were examined, summer and winter. The initial TCN concentrations, presented in Table 6, were the real mean values from a similar system at a Canadian gold mine (MCN/TCN = 0.6).

Assuming steady state conditions and using the previously derived model based on first order kinetics, the concentration of TCN was calculated for four different retention times (Table 6), and plotted in Figure 6. The predicted TCN concentration after three days during winter would be 32.8%, and for summer 43%. In the actual system, the corresponding values were 43.6% and 73.1% respectively. The difference between the predicted and observed values may be explained by the following: the actual system is probably not under steady state conditions, it is not represented by a true CSTR, and solid particles are present.

TABLE 6. CALCULATED TCN FOR THE TAILINGS POND

Retention Time (d)		0	1	3	7	30
Winter	Average input TCN_o = 14 mg/L	Calculated TCN_F concentration (mg/L)	11.7	9.4	7.4	3.9
	% removal		16.4	32.8	47.1	72.1
Summer	Average input TCN_o = 22.3 mg/L	Calculated TCN_F concentration (mg/L)	17.2	12.7	8.9	3.9
	% removal		22.9	43.0	60.1	82.5

F - Final concentration

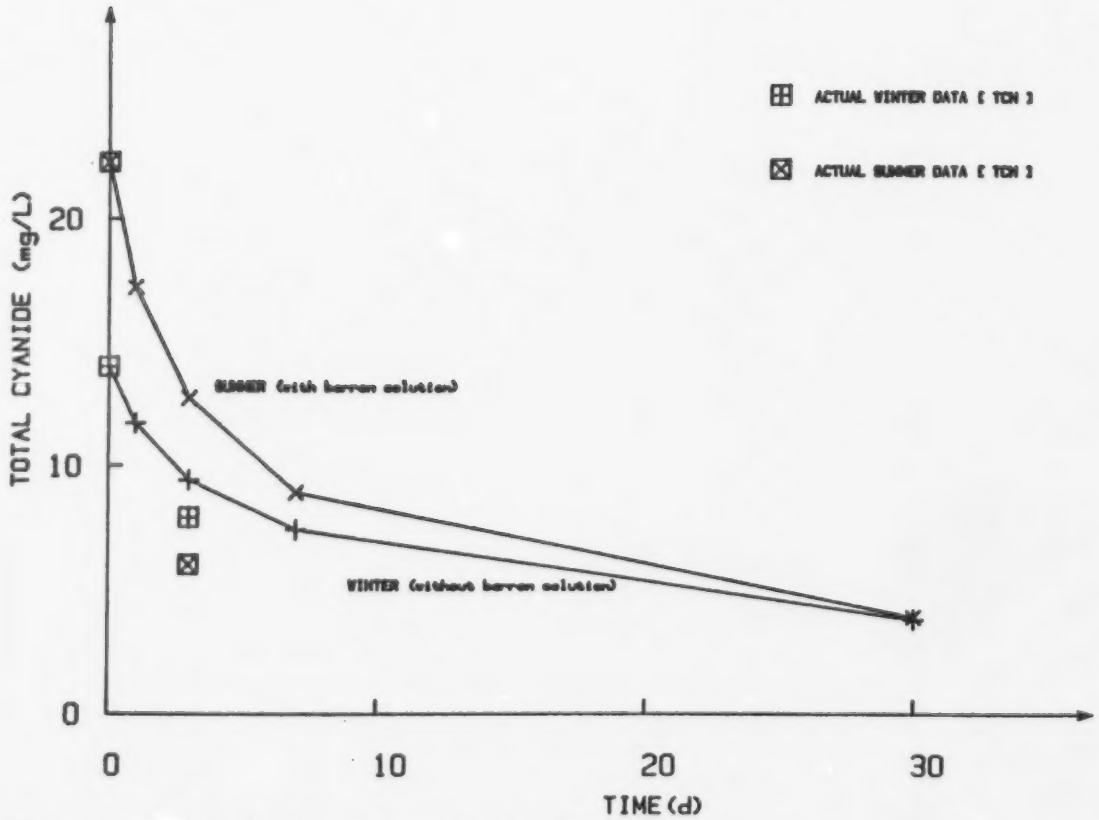

FIGURE 6. CYANIDE DEGRADATION - DESIGN CALCULATION

CONCLUSIONS

The conclusions from this study are:

1) Volatilization of free cyanide and metallo-cyanide decay are the mechanisms used to explain cyanide removal from solution during natural degradation. Volatilization is a rapid process, thus metallo-cyanide decay will be the rate limiting mechanism for many conditions.

2) Analysis of the experimental results conducted on laboratory solutions show that temperature appears to have had the greatest effect on the volatilization rate of both NaCN and metallo-cyanide solutions. Aeration had a lesser effect than temperature on the volatilization of free cyanide from NaCN solutions. Volatilization was essentially complete within the first 48 to 72 hours of the removal process.

3) Temperature had a large effect upon the metallo-cyanide decay rate in most of the solutions. UV light had a large effect only on the Fe-CN and "low mix" solutions containing low quantities of iron. It had no significant effect upon a "high mix" solution containing a high concentration of iron.

4) A mathematical model, developed for the degradation of a single metallo-cyanide complex solution in a batch reactor, supported the assumptions that the volatilization of free cyanide and metallo-cyanide complex decay controlled the cyanide degradation process, and that a chemical equilibrium existed between HCN and cyanide ion.

5) By using the best estimates of the reaction rate coefficients determined for the single metallo-cyanide solutions to simulate the experimental data of the mixed synthetic metallo-cyanide complex solution, it was found that the model predictions fitted the data at the 95% confidence level in five of the eight test conditions, however, for the other three, it did not fit as well.

6) The model derived from the synthetic solutions was applied to two gold mill effluents. In the case of modelling tailings pond water containing a very low level of total cyanide, the results showed that the model can be used successfully to estimate the cyanide degradation rate. For barren solution, although the model predictions generally fitted the data well, recalibration of the rate constants was considered necessary.

7) The model derived for batch reactors, can be used at this stage of its development, for design purposes.

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Environment Canada / Environnement Canada
Environmental Protection / Protection de l'environnement

Wastewater Technology Centre,
P.O. Box 5050,
Burlington, Ontario. L7R 4A6

October 22, 1984

Your file / Votre référence

Our file / Notre référence

81

Mr. H. von Michaelis
President
Randol International Ltd.,
21578 Mountsfield Drive
Golden, Colorado 80401
U.S.A.

Re: Your letter 3 October, 1984 - Natural Degradation of Cyanide

In response to your question concerning the location of the "final effluent" sampling point (3A), I would advise that it was located near the toe of the tailings dam. There was no dilution of the effluent at this location and the residence time in the decant structure was perhaps of the order of a few seconds. As tailings ponds III and IV were not used simultaneously the same comment applies to sampling location 3B.

I cannot give you a definitive answer to the first sentence in your fourth paragraph. The reason for this is that two gold mills located in the Northwest Territories (N of 60° latitude) have, in fact, proposed to use this method as the "sole means" of treatment. Both mines have been operating for a period of about two years and their tailings ponds are of such a size that they will not have to decant any water for a period of several years. We are collaborating with both mines on "natural degradation" studies and they are also undertaking on-site test work to determine whether or not "natural degradation" will be an adequate "sole treatment" process. Because both these mines are very isolated the cost of any chemical treatment would be quite substantial. We are also aware that other operators are or intend to use "natural degradation" as an element of their treatment systems.

Since presentation of our paper on natural degradation, we have carried out additional laboratory and field studies with a view to developing a model for design purposes. I regret, however, that this information is not yet readily available but will be published in several different reports and papers in the next few months and we will be pleased to forward this information to you when it becomes available. A major paper summarizing most of the work will be presented at the "Cyanide and the Environment" Conference being held in Tucson

In order to conserve energy and resources, this paper contains post-consumer fibre.

A des fins de conservation de l'énergie et des ressources, ce papier contient des fibres recyclées.

Mr. H. Von Michaelis October 22, 1984

in December, by Mrs. L. Simovic, the project leader for our natural degradation studies. Much of the information to be presented will be from her M.Eng. thesis (a 350 page document) which she recently completed.

The document which you are compiling looks as though it would be of interest to us and we would appreciate being advised when it is completed. } Sadly Not possible *

We thank you for your interest in our program and if we can be of additional assistance (with respect to this topic or minewater treatment generally, please do not hesitate to contact us.

Yours very truly,

J.W. Schmidt, P.Eng.,
Head,
Physical/Chemical Processes Section

cc: L. Simovic

* Reads: [illegible] Agency:

HEAP LEACHING

Most heap leaching operations to date have been located in parts of the country with net evaporation, and it is reasonable to expect that cyanide will be destroyed by natural degradation in these heaps on abandonment. The question has been raised that if a heap is drained, there will still be cyanide left in the pores of rock particles and the residual moisture content of the material. As this dries out and water evaporates, cyanide will be left as soluble salts. If dry, it will remain forever, and the question is asked as to its fate if some years later there is a torrential downpour. This aspect is under investigation. To date, Dave Milligan is the only person known to have actually sampled material from the inside of abandoned heaps to measure its cyanide content on one dump.

It is reasonable to speculate that the fate of cyanide in abandoned heaps will be one of three:

1) Natural degradation will cause cyanide to be lost as the heap dries out. There will always be some residual moisture left, and atmospheric CO_2 will reduce the pH low enough to volatize cyanide.

   Also, bacterial action in the heap with its large surface area will consume cyanide as an energy source in some cases.

2) Where small amounts of sulfides are present in the tailing material, oxidation thereof in the dam material exposed to the air will cause a pH drop in the residual interstitial moisture which will slowly volatilize residual cyanides which will be lost.

3) If the pH stays high at around pH 10 or so, there is a possibility that some residual cyanide values could reside in the heap for some time until precipitation flushes it out. This has not been studied or confirmed, however.

With the third possibility in mind and for heap leaching operations in parts of the world with net precipitation, there are two possible approaches:

1) Rinse the heap with alkaline hypochlorite solution before abandonment as at Superior Mining, Idaho--see Appendix I.

2) Use the heap material as a giant trickle filter.

By irrigating solutions onto the heap that are innoculated by appropriate bacteria and nutrients, the biological oxidation of residual cyanide can likely be enhanced.

This concept emerged at the RANDOL Water Workshop, Beaver Creek, in October, 1984. It is now being tested at a New Mexico heap leaching operation by:

ENVIROLOGIC SERVICES INTERNATIONAL
Div. of J. H. Kleinfelder and Associates
2425 South Colorado Blvd.
Denver, CO 80222
(303) 759-2611
Jim V. Rouse
David Brooman

HOMESTAKE MINING COMPANY, LEAD, SOUTH DAKOTA

Following the imposition of relatively strict effluent limits by the state of South Dakota in 1976 a major effort has been underway to meet the regulatory demands. The various processes tested have been described by HALBE et. al. (1979); TRAUTMAN & OMMEN (197?); MUDDER & WHITLOCK (1984) and WHITLOCK & MUDDER (1984). The historical battles between the company and the regulatory authorities in trying to gain relief from limits that appear almost impossible to meet by any known technical process that could be afforded were described by EDELMAN & WALLINE (1981)

Parameter	BPT Limit (40 CFR 440.22)* mg/l	WQS Limit mg/l	Permit
Total Suspended Solids	30	10	10
Arsenic	N/A	0.38	0.38
Cadmium	0.1	0.00025	0.00025
Chromium	N/A	0.85	0.85
Copper	0.1	0.009	0.009
Lead	0.4	0.28	0.28
Mercury	0.002	0.001	0.001
Nickel	N/A	1.25	1.25
Silver	N/A	0.001	0.001
Zinc	1.0	0.020	0.020
Cyanide	0.02	**	0.02
pH	6 to 9	N/A	6 to 9

* 40 Fed. Reg. 61722 (Nov. 6, 1975).

** "Quality Criteria for Water," United States Environmental Protection Agency (July 1976), indicated that an instream value of 0.005 mg/l total cyanide would be necessary to protect fresh water aquatic life. With the available dilution ratio, this would require and effluent limitation of approximately 0.017 mg/l.

Source: EDELMAN & WALLINE

Since 1981 or 1982 Homestake Mining Company redirected its cyanide removal development and search towards biological processes. The laboratory and pilot scale test program has culminated in a commercial scale plant to treat a maximum of 21,000 m^3d (3800 USgpm) of mine and tailings decant water by biological processes employing 48 rotating biological contactors in a plant rumored to cost somewhere between $5.5 million and $10.0 million depending on the source.

MUDDER & WHITLOCK (1984) and WHITLOCK & MUDDER (1984) have provided a glimpse at the broad principles of the process and have also discussed some of the shortcomings of other processes that have been tested or evaluated. Their papers describe the basic process details but since the plant has been operating less than one month at the time of writing it is too soon to determine what performance can be achieved. Bacterial colonies take several months to stabilize.

FEED SOLUTION AT LEAD, SOUTH DAKOTA

Wastewater Characteristics

PARAMETER	MINEWATER[1]	TAILINGS IMPOUNDMENT WATER[1]
Thiocyanide	1.0 - 16.0	110.0 - 240.0
Total Cyanide	.10 - .50	7.00 - 30.00
Method-C Cyanide	.02 - .10	4.00 - 20.00
Iron	.10 - 10.00	1.50 - 6.00
Copper	.07 - 1.60	1.40 - 6.00
Nickel	.01 - .04	.20 - .40
Zinc	.01 - .10	.01 - 1.50
Ammonia-N	5.0 - 6.0	less than 1.0
Phosphorous-P	trace	trace
pH	5.0 - 6.5	7.00 - 9.5
Temperature (F°)	70 - 85	34.70

1 - All values in mg/l except temperature and pH.

Note: The actual wastewater ratio is varied throughout the year from 70/30 mine/tailings impoundment wastewater ratio in the winter to 50/50 mine/tailings impoundment wastewater ratio in the summer.

Source: WHITLOCK & MUDDER (1984)

POTENTIAL SUITABILITY

Suitability of Bacteria for Removal of

Total Cyanide CN_T	Thiocyanate CNS^-	Method-C Cyanide	Ammonia	Metals
Yes	Yes	Yes	Yes	Yes

MUDDER & WHITLOCK (1984) showed that acclimatized strain of bacteria could remove all the items of major concern in the Homestake effluent. Ammonia in the minewater and ammonia generated in the biodegradation of cyanide could be removed in a second stage biodegradation step to yield NO_3^-.

WASTE WATER TREATMENT USING ACCLIMATIZED PSEUDOMONAS PAUCIMOBILIS

84-06156 M1

Biological degradation of free or complex cyanide and thiocyanate - waste-water treatment using acclimatized Pseudomonas paucimobilis (En)

/Homestake-Mining/ US 4440-844: 20.04.83-US-486610 (03.04.84) 20.04.83 as 486610. *84-100770/16*

The strain Pseudomonas pausimobilis (Mudlock) ATCC 39204 is used in the degradation of cyanides, thiocyanates and metal cyanide complexes in aqueous waste. The aqueous waste is contacted with this flora to cause conversion of harmful cyanides etc. to environmentally safe products. Preferably contact is in a rotating biological contactor where the flora is attached to a rotating disk so that part of the disk is in the waste and part in the air. Alternatively, an activated sludge method is used where the flora and waste are alternately agitated and settled with continuous aeration. The wild type strain is preferably acclimatized in a medium containing 5-15 mg/l total cyanide and 30-70 mg/l thiocyanate. The process is used for treating mining and electroplating waste-water. The pollutants (including stable Fe complexes) are oxidized to bicarbonates, sulfates and nitrates without generating ammonia. (6pp)

MICROBIOLOGICAL PROCESS

MUDDER & WHITLOCK isolated a specific strain of bacteria indigenous to process waters at the Homestake Mine. These were acclimated to increased concentrations of cyanide and thiocyanate to develop a mutant strain with increased capacity to degrade cyanides.

The bacteria species developed are unable to grow in the presence of low oxygen atmospheres or in a hydrogen atmosphere and are described as aerobic heterotrophs.

The predominant bacterium is a gram negative rod (0.7-1.4 micrometers) mobile by means of a single polar flagellum approximately three times the body length. Optimum growth occurs at 30°C with limitations at 5-42°C. Metabolism is respiratory, never fermentative. The optimum pH range for the bacteria is 7.0-8.5. Nitrates and nitrites are not reduced and H_2S is not produced; all of these factors are critical to both the treatment process and the structural features of the plant.

The bacteria oxidize free and complexed cyanides to carbonate and ammonia and metals are absorbed, ingested and precipitated as follows:

$$(1)\quad M_xCN_y + 4H_2O + O_2 \xrightarrow{\text{Bacterium}} \text{M-biofilm} + 2HCO_3^- + 2NH_3$$

The order of rate of degradation increases from Zn, Ni, Cu to Fe for metal complexed cyanides in lime with the complex stability sequence.

Iron cyanides have been shown to be degraded as well as adsorbed at rates of degradation exceeding those previously reported.

Thiocyanate degradation is similar and rapid and occurs in the pH range 7.0 - 8.5 also which is higher than the range reported in the literature.

$$(2)\quad 2SCN^- + 5O_2 + 4H_2O \xrightarrow{\text{Bacterium}} SO_4^{-2} + HCO_3 + NH_3$$

Following the degradation of thiocyanate, cyanides and metals removal through adsorption, the NH_3 must be removed. This is achieved in the nitrification stage by means of a common pair of anaerobic autotrophic bacteria (using inorganic carbon as sole source of carbon and inorganic materials as their sole nutrient source.)

Degradation and nitrification of ammonia are similar to that in activated sludge nitrification plants at the end of more modern sewage treatment plants.

$$(3)\quad 2NH_4^+ + 3O_2 \xrightarrow{\text{Bacterium}} 2NO_2^- + 4H^+ + H_2O$$

$$(4)\quad 2NO_2^- + O_2 \xrightarrow{\text{Bacterium}} 2NO_3^-$$

Ammonia is oxidized to nitrite slowly and then rapidly to nitrate. According to WHITLOCK & MUDDER (1984) the two microbial flora in the degradation stage and nitrification stage are normally non-competitive and are limited by the change in thiocyanate/cyanate concentrations.

Thiocyanate and cyanide are nutrients for the degradation stage bacteria and are toxic to the nitrifying bacteria. Ammonia acts as a nutrient for the nutrifiers and along with diminishing food source may act to control competition from cyanide degrading bacteria. An upset in the effectiveness of cyanide degradation would adversely affect the nitrificaiton stage and recovery of the nitrifying bacteria is several times slower than recovery for cyanide degraders. Hence the rate limiting factor incorporated into the plant design is based on the slower recovery rate of the nitrifiers. Reaction rates for thiocyanate, cyanide and ammonia are usually zero order down to low concentrations.

This means that the process is divided basically into two sections - the first to degrade cyanide and thiocyanate and adsorb and metabolize metals - the second to nitrify the ammonia byproduct.

TREATMENT PLANT DESIGN

Testwork by MUDDER & WHITLOCK (1981) showed that an activated sludge will work, but even with aeration periods ranging from 6 - 24 hours, the system fails after about 60 days due to metal overload.

The system employed uses 48 rotating biological contactors (RBCs) followed by clarification and pressure sand filters with dual media beds.

PILOT PLANT RBC RESULTS AT HOMESTAKE, LEAD, SOUTH DAKOTA (ppm)

	CNS	CN_T	Method-C Cyanide	Ammonia	Copper
Pilot Plant Influent	60.0 ± 10.0	6.50 ± 2.10	4.10 ± 1.30	6.0 ± 1.0	1.00 ± 0.40
2.0m RBC Pilot Plant Effluent	less than 1.0	0.35 ± 0.0	0.05 ±0.02	less than 0.50	0.04 ± 0.02

Source: MUDDER & WHITLOCK (1984)

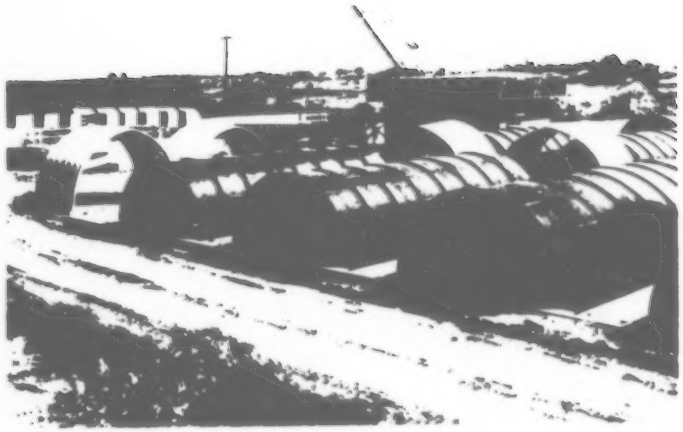
WALKER PROCESS

Dedicated to the Water & Wastewater Industry

BIOSPIRAL

ROTATING BIOLOGICAL CONTACTOR

2620



INTRODUCTION

Rotating Biological Contactor systems (RBC's) are widely applied in municipal and industrial wastewater treatment where a high degree of BOD and NH_3 removal is required. RBC technology is based on the "dynamic" fixed film principle in which media, mounted on a slowly rotating horizontal shaft, is alternately submerged in a tank of wastewater and then exposed to the atmosphere. Microorganisms attach themselves to the media where they oxidize organic pollutants contained in the wastewater.

RBC systems offer several significant advantages over other types of secondary treatment processes including

- **Low energy requirements**
- **Low space requirements**
- **Operational simplicity**
- **Low maintenance requirements**
- **Low system headloss**
- **High treatment efficiency**
- **Good resistance to shock loads**

RBC systems are applied in a variety of configurations including new plant construction, trickling filter or activated sludge plant upgrades and polishing for municipal treatment systems. They have also been used in the petrochemical, textile, food and beverage industries and others. RBC systems available include smaller diameter treatment modules in steel tanks for commercial treatment applications to multiple full-size shafts for large treatment plants.

RBC systems are a proven, effective treatment alternative for biological reduction of organic pollutants.

The Walker Process BioSpiral RBC provides the mechanical and structural reliability we have been known for in the wastewater field since 1946. Our BioSpiral combines the largest structural components standardly available with a superior design to produce a rugged RBC capable of the sustained performance you require in your plant. The Walker Process engineering staff will provide the designer with necessary assistance in developing the most efficiently sized RBC system for his particular treatment requirements. Our unique media arrangement provides the capability to custom design a system for any application.

The following pages will introduce you to our BioSpiral RBC and highlight the beneficial features available with the BioSpiral. For further information please contact your local Sales Representative or Walker Process in Austin, Minnesota or Aurora, Illinois.

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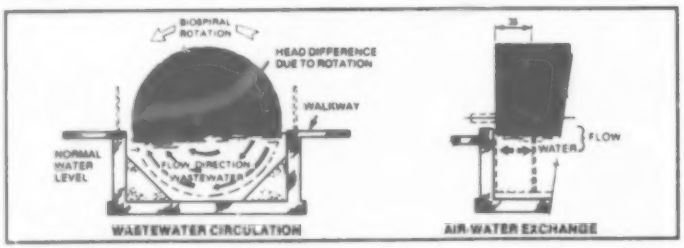
GENERAL DESCRIPTION

The Walker Process BioSpiral utilizes a patented media and manufacturing process which provides a configuration that limits stresses in the polyethylene media to very low levels and provides a short flow path for air and water exchange through the media. The media is thermally welded in 36 inch wide modules in a continuous spiral wrapping process to produce a monolithic, self-supporting structure. This fabrication technique eliminates the need for media supports or torque transmitting devices which require periodic maintenance and produce localized stress concentrations in the media. The short flow path and open media construction also produce improved media scour and higher dissolved oxygen levels in the wastewater.

RBC's, like any major item of wastewater equipment, must be built to last to maintain the successful performance of the plant. Competent manufacturers design their RBC's to provide reliable performance and longevity based on applicable codes. Walker Process was the first to design its RBC shaft based on the fatigue provisions of The American Welding Society Structural Steel Welding Code D1.1, Chapter 10.

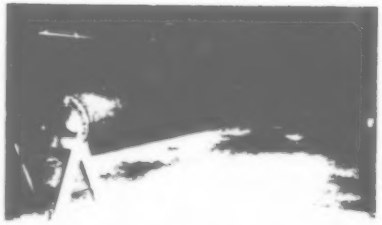
This design code is now widely recognized in the industry and by the USEPA as a necessary technique to assure reliable structural designs. Low shaft and media stress levels, good quality control and competent design are built into the BioSpiral to assure a design life of over 20 years. Fabrication is strictly controlled with our in-house Q.A. program to assure that the quality designed for is built into each BioSpiral. Pipe for the main shaft is purchased from the mill fully tested, meeting the requirements of API5L. Stub end machining, welding and media fabrication are checked at each step in the manufacturing process. Design stress values have been fully confirmed with full-scale testing.

BioSpiral standard shafts are approximately 26 feet long and 11 feet 10 inches in diameter, with either standard density media modules for 100,000 $ft.^2$ or high density media modules for 150,000 $ft.^2$ or more of effective surface area. The spiral media module design incorporated into the BioSpiral allows custom fabrication of shafts for specific applications. Process loadings, space availability, or existing structures may require special areas or special media diameters. The BioSpiral can be fabricated to any diameter between 6 and 12 feet and any shaft length to 26 feet, using from one to eight modules. The following pages further discuss the advantages available with the BioSpiral.

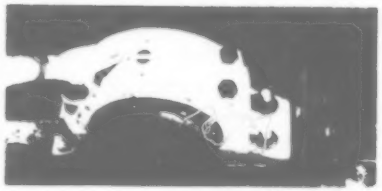


FEATURES

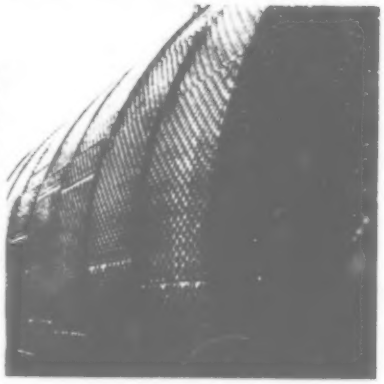
The main shaft is a 30 inch diameter, 3/4 inch wall pipe section with one-piece cast steel stub ends. The stub ends are first machined over their full surface to remove all surface imperfections and then tested to locate and eliminate any casting flaws. With our unique media design, no welded media attachment collars or clips are necessary on the main shaft. This eliminates the potential for stress concentrations which exist at such discontinuous attachments. The BioSpiral provides the largest shaft section modulus available in the industry at 492 in.^{3}. This, combined with good welding design, produces low stress levels to insure long shaft life.

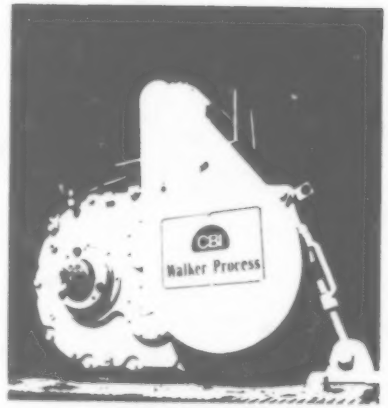


Bearings provided with the BioSpiral are also the largest available in the industry at 7 inch diameter on full size shafts. This results in lower unit loadings and longer bearing life. Bearings are self-aligning, tapered roller pillow block units with a minimum AFBMA B_{10} life rating of over 200,000 hours at normal rotational speeds and loads. Fixed bearings are used at the drive end with expansion bearings on the idle end. The BioSpiral is manufactured and shipped with bearings in place permitting offloading directly to the anchorage.



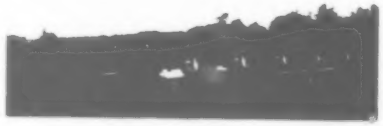
Media is vacuum formed, high density polyethylene continuously wound and thermally welded within itself to produce a self-supporting structure. Every point of contact in the media structure is welded to assure media strength. Tested weld strength exceeds all design operating loads by a factor of 10 or more. A two-part system provides positive attachment of the media to the main shaft with the use of stainless steel straps, and an epoxy adhesive. Media is stabilized with carbon black to resist exposure to ultraviolet degradation and maintain tensile strength. The short air-water flow path and open construction of the media has been shown to provide good media scouring action and somewhat higher dissolved oxygen levels than produced with a more closed type of media.





Direct mechanical drive is used with a triple reduction helical torque arm reducer mounted directly on the stub end extension. Positive mechanical drive has been shown to be the most reliable and energy efficient, RBC drive system available. The shaft mounted drive is a significant improvement over the chain and sprocket designs which require an oil bath chain guard submerged in the tank. The reducer is driven through V-belts by a five horsepower motor to produce the desired rotational speed. Although not normally necessary, speed variation can be obtained by changing sheaves, a more economical and trouble free method than using variable speed drives.

Fiberglass enclosures can be provided for protection of the process against weather and for temperature and odor control. Enclosures can be provided which also enclose the RBC drive, if desired. BioSpiral enclosures consist of free standing arch sections with tongue and groove joints requiring no bolting for ease of assembly. Joint design allows for air infiltration to provide oxygen for the biological process. Enclosures are designed for normal wind or snow and live loads and are provided with access doors and inspection ports.



DESIGN CONSIDERATIONS

Proper evaluation and application of an RBC system requires careful consideration of many factors that affect system sizing and performance. The first step in properly designing a system is to determine the basic wastewater characteristics and effluent requirements. Design can be completed with the following parameters:

INFLUENT TO RBC SYSTEM

Flow, daily average	_____	GPD
Flow, peak two hour duration	_____	GPD
Flow, minimum	_____	GPD
Total BOD_5	_____	mg/l
Soluble BOD_5	_____	mg/l
TSS	_____	mg/l
*TKN	_____	mg/l
*NH_3N	_____	mg/l
*Alkalinity ($CaCO_3$)	_____	mg/l
Temperature/summer	_____	°F
Temperature/winter	_____	°F
pH	_____	

EFFLUENT

Total BOD_5	_____	mg/l
*NH_3N/summer	_____	mg/l
*NH_3N/winter	_____	mg/l

In evaluating these parameters, the designer will also rationally apply loading values, temperature corrections, staging and other design considerations to arrive at the proper RBC system size and arrangement.

For purposes of allowing the designer to gain a rough approximation of the RBC system for his application, Walker Process has developed sizing charts for determining surface area required for various BOD_5 and NH_3N loadings. These are preliminary design values, of course, and the designer should contact his local Walker Process Sales Representative for specific information. Walker Process engineers will assist the designer and will perform a careful analysis of each particular application and provide specific information suitable for that application. Proper shaft arrangement, staging and exact design application can significantly affect the surface area selected from the charts. Consult Walker Process for flows or influent loadings beyond the limits of the curves.

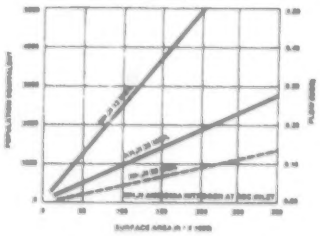
* *When ammonia nitrogen reduction is required.*

2623

SIZING CHARTS

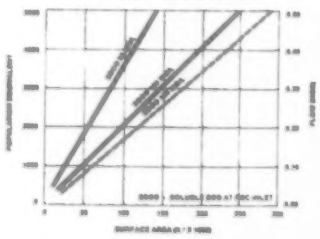
NH_3N REMOVAL

FOR EFFLUENT NH_3N OF 4 MG/L



BOD REMOVAL

FOR EFFLUENT SBOD OF 15 MG/L



TEMPERATURE CORRECTION TABLE

45	0.56
50	0.79
55	1.00

TEMPERATURE CORRECTION TABLE

45	0.73
50	0.87
55	1.00

FOOTNOTES

1. Charts are based on 100 GPD/capita.
2. Temperature correction must be applied to values from charts below temperatures of 55° F.
3. Effluent total BOD is 30 mg/l with soluble BOD of 15 mg/l.
4. Normally, and for purposes of approximation, standard density media is applied for BOD removal and high density media for NH_3H removal.
5. Standard shafts normally utilize 100,000 ft.² (standard density) and 150,000 ft.² (high density) maximum media surface area per shaft. For total surface areas beyond these values apply multiple shafts.
6. NH_3N removal chart assumes SBOD level is reduced to about 15 mg/l.
7. For purposes of approximation, add surface areas obtained from the charts for combined BOD and NH_3N removal. In actual practice this is generally conservative.
8. Flowrates may have to be adjusted prior to entering the charts if the peak to average ratio exceeds 2.5.
9. Consult Walker Process for values not listed in the charts, for specific design applications, and staging arrangements.

EXAMPLES

Example 1: (BOD removal only)

Flow = 0.28 MGD

SBOD = 100 mg/l (RBC influent)

TBOD = 30 mg/l (effluent)

Winter temperature = 45° F

From chart; 140,000 ft.² is required applying temperature correction;

$$\frac{140,000}{0.73} = 191,800 \text{ ft.}^2$$

Use two standard density shafts @ 100,000 ft.² each; 200,000 ft.² total; two parallel tanks.

Example 2: (BOD and NH_3N removal)

Flow = 0.45 MGD

SBOD = 50 mg/l (RBC influent)

NH_3N = 12 mg/l

TBOD = 30 mg/l (effluent)

NH_3N = 4 mg/l

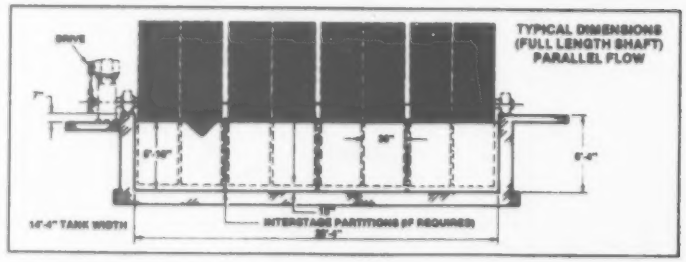
Winter temperature = 48° F

From charts and applying correction factors;

For BOD removal; $\frac{130,000}{0.73}$ = 178,000 ft.² required

For NH_3N removal; $\frac{180,000}{0.56}$ = 321,000 ft.² required

Use two standard density shafts @ 100,000 ft.² each; two high density shafts @ 150,000 ft.² each; 500,000 ft.² total; two parallel tanks.



In addition to BioSpiral Rotating Biological Contactors, Walker Process supplies a full line of water and wastewater components and systems including clarifiers, anaerobic digestion equipment, ClariCone Reactor Clarifiers, Filters and much more.

Sales Representatives are located throughout the United States and in foreign countries. For specific recommendations or for further information and assistance on this product or any other, write or call your local Sales Representative or the offices listed below.

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Aurora, Illinois 60507 *(All Products)*
(312) 892-7921

Walker Process Corporation
P.O. Box 652
Austin, Minnesota 55912 *(RBC's Only)*
(507) 433-7345

Feed to the plant consists of a proportioned blend of tailings impoundment decant water and mine water the proportion monitored and regulated by an on-line automated thiocyanate monitor developed in-house. The blended water is regulated to control the incoming nutrient stream concentration and temperature of the blend. Minewater is at an almost constant 26°C, so the waters are blended to average 70:30 mine to tailings water in winter and 50:50 in summer still keeping within the bacterial limits.

Much of the nutrient requirement is in the water already although phosphorous for energy and carbonate as an essential source of inorganic carbon are supplemented by chemical addition in the form of phosphoric acid and soda ash.

Provision is made to add ferric chloride and polymer for additional metals removal and for clarification as needed.

The 48 RBC's are set in two identical mirror image arrangements of 24 each. Feed flows perpendicularly to the disc with five discs per train.

In general, the first two discs per train remove CNS^- and CN^- and accumulate metals while the remaining three are for nitrification.

Each disc is fitted with aeration headers and load cells for supplemental aeration and biofilm thickness monitoring.

Discs are about 40% submerged and rotate at variable speeds of 0.5-1.5 RPM driven by reversible drives. Physical dimensions of each disc is 3.65 mØ and 7.6 m long constructed of corrugated plastic media on a central shaft to present a surface area of 9.290 m^2 (100,000 ft^3) to 13,935 m^2 (150,000 ft^3) depending on the density of the media.

The first two cyanide and thiocyanate degradation discs are low density and the last three are high density to accommodate the weight of the biofilm. Each RBC is individually housed in its own insulated fiberglass cover as illustrated in the brochure. The bacterial biomass attached to the RBC should average 18,000 Kg (20 net tons).

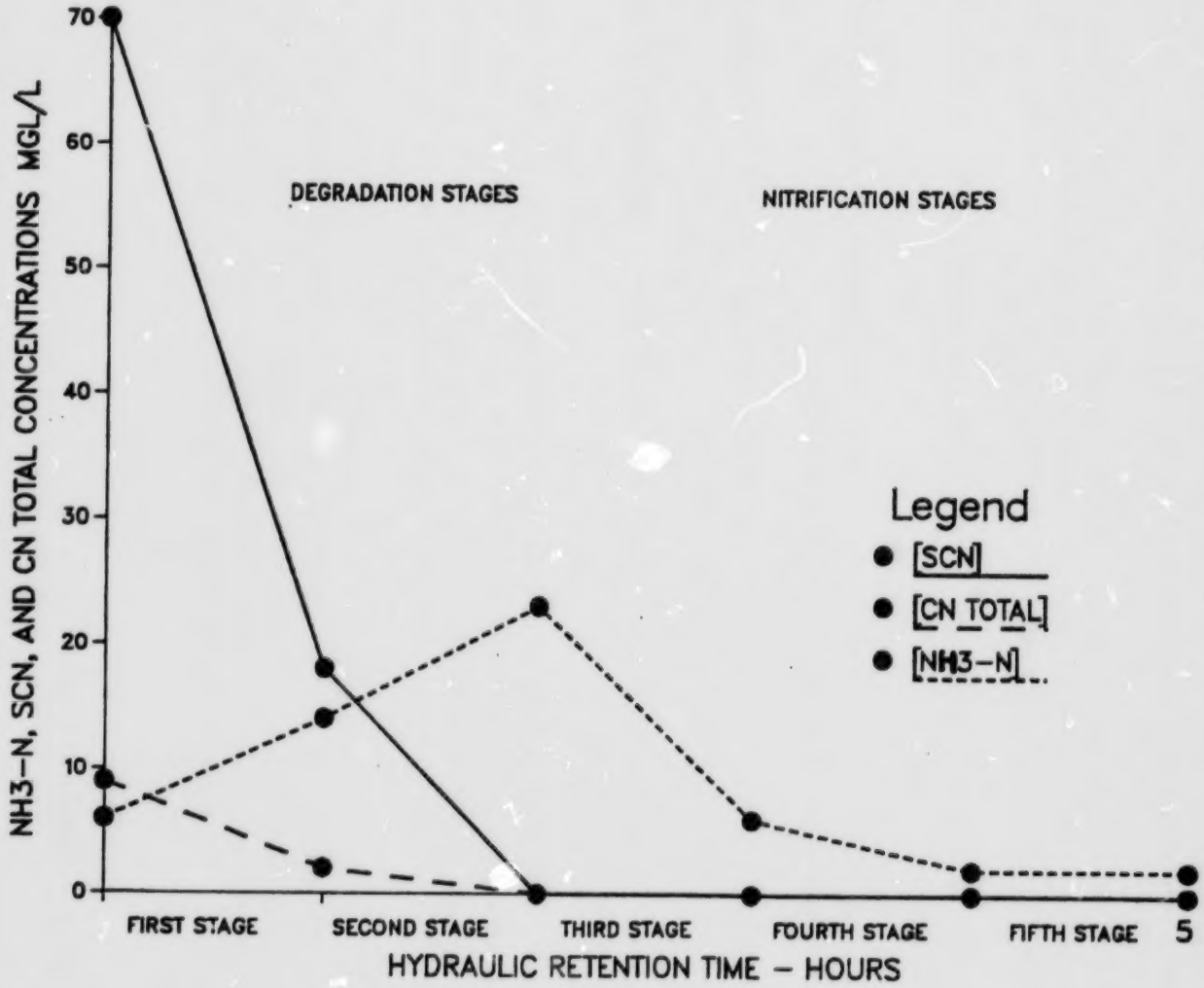
CYANIDE DETERMINATIONS

Considering the complexity and variability of wastewater measurement, reliable means of reproducibly analyzing the flows were found essential especially at trace levels.

HOMESTAKE MINING COMPANY found that the EPA total cyanide method substituting H_3PO_4 for sulfuric acid works reliably for total cyanide including iron cyanides. The

FIGURE 2

BIOLOGICAL DEGRADATION OF AMMONIA, CYANIDE, AND THIOCYANATE



SOURCE: WHITLOCK & MUDDER (1984)

ASTM Method C was found satisfactory for available cyanide in Homestake's particular wastewater. Method C measures total cyanide less iron cyanide. It was found that Method-C cyanide measurement avoids many of the interferences which complicate the total cyanide method.

TOXICITY TESTING

WHITLOCK & MUDDER (1984) stressed that treatment methods which rely solely on chemical analyses of the treated effluent may result in unexpected toxicity due to the sporadic presence of an overlooked toxic contaminant, or due to synergistic/antagonistic effects.

Homestake has constructed an on-line bioassay facility to test the effluent stream using trout, daphnia and macroinvertebrates collected from the actual receiving stream.

Through use of the on-line bioassay laboratory Homestake Mining Company has been able to develop information on meaningful site specific water criteria to determine the effect of water on that particular stream.

WHITLOCK & MUDDER (1984) have made a major contribution both in developing a biological process to treat a toxic stream, but also in developing the concept of an on-line bioassay laboratory to obtain a much better picture of the usefulness and effectiveness of the treatment program.

BIOLOGICAL PROCESSES FOR CYANIDE REMOVAL (TENTATIVE)

Advantages

1) Bacterial processes remove chemical species from water while adding very little back in the way of chemical species unlike chemical treatment processes.

2) The acclimated bacteria serve to remove all the main contaminants from the stream, albeit in two separate bacterial processes in series. These include CN_T, CN^-, Cu, Ph, Zn, As, and NH_3.

3) Once established the cost of chemical additions will be minimal. (Data on amount and cost of H_3PO_4 and Na_2CO_3 addition was not yet released.

4) This process is a bold pioneering work and represents real progress. Biological processes akin to this are routinely used in several other industries and the RBC equipment is already available as a standard item if not already completely "debugged."

5) Minimal pH adjustments up or down are required.

Disadvantages

1) The capital cost of the plant appears to be high although the inventors claim that it was the least costly of the available process combinations able to achieve the same levels.

2) The two step process is vulnerable in that if the CN degradation step should upset, the second denitrification step will be interfered with too and it takes longer to be restored.

3) General applicability of the biological processes may not be possible in cold climates. The Homestake Mining Co. minewater at a constant 26°C (79°F) enables the mixture of mine and tailings effluent to be within the optimum temperature range year round.

   Biological processes generally slow down at lower temperatures and for most operations which do not have a source of heated effluent, winter temperatures of solutions will drop below the 10-11°C at which point the process will slow down to be less effective, even though WHITLOCK & MUDDER claim the bacteria function down to 5°C.

4) Being biological in nature the processes are subject to upsets. Discharging inadequately treated water to the creek for one 24 hour period will likely do as much damage as for a year long period. A means of testing water quality continuously and provision for returning it to the tailings dam when it does not meet discharge criteria is essential.

5) Long and short term toxicological characteristics of the effluent product have not yet been proven.

6) Probably it would be difficult or impossible to treat tailings pulp directly for cyanide degradation in RBCs because of the high solids levels.

FeS DESTRUCTION OF CYANIDES

The use of freshly made ferrous sulfide in the presence of a reducing agent i.e., excess ferrous sulfate for cyanide removal is described in the following patent by KUIT and BABCOCK (1981) of COMINCO LTD. The CON Mine cyanide treatment process is a combination of chemical treatment and natural degradation in a large shallow pond.

CYANIDE

This process is employed at COMINCO's Con Mine in Yellowknife Northwest Territories which was visited by RANDOL in June 1984 and is the subject of a trip report. Unfortunately, at the time of the visit the personnel who are knowledgeable about the process were on summer vacation and operating parameters and performance data were not available on site. Composition of the CON Mine influent solution composition as well as their tailings pond decant and permit limits are included in the paper by SCOTT (1984) inserted above.

Sponsors interested in gaining details of how this process works in practice may get in touch with the following people:

WALTER J. M. KUIT
Cominco Ltd.
200 Granville Street
Vancouver, BC V6C 2R2
(604) 682-0611

JIM GOWANS
Surface Superintendent
Con Mine
Cominco Ltd.
Yellowknife, NWT
(403) 873-2783

DR. LORNE BALL
Group Leader - Research
Cominco Ltd.
Trail, BC
(604) 364-4419

In practice at the Con Mine, tailings are discharged at the mill end of a very large shallow tailings impoundment using the downstream impoundment principle. Solution is decanted and flows to the impoundment overflow weir at the far end where it is discharged to the Great Slave Lake via a creek.

The tailings decant is treated by addition of ferrous sulfate and sodium sulfide directly to the tailings pond in two steps.

1) Ferrous sulfate and sodium sulfide are added near the point of discharge from the mill. At this point, the pH is 10.5 - 11.0.

2) Ferrous sulfate and lime are spread into the tailings pond at the discharge end into the decant solution close to the decant overflow weir. The reagents are delivered in bags which are spread over the solution surface from a mobile raft.

Total tailings from the Con Mine are generated at the rate of 750 tpd but after a sand/slime splip for backfill, only 400 stpd slimes reach the tailings pond at 25% solids, i.e., 1,100 m^3/d (1,200 stpd) water. Because of the 6 months frozen season, tailings

United States Patent [19]

Kuit et al.

[11] **4,250,030**

[45] **Feb. 10, 1981**

[54] **PROCESS FOR THE REMOVAL OF CYANIDES FROM EFFLUENT**

[75] Inventors: **Wouterus J. M. Kuit, Trail; Alan R. Babcock, both of Trail, Canada**

[73] Assignee: **Cominco Ltd., Vancouver, Canada**

[21] Appl. No.: **113,993**

[22] Filed: **Jan. 21, 1980**

[30] **Foreign Application Priority Data**

Oct. 26, 1979 [CA] Canada 338593

[51] **Int. Cl.**[3] **B01D 15/00**

[52] **U.S. Cl.** **210/684**; 210/904; 210/716; 210/722

[58] **Field of Search** ..... 210/38 B, 37 B, DIG. 31, 210/24, 45, 47, 50, DIG. 30, 51, 52, 57, 59; 423/364, 367, 236

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,194,438	3/1940	Wernlund et al.	210/DIG. 31
2,845,330	7/1958	Zabban	423/43
3,736,239	5/1973	George et al.	210/DIG. 31

FOREIGN PATENT DOCUMENTS

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2307669	8/1974	Fed. Rep. of Germany	210/DIG. 31
49-69544	7/1974	Japan	210/DIG. 30

Primary Examiner—Benoit Castel

Attorney, Agent, or Firm—Arne I. Fors; Robert F. Delbridge

[57] **ABSTRACT**

A method is disclosed for removal of free and complex cyanides from water-containing industrial effluents and wastes by treatment with insoluble solid iron sulfides at a pH in the range of about 7.0 to 8.5. The insoluble solid iron sulfides can be chemically prepared prior to treatment or prepared in situ, usually of a particle size smaller than about 5μ, or supplied in the form of naturally occurring iron sulfides such as pyrrhotite or pyrite having a particle size smaller than about 300μ, preferably smaller than about 150μ. The weight ratio of iron sulfide to total cyanide in the effluent is greater than 2:1, preferably greater than about 5:1 for prepared iron sulfides and greater than about 100:1 for mineral sulfides. The presence of a reducing agent such as ferrous ions or sodium sulfite to maintain a non-oxidizing environment during treatment enhances removal of cyanide.

22 Claims, No Drawings

PROCESS FOR THE REMOVAL OF CYANIDES FROM EFFLUENT

BACKGROUND OF THE INVENTION

This invention relates to the removal of cyanide from effluents and wastes and, more particularly, relates to a method for the removal of free and combined dissolved cyanides from aqueous industrial effluents and wastes.

Due to increasingly stringent requirements for the disposal of noxious materials in waste waters and effluents from industrial processes, considerable effort has been expended, especially during the last ten years, to detoxify effluents that contain cyanides. As a result, many methods are reported in the literature that disclose the removal of free and combined cyanides from such effluents. These methods include oxidation of cyanide by treatment with chlorine, hypochlorite or ozone, treatment with an aldehyde, treatment with activated carbon or silica, removal as precipitated metal cyanides, treatment with fly ash or flue gas, and removal by irradiation, chelating, ion exchange or heating. However, in practice, most of the reported methods do not achieve the removal of cyanides and complex cyanides to levels that satisfy the requirements for safe disposal of aqueous effluents, while many methods are economically unattractive for the removal of small concentrations of cyanides from large quantities of effluent. Moreover, most methods are unsuitable to remove cyanides from slurries and solids such as flotation tailings.

We have now discovered that free cyanide as well as combined cyanides can be effectively and economically removed from effluents by treating the effluents with iron sulfides.

In the flotation concentration of mineral values in ores, cyanide ions are often used to depress certain sulfides such as, for example, iron sulfides in the concentration of lead sulfide. The depression of sulfides with cyanide ions is usually carried out at pH values of from 8 to 12.

Several methods have been disclosed that relate to the treatment of effluents with iron sulfides. According to U.S. Pat. No. 3,294,680, there is disclosed a method for reducing and removing chromate from solution by contacting the solution with a mass of hard metal sulfide, such as iron sulfide granules, at a pH of about 7.5.

According to U.S. Pat. No. 3,740,331, there is disclosed a method for the removal of heavy metal pollutant ions in a sulfide precipitation wherein sulfide ion and a heavy metal ion, which form a sulfide having a higher equilibrium sulfide ion concentration than the sulfide of the heavy metal pollutant, are added to the solution. In U.S. Pat. No. 3,901,802 there is disclosed a process for extracting heavy metal ions from solution wherein solution is contacted with an insoluble mixed salt of iron sulfide and barium sulfate containing a surplus of sulfide ions. According to U.S. Pat. No. 4,102,784, heavy metal pollutant ions are precipitated from solution by adding a slurry of large particle size ferrous sulfide precipitate to the solution in the presence of a polyelectrolyte to form a colloid-free metal ion precipitate. The foregoing methods are strictly related to the removal of heavy metal ions.

In a Technical Bulletin issued by the Permutit Co., on the Sulfex (Trade Mark) Heavy Metals Waste Treatment Process, it is stated that the process for removal of heavy metals with freshly precipitated iron sulfides at pH 8-9 is a heavy metal removal system, and that any

cyanides must be oxidized in a pretreatment step. According to Japanese Kokai No. 53 101 846, which issued on Sept. 5, 1978, there is disclosed a method for the inhibition of corrosion of waste water treatment apparatus in which ferrous ions are added to waste water that contains hydrogen sulfide, ammonia and cyanide corrosion inhibitor. The water is filtered to remove iron sulfide and then treated in a stripper.

STATEMENT OF INVENTION

We have now discovered that free cyanide ions and complex cyanide ions can be effectively and economically removed from effluents and wastes by treatment with iron sulfides under carefully controlled conditions.

Accordingly, there is provided a method for the removal of dissolved free and complex cyanides from water-containing effluent which comprises controlling the pH of said effluent in a range of about 7.0 to 8.5 and treating said effluent with an effective amount of an insoluble iron sulfide chosen from at least one of ferrous sulfide and ferric sulfide having particle sizes smaller than about 300μ for a period of time of at least about 5 minutes to remove said dissolved free and complex cyanides to a desired level, said effective amount being sufficient to give a weight ratio of said iron sulfide to total cyanide in said effluent of greater than 2:1.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention will now be described in detail. Effluents that may be treated according to the method of the invention are aqueous solutions, suspensions and slurries that are encountered in the metallurgical and metal processing industries. Such effluents comprise, for example, tailings and solutions from flotation processes for concentrating metal values in ores and electro-plating waste solutions which contain cyanides as free cyanide ions and/or metal cyanide complex ions of such metals as iron, copper, nickel and zinc. Effluents may be treated as such or may be pretreated for removal of at least a portion of the solids such as by settling or thickening and decantation, or filtration, with or without the use of flocculants or filter aids.

Effluent is treated with solid iron sufides under controlled conditions whereby a major portion of the free and complex cyanides is removed from the effluent. Without being bound by theoretical considerations, the removal is believed to be mostly due to adsorption of free and complex cyanides on the surface of the insoluble solid iron sulfide particles. The treatment is conducted by contacting an effective amount of finely divided solid iron sulfides with effluent for a period of time sufficient to reduce the cyanide content of the effluent. The contacting is performed by using known methods for obtaining intimate contact between effluent and iron sulfides. For example, effluent is agitated with solid iron sulfides, or effluent is agitated with a slurry of solid iron sulfides, or effluent is percolated through a body containing solid iron sulfides. The contacting by agitation with iron sulfide may be performed in a single stage, or may be performed in two or more stages in co-current or counter-current fashion.

Suitable iron sulfides are ferrous sulfide and ferric sulfide which may be used in the form of prepared compounds, i.e. chemically prepared iron sulfides, either as purchased or freshly prepared prior to the treatment of effluent or prepared in situ, or in the form of

naturally occurring mineral iron sulfides such as pyrrhotite and pyrite. Freshly prepared iron sulfides are made by conventional methods, while iron sulfides prepared in situ are preferably obtained by adding to the effluent a predetermined amount of ferrous sulfate or ferric sulfate and a stoichiometric amount of sodium sulfide or other suitable soluble sulfide that forms ferrous sulfide or ferric sulfide with the ferrous sulfate or ferric sulfate, respectively. The mineral iron sulfides are preferably used in the form of tailings or concentrates which contain at least one of pyrrhotite and pyrite.

The degree of cyanide removal is a direct function of the mass to surface area ratio of the iron sulfides. The lower the ratio, i.e. the finer the size of the iron sulfides, the more efficient and complete will be the cyanide removal. Prepared iron sulfides have particle sizes that are usually smaller than about 5μ (microns). Mineral iron sulfides in the form of tailings or concentrates are usually also finely divided, i.e. have particle sizes that are smaller than about 300μ, usually smaller than 150μ. If desired, coarse mineral sulfides may be subjected to a particle size reduction operation. A size reduction to particle sizes smaller than at least about 300μ, preferably smaller than about 150μ, is advantageous.

The choice of whether to use prepared or mineral iron sulfides depends on the manner in which effluent is contacted with iron sulfides, as well as on economic considerations. Mineral sulfides may be advantageously used where they are readily available. Because mineral iron sulfides have generally larger particle sizes than prepared sulfides, the use of mineral sulfides in the form of tailings and concentrates requires larger amounts and longer contact periods to attain the same degree of cyanide removal than the use of prepared sulfides. The lower efficiency of mineral sulfides may also be due to the presence of aged surface areas and residual flotation agents. The effectiveness of mineral iron sulfides in the process of the invention may be increased by subjecting the sulfides to milling whereby not only particle sizes are reduced but also fresh surface areas are exposed.

Mineral iron sulfides are advantageously used when effluent is treated by percolating effluent through a body of iron sulfides. The body of iron sulfides consists of a column or bed of finely divided solid mineral iron sulfides having particle sizes generally larger than about 44μ, preferably in the range of about 44 to 300μ, most preferably in the range of about 44 to 150μ. Too large a content of mineral sulfide particles smaller than about 44μ causes too rapid a decrease in the effectiveness of the percolation body due to plugging of the interstices in the body and a consequent diminishing of the percolation rate, while particles larger than 300μ have a high mass to surface area ratio which is less effective than a lower ratio. The method of contacting by percolation is suitable when treating aqueous effluents that are substantially free of solids or have a low solids content. It is reiterated that effluents may be treated for removal of at least a portion of contained solids prior to being subjected to percolation.

Prepared iron sulfides are used when cyanide levels must be reduced to very low levels in effluents that contain solids and in cases where mineral sulfides re not available or are uneconomical to use. Ferrous sulfide and ferric sulfide may be used singly or as a mixture. As stated hereinabove, prepared iron sulfides can be readily obtained by purchase or can be prepared prior to treatment of effluent or in situ. Preferably, iron sulfides are prepared in aqueous solution by reacting ferrous sulfate and/or ferric sulfate, or other suitable ferrous and/or ferric salt, with a soluble sulfide causing precipitation of finely divided solid ferrous and/or ferric sulfide. The resulting reaction mixture is subsequently added to the effluent in the form of a slurry or suspension either batchwise in a predetermined amount or in continuous or semi-continuous fashion at a predetermined rate. Alternatively, iron sulfides are prepared in situ by adding predetermined amounts of ferrous and/or ferric sulfate or other suitable ferrous and/or ferric salts and a suitable soluble sulfide causing precipitation of ferrous and/or ferric sulfide. The effluent and added or in situ-prepared iron sulfides are thoroughly agitated to ensure intimate contact between effluent and iron sulfide particles. After a suitable contact time, the mixture may be separated into treated effluent and iron sulfide components. The iron sulfides may be impounded or, if desired, a portion of the iron sulfides may be recycled after separation from treated effluent for treatment of further amounts of effluent.

The amount of prepared or mineral sulfides to be used depends on the physical characteristics of the effluent, the amounts and nature of the cyanides in the effluent, the origin and nature of the iron sulfides and, in the case of mineral sulfides, on the amount of iron sulfides present in the concentrate or tailings employed.

Generally, the amount of iron sulfides must be used or added in an effective amount, i.e., an amount that is at least sufficient to remove dissolved free and complex cyanides from the effluent to the desired level. Preferably, iron sulfides are used in excess. The excess may be expressed as the weight ratio of iron sulfides, i.e. ferrous sulfide and/or ferric sulfide, to the total cyanide content of the effluent, denoted hereinafter as the FeS/CN ratio. For percolation, this ratio will, of course, be very high, such as 100:1, and as high as 10^6:1, while for agitating iron sulfides with effluent the ratio should be at least about 2:1, i.e. provide a 100% excess of sulfides. When using prepared iron sulfides, the ratio is preferably in the range of about 5:1 to 20:1, while when using mineral sulfides, the ratio is preferably at least 100:1.

The pH during contacting of effluent with iron sulfides is critical and must be carefuly controlled. The pH is to be controlled in the range of about 7.0 to 8.5. Below a pH of about 7, hydrogen cyanide is liberated and cyanide complexes are not removed effectively. At a pH above about 8.5, cyanide removal is incomplete due to increased competition of cyanide and complex cyanide ions with hydroxyl ions for adsorption on the iron sulfide surfaces. The value of the pH is preferably maintained in the range of about 7 to 8, and most preferably at a value of about 7.5 which results in optimum removal of free and complex cyanides. We have found that cyanide ions are most strongly adsorbed in the pH range of 7 to 8 and that, for example, cuprocyanide is dissociated by ferrous sulfide and pyrrhotite leaving the cyanide strongly bound to the adsorbent. Copper is removed from solution by precipitation. The pH of the effluent is adjusted to a pH in the range of about 7 to 8, preferably to a value of about 7.5, prior to or during contacting with iron sulfides and the pH is maintained in this range during the contacting step. The adjusting and maintaining of the pH in the preferred range is accomplished by adding either an acid, such as dilute sulfuric acid, or an alkali, such as sodium hydroxide or lime, as required.

Although the adsorption process is temperature dependent, the treatment of effluent is carried out at ambi-

ent temperatures using the effluent at the temperature at which it is obtained. The contacting is carried out over a period of time that is sufficient to reduce the cyanide content of the effluent to the desired level. Using prepared iron sulfides which have particle sizes smaller than 5μ, a contact time of at least 5 minutes is required to obtain removal of cyanides. When agitating effluent with prepared iron sulfides, the contact time is preferably in the range of about 15 to 180 minutes and, most preferably, in the range of 15 to 60 minutes. For mineral iron sulfides which have particle sizes in the range of 44 to 300μ, the contact time is preferably at least 30 minutes and most preferably in the range of about 30 minutes to 10 hours. When percolating effluent through a body of particulate iron sulfides, the contact time is preferably at least 30 minutes and is most preferably in the range of about 1 to 24 hours.

We have found that the presence of a reducing agent will further depress the amount of cyanide in solution. Suitable reducing agents, eg. ferrous ions and sodium sulfite, are added in a quantity to maintain a non-oxidizing environment. We have also found that in the case of high concentrations of the ferrocyanide complex in the effluent, the presence of free, i.e. excess, ferrous ions will cause precipitation of prussian blue-type compounds. Thus, the presence of added free ferrous ions further depresses the total cyanide content of the effluent. Free ferrous ions are added in the form of a suitable, soluble ferrous salt.

The invention will now be illustrated by means of the following non-limitative examples.

EXAMPLE 1

Effluent containing 38 mg/L total cyanide (T/CN), of which 14.4 mg/L was free CN and 23.6 mg/L was CN as cuprocyanide ($Cu(CN)_3^{2-}$), and having a pH of 9.5, was percolated through a bed of mixed pyrrhotite-pyrite concentrate. The concentrate was screened to particle sizes in the range of 44 to 74μ. The bed volume was 600 mL and the retention time of the effluent, which was pumped upwardly through the bed, was 30 minutes. 500 mL percolated effluent was collected which analyzed 0.08 mg/L T/CN and <0.01 mg/L as $Cu(CN)_3^{2-}$ and had a pH of 7.0.

EXAMPLE 2

The test of Example 1 was repeated but the concentrate was screened to remove particles smaller than 74μ. The percolated effluent had a pH of 7.5 and contained 0.68 mg/L T/CN and 0.05 mg/L CN as $Cu(CN)_3^{2-}$.

The tests of Examples 1 and 2 show that free and complex cyanides can be effectively removed from effluent by percolating through a bed of finely divided iron sulfides and that smaller particle sizes are more effective in the removal.

EXAMPLE 3

This example illustrates the removal of free and complex cyanides from tailings from a metallurgical operation by percolating tailings solution through a bed of pyrrhotite-pyrite concentrate. The tailings were settled and the decanted solution was filtered through a bed of diatomaceous earth to remove colloidal matter. The clarified solution contained 21 mg/L total cyanide (CN), 0.9 mg/L free CN, 10.3 mg/L CN as cuprocyanide ($Cu(CN)_3^{2-}$) and 9.8 mg/L CN as ferrocyanide ($Fe(CN)_6^{4-}$), and had a pH of 9.5. The percolation bed was prepared by wet screening the concentrate to remove particles smaller than 44μ and the remaining slurry was poured into a 4.6 cm diameter percolation column. After settling, the excess water was decanted. The final bed depth was 36 cm giving a bed volume of 600 mL. In a first test clarified solution was percolated at its natural pH of 9.5 and in a second test the solution was adjusted to pH 7.5 before being percolated.

The clarified solution was pumped upwardly through the bed at a rate of 3.75 mL/min. The treated effluent was collected in 600 mL portions over a period of 45 hours and analyzed. The retention time was one hour. The test results are given in Table I.

TABLE I

Test No	Cumulative volume of effluent in ml	pH	CN in treated effluent in mg/L: Total	free	as $Cu(CN)_3^{2-}$	as $Fe(CN)_6^{4-}$
1	600	9.5	0.24		0.01	0.45
	1200	9.5	2.0	0.4	0.06	1.54
	1800	9.5	5.1	1.1	0.04	4.0
	2400	9.5	6.3		0.01	6.5
	2700	9.5	8.5	0.4	0.01	8.1
2	300	7.5	0.60	0.18	0.03	0.39
	900	7.5	0.75	0.21	0.01	0.54
	1500	7.5	1.50	1.11	0.03	0.36
	2100	7.5	0.25		0.05	0.45
	2700	7.5	2.00	1.24	0.03	0.73

The results show free and complex cyanides can be effectively removed by percolation of effluent through a body of finely divided iron sulfides and that the removal is more effective at pH 7.5.

EXAMPLE 4

One liter of the effluent as used in Examples 1 and 2 was agitated for a period of 24 hours with 800 g of a mixed pyrite-pyrrhotite concentrate. The treated effluent had a pH of 7.5 and contained 0.08 mg/L total CN and <0.01 mg/L CN as $Cu(CN)_3^{2-}$. The FeS/CN weight ratio was 20000:1.

EXAMPLE 5

This example illustrates the removal of cyanide from tailings from a metallurgical operation by mixing tailings solution with varying amounts of an iron sulfide concentrate. The tailings were settled and one liter portions of the decanted solution containing 55 mg/L T/CN were mixed with concentrate for a period of 10 hours, while maintaining the pH at a value of 7.5. Samples were taken after 2, 4, 6 and 10 hours. The samples were filtered and analyzed for total cyanide (T/CN) content. The results are given in Table II.

TABLE II

Amount of Sulfides Concentrate in g	Weight Ratio iron sulfides to cyanides	T/CN in mg/L: 0 hr	2 hr	4 hr	6 hr	10 hr
250	4000:1	55	11	8	20	
667	10000:1	55	5.7	6.4	3.0	5.0
1500	23000:1	55	2.6	1.2	0.2	0.1
4000	62000:1	55	<0.2	1.5	1.5	

The results of the tests in Examples 4 and 5 show that cyanides can be effectively removed from effluent by agitating effluent with finely divided mineral iron sulfides at a pH of 7.5 using retention times of 2 to 19 hours at ratios of iron sulfides to total cyanides (FeS/CN) of 4000:1 to 62000:1.

EXAMPLE 6

400 mL portions of an effluent containing 100 mg/L T/CN, 16.7 mg/L free CN, 33.2 mg/L CN as $Cu(CN)_3^{2-}$ and 50 mg/L CN as $Fe(N)_6^{4-}$, and having a pH of 9.5, were adjusted to different pH values. The portions were each mixed with an amount of freshly prepared solid ferrous sulfide to give an iron sulfide to cyanide (FeS/CN) ratio of 8.33:1. The mixtures were each agitated for 15 minutes, a sample taken, agitated for a further 45 minutes, and a second sample taken. The samples were filtered through a 0.45μ filter and analyzed for cyanides. The results are given in Table III.

TABLE III

Retention time in min	Adjusted pH of Effluent	CN in Treated Effluent in mg/L			
		Total	Free	as $Cu(CN)_3^{2}$	as $Fe(CN)_6^{4}$
15	7.0	5.6	4.1	0.05	1.5
60	7.0	4.3	2.3	<0.02	2.0
15	8.0	4.7	1.1	0.06	3.6
60	8.0	1.9		<0.02	4.1
15	8.5	15	0	<0.02	15
60	8.5	9	0	<0.02	9
15	9.0	68	0	0.07	68
60	9.0	53	0	<0.02	53

It can be seen from the data given in Table III that a major portion of the cyanides can be removed from effluent by mixing with prepared ferrous sulfide at a pH in the range of 7.0 to 8.5 and that best results are obtained at a pH of from 7.0 to 8.0. A retention time of 60 minutes gives better results than one of 15 minutes. The data also show that copper and cuprocyanide are substantially removed from the effluent. The high figures for ferrocyanide at pH 9.0 indicate that ferrocyanide is formed and incompletely adsorbed on the sulfide.

EXAMPLE 7

This example illustrates that an excess of ferrous sulfide improves the removal of cyanide and that cyanide removal increases with increasing FeS/CN ratios. Portions of effluent containing 100 mg/L free CN at pH 7.5 were contacted with amounts of prepared ferrous sulfide to give predetermined FeS/CN weight ratios. The mixtures were agitated for 60 minutes, filtered and the treated effluent analyzed for total CN. The results are given in Table IV.

TABLE IV

Weight Ratio FeS/CN	Total CN in Treated Effluent in mg/L
1.0	38
3.0	23
4.0	12
5.0	3.5
6.3	0.48

EXAMPLE 8

Effluent containing 96 mg/L free CN and having a pH of 10.0 was adjusted to pH 7.5 using dilute sulfuric acid. Ferrous sulfide was prepared in the effluent by adding a solution of sodium sulfide and a solution containing ferrous sulfate in a stoichiometric amount to form ferrous sulfide in an amount to give a FeS/CN ratio in the effluent of 6.28:1. The mixture was agitated and samples taken after 15, 30, 60 and 180 minutes. The samples were filtered using a 0.45μ filter and the filtered samples were analyzed. The results are given in Table V.

TABLE V

Retention Time in min.	Treated Effluent Total CN in mg/L
15	1.9
30	1.0
60	0.48
180	0.84

The results show that free cyanide can be effectively removed by agitating effluent with ferrous sulfide prepared in situ for periods of time in the range of 15 to 180 minutes with best results obtained at 60 minutes.

EXAMPLE 9

Effluent containing 96 mg/L T/CN, 55 mg/L free CN and 41 mg/L CN as $Cu(CN)_3^{=}$ and having a pH of 9.5 was adjusted to pH 7.5 by adding the necessary amount of dilute sulfuric acid. Previously prepared ferrous sulfide having particle sizes of less than 5μ was added to the effluent in an amount to give a ratio of ferrous sulfide to total cyanide of 6.4:1. The mixture was agitated and samples taken after 15, 30, 60 and 180 minutes. The samples were filtered using a 0.45μ filter and the filtered samples were analyzed. The results are given in Table VI.

TABLE VI

Retention Time in min.	CN in Treated Effluent in mg/L	
	Total	as $Cu(CN)_3^{=}$
15	4.8	0.09
30	4.0	<0.01
60	1.2	<0.01
180	1.4	<0.01

The results show that free cyanide and cuprocyanide can be effectively removed by agitating effluent with prepared ferrous sulfide using retention times of from 15 to 180 minutes with best results obtained at 60 minutes retention.

EXAMPLE 10

Effluent containing 94 mg/L CN as $Fe(CN)_6^{4-}$ and having a pH of 9.5 was adjusted to pH 7.5. Prepared ferrous sulfide was added to the effluent in an amount sufficient to give a FeS/CN ratio of 6.4:1. The mixture was agitated and samples taken after 15, 30, 60 and 180 minutes. The samples were filtered through a 0.45μ filter and analyzed for T/CN. The results are given in Table VII.

TABLE VII

Retention Time in min.	Treated Effluent T/CN in mg/L*
15	0.15
30	0.10
60	0.09
180	5.5

*All cyanide was adsorbed as the ferrocyanide complex.

The results shown in Table VII indicate that ferrocyanide can be substantially removed from effluent by treating the effluent with prepared ferrous sulfide at pH 7.5 and with agitation for a retention period of 15 to 60 minutes. At retention times appreciably longer than 60 minutes, the cyanide content of the treated effluent increases because of oxidation.

ent temperatures using the effluent at the temperature at which it is obtained. The contacting is carried out over a period of time that is sufficient to reduce the cyanide content of the effluent to the desired level. Using prepared iron sulfides which have particle sizes smaller than 5μ, a contact time of at least 5 minutes is required to obtain removal of cyanides. When agitating effluent with prepared iron sulfides, the contact time is preferably in the range of about 15 to 180 minutes and, most preferably, in the range of 15 to 60 minutes. For mineral iron sulfides which have particle sizes in the range of 44 to 300μ, the contact time is preferably at least 30 minutes and most preferably in the range of about 30 minutes to 10 hours. When percolating effluent through a body of particulate iron sulfides, the contact time is preferably at least 30 minutes and is most preferably in the range of about 1 to 24 hours.

We have found that the presence of a reducing agent will further depress the amount of cyanide in solution. Suitable reducing agents, eg. ferrous ions and sodium sulfite, are added in a quantity to maintain a non-oxidizing environment. We have also found that in the case of high concentrations of the ferrocyanide complex in the effluent, the presence of free, i.e. excess, ferrous ions will cause precipitation of prussian blue-type compounds. Thus, the presence of added free ferrous ions further depresses the total cyanide content of the effluent. Free ferrous ions are added in the form of a suitable, soluble ferrous salt.

The invention will now be illustrated by means of the following non-limitative examples.

EXAMPLE 1

Effluent containing 38 mg/L total cyanide (T/CN), of which 14.4 mg/L was free CN and 23.6 mg/L was CN as cuprocyanide ($Cu(CN)_3^{2-}$), and having a pH of 9.5, was percolated through a bed of mixed pyrrhotite-pyrite concentrate. The concentrate was screened to particle sizes in the range of 44 to 74μ. The bed volume was 600 mL and the retention time of the effluent, which was pumped upwardly through the bed, was 30 minutes. 500 mL percolated effluent was collected which analyzed 0.08 mg/L T/CN and <0.01 mg/L as $Cu(CN)_3^{2-}$ and had a pH of 7.0.

EXAMPLE 2

The test of Example 1 was repeated but the concentrate was screened to remove particles smaller than 74μ. The percolated effluent had a pH of 7.5 and contained 0.68 mg/L T/CN and 0.05 mg/L CN as $Cu(CN)_3^{2-}$.

The tests of Examples 1 and 2 show that free and complex cyanides can be effectively removed from effluent by percolating through a bed of finely divided iron sulfides and that smaller particle sizes are more effective in the removal.

EXAMPLE 3

This example illustrates the removal of free and complex cyanides from tailings from a metallurgical operation by percolating tailings solution through a bed of pyrrhotite-pyrite concentrate. The tailings were settled and the decanted solution was filtered through a bed of diatomaceous earth to remove colloidal matter. The clarified solution contained 21 mg/L total cyanide (CN), 0.9 mg/L free CN, 10.3 mg/L CN as cuprocyanide ($Cu(CN)_3^{2-}$) and 9.8 mg/L CN as ferrocyanide ($Fe(CN)_6^{4-}$), and had a pH of 9.5. The percolation bed was prepared by wet screening the concentrate to remove particles smaller than 44μ and the remaining slurry was poured into a 4.6 cm diameter percolation column. After settling, the excess water was decanted. The final bed depth was 36 cm giving a bed volume of 600 mL. In a first test clarified solution was percolated at its natural pH of 9.5 and in a second test the solution was adjusted to pH 7.5 before being percolated.

The clarified solution was pumped upwardly through the bed at a rate of 3.75 mL/min. The treated effluent was collected in 600 mL portions over a period of 45 hours and analyzed. The retention time was one hour. The test results are given in Table I.

TABLE I

Test No.	Cumulative volume of effluent in mL	pH	CN in treated effluent in mg/L: Total	free	as $Cu(CN)_3^{2-}$	as $Fe(CN)_6^{4-}$
1	600	9.5	0.24	—	0.01	0.45
	1200	9.5	2.0	0.4	0.06	1.54
	1800	9.5	5.1	1.1	0.04	4.0
	2400	9.5	6.3	—	0.01	6.5
	2700	9.5	8.5	0.4	0.01	8.1
2	300	7.5	0.60	0.18	0.03	0.39
	900	7.5	0.75	0.21	0.01	0.53
	1500	7.5	1.50	1.11	0.03	0.36
	2100	7.5	0.25	—	0.05	0.42
	2700	7.5	2.00	1.24	0.03	0.73

The results show free and complex cyanides can be effectively removed by percolation of effluent through a body of finely divided iron sulfides and that the removal is more effective at pH 7.5.

EXAMPLE 4

One liter of the effluent as used in Examples 1 and 2 was agitated for a period of 24 hours with 800 g of a mixed pyrite-pyrrhotite concentrate. The treated effluent had a pH of 7.5 and contained 0.08 mg/L total CN and <0.01 mg/L CN as $Cu(CN)_3^{2-}$. The FeS/CN weight ratio was 20000:1.

EXAMPLE 5

This example illustrates the removal of cyanide from tailings from a metallurgical operation by mixing tailings solution with varying amounts of an iron sulfide concentrate. The tailings were settled and one liter portions of the decanted solution containing 55 mg/L T/CN were mixed with concentrate for a period of 10 hours, while maintaining the pH at a value of 7.5. Samples were taken after 2, 4, 6 and 10 hours. The samples were filtered and analyzed for total cyanide (T/CN) content. The results are given in Table II.

TABLE II

Amount of Sulfides Concentrate in g	Weight Ratio iron sulfides to cyanides	T/CN in mg/L: 0 hr	2 hr	4 hr	6 hr	10 hr
250	4000:1	55	11	8	20	—
667	10000:1	55	5.2	6.4	3.0	5.0
1500	23000:1	55	2.6	1.2	0.2	0.1
4000	62000:1	55	<0.2	1.5	1.5	—

The results of the tests in Examples 4 and 5 show that cyanides can be effectively removed from effluent by agitating effluent with finely divided mineral iron sulfides at a pH of 7.5 using retention times of 2 to 10 hours, at ratios of iron sulfides to total cyanides (FeS/CN) of 4000:1 to 62000:1.

EXAMPLE 11

Two portions of effluent containing 35 mg/L total CN, 15.4 mg/L free CN, 4.1 mg/L CN as $Cu(CN)_3^{2-}$ and 15.5 mg/L CN as $FE(CN)_6^{4-}$ were adjusted to pH 7.5 and treated with prepared ferrous sulfide to yield varying FeS/Cn ratios and varying amounts of free ferrous ions were added. A third portion of effluent was similarly treated but no excess ferrous ions was present. The results are given in Table VIII.

TABLE VIII

Retention Time in min.	Ratio FeS/CN	Excess Fe^{2+} in mg/L	CN in Treated Effluent in mg/L Total	Free	$Cu(CN)_3^{2-}$	as $Fe(CN)_6^{4-}$
15	2	22.3	12	1.3	0.17	10.5
30	2	22.3	11	1.0	0.80	9.2
15	13.35	164.0	3.5	3.4	0.02	<0.1
30	13.35	164.0	2.2	2.1	0.02	<0.1
15	13.35	0	4.6	4.3	0.03	0.3
30	13.35	0	4.5	4.0	0.02	0.5

The data in Table VIII indicate that better removal of cyanides is obtained at high FeS/CN ratios and that the presence of free ferrous ions effectively reduces the cyanide content of the effluent.

EXAMPLE 12

Portions of a high cyanide containing effluent containing 560 mg/L total CN, 162 mg/L free CN, 51 mg/L CN as $Cu(CN)_3^{2-}$ and 347 mg/L CN as $Fe(CN)_6^{4-}$ were treated with prepared ferrous sulfide with and without the addition of excess ferrous ions. The FeS/CN ratio, effluent pH and retention times while agitating were varied. The results are given in Table IX.

TABLE IX

Retention Time in min	FeS/CN ratio	excess Fe^{2+} in g/l	pH	CN in Treated Effluent in mg/L Total	as $Cu(CN)_3^{2}$	as $Fe(CN)_6^{4-}$
60	2	0	7.5	156	<0.01	0.48
30	8.9	0	7.5	16	0.02	0.28
30	8.9	0	8.5	38	0.02	3.3
20	13.35	0	7.5	29	0.05	0.22
30	13.35	0	8.5	24	0.05	0.64
30	2	0.47	7.5	33	<0.01	0.22
30	5	1.18	7.5	31	<0.01	0.34
60	5	1.18	7.5	13	<0.01	

The tabulated results show that best results are obtained with retention times of 20 to 60 minutes at pH 7.5 using FeS/CN ratios of 5:1 to 15:1, that cuprocyanide and ferrocyanide are effectively removed from the effluent and that cyanide can be more effectively removed when free ferrous ions are present.

EXAMPLE 13

In a continuous operation for the treatment of cyanide containing effluent from a metallurgical operation, 91 L/min effluent, containing varying amounts of cyanides, was fed to an agitated reaction vessel. A slurry of ferrous sulfide was prepared in a separate vessel by mixing stoichiometric amounts of ferrous sulfate heptahydrate and sodium sulfide, both in aqueous solution. Slurry containing 54 g/L ferrous sulfide was continuously added to the reaction vessel in an amount sufficient to maintain the FeS/CN ratio as predetermined values. The pH of the mixture in the reaction vessel was maintained at 7.5 by adding an 18.6% solution of H_2SO_4 as required. During periods of the operation, excess free ferrous ions was added to the reaction vessel. The retention time of the effluent in the reaction vessel was 90 minutes. The discharging effluent was periodically sampled and the samples were filtered and analyzed. Operating parameters and analysis results are shown in Table X.

TABLE X

FeS in mg/L	FeS/CN weight ratio	Excess Fe^{2+} g/L	CN in effluent in mg/L free	$Cu(CN)_3^{2-}$	$Fe(CN)_6^{4-}$	CN in treated effluent in mg/L free	$Cu(CN)_3^{2-}$	$Fe(CN)_6^{4-}$
0.94	1.20	Nil	618.2	64.9	99.5	140.3	38.5	241.2
0.94	1.28	0.20	492.7	64.1	175.8	29.4	11.1	104.6
1.26	2.10	Nil	110.5	71.2	418.3	20.4	9.3	180.3
1.28	2.15	0.23	75.8	65.1	454.1	8.8	0.1	60.4
1.95	3.20	Nil	135.5	61.4	413.1	19.5	2.8	146.7
1.90	3.07	0.39	201.4	68.6	350.0	Nil	0.04	10.0

The data presented in Table X clearly demonstrate that in excess of 98% removal of T/CN was attained with an FeS/Cn weight ratio of about 3:1 and an excess of about 0.4 g/L ferrous ions.

EXAMPLE 14

One L effluent containing 100 mg/L T/CN and having a pH of 7.5 was agitated with an amount of prepared ferric sulfide sufficient to give a FeS/CN weight ratio of 10:1. The mixture was sampled after 15, 30 and 180 minutes retention and the samples, filtered and analyzed, were found to contain 23.0, 10.5 and 1.6 mg/L T/CN, respectively.

This example illustrates that cyanide can be effectively removed from effluent by treating with ferric sulfide.

EXAMPLE 15

One L portions of effluent containing 100 mg/L T/CN were treated with either 1 g prepared ferrous sulfide or ferric sulfide with and without a reducing agent. 120 mg SO_3 as sodium sulfite was used as reducing agent. The mixtures were periodically sampled and the samples were filtered and analyzed. The results are shown in Table XI.

TABLE XI

Retention Time in min	T/CN in mg/L Ferrous Sulfide without Reducing Agent	Ferrous Sulfide with Reducing Agent	Ferric Sulfide without Reducing Agent	Ferric Sulfide with Reducing Agent
15	0.76	0.20	23.0	21.0
30	0.32	0.20	10.5	9.3

TABLE XI-continued

Retention Time in min.	T/CN in mg/L			
	Ferrous Sulfide		Ferric Sulfide	
	without Reducing Agent	with Reducing Agent	without Reducing Agent	with Reducing Agent
60	0.30	<0.04	—	3.4
180	0.23	0.16	1.6	1.8

As can be seen from the results presented in Table XI, the presence of a sodium sulfite as a reducing agent further improves the removal of cyanide from effluent when the effluent is treated with ferrous sulfide. Little or no improvement was obtained in this example when effluent was treated with ferric sulfide.

It will be understood, of course, that modifications can be made in the embodiment of the invention described and illustrated herein without departing from the scope and purview of the invention as defined by the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A method for the removal of dissolved free and complex cyanides from water-containing effluent which comprises controlling the pH of said effluent in a range of about 7.0 to 8.5 and contacting said effluent with an effective amount of an insoluble solid iron sulfide chosen from at least one of ferrous sulfide and ferric sulfide having particle sizes smaller than about 300μ for a period of time of at least about 5 minutes to remove said dissolved free and complex cyanides to a desired level, said effective amount being sufficient to give a weight ratio of said iron sulfide to total cyanide in said effluent of greater than about 2:1.

2. A method as claimed in claim 1, wherein the effluent contains cyanides of at least one of cyanide ions, complex cyanide ions of iron, copper, nickel and zinc, or mixtures thereof.

3. A method as claimed in claim 1, wherein said iron sulfide is prepared prior to treatment of effluent or in situ during treatment of effluent and has a particle size smaller than about 5μ.

4. A method as claimed in claim 3, wherein said weight ratio is in the range of about 5:1 to about 20:1.

5. A method as claimed in claim 4, wherein the effluent is contacted with the iron sulfide in a single stage, or in two or more co-current or counter-current stages.

6. A method as claimed in claim 3, 4 or 5, wherein the effluent and iron sulfide are agitated to ensure intimate contact between said effluent and iron sulfide particles and said pH is controlled in a range of about 7 to 8.

7. A method as claimed in claim 6, wherein iron sulfide is separated from effluent after contacting with said

iron sulfide and at least a portion of the separated iron sulfide is returned to said treatment.

8. A method as claimed in claim 3, 4 or 5, wherein said contacting is carried out for a period of time in the range of about 15 to about 180 minutes.

9. A method as claimed in claim 3, 4 or 5, wherein said contacting is carried out for a time in the range of about 15 to 60 minutes.

10. A method as claimed in claim 1, wherein the effluent is contacted with a particulate material chosen from concentrate and tailings, said material containing at least one mineral iron sulfide chosen from pyrrhotite and pyrite.

11. A method as claimed in claim 10, wherein said particulate material has particle size smaller than 150μ.

12. A method as claimed in claim 11, wherein said weight ratio is at least about 100:1.

13. A method as claimed in claim 1, wherein said contacting is carried out for a time in the range of about 30 minutes to 10 hours.

14. A method as claimed in claim 11, 12 or 13, wherein the effluent and iron sulfide are agitated to ensure intimate contact between said effluent and iron sulfide particles and said pH is controlled in a range of about 7 to 8.

15. A method as claimed in claim 1, wherein effluent is percolated at a pH in the range of about 7 to 8 through a particulate body containing mineral iron sulfide.

16. A method as claimed in claim 15, wherein said effluent is percolated through a particulate body of material chosen from concentrate and tailings containing at least one iron sulfide chosen from pyrrhotite and pyrite, and wherein the contact time of effluent with said body is at least about 30 minutes.

17. A method as claimed in claim 16, wherein said contact time is in the range of about one to 24 hours.

18. A method as claimed in claim 17, wherein said particulate body has particle sizes in the range of about 44 to 300μ.

19. A method as claimed in claim 15, 16 or 17, wherein said particulate body has particle sizes in the range of about 44 to 150μ.

20. A method as claimed in claim 15, 16 or 17, wherein said weight ratio is at least about 100:1.

21. A method as claimed in claim 1 or 2, wherein the effluent contains ferro-cyanide and wherein the effluent is treated with an excess of free ferrous ions.

22. A method as claimed in claim 1 or 2, wherein the iron sulfide is ferrous sulfide and the effluent is treated in the presence of sodium sulfite.

* * * * *

and solution are accumulated during the winter months. The liquid effluent decant is treated and discharged during the 6 warmer months.

The following rate of reagent consumption was reported for Con Mine which gives an idea of the amount of cyanide in the system and the reagents required to remove it:

Reagent Consumption at Con Mine, NWT
June 1984

Cyanide		1000	lbs	NaCN/day
Lime	1065	lbs		/day
$FeSO_4$	920	lbs	/day	
Na_2S	179	lbs	/day	
Zn dust		56.4	lbs	/day
Pb Acetate		14.0	lbs	/day

Notes

1) Because of the very large, shallow dam and because secondary treated is applied in summer only, there can be expected to be a significant natural cyanide degradation in the pond.

2) Because of the addition of sulfides and ferrous ions to the tailings dam, the decant water is unlikely to be suitable for recycling to the mill. In the NWT water is not in short supply.

3) Because of the sand/slime split and underground backfill, it is likely that minewater will contain some free cyanide.

CYANIDE DESTRUCTION BY PEROXIDE

Degradation of cyanide by hydrogen peroxide has been tested by several companies and recently installed on a commercial basis at the huge OK Tedi gold leaching operation in Papua, New Guinea.

The copper catalyzed hydrogen peroxide process is patented in the USA by DuPont and is known as the Kastone process. It is described by MATHRE & DEVRIES (1981) inserted below.

HOMESTAKE PILOT TESTS

MUDDER & WHITLOCK (1984) tested the DuPont Kastone process for the Homestake Lead effluent discussed above with thiocyanate and cyanide as well as copper and iron in relatively low levels, but still over effluent limits and 2-3 mg NH_3/l. It was found in a pilot plant test that this process provided the best solution to Homestake's treatment problem based on numerical and toxicological evaluations.

Suitability of DuPont Kastone Cayalyzed Peroxide Process for Removal of:

Thiocyanate	Total Cyanide CN_T	Method-C Cyanide	Ammonia	Metals	Ferrocyanides
NO	YES	YES	NO	YES	YES

The process did not remove thiocyanate, byproduct ammonia or residual copper all of which are potentially toxic and require additional treatment for their removal.

It was found that "the process required large quantities of expensive chemicals resulting in expected high operating costs."

The Homestake pilot plant consisted of several 0.2m³ (55 US gallon) Nalgene barrels operated in series to achieve a 2.5 hour contact period. The pilot flow rates varied from 125-200 ml/s (2.0-3.0 gpm). 100 mg H_2O_2/l, 10 mg Cu/l and 20.0 mg $FeCl_3$ were added.

The pH was maintained at 9.0 with either caustic or lime. The process was operated at ambient temperatures.

Following the oxidation sequence, the solutions were clarified and filtered under pressure through a sand filter. "Excessive chemical requirements and costs rendered the processes cost prohibitive for this application."

TRAUTMAN & OMMEN (1981) reported the same tests using 2.5 hour residence times in the reaction tanks. Altogether, 14 test programs were completed at various flow combinations. Total cyanide was reduced from 10.5 ppm to 0.5 ppm. Weak acid dissociable cyanide was reduced from 8.1 ppm to 0.2 ppm. When scale control using phosphonate was attempted, higher copper values were found in the effluent.

OK TEDI PEROXIDE DECOMPOSITION OF CYANIDE

LAMMERS (1984) mentioned the use of hydrogen peroxide for cyanide destruction in a major project milling 22,500 tpd ore with cyanide addition of about 11,250 Kg/d. The screened tailings are pumped to a tank 13 mØ x 24.5 m high agitated by a Denver draft tube agitator with 3.66 m impeller and powered by a 75 kilowatt motor.

About 1.2 Kg hydrogen peroxide solution (70%) is added per ton of ore. Sufficient copper ions are already in the solution to provide the catalyst for the reaction.

The peroxide addition is controlled automatically based on the oxidation-reduction potential of the feed to the tailings tank. This control system was developed by Degussa, the supplier of the hydrogen peroxide, and is proprietory.

KNORR & GRIFFITHS (1984) of Degussa discussed peroxide oxidation of cyanide at the Cyanide Conference held in December 1984 in Tucson, Arizona. Their process is made feasible through the use of their on-line analysis and automated process controlls described in the patent inserted below.

LAMMERS (1984b) pointed out that the Degussa peroxide addition controller was essential to achieve an affordable reagent consumption for this process.

Information on the DuPont copper catalyzed hydrogen peroxide cyanide destruction process can be requested from:

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Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Telefon-Durchwahl	Datum
		IC-ATA/Dr.Gr-sch	59- 3289	01.02.85

Dear Hans,

it was very interesting meeting you in Tucson, at the conference on "Cyanide and the Environment". We hope you enjoyed the conference as much as we did, and look forward to more such stimulating meetings in the future.

We promised to send you a copy of the U.S. Patent covering the application of our cyanide detoxification process with hydrogen peroxide, and we enclose it herewith. We also take the opportunity to include some further information on Degussa and the products and processes which we offer.

Kind regards

D e g u s s a AG
Industrial and Fine Chemicals Division
Product Development and Technical Service

ppa. Dr. Knorre i. A. Dr. Griffiths

Enclosure
"Mining and Degussa"
U.S. Patent No. 4,416,786
List of Products
Annual Reports 1980/81 and 1982/83

Degussa Aktiengesellschaft · Sitz: Frankfurt (Main) · Registergericht: Amtsgericht Frankfurt (Main) · Eintragungs-Nr. 72 HRB 8239
Vorsitzender des Aufsichtsrats: Dr. Konrad Henkel · Vorstand: Gert Becker (Vorsitzender), Dr. Robert Ehrt, Dr. Karl Feldmann, Herbert Hartmann, Prof. Dr. Bernhard Liebmann, Dr. Heribert Offermanns, Dr. Erich Sattler-Dornbacher, Dipl.-Ing. Hanns E. Sohn, Günter Wohlenberg

0882

United States Patent [19]

Knorre et al.

[11] **4,416,786**

[45] **Nov. 22, 1983**

[54] **PROCESS FOR THE TREATMENT OF CONTINUOUS WASTE WATER STREAMS HAVING CHANGING CONTENTS OF DIFFERENT OXIDIZABLE MATERIALS WITH HYDROGEN PEROXIDE**

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[73] Assignee: **Degussa, Frankfurt, Fed. Rep. of Germany**

[21] Appl. No.: **392,464**

[22] Filed: **Jun. 28, 1982**

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**[3] **C02F 1/72**

[52] **U.S. Cl.** **210/746; 210/759; 210/908; 210/904; 210/916**

[58] **Field of Search** 210/739, 743, 758–760, 210/790, 904, 908, 916, 746

[56] **References Cited**

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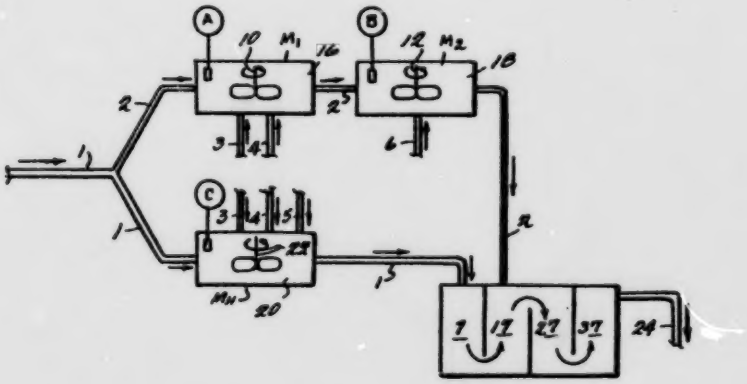
Primary Examiner—Thomas G. Wyse

Attorney, Agent, or Firm—Cushman, Darby & Cushman

[57] **ABSTRACT**

There is provided a continuous process for the lowering of the content of toxic materials in waste waters which also contain other oxidizable materials by quickly and continuously ascertaining the requirement of hydrogen peroxide, namely by potentiometric determination of the oxidizing agent requirement in a branched-off side-stream using a strong oxidizing agent, such as peroxymonosulfate, peroxydisulfate, permanganate, hypochlorite or ozone, which acts more quickly than hydrogen peroxide under comparable conditions.

20 Claims, 2 Drawing Figures



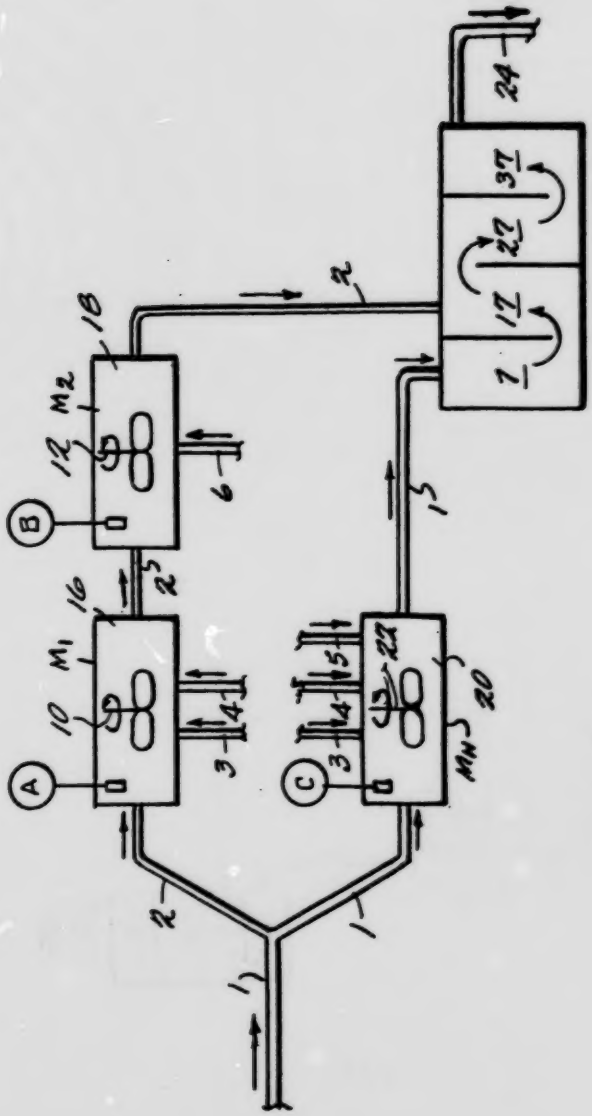


FIG. 1

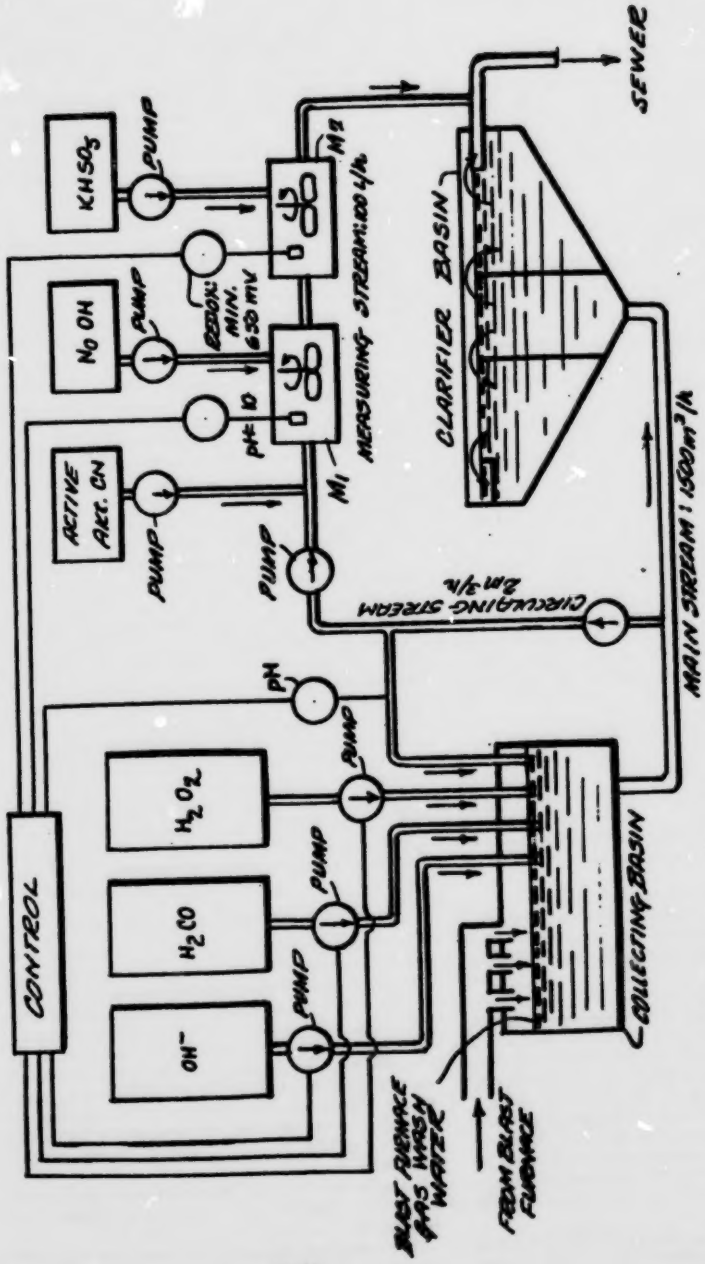

CONTROL
OH^-
H_2CO
H_2O_2
$NaOH$
$KHSO_3$
ACTIVE ALC. CN
PUMP
pH
pH=10
REDOX: MIN. 650 mV
M_1
M_2
MEASURING STREAM: 100 l/h
CIRCULATING STREAM 2m³/h
CLARIFIER BASIN
SEWER
MAIN STREAM: 150m³/h
COLLECTING BASIN
BLAST FURNACE GAS WASH WATER
FROM BLAST FURNACE

FIG. 2

PROCESS FOR THE TREATMENT OF CONTINUOUS WASTE WATER STREAMS HAVING CHANGING CONTENTS OF DIFFERENT OXIDIZABLE MATERIALS WITH HYDROGEN PEROXIDE

BACKGROUND OF THE INVENTION

The use of hydrogen peroxide as an agent for the oxidative treatment of waste water takes on increasing significance under today's aspects of environmental protection, since hydrogen peroxide itself does not cause additional salting of the waste water but splits into water and oxygen. However, an essential condition is that the necessary amount of hydrogen peroxide can be determined automatically and controlled.

This requirement is especially true for the treatment of continuous waste water streams which contain variable amounts of different oxidizable toxic materials and only permit a relatively short time for treatment. In such cases the success of waste water treatment with hydrogen peroxide depends highly on how quickly and reliably the total requirements of oxidizing agent can be determined in the incoming waste water stream in the treatment plant. As total oxidizing agent demand (requirement) we understand that amount of active oxygen or H_2O_2 which is needed in order to be able to convert the oxidizable material in the waste water under the chosen reaction conditions into the appropriate oxidation products in each case.

Little information can be found in the technical literature as to how the total oxidizing agent requirement of a waste water can be determined automatically. The reason for this is that most of the materials occurring in waste water only contribute in small and very variable manner to the formation of a definite redox potential, that e.g. can be measured with a platinum/reference electrode pair. Therefore the oxidative waste water treatment process is operated in such a way that, while following the redox potential of the waste water, oxidizing agent is added successively until due to the presence of an excess a constant end point is established. However, in most cases this process is usable only for a batchwise treatment of waste water, since the oxidation of the various materials with H_2O_2 requires variable reaction times and therefore a constant end potential is not established immediately, even in the presence of excess H_2O_2, but only when the oxidation reactions are completed.

Thus, e.g., there is described in German Pat. No. 2,352,856 and related Fischer U.S. Pat. No. 3,970,554 a process for the detoxification of cyanide-containing waste water with H_2O_2 that permits the monitoring and control of the detoxification process and the addition of the H_2O_2 by measuring the redox potential with a silver electrode and any desired reference electrode, preferably a thalamide electrode. (The entire disclosure of the Fischer U.S. patent is hereby incorporated by reference and relied upon). However, this process is only employable in most cases for a batchwise treatment of waste water since the measurement of the redox potential shows the free cyanide content in the waste water, but permits no conclusions regarding the total oxidizing agent requirement if, besides free cyanides, other consumers of hydrogen peroxide are also contained in the waste water.

The single addition of an amount of oxidizing agent corresponding to the indication of free cyanide content

at the beginning of the waste water treatment would accordingly lead to insufficient detoxification results, because the other consumers of H_2O_2 use up a portion of the hydrogen peroxide which is needed for the cyanide oxidation. Only through multiple subsequent dosing of oxidizing agent at fixed time intervals can in these cases bring about both the desired breakdown of cyanide as well as of other oxidizable materials present. Such a stepwise approach to the goal of the process, as necessary because of the reaction time needed for the oxidation of the cyanide, does not usually permit the continuous treatment of large waste water streams because the treatment plant must be constructed so large in order to guarantee sufficient treatment time.

In Belgian Pat. No. 883,046 there is given a process for the measurement of the concentration of a specific dissolved component with redox- or ion-sensitive electrodes for the purpose of monitoring or regulating chemical processes, among others in the treatment of waste water. This process is characterized by the determination of the maximum attainable potential value by addition of excess reagent to a side stream of the system and evaluating the deviation of the starting potential as a measure of the reactive material content. For example, in this way the free cyanide content can be ascertained quickly and reliably in a continuous waste water stream and the amount of hydrogen peroxide shown to be required for the oxidation can be added. However, the process described according to Belgian Pat. No. 883,046 fails to work if there are present in waste water different oxidizable toxic materials in varying concentrations together which contribute different amounts to the formation of the redox potential. Thus, e.g., in the measurement of the cyanide potential with a silver electrode and a thalamide reference electrode under the conditions of the process described in German Pat. No. 2,352,856 (and related Fischer U.S. patent) approximately the same redox potential of about 350 mV is produced by 1 mg S^{2-}/l as by 50 mg Cn/l. Other oxidizable materials, such as sulfite, on the other hand are practically not detected at all by this redox system.

Therefore the invention is based on the problem of developing automatic system which makes possible quick and reliable determination of the oxidizing agent requirement which is needed for decreasing the toxic material concentration of a waste water under a desired limit in a continuous oxidative treatment of the waste water under fixed pH and temperature conditions.

SUMMARY OF THE INVENTION

It has now been found that this problem of the treatment of continuous waste water streams with varying contents of different oxidizable materials, especially cyanides, sulfides, sulfites, thiosulfates, thiocyanates and/or organic materials, with hydrogen peroxide for the purpose of the detoxification and reduction of the chemical and biological oxygen demand can be solved if the dosing of the H_2O_2 to the continuous waste water stream (main stream) is controlled by ascertaining the oxidizing agent demand in a small, continuously branched-off side-stream (measuring stream) parallel thereto by:

(a) adjusting the pH of the waste water in the side-stream by dosing of alkali or acid to a definite value between pH 3 and 12;

(b) continuously measuring the redox potential in the side-stream in the known manner with a platinum, sil-

ver, gold, or ion-selective electrode and any suitable reference electrode and dosing an aqueous solution of a strong oxidizing agent acting more quickly than H_2O_2 under comparable conditions, such oxidizing agent preferably being a peroxymonosulfate, peroxydisulfate, hypochlorite, permanganate or ozone, until the desired redox value is reached corresponding to the sought breakdown of the toxic material, and then always, when the strong oxidizing agent is dosed into the side-stream (measuring stream) simultaneously adding proportional amounts of H_2O_2 and other chemicals if necessary, e.g., for pH regulation, into the main-stream.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow diagram of one form of the process of the present invention; and

FIG. 2 is a schematic flow diagram of the decyanization of blast-furnace gas wash-water by the process of the invention.

DETAILED DESCRIPTION

Referring to FIG. 1, a constant amount of waste water per unit time is continuously branched off from the waste water stream 1 (main stream) and is led as so-called measuring stream 2 separately through two measuring cells M_1 (also identified as 16) and M_2 (also identified as 18), fitted with stirring or mixing devices 10 and 12. In the measuring cell M_2, the pH and redox values of the waste water are continuously measured with pH and redox measuring devices. In measuring cell M_1 the dosing of acid or alkali takes place, which continuously establishes the pH required for measuring the redox potential. Besides this, the strong oxidizing agent is added to the measuring stream, if the measured redox potential in cell M_2 deviates from the desired redox value (set point).

Synchronous with the dosing of the strong oxidizing agent into the measuring stream 2 there is dosed into the waste water stream 1 (main stream) a proportional amount of H_2O_2. Additionally, the chemicals needed to regulate the pH in the main stream are added as soon as the strong oxidizing agent is dosed into the measuring stream 2 and H_2O_2 is dosed into waste water stream 1 (main stream).

For the exact and quick determination of the H_2O_2 requirement which is needed for decreasing the toxic material concentration to the desired limit there must be chosen a strong oxidizing agent which on the one hand reacts practically instantaneously with the toxic materials in the waste water and on the other hand has a comparable oxidation power, to that which is reached by dosing H_2O_2 into the waste water stream 1 (main stream) within the available treatment time. As indicated above, under these conditions, the most suitable strong oxidizing agents are the soluble salts of peroxymonosulfuric acid, e.g. sodium monoperoxysulfate and potassium monoperoxysulfate (caroate). However, there can also be used other strong oxidizing agents such as salts of peroxydisulfuric acid, e.g. sodium peroxydisulfate and potassium peroxydisulfate, permanganates, e.g. sodium permanganate and potassium permanganate, ozone and hypochlorites of the alkali metals and alkaline earth metals.

The addition of the H_2O_2 as well as the chemicals for pH regulation in the waste water stream 1 (main stream) is undertaken in a mixing vessel M_H (also identified as 20) containing stirring device 22 from which mixing vessel the waste water stream 1 is led into one or more reaction basins 7, 17, 27, and 37 connected in series, in which the oxidation of the various materials present can be carried out simultaneously. In the course of passing these reaction basins, can also, if necessary, a correction of the pH or subsequent dosing of oxidizing agent be carried out.

If insoluble compounds are formed in the oxidative treatment, the waste water stream must subsequently be led to devices for the separation of the sediment (not shown) before the waste water can be led into the sewer. It is also necessary to adjust the pH to the permissible range if it deviates therefrom.

The measuring stream, after passing through the measuring cells M_1 and M_2, also rejoins the waste water stream 1 (main stream) and the combined treated stream leaves through line 24.

In FIG. 1 the measuring devices are designated by the letters A, B, and C. The lines for dosing of acids, alkali, H_2O_2 and caroate into the measuring stream 2 or waste water stream 1 (main stream) are denoted by 3, 4, 5, and 6.

The process of the invention has proved successful above all in the decyanization of blast-furnace gas wash-waters. Such waste waters arise in blast furnace processes in amounts of several hundreds to over one thousand m^3/h. They contain besides considerable amounts of flue dust varying amounts of alkali cyanides, heavy metal cyanides, sulfides, sulfites, thiocyanates and other sulfur compounds as well as phenols and other organic compounds. The content of easily-liberated cyanide in these waste waters normally lies in the range of 0–10 mg CN^-/l; in disturbances of the blast furnace process or in starting up or shutting down the blast furnace the cyanide content, however, can also increase to a substantially higher value (over 100 mg CN^-/l).

For the decyanization of such waste water there has been up to now no suitable process available. The known process of chlorination has disadvantages such as the formation of toxic chlorination products, operation at very high pH values and because of this the formation of additional amounts of neutral salts in the necessary neutralization of the waste water after the detoxification before entering the sewer, which increases the amount of neutral salts arising from the chlorination reagents as well as the known dangers due to the presence of excess chlorine or hypochlorite, entirely apart from the difficulties in automatic monitoring and control of operations with these materials.

In contrast, hydrogen peroxide does not form toxic products or cause additional salting. The presence of an excess is not injurious since hydrogen peroxide decomposes to water and oxygen. The cyanide oxidation with hydrogen peroxide can also be carried out at lower pH values, preferably at pH 10; therefore less chemicals are needed for the alkalization and neutralization of the waste water and therefore less neutral salt is produced. Simultaneously, hydrogen peroxide oxidizes sulfur compounds in a lower stage of oxidation to elemental sulfur or sulfates and thiocyanates are converted into cyanates. In the presence of metallic iron or copper or iron-III ions phenols are also oxidatively broken down by H_2O_2 forming mainly dicarboxylic acids. The oxidation of organic compounds takes place partly up to CO_2 so that a significant reduction in Chemical Oxygen Demand (COD) is effected by H_2O_2 without additional increase in salt content. Aldehydes are also oxidized by H_2O_2.

Preliminary experiments have shown that for reduction of the cyanide content in blast-furnace gas washwater a significantly higher amount of H_2O_2 relative to the amount of cyanide is needed because other oxidizable materials sometimes react with the hydrogen peroxide more quickly than cyanide. Such a waste water treatment with H_2O_2 can therefore only be carried out if the addition of H_2O_2 can be controlled automatically and adjusted according to the total oxidizing agent requirement. This was made possible for the first time through use of the present invention as described in Example 2.

A further field of use for the process of the invention is e.g. the treatment of waste waters from the reproduction section of graphic plants and from film copying works whose content of toxic material in the individual waste water streams as well as in the form of waste water mixtures can be reduced to the desired limit. Besides inorganic sulfur compounds in lower oxidation stages, such waste waters always contain varying amounts of organic compounds which because of their high oxygen demand (COD, BOD) are a great stress for the biological sewage treatment plants. With the help of hydrogen peroxide, it is possible to treat such waste water from fixing, developing and clearing baths and other processes so that the biological load is substantially lower. Thus, by means of the treatment with H_2O_2 reducing substances such as thiosulfates and sulfites which are present in fixing, developing, and clearing baths can be finally oxidized up to sulfates. Simultaneously in the oxidation treatment with H_2O_2 the dissolved silver is precipitated as an insoluble mixture of Ag_2O, AgBr and Ag_2S. The recovery of silver from the sludge thus contributes to the cost of the waste water treatment.

In concentrated waste waters from such photo processes the changes in pH or redox potential occurring during the treatment with H_2O_2 can frequently be used for control of the oxidative waste water treatment, especially as these treatments can be carried out for the most part batchwise. However, such a waste water treatment is substantially more difficult if a dilute waste water with relatively low concentrations of oxidable materials is used and which, because of the large amounts of waste water, cannot be treated batchwise but must be treated continuously.

In this case the invention is based on the problem of finding a monitoring and regulating concept with whose help it is possible, by dosing H_2O_2 into a continuous waste water stream, to lower the iodine value, used here as a measure for the content of oxidizable material, from e.g. above 10 mg iodine/l to 10 mg iodine/l or lower.

To carry out the process of the invention the pH is selected in such a way that the oxidizing agents added to the measuring and waste water main streams can act optimally. This pH value or pH range can be different in the waste water main stream from that in the measuring stream.

Thus, it has been shown that in the oxidation of cyanide-containing waste water the pH in the main stream and in the measuring stream can be in the range of 6 to 12, preferably at about 9-12, the value of about 10 has proved to be especially favorable.

As redox measuring electrodes, platinum, gold, or silver electrodes or an ion sensitive electrode may be used at will and connected with any reference electrodes, e.g. a thalamide electrode.

In employing hydrogen peroxide it may also be of advantage to use activators, e.g. the substances described in German Pat. No. 2,352,856 and Fischer U.S. Pat. No. 3,970,554.

The hydrogen peroxide is employed in the normal commercial concentrations, e.g. in solutions containing 30-70 weight % H_2O_2. Higher or lower concentrations are possible, but not usual.

The materials used as strong oxidizing agent such as peroxymonosulfates, peroxydisulfates, potassium permanganate, hypochlorites or ozone are employed in concentrations which are adjusted to the oxidizing agent requirement in each case. In using potassium caroate a concentration of 45 grams $KHSO_5$/l has proven suitable.

Per mole of peroxymonosulfate there are employed 1-10 moles of H_2O_2, whereby the ratio of liters of measuring stream to liters of main stream must of course be considered.

For the decyanization of waste waters with H_2O_2 in a given case there can also be added a small amount of formaldehyde as an aid, with which the cyanide is partially converted into glycolic acid. The formaldehyde is employed in the form of commercial aqueous solutions which preferably contain 30-40 weight % H_2CO. According to the process of the invention additions of 0.1-1 mole of H_2CO/mol of peroxymonosulfate are advantageous, in which case again the ratio of liters of measuring stream to liters of main stream must be considered.

The advance in the art of the process of the invention consists essentially of the possibility of ascertaining the requirement of H_2O_2 needed for lowering the concentrations of various toxic materials in continuous waste water streams quickly and continuously as well as being able to undertake simultaneously the dosing of the hydrogen peroxide as well as the chemical aids, e.g. for regulation of the required pH in the waste water, so that it is guaranteed that, even at changing concentrations of toxic materials in the waste water, there will always take place the desired breakdown to the required limit of concentration. The process of the invention also has the advantage that the pH regulation in the waste water main stream is only then undertaken if a treatment with hydrogen peroxide is necessary. In this way reagents are saved, as well as unnecessary salting of the waste water.

Unless otherwise indicated all parts and percentages are by weight.

The process of the invention can comprise, consist essentially of, or consist of the stated steps with the stated materials.

The invention is explained more closely in the following examples.

EXAMPLE 1

There should be automatically added to a continuous waste water stream from a film copying plant an amount of H_2O_2 corresponding to the varying content of oxidizable materials with substantial avoidance of over and under dosaging. The iodine value serving here as the measure for the content of oxidizable materials should be regulated to a maximum of 10 mg of iodine per liter.

It was established in preliminary tests that the changes of the redox potential at the relatively low concentrations of oxidizable materials (iodine value 100-200 mg per liter) present in the untreated waste

water by addition of the H_2O_2 were only small and could not be utilized for automatic regulation. The pH of 6–7 present in these water samples did not change substantially during the addition of H_2O_2.

However, it was established that, even in these waste waters, significant pH-dependent changes of the redox potential (about 300–400 mV) occur if there is added to the waste water in place of H_2O_2, the solution for example of an alkali metal salt of peroxymonosulfuric acid (Caro's acid) such as potassium caroate, $KHSO_5$ (or sodium caroate). This change of the redox potential in the addition of caroate can be used as quantitative control for the treatment of waste water with H_2O_2 if the caroate addition is carried out at constant pH and the pH change caused by the addition of the acid-reacting caroate solution is compensated for by addition of caustic soda (aqueous sodium hydroxide). A platinum/calomel-electrode pair is suitable in this case for the potential measurement.

For the principle of the process of the invention see FIG. 1.

For the present example there were branched off from the waste water stream of a film copying plant (about 40 cubic meters per hour) a measuring stream (50 liters per hour) and a main stream with 2300 liters per hour. The measuring stream was led through two series-connected stirrer cells (M_1 and M_2). There was dosed into the stirrer cell M_1 the caroate solution (150 grams of caroate per liter=6.32 grams of active oxygen per liter) and in the stirrer cell M_2 there was dosed 1 N aqueous sodium hydroxide (40 grams of NaOH per liter). The stirrer cell M_2 also contains a combined pH-measuring electrode (one-line) and a platinum/calomel redox electrode pair.

With the help of a measuring and controlling apparatus the dosing of the aqueous sodium hydroxide and caroate solution into the measuring stream was controlled in such a manner that, at a constant pH of 8, there was maintained a redox potential of +150 mV. (Under these conditions with potassium iodide-starch paper there was always established a small caroate excess in the measuring stream).

Synchronous with the dosing of caroate into the measuring stream there was added to the main stream a proportional amount of H_2O_2 (50 weight % with 281 grams of active oxygen per liter). The waste water treated with H_2O_2 flowed through the reactor M_H which consisted of two series-connected reactors, each having a volume of about 750 liters of which the first reactor was equipped with a stirrer. The theoretical residence time amounted to about 20 minutes per reactor.

By determination of the iodine value of the waste water in the main stream treated with H_2O_2, the H_2O_2 dosage was adjusted so that the iodine value, which in the untreated waste water on the average amounted to 200 mg I_2 per liter, was reduced to 10 mg of iodine per liter.

The consumption of chemicals needed to reach this iodine value amounted on the average to:

(a) 400 ml of 1 N-NaOH per hour and 680 ml of caroate solution (150 grams per liter) per hour for the measuring stream (50 liters per hour) and

(b) 940 ml of H_2O_2, 50 weight %, per hour for the main stream (2.3 cubic meter per hour).

EXAMPLE 2

At the blast furnace of a metallurgical plant for the production of pig iron there arise per hour about 1,400–1,800 cubic meters of blast-furnace gas wash-water which contains, besides iron oxide and zinc oxide ore and slag particles, calcium compounds etc, varying amounts of dissolved oxidizable materials such as sulfites, sulfides, phenols and also alkali cyanides in the order of magnitude of 0–10 mg CN^- per liter. For example, the total analysis of such a waste water showed the following contents:

2.15 mg CN^-/l total cyanide according to DIN 38 405-D 13.1

1.95 mg CN^-/l direct argentometrically determinable cyanide

16 ml sediments per liter waste water

0.5 mg Cu/l total

0.3 mg Ni/l total

17 mg Zn/l total

168 mg Fe/l total

0.3 mg Cu/l dissolved in the filtrate

0.2 mg Ni/l dissolved in the filtrate

<0.05 mg Zn/l dissolved in the filtrate

<0.3 mg Fe/l dissolved in the filtrate

The pH of the waste was about 6. The permanganate consumption was 1049 mg $KMnO_4$ per liter of waste water corresponding to 265.6 mg active oxygen per liter or 1,130 mg H_2O_2 (50 weight percent) per liter or 5,600 mg potassium caroate (45 percent $KHSO_5$) per liter of waste water.

During the temporary shutting-down of the blast furnace for the purpose of repair there was established in the blast-furnace gas wash-water the following maximum content of unwanted substances:

197 mg CN^-/l direct argentometrically determinable cyanide

142 mg CN^-/l easily-liberated cyanide according to DIN 38 405-D 13.2

820 mg Fe/l total

7.6 mg Pb/l

87.2 mg Zn/l

39 mg S^{--}/l

DIN stands for German Industrial Standard.

Up to now, the waste water of this blast furnace was merely continuously clarified in a sedimentation plant (Bischoff-basin) and, mixed with other process waters, led into a river; only during the starting-up and shutting-down of the blast furnace, i.e. at higher cyanide contents in the blast-furnace gas wash-water, there was carried out a treatment with hypochlorite bleach solution. This process, however, was not satisfactory because of the above-mentioned side effects.

In the course of investigating all possible processes for the decyanization of this waste water there could also be tested the treatment with hydrogen peroxide using the measuring and control techniques of the invention. Thereby it was found that the content of easily liberated cyanide, (using the residence time in the sedimentation basin, can be quickly and safely reduced to values below 0.1 mg CN^- per liter (according to DIN 38405-D. 13.2) if the ascertained amount of H_2O_2 in the waste water determined by redox controlled addition of potassium caroate in a side-stream (measuring stream) is added to the collecting tank installed before the sedimentation plant and simultaneously there is added a less than stoichiometric amount of formaldehyde relative to the amount of H_2O_2. In this way, above all at low cya-

nide concentrations, there is caused a partial conversion into glyconitrile which, under the action of H_2O_2, very quickly hydrolyzes to glycolic acid and in the presence of calcium ions substantially precipitates as insoluble calcium glycolate.

The principle of the measuring and control technique which is employed for the decyanization of the blast-furnace gas wash-water with H_2O_2 and H_2CO is represented in FIG. 2.

For the control of the addition of chemicals there is branched off from the blast-furnace gas wash-water stream a side-stream of about 2 cubic meters of waste water per hour and led back again as a loop stream into the collecting tank. From this loop stream there is continuously drawn off exactly 100 liters of waste water per hour and led as a measuring stream through two mixing cells M_1 and M_2. In the mixing cell M_1 the pH of the waste water is continuously measured with a glass electrode and regulated by automatically dosing 10% aqueous sodium hydroxide to pH 10±0.5. In the mixing cell M_2 the redox potential of the waste water is continuously measured with a silver and a thalamide reference electrode and regulated by automatically dosing a 10% caroate solution containing 4.5% $KHSO_5$ to at least +650 mV. This potential corresponds to the desired degree of detoxification. In order to be able to measure this potential there is continuously dosed into the measuring stream 2 at least 0.001 mg Ag NO_3 and 2.5 mg KI per liter. The output of the metering pump for the caroate solution was regulated so that in normal operation of the blast furnace the toxic material content could be reduced from maximally 10 mg CN^- per liter in the presence of other oxidizable materials practically instantaneously to a residual content of <0.1 mg CN^- per liter through the added amount of caroate solution, (e.g. dosing output 1 liter of 10% caroate solution per hour). The pump for dosing of caroate solution into the measuring stream is controlled via the set point of the redox measuring device. When the potential falls below the set point (=specified mV value) the pump is switched on, on exceeding the same set point it is switched off again.

Parallel to the dosing of the caroate solution if the potential falls below the set point of the redox measuring amplifier the addition of chemicals into the main stream is also controlled. The pH of the waste water main stream, which already is partly alkalized by lime, is regulated by dosing aqueous sodium hydroxide into the collecting tank to pH 10±0.5 with the aid of a pH measuring device in the loop stream line, and proportional amounts of 37% formaldehyde solution and 50 weight percent hydrogen peroxide are also dosed to the collecting tank. The dosing output of the chemical pumps was thereby chosen, so that in the normal operation of the blast furnace and a waste water amount of 1,500 cubic meters per hour there could be dosed per liter of caroate solution (in the measuring stream) 620 liters of H_2O_2 (50 weight percent) and 170 liters of H_2CO (37 weight percent) as well as about 3000 liters of NaOH (20 weight percent) in the main stream.

The effective consumption of chemicals in the normal operation of the blast furnace is about 250 liters of H_2O_2 (50 weight percent) per hour and 70 liters of H_2CO (37 weight percent) per hour; additionally there is needed on the average 840 liters of NaOH (20 weight percent) per hour for the final alkalization. A re-neutralization of the waste water after the oxidative treatment was not necessary; the pH of the treated waste water after the separation of sediment is always below 9.

An analytical investigation of the degree of detoxification according to DIN 38 405-D 13.2 carried out at regular intervals showed that under these conditions the content of easily-liberated cyanide in the waste water could always be reduced to a value below 0.1 mg CN^-/l. The treatment thus fully met the requirements.

If the content of oxidizable material in the waste water increases, both the output of the caroate pump and proportionally that of the chemical pumps for the main stream must be increased. The signal for this is given when, during permanent operation of the chemical dosing pumps, the specified redox potential is no longer exceeded.

In the treatment of blast-furnace gas wash-water it is also necessary to ensure the correct functioning of the measuring electrode by cleaning at regular intervals (about 1 hour), since some materials in the waste water (above all the alkaline earth metal compounds and the CO_2) lead in the alkaline pH range to scale formation. Such a cleaning of the electrodes can be effected very easily by dosing into the mixing cell M_1 of the measuring stream at regular intervals a small amount of medium strength hydrochloric acid or nitric acid. This dosing is controlled automatically by a time switch.

The entire disclosure of German priority application P 3125452.7 is hereby incorporated by reference.

EXAMPLE 3

In the synthesis of an intermediate for the production of herbicides there arise 1000 l/h of waste water which, in addition to neutral salts and sulfur compounds, also contain other organic reaction products. As a result there is a high COD value of about 17,000 mg O_2/l. The pH of the waste water is 7.

Difficulties occurred in treating this waste water in a biological purification plant because of the high COD value. The lowering of the COD value by a complete oxidative treatment with chemicals was excluded for reasons of cost. Therefore the possibility was investigated of changing the materials contained in the waste water by a chemical treatment in such a way that they could be completely broken down in a subsequent biological purification plant.

It was established in preliminary tests that in the treatment of the waste water with H_2O_2 in the acid pH range there occurred an intermediate precipitation of certain substances, which in the further oxidation either partially or completely redissolved. However, if the reaction was carried out with less than stoichiometric amount of H_2O_2 based on the initial COD of the waste water and the intermediately formed precipitate was separated off, then a substantially greater reduction of the COD was produced than would be expected from the oxidation agents alone. However, this oxidation reaction could not be followed and controlled up to now. Therefore the practical use of these oxidation reactions was linked to high analytical expense. By using the principle of the invention described herein for controlling waste water treatment processes with H_2O_2, in this case also a simple and economical solution of the waste water problem was found.

To ascertain the maximum amount of oxidizing agent required, there was continuously branched off from the waste water stream of 1,000 l/h a side-stream of 1 l/h and fed into a diluting water stream of 100 l/h. This diluted waste water side stream was then adjusted to a

pH of 12 by dosing aqueous sodium hydroxide solution and there was continuously dosed a caroate solution (45 grams $KHSO_5$/l) until the redox potential measured with a Pt-thalamide electrode pair increased from +700 mV to +800 mV.

Parallel to the diluted waste water side stream, the waste water main stream (1000 l/h) was first adjusted to a pH of 3 by dosing sulfuric acid, and then 50% H_2O_2 was always dosed when caroate solution was dosed into the diluted waste water side stream. The ratio of caroate dosed into the diluted waste water to H_2O_2 dosed into the waste water main stream was hereby so regulated that in dosing 1 liter of caroate solution into the diluted waste water side stream, there were introduced 16 liters of 50 weight % H_2O_2 into the main waste water stream. This amount of H_2O_2 corresponds to about 55% of the oxidizing agent requirement for the total oxidation based on the initial CGD of the waste water of 17,000 mg O_2/l.

After a reaction time of 1.5 hours and separation of the precipitates formed in the course of this treatment, the filtrate of the waste water main stream had a COD value of only 3,570 mg O_2/l; this corresponds to a reduction in COD of 79% based on the original COD, or 144% based on the amount of oxidizing agent used.

It was also determined, that the waste water after this treatment could be completely treated in a biological sewage plant without difficulty.

EXAMPLE 4

A continuous waste water stream from a hardening shop which contains varying amounts of nitrite (15 to 120 mg $NO^-{}_2$/l) should be treated by automatically controlled addition of H_2O_2 so that, on the one hand there is guaranteed a complete oxidation of the nitrite to nitrate, and on the other hand that H_2O_2 is not dosed in excess.

In preliminary tests on a laboratory scale it was established that in the oxidation of this waste water with H_2O_2 in the acid pH range there occurred only a very small change of the redox potential measured with a gold-thalamide electrode pair. This small change could not be used for control.

However, it was also established that in the oxidative treatment of this hardening-shop waste water there always occurred a clear jump in potential (from 320 to 640 mV) if, instead of H_2O_2, sodium hypochlorite was used as the oxidizing agent. This change of redox potential can be used as a standard for the treatment of waste water with H_2O_2 if the NaOCl addition takes place at a pH below 3 and the change in pH caused by the addition of alkaline NaOCl solution is compensated for by the addition of acid. For the measurement of the potential gold or platinum electrodes are suitable in conjunction with the customary reference electrodes employed in the practice.

CARRYING OUT OF THE OXIDATIVE TREATMENT

There was branched off from the waste water stream of a hardening shop (6 m^3/h) for the present example a measuring stream of 100 liters per hour which was led through two measuring cells connected in series. There were fed into the stirrer cell 1 sulfuric acid (accumulator acid) and sodium hypochlorite solution (25 grams NaOCl/l). The stirrer cell 2 contained a combined pH measuring electrode and a gold/thalamide electrode pair.

By using a suitable measuring and control apparatus of customary construction the dosing of acid and NaOCl into the measuring stream was controlled so that at a pH of 3 or below there was maintained a redox potential of above +1600 mV. (Under these conditions with potassium iodide-starch paper there was always established only a slight excess of NaOCl in the measuring stream.)

Parallel to the dosing of NaOCl into the measuring stream, the pH in the main stream was first regulated to 3.5 or below and then there was always dosed a proportional amount of H_2O_2, 50 weight %, when NaOCl was dosed into the measuring stream. The thus treated waste water was then led into a further reaction basin (1.5 m^3) and from there into final stirrer container (1.5 m^3) in which the neutralization with milk of lime was carried out. Then the sediment ($CaSO_4$) contained in the waste water (mainstream and measuring stream) was separated off by means of an inclined clarifier and substantially dewatered in a filter press. In this manner there was always observed in the discharges from the starting clarifier and the filter press a nitrite content below 1 mg $NO^-{}_2$/l; the excess content of H_2O_2 was likewise only less than 5 mg H_2O_2/l.

In order to obtain these discharge values there were only needed on the average the following amounts of oxidizing agents

(a) 420 ml of hypochlorite solution per hour containing 25 grams NaOCl/l for the measuring stream (100 l/hour).

(b) 520 ml H_2O_2, 50 weight %, per hour for the mainstream (6 cbm/hour).

What is claimed is:

1. A process for the treatment of a continuous main waste water stream having a varying content of different oxidizable materials with hydrogen peroxide for the purpose of detoxification and reduction of the chemical oxygen demand and biological oxygen demand, comprising diverting a small portion of the main waste water stream to form a side stream and controlling the amount of hydrogen peroxide added to the main stream by ascertaining the oxidizing agent demand in the side stream by:

(a) adjusting the pH of the waste water by dosing of alkali or acid continuously to a constant pH value between 3 and 12,

(b) continuously measuring the redox potential with a platinum, silver, gold, or ion selective electrode and a reference electrode and dosing an aqueous solution of a strong oxidizing agent acting more quickly than H_2O_2 under comparable conditions until the desired redox value is reached corresponding to the sought breakdown of the toxic material, and then always when the strong oxidizing agent is dosed into the side stream simultaneously adding into the main stream proportional amounts of H_2O_2 and any necessary further chemicals.

2. A process according to claim 1 wherein the materials to be removed are selected from the group consisting of cyanides, sulfides, sulfites, thiosulfates, thiocyanates, and/or organic oxidizable material.

3. A process according to claim 2 wherein the material to be removed includes cyanide.

4. A process according to claim 3 wherein there is added to the main stream a chemical reagent which regulates the pH.

5. A process according to claim 3 wherein the strong oxidizing agent is a peroxymonosulfate, peroxydisulfate, permanganate, hypochlorite or ozone.

6. A process according to claim 5 wherein the strong oxidizing agent is a salt of peroxymonosulfuric acid.

7. A process according to claim 6 wherein the salt is potassium caroate.

8. A process according to claim 6 comprising lowering the cyanide content in the waste water by

(a) continuously controlling the pH of the side stream to 10±0.5 by adding alkali or acid thereto;

(b) continuously following the cyanide content in the side stream by measuring the cyanide-specific redox potential with a silver-thalamide electrode pair and dosing an aqueous solution of peroxymonosulfate until there is indicated a redox potential of at least +650 mV; and

(c) adding to the main stream an amount of hydrogen peroxide potential to the amount of peroxymonosulfate used in the side stream and controlling the pH during the addition to a value between 9 and 12.

9. A process according to claim 8 wherein the pH is controlled in the main stream to 10±0.5.

10. A process according to claim 9 wherein per mole of peroxymonosulfate used in the side stream there is fed into the main stream 1-10 moles of H_2O_2 times the ratio of liters in the main stream to the liters in the side stream.

11. A process according to claim 10 wherein there is fed into the main stream 0.1-1 mole of formaldehyde per 1-10 moles of H_2O_2.

12. A process according to claim 8 wherein per mole of peroxymonosulfate used in the side stream there is fed into the main stream 1-10 moles of H_2O_2 times the ratio of liters in the main stream to the liters in the side stream.

13. A process according to claim 12 wherein there is fed into the main stream 0.1-1 mole of formaldehyde per 1-10 moles of H_2O_2.

14. A process according to claim 2 wherein there is added to the main stream a chemical reagent which regulates the pH.

15. A process according to claim 2 wherein the strong oxidizing agent is a peroxymonosulfate, peroxydisulfate, permanganate, hypochlorite or ozone.

16. A process according to claim 15 wherein the strong oxidizing agent is a salt of peroxymonosulfuric acid.

17. A process according to claim 16 wherein the salt is potassium caroate.

18. A process according to claim 15 wherein there is employed as the strong oxidizing agent a peroxymonosulfate and per mole of peroxymonosulfate used in the side stream there is fed into the main stream 1-10 moles of H_2O_2 times the ratio of liters in the main stream to the liters in the side stream.

19. A process according to claim 15 wherein the waste water contains a sulfur compound which is a sulfide, sulfite, or thiosulfate and the content of the sulfur compound can be expressed by the iodine value which is the iodine consumption of the waste water in mg I/l and the process comprising reducing the iodine value by

(a) continuously controlling the pH of the side stream to a constant pH in the range of 3 to 12 by adding acid or alkali;

(b) continuously feeding into the side stream an aqueous solution of peroxymonosulfate whose amount is regulated so that therewith the redox potential of the side stream is continuously maintained at a constant mV value which is characteristic for a specific predetermined reduction of the iodine value;

(c) adding to the main stream an amount of hydrogen peroxide proportional to the consumption of peroxymonosulfate in the side stream and controlling the pH to a value between 3 and 12.

20. A process according to claim 19 wherein the pH in the side stream is controlled to a value between 6 and 10 and the pH in the main stream is controlled to a value between 6 and 10.

* * * * *

DESTRUCTION OF CYANIDE IN GOLD AND SILVER MINE PROCESS WATER

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ABSTRACT

Addition of Kastone® peroxygen compound and formaldehyde to cyanide gold extraction process effluents, containing at least 5 mg soluble copper per liter, will oxidize acid-dissociable cyanide to levels less than 0.2 mg per liter, without appreciable oxidation of thiocyanate. Most of the copper precipitates and is removed by filtration of the treated solutions. The treatment can be completed in less than 2 hours when the excess of hydrogen peroxide over the cyanide is about 75-100 mg per liter. The excess hydrogen peroxide destroys residual formaldehyde and then is catalytically decomposed by the copper-containing solids that separate, so it will not interfere with subsequent operations.

A pilot plant using this technology has been operated for more than four months at rates from 1-2 gpm. Clear, filtered effluent containing less than 0.2 mg acid-dissociable cyanide per liter has been produced.

A paper presented at the annual meeting of the Metallurgical Society of AIME, February 23, 1981, Chicago, IL.

Introduction

The extraction of gold and silver from ore with alkaline cyanide solutions has been an important process for about ninety years. The waste water from this operation generally contains variable amounts of sodium cyanide, acid-dissociable complex metal cyanides and thiocyanate. Some waste waters may also contain oxidizable sulfur species such as sulfide, polysulfide, sulfite and thiosulfate. Routes for the formation of copper cyanide, refractory iron cyanides and thiocyanates in gold and silver extraction are shown in figure 1.

Figure 1

Gold and Silver Extraction

$$FeS + xs\ CN^- + Air \xrightarrow{OH^-} Fe(CN)_6^{-4} + CNS^-$$

$$Copper\ (Carbonate\ ore) + xs\ CN^- \xrightarrow{OH^-} Cu(CN)_2^- + CNO^-$$

$$S_n^{-2} + n\,CN^- \longrightarrow n\,CNS^- + S^{-2}$$

State and Federal guidelines and regulations propose or specify limits on the concentration of cyanide, free and complexed, that may be discharged to streams and in some cases sanitary sewers. The limits set by the regulatory authorities are generally at levels that require some type of cyanide analysis methodology that is used to define the cyanide content of the stream.

Oxidation with Chlorine

Alkaline chlorination is commonly used to destroy cyanide in waste process water. It destroys free cyanide and cyanide complexed with common metals such as cadmium, chromium, copper, gold, nickel, silver and zinc. It does not destroy the cyanide present as ferrocyanide or ferricyanide. It also reacts with thiocyanates and other components of waste streams, which may not require destruction and can produce undesirable by products. The net chemical reactions are shown in figure 2.

Figure 2

Process Effluent Treatment Alkaline Chlorination

$$CNS^- + 4\,OCl^- + 2\,OH^- \longrightarrow CNO^- + SO_4^{-2} + 4\,Cl^- + H_2O$$

$$CN^- + OCl^- \longrightarrow CNO^- + Cl^-$$

$$2\,Fe(CN)_6^{-4} + OCl^- + H_2O \longrightarrow 2\,Fe(CN)_6^{-3} + 2\,OH^- + Cl^-$$

$$2\,Cu[I] + OCl^- + H_2O + 2\,OH^- \longrightarrow 2\,Cu(OH)_2 + Cl^-$$

It was known that thiocyanate, a common by-product of cyanide ore leaching, would react with hypochlorite under conditions used for alkaline chlorination of cyanide compounds. Since waste water from cyanide gold and silver extraction processes usually contains thiocyanate in substantial quantities, it is necessary to add enough alkaline hypochlorite to destroy both the compounds. These reactions proceed in steps, but we will consider the net reactions shown in the first two equations in figure 2. It is apparent that the presence of moderate amounts of thiocyanate in a waste stream will substantially increase the chlorine demand of the waste stream.

Both synthetic and real process solutions were subjected to standard alkaline chlorination conditions, except that the amount of hypochlorite added was limited to that required for cyanide destruction plus an excess that ranged from 10-100% of the calculated value. Analysis of the solutions for cyanide and thiocyanate showed that the thiocyanate reacted preferentially with the hypochlorite and that the cyanide concentration was almost unchanged. This observation confirms other data that enough hypochlorite must be added to the waste stream to destroy both the thiocyanate and the cyanide to reduce the measured levels of acid-dissociable cyanide in the treated effluent. Figures 3 and 4 show typical results.

Figure 3

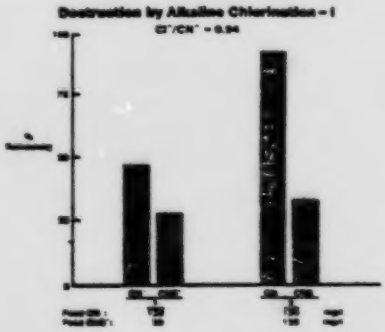
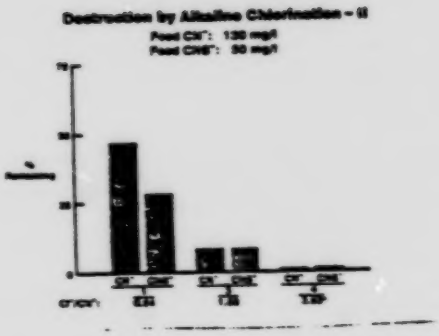


Figure 4



Even if sufficient chlorine has been added to destroy the thiocyanate as well as the cyanide, there is a further problem: It has been found in analytical method evaluation that solutions containing 0.1-5 mg cyanide per liter and more than 10 mg thiocyanate per liter will show a positive test for cyanide after treatment with an excess of chlorine even for 30 minutes. The analytical samples were dechlorinated with either ascorbic acid or sodium arsenite, preserved with sodium hydroxide and analyzed for acid-dissociable cyanide and for total cyanide by the official methods. Cyanide values greater than 0.1 mg/l were obtained. This suggests that alkaline chlorination of waste waters that contain substantial quantities of thiocyanate can yield effluents that may not meet regulatory requirements for discharge unless different alkaline chlorination process conditions or sample-handling techniques are used.

Oxidation with Peroxide

It was reported by Masson in 1907 that hydrogen peroxide would react with alkaline sodium cyanide solutions.(1) The kinetics of the reaction given in the paper showed that the time required for reduction of cyanide from 50 mg/l to less than 0.5 mg/l would be more than 3 hours even when the initial molar ratio of hydrogen peroxide to cyanide was as high as five. During the period 1968-1971 it was reported that the reaction between hydrogen peroxide and cyanide was promoted by addition of compounds such as formaldehyde and soluble copper salts.(2-5) The reaction rate was increased so that it became a viable candidate for destruction of cyanide in process effluents. It also was shown that substantially improved hydrogen peroxide reaction efficiency could be obtained by addition of decomposition stabilizers. This stabilized hydrogen peroxide, known as Kastone® peroxygen compound, is used in combination with formaldehyde promoter for commercial destruction of cyanide. The net chemical reactions are given in figure 5.

Figure 5

Process Effluent Treatment - Hydrogen Peroxide

$$2Cu(CN)_2^- + 5H_2O_2 \longrightarrow 2Cu^{+2} + 4CNO^- + 5H_2O$$

$$2Cu^{+2} + 5CN^- + 2OH^- \longrightarrow 2Cu(CN)_2^- + CNO^- + H_2O$$

$$CN^- + H_2O_2 \longrightarrow CNO^- + H_2O$$

$$CN^- + HCHO + H_2O \longrightarrow HOCH_2CN + OH^-$$

$$HOCH_2CN + H_2O \xrightarrow[OH^-]{H_2O_2} HOCH_2CONH_2$$

Since Kastone® technology was developed for the plating industry, the effect of thiocyanate on the process had not been examined. We found that cyanide was selectively oxidized in alkaline solution by formaldehyde or soluble-copper promoted hydrogen peroxide in solutions containing thiocyanate. Analysis showed that generally less than 10 percent of the thiocyanate was destroyed. The cyanide found in the treated solutions was less than 0.2 mg per liter. The copper-promoted system generally gave cyanide residual values below 0.05 mg per liter. The results obtained for several typical tests are given in figure 6.

Figure 6

Lab Tests - Synthetic

	mg/l			
	CN^-	CNS^-	H_2O_2	Cu
Feed	20	50	155	10
Effluent @ 36 min	0.04	49	-	-
Feed	10	100	155	5
Effluent @ 29 min	0.01	99	-	-
Feed	20	50	211	10
Effluent @ 211 min	0.03	48	-	-
Feed	20	50	196	2
Effluent @ 142 min	≤0.01	51	-	-
Feed	10	50	128	5
Effluent @ 57 min	0.01	50	-	-

Treatment of Field Samples

Cyanide gold and silver mine process effluents frequently contain soluble copper cyanide complexes. Synthetic process solutions containing sodium cyanide, copper cyanide complex, ferrocyanide and thiocyanate were treated with Kastone® peroxygen compound at pH = 8.5-10.0 and 30°C. The addition of as little as 5-10 mg formaldehyde per liter to these solutions reduced the treatment time by as much as 40% to less than 2 hours and reduced the final level of cyanide as measured to less than 0.1 mg per liter. The thiocyanate measured at the end of the reaction was generally within 2-5% of the value of the initial sample (25-150 mg/liter). For samples containing 5-10 mg

cyanide per liter as sodium and copper cyanide, 75-125 mg hydrogen peroxide per liter was adequate for reduction of cyanide to levels below 0.1 mg/l in 2 hours.

Cyanide gold extraction process effluents containing 8-25 mg acid-dissociable cyanide, 3-10 mg soluble copper per liter and 75-250 mg thiocyanate per liter, were treated with formaldehyde and hydrogen peroxide under conditions used for the synthetic process solutions. It was shown that the acid-dissociable cyanide could be reduced to levels below 0.1 mg/liter in these solutions in less than two hours.

No destruction of thiocyanate was found by the colorimetric iron method. Based on this work it is concluded that the addition of 5 mg formaldehyde per liter and 75-100 mg hydrogen peroxide per liter to an effluent containing 4-6 mg soluble copper per liter and 5-20 mg acid-dissociable cyanide per liter is a good choice. The pH should be maintained between 9 and 10, and the temperature should preferably be between 20°C and 40°C to reduce cyanide levels to below 0.1 mg/l within 2 hours. The results obtained on mill effluents, some of which contained additional cyanide and copper (I) to cover anticipated operating ranges, are summarized in figures 7 and 8. The data are consistent with these obtained with synthetic solutions.

Figure 7

Lab Tests - Mill Water - I

Feed: 18 mg/l CN^-
147 mg/l CNS^-
36 mg/l Cu

mg/l

Feed		Effluent		
H_2O_2	HCHO	CN^-	CNS^-	Time (min)
146	-	0.04	145	111
145	5.0	0.11	144	79
96	-	0.06	143	176
87	5.0	0.07	141	119

Figure 8

Lab Tests - Mill Water - II

Feed: 147 mg/l CNS^-
3.6 mg/l Cu
5.0 mg/l HCHO

mg/l

Feed		Effluent		
CN^-	H_2O_2	CN^-	CNS^-	Time (min)
18	87	0.07	141	119
8	89	0.06	146	19
8	42	0.06	142	40

Addition of only 5 mg formaldehyde per liter to a natural mill effluent provided rapid destruction of acid dissociable cyanide to levels below 0.1 mg per liter in less than two hours. Figure 7 shows that cyanide destruction to levels below 0.1 mg per liter can be achieved even when the copper present in a mill effluent is much higher than required for efficient process operation.

Kinetics

It is important to provide sufficient time for the reaction to proceed as shown in figures 9 and 10. The rate of destruction of cyanide is increased towards the end of this reaction because of the increase in the ratio of hydrogen peroxide to residual cyanide. This can be explained by the kinetic rate equation derived by Masson(1):

$$\frac{d\left[(CNO^-) + (CO_3^{-2})\right]}{dt} = k\,(H_2O_2)\,\left[(CN^-) + (\text{formate})\right]$$

An excess of 40-70 mg hydrogen peroxide per liter over that required for the oxidation of solution components has been sufficient to provide an effluent containing less than 0.1 mg acid-dissociable cyanide per liter.

Figure 9

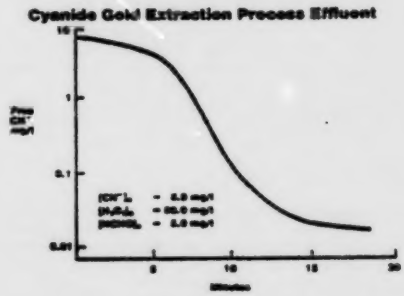
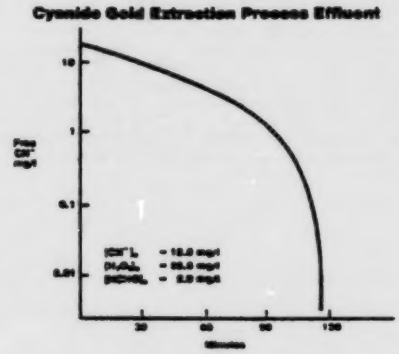


Figure 10



Treatment of both synthetic and real effluents with Kastone® peroxygen compound with or without formaldehyde yielded a precipitate that contained a mixture of basic salts that contained copper, iron, calcium, nickel and zinc salts that were quite easy to filter. Samples were analyzed for copper, iron and nickel by atomic absorption spectroscopy. Copper and nickel levels obtained were less than 0.1 mg/liter and iron levels were reduced to less than 0.3 mg/liter. The data in figure 11 shows typical data obtained in lab tests with synthetic solutions.

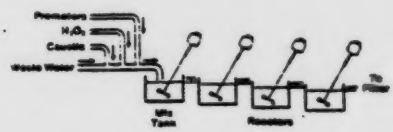
Figure 11

Filtered Effluent

	mg/l	
	CN^-	Cu
Lab	0.04	0.12
Pilot Plant	0.15	0.15

Figure 12

Pilot Plant Schematic



Pilot Plant Operation

This work has been done using a batch treatment concept. Based on experience with cyanide waste treatment installations, this chemistry can be scaled up on a batch basis or in a continuous treatment process if sufficient residence time is provided to allow the reaction to go to completion. The process is currently being evaluated in a pilot plant located at the Homestake Mining site in Lead, South Dakota. It has a 9-stage, cascaded, stirred-reactor design. A schematic of the feed, mixing and the first three reactor stages is shown in figure 12. The cascaded reaction system was designed to treat 1-2 gpm. It has operated continuously for more than 4 months treating mixed effluent from the mill and the mine. Filtered effluent has been clear. Acid-dissociable cyanide has been reduced to levels below 0.2 mg per liter but has not yet reached 0.05 mg per liter.

Since mill effluent has been treated in the laboratory to give lower levels of acid-dissociable cyanide than that obtained from the pilot plant, it is concluded that a component in the mine effluent is a contributing factor to the higher cyanide content (figure 11). Work on this problem is in progress.

Analytical

During this study a simplified process control technique was developed. A silver/sulfide ion-specific electrode was used to monitor the change in cyanide ion concentration in the solution. A change in concentration by a factor of 10 changes the electrode potential (vs. a reference electrode) by about 118mV. This electrode has been particularly useful in determining when the reaction between the cyanide and the hydrogen peroxide is rapid and when it has gone to its final level. Reflux distillation analysis generally gave higher values of measured cyanide than the free cyanide ion calculated from direct electrode measurements. We conclude that the silver/sulfide ion-specific electrode is a useful process monitoring tool, but actual cyanide concentration in treated water should be measured in samples taken from the process and analyzed by tested methodology.

Conclusion

Copper-formaldehyde promoted hydrogen peroxide selectively destroys cyanide in the presence of thiocyanate in a "clear" gold milling process effluent. Laboratory tests have given clear filtered effluents containing less than 0.05 mg acid-dissociable cyanide per liter and 0.12 mg dissolved copper per liter. Pilot plant operation with mixed gold mill and mine effluent has given filtered effluents containing 0.15 mg acid-dissociable cyanide per liter and 0.15 mg dissolved copper per liter. The clarity of the pilot-plant filtered effluent has been below 5 NTU turbidity units.

Acknowledgements

We would like to acknowledge the participation of C. Sharpe Beltsch, R. Osman and L. Trautman of the Homestake Mining Company at Lead, SD, for their contributions to the laboratory programs and for construction and operation of the pilot plant.

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(2) J. Zumbrunn, AITE International Conference of Nov. 15, 1968.

(3) B. C. Lawes, L. B. Fournier and O. B. Mathre, "Plating", Sept., 1973.

(4) U. S. Patent 3,617,567.

(5) U. S. Patent 3,617,582.

ERGO FREE CYANIDE REMOVAL WITH IRON

At ERGO (East Rand Gold and Uranium Company Ltd.), 50 m^3/hour of raffinate from the acid uranium recovery plant containing 6,400 mg/l iron due to acid leaching of concentrate at a low pH of less than 2 is added to the gold plant residue containing repulped calcine which has been leached at pH 10.5 with cyanide and filtered for pregnant gold solution recovery. The raffinate drops the pH of the calcine residue to about 7.5. The low pH and the air agitation in the pachuca destroy most of the free cyanide, and the balance is converted by the high iron concentration in the raffinate to stable iron cyanide complexes.

Raffinate-treated gold plant residue was, until recently, pumped to a separate calcine tailings dam with the decanted water as effluent being injected into the tailings dam feed pipelines. Currently, the cyanide-free calcine residue is deposited directly with the flotation tailings to the ERGO tailings dam.

ERGO CYANIDE REMOVAL BY ACTIVATED CARBON

The new CIL installation for the recovery of additional gold from flotation tailings at ERGO utilizes the last seven of eleven carbon contacting stages for cyanide removal at the time of the visit to this plant, the CIL installation had not yet been installed, and no information was available about how carbon reduces cyanide levels in a pulp. However, it is known that at near neutral or slightly acid pH, activated carbon in the presence of low base metal levels will cause cyanide degradation at a rapid rate. At the end of this chapter, reference is made to reputed methods of recovering cyanide using activated carbon. It is not known which of these approaches is used at ERGO, although it is suspected that it is the former destruction process. After treatment, these tailings advance to the new disposal dam.

The ERGO pulps contain very low gold values in the first place. It is found that the lower the cyanide tenor in a pulp, the more effectively gold adsorbs onto carbon.

Details of ERGO's cyanide destruction process will likely be published in due course; meanwhile, information could be requested from:

EAST RAND GOLD AND URANIUM
COMPANY LTD.
Post Office Box 980
Boksburg 1540
(011) 55-9050
Ken Henderson
Metallurgical Manager

ANGLO AMERICAN RESEARCH LABORATORIES
Post Office Box 106
Crown Mines 2025
(011) 835-3251
Ray J. Davidson

PRUSSIAN BLUE PRECIPITATION OF CYANIDE

A second process employing sodium sulfite has been developed and patented as a joint program between a California consulting firm, Engineering & Technical Consultants Inc. and Homestake Mining Company. It is also known as the ETC-HMC Process.

The process has been developed to treat mine effluents containing 10-200 ppm total cyanide.

The process requires five steps which have been piloted on a continuous basis at up to 5000 gallon tank capacities (residence time not specified).

The technology is owned jointly by Homestake Mining Company and Engineering & Technical Consultants Inc.:-

ENGINEERING AND TECHNICAL
CONSULTANTS, INC.
1068 Edenbowers Lane
Redwood City, CA 94061
(415) 364-5549
Dr. Roy G. Neville

DR. NEVILLE is actively marketing the process in Canada and the U.S.A.

Step 1

Adjust the pH of the solution or pulp to pH 7 or 7.5.

Step 2

Add 100-300 ppm sodium metabisulfite. The amount to be added can be determined experimentally for each solution.

The $Na_2S_2O_5$ dissolves in water to form 2 molecules of sodium bisulfite while further reducing the pH to around 5. Some buffering effects also take place.

$$Na_2S_2O_5 + H_2O = 2\ NaHSO_3$$

Step 3

This stage is operated at pH 5-5.2. Ferrous sulfate is added at 200-300 ppm, again the precise amount depends on the specific solution.

$$Fe^{II} + 6\ CN^- \text{ (free)} = [Fe(CN)_6]^{4-}$$

Engineering & Technical Consultants, Inc.

Management • Engineering, Metallurgical & Chemical Process Development • Environmental Pollution Control • Toxicological & Analytical Services

1068 Eden Bower Lane, Redwood City, California 94061 • Telephone (415) 364-5549

THE E.T.C./HOMESTAKE CYANIDE REMOVAL PROCESS

In response to numerous inquiries regarding the cyanide removal process the following information is presented.

The process was developed by Engineering & Technical Consultants and Homestake Mining Company as part of an extensive experimental study to discover a method which would effectively remove free cyanide, and the complex cyanides of various metals, from waste water produced in the extraction of gold, by treating gold-bearing ores with sodium cyanide. In addition to free cyanide (CN^-), and complex cyanides (e.g. ferrocyanide, cuprocyanide, etc.), the waste water typically contains thiocyanate (SCN^-), as well as several hundred parts per million (ppm) of other anions (e.g. sulfate, chloride, bicarbonate, etc.), and cations (e.g. sodium, calcium, magnesium, etc.). A cyanide removal process was sought which would be rapid, dependable, economically feasible, and which would reduce or completely eliminate "total" cyanide (i.e. free cyanide and complex metal cyanides), without unnecessarily reacting with non-toxic ions present in the water.

Chemistry of the Process

After a thorough experimental study of several potentially feasible chemical processes (e.g. chlorination, peroxidation, ozonation, etc,), it was discovered that treatment of cyanide-containing waste water with ferrous ion (Fe^{2+}) and sulfurous acid (H_2SO_3, from sulfur dioxide),

or bisulfite ion (HSO_3^-, from $Na_2S_2O_5$), removed total cyanide to levels that meet most environmental regulations. The following chemical equations illustrate the sequence of reactions that occur:

1. Addition of ferrous ion (e.g. Fe^{2+} as $FeSO_4$) converts the free cyanide (CN^-) to ferrocyanide ion ($[Fe(CN)_6]^{4-}$):

$$Fe^{2+} + 6\ CN^- = [Fe(CN)_6]^{4-} \qquad (1)$$

2. Excess ferrous ion reacts immediately with ferrocyanide ion to produce Prussian blue (ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$), by reaction with dissolved atmospheric oxygen in the water:

$$2\ FeSO_4 + 2\ Fe(HSO_4)_2 + 3\ Na_4[Fe(CN)_6] + O_2 = Fe_4[Fe(CN)_6]_3 + 6\ Na_2SO_4 + 2\ H_2O \qquad (2)$$

3. A very small amount of free cyanide (ca. 0.1-0.2 ppm) remains in equilibrium with ferrocyanide ion after ferrous treatment. This minute concentration of free cyanide ion is reduced by the sulfurous acid (or bisulfite ion) present to non-toxic ammonium formate, which rapidly decomposes in the environment to ammonia, carbon dioxide and water. Catalyzed by the ferrous ion, sulfurous acid (or bisulfite ion) adds across the triple bond of the cyanide ion; to form a transitional, unstable intermediate aminomethanedisulfonate ion, which immediately decomposes to ammonium formate:

$$4\ H_2O + 2\ SO_2 + CN^- = H.COONH_4 + H_2SO_3 + HSO_3^- \qquad (3)$$

Reactions 1, 2, and 3 occur simultaneously in the mildly acidic (ca. pH 4-5) solution. In dilute aqueous cyanide solutions, the amount of Prussian blue formed is very small. Consequently, although it is extremely insoluble, it does not quantitatively precipitate.

However, merely by raising the pH of the solution to 8.0-9.0, the excess ferrous ion is immediately precipitated as ferrous hydroxide, which encapsulates the Prussian blue particles and quantitatively precipitates them.

The mild alkalinity of the solution has the additional advantage that the very minute amount (usually less than 0.1 ppm) of ammonium formate (produced by catalytic reduction of CN^- by H_2SO_3 or HSO_3^-) is decomposed to environmentally acceptable levels of ammonia, which is rapidly lost to the atmosphere:

$$H.COONH_4 + OH^- = H.COO^- + H_2O + NH_3 \qquad (4)$$

By means of these very fast, simultaneous reactions, both the free and complex metal cyanides are removed from solution. The resulting clear, colorless solution, on analysis, is found to contain total cyanide that is either undetectable, or virtually undetectable, by the so-called "standard reflux method", as recommended by the United States Environmental Protection Agency, and as described in the textbook, Standard Methods for the Analysis of Waste Water. Depending on the concentration of cyanide in the waste water, different concentrations and ratios of ferrous and bisulfite ions are used. For efficient removal of total cyanide the relative concentrations of ferrous and bisulfite ions are determined experimentally for each type of waste water. Typically, the concentrations of ferrous and bisulfite ions are ca. 100-200 ppm, but they may be higher or lower, depending upon the chemical characteristics of the waste water being treated.

Advantages of the Process over other Cyanide Removal Processes

1. Uses cheap, readily available industrial chemicals.
2. Total cyanide removal is rapid.
3. Minimal pH adjustment required.
4. Minimal production of solids, as total amount of added ferrous and bisulfite ions is small.
5. Process works in cold climates, near the freezing point of water.
6. Other ions (e.g. SCN^-) do NOT interfere (cf. chlorination, peroxide, ozone, etc., which react with SCN^-).
7. Removes ALL FORMS OF CYANIDE (free and complex metal cyanides). (cf. chlorination, peroxide, ozone, etc., which do not remove ferrocyanide, cuprocyanide, etc.).
8. Can be applied to batch operations or continuously flowing waste cyanide-containing streams.
9. Most importantly, no specialized equipment is required (often just a mixing tank and a settling tank are sufficient), and the process can be carried out by unskilled or semi-skilled operators.

Further Information

E.T.C., Inc. and Homestake Mining Company jointly own a United States patent on this process, and patents are pending in other countries.

The process is available for licensing to any interested companies or potential users. Technical assistance is available, to enable the process to be correctly adapted to each user's cyanide-containing waste water, in order to achieve optimum removal.

For further information, please contact:

Dr. Roy G. Neville
President
Engineering & Technical Consultants, Inc.
1068 Eden Bower Lane
Redwood City, California 94061, U.S.A.

Excess ferrous iron combines with the ferro-cyanide to form ferrous ferrocyanide.

$$2\ Fe^{II} + [Fe(CN)_6]^{4-} = Fe_2\ [Fe(CN)_6]$$

Some excess ferrous ions are oxidized by oxygen in the solution to yield a series of ferric ferrous cyanide complexes ultimately forming an almost insoluble precipitate Prussian Blue $Fe_4\ [Fe(CN)_6]_3$.

A very small amount of free cyanide (0.1 - 0.2 ppm) remains in equilibrium with ferrocyanide after the reaction with ferrous sulfate.

This remaining free cyanide reacts with excess ferrous bisulfite to form ammonium formeate which is non-toxic and in the ultimate alkaline solution decomposes to ammonia and is lost to the atmosphere (hopefully).

Step 4

Because the cyanide solution is so dilute, all the Prussian Blue does not precipitate even though it is very insoluble.

The pH is next raised from pH 4-5 to pH 8-8.5. This can be done using lime, caustic soda, soda ash, etc.

Ferrous hydroxide encapsulates the Prussian Blue which is now quantitatively precipitated. Any ferric ions present will also precipitate (at the lower pH) as ferric hydroxide which when nucleated on the Prussian Blue and flocculated with a small amount of Superfloc 127 are easily settled and filtered.

Any nickel, copper, zinc, etc. are present as anionic complexes and will be precipitated when the ferrous bisulfite is added in the presence of a little oxygen already in the solution.

Cupro cyanide + ferrous = Ferro-cupro-cyanide.

Nickel, zinc, chromium, cobalt, etc. all behave similarly and co-precipitate with the Prussian Blue.

Step 5

The precipitate is settled out in a settling tank from which the clear treated solution is decanted. Very small amounts of precipitate are formed and it can be allowed to accumulate for a long time without filtering.

It is claimed that by first forming Prussian Blue at a lower pH, a very large amount of the cyanide is removed early leaving a very much smaller amount to be decomposed. If the pH is high when the ferrous sulfate is added then ferrous hydroxide forms, which does not react with cyanide to form Prussian Blue.

At the low pH $SO_3^{=}$ is present as HSO_3^- in the presence of which Prussian Blue is formed. HSO_3^- is also necessary to decompose the residual cyanide to ammonium formeate.

The ETC-HMC process does not affect thiocyanate ions.

According to TRAUTMAN & OMMEN (1981) of Homestake Mining Co., the Prussian Blue pilot plant was difficult to operate and was very temperature dependent. During winter, the cold water temperatures resulted in a much slower reaction. Also, the effluent from the thickener after precipitation with ferrous hydroxide contained fine precipitated particles which required sand filtration. After sand filtration the Prussian Blue precipitation process reduced the total cyanide concentration to about 2.5 ppm. It is not known whether the ETC-HMC process has been modified or improved since the pilot operation was carried out.

More information could be obtained from the vendor of the process, DR. ROY NEVILLE, and also from:-

HOMESTAKE MINING COMPANY
Post Office Box 875
Lead, SD 57754
Harry Hinds
Larry L. Trautman
(605) 584-1020

REMOVAL OF IRON CYANIDES FROM WASTEWATER

The Prussian Blue process described above amounts to a method of converting cyanides to iron cyanide and precipitating them as a means of removing cyanide from solution.

Iron cyanides are often generated in gold recovery solutions and discharged with effluents. The toxicity of iron cyanides which, in themselves, have a very low solubility hangs on their instability in ultraviolet light. If present in shallow sundrenched streams, the concern is that under UV-light, the iron cyanides will decompose to release free cyanide.

TANIHARA, KOICHI, et al. (1983) described a process for "Treatment of Wastewater Coontaining Iron Cyanide Complexes: II - Precipitation and Removal of Iron Cyanide Complexes by Simultaneous Dosage of Zinc Sulfate and Sodium Thiosulfate." Government

Industrial Research Institute, Kyushu Kogyo Gijutsu Shikensho, Hokoku, Vol. 31, pp2005-2011, 1983 (Japanese).

CARO'S ACID - SALSIGNE

It has been learned that at the Salsigne gold mine in France, cyanidation is employed on a small scale. Salsigne effluents discharge to a trout stream.

Although no details were obtained, it is believed that cyanide is destroyed in their effluents by reaction with CARO's ACID (H_2SO_4 + H_2O_2). Apparently, it is not necessary to add an excess to the point of rendering the effluent acid. Details may be available from:

J-L RICHARD
Mines et Produit Chimique de Salsigne
BP 2-1160 Conques-sur-Orbiel
France
(68) 771022
Telex: 500-465-F MINSIGN

Wet Air Oxidation

Wet air oxidation is now conventionally used in the U.S.A. for treatment of hazardous wastes and also sewage sludge oxidation. In all, about 250 plants have been installed.

One of these plants is installed in California to destroy cyanide at a hazardous waste site:

CASMALIA RESOURCES, INC.
Post Office Box E
Casmalia, CA 93429
(805) 937-8449
Al Brandt

The head office is in Santas Barbara and can be reached as follows:

CASMALIA RESOURCES, INC.
Post Office Box 5275
Santa Barbara, CA 93150
(805) 969-5897
Jim McBride
Technical Director
Ken Hunter
President

The small 10 gpm ZIMPRO Wet Air Oxidation Plant is used primarily to destroy cyanide wastes. No waste with over 100 ppm CN is allowed to be dumped at their hazardous waste site.

Wastes in excess of 100 ppm CN are detoxified in the ZIMPRO unit after which the wastes are considered detoxified sufficiently to be discarded.

Casmalia Resources tarif for cyanide detoxification starts at $120/ton so not too many gold operations could afford to take waste there, but this installation demonstrates that the method is in use.

Cyanide destruction requires 450°-500°F which equates to a pressure of 900-1,200 psig according to the vendors of this process who supply the design of the equipment:

ZIMPRO, Inc.
Military Road
Rothschild, WI 54474
(715) 359-7211
Al Wilhelmi
Bill Copa
Technical Director

A flowsheet of the ZIMPRO Wet Air Oxidation Process is inserted below. The process employs a stainless steel pressure tower or tube as the reactor.

According to ZIMPRO, the operating cost for these units is 1-2¢/gallon, i.e., $20-$40/1,000 gallons [$8-$16/m^3], which is relatively high. Of these costs, energy amounts to about $10/1,000 gallons ($2.50/m^3) for an effluent which contains no calorific value. If sewage is added, the oxidation thereof will contribute to the energy requirement. The major cost item is in pumping high pressure air into the system.

ZIMPRO WET Air Oxidation Units are capital intensive. For example, very rough ballpark estimates were provided as follows:

330 U.S. gpm - $10 Million
15-20 U.S. gpm - $2.5 Million

ZIMPRO, INC. is a subsidiary of Michigan Tech Ventures of Houghton, Michigan, which also offers a wet air oxidation process employing stirred reactors under the process name WETOX. Ontario Research Foundation in Mississauga, Ontario, is a licensee of this company.

Temperature achievable is, of course, a function of pressure applied, ranging as follows:

400°F - P=400-500 psig
450°F - P=900 psig
600°F - P=2,500-3,000 psig

Heat is recovered to preheat the feed. If excess heat is generated, it can be used as a source of steam.

GEOCLAVE OXIDATION

There are other innovative configurations of wet air oxidation reactors that have been installed on an experimental basis. In Colorado, two experimental geoclaves have been installed:

1) City of Longmont Geoclave

An EPA financed demonstration geoclave was in Longmont, Colorado, to test the combustion of sewage sludges and hazardous waste in a hole one mile deep. This geoclave requires 575°F to achieve an exothermic reaction, and it uses a G.E. heat exchanger to preheat feed material. These conditions would also decompose cyanide to CO_2 and ammonia.

The inner heat exchanger tube has a 5" diameter. The downcomer is 7" in diameter inside a 10" upcomer. Pressures of 1,500 psi are reached at a depth of 1 mile. Compressed air is injected at 40 ft. depth. The unit can handle 4-5 tons per day of solids and a volume reputed to be 120 U.S. gpm at 1% solids.

The Longmont geoclave is owned and operated by:

VERTECH TREATMENT CO.
Sub of Bow Valley Resource Services
2006 West 120 Avenue
Westminster, CO 80234
(303) 452-8800
Gerry Rappe

It is not known whether this geoclave has been tested for cyanide destruction.

2) Resource Technology Associates
11728 Highway 93
Boulder, CO 80303
(303) 499-1032
Dr. Mark A. Peters

This company constructed a test geoclave on the property of Hazen Research, Inc., Golden, Colorado. No details of test results have been released. It is not known whether it has been tested for cyanide destruction.

Conclusions on Wet Air Oxidation

1) To benefit from hydrostatic pressure, geoclaves must be very deep--3 to 5,000 feet. To contain corrosive fluids at high pressures and temperatures in such deep reactors means that large quantities of expensive exotic materials are required. This adds to the capital expense.

2) According to ZIMPRO, the operating costs of a wet air oxidation plant are small compared with capital cost items. A deep geoclave results in energy cost savings but increases the capital considerably. Therefore, it is unlikely that a geoclave will be less expensive overall than an above-ground reactor.

3) Operating costs of \$20-\$40 per 1,000 gallons (\$5-10/m^3) is high as far as effluent treatment for mine-mill effluents is concerned and, therefore, this technology does not appear to be attractive at this time for cyanide destruction, unless there already happened to be a wet air oxidation plant on site for sewage sludge oxidation which could combine the cyanide effluent in its feed.

ELECTROLYTIC CYANIDE DESTRUCTION

HSA Reactors Ltd's high surface area cathodes have been tested at the Pamour Schumacher Mill in Ontario as a means of destroying cyanide while recovering base metals. Cyanide is electro-oxidized to cyanate.

The desirable temperature of operation is about 60°C. The oxidation of cyanide is enhanced by the addition of salt to provide chloride ions. A metal stripping stage is also required to periodically remove the deposited metals. The metals may be recovered from the stripping solution by conventional electrolytic practice or by chemical precipitation.

MOHANTA et al (1980) submitted the following results of the pilot plant tests at the Pamour Schumacher mill to ENVIRONMENT CANADA:-

	Influent	Effluent
pH	11.7	9.8
Copper	450 mg/L	0.14 mg/L
Zinc	54	0.06
Total Cyanide	1300	2.8
Free Cyanide	733	0.3
Cyanate	72	1120
Thiocyanate	756	68
Sulphate	1625	2826
Chloride	1400	5400

HSA Reactors Ltd., claim that its process can destroy cyanide at about one-half the cost of that by alkaline chlorination, although RANDOL believes that at the extremely low cyanide levels, current efficiency might not be so good. However, the real merit in the electrochemical system stems from the possibility to recover cyanide by removing fouling metals when applied in a different way.

The HSA cyanide destruction process still requires further development to reach the anticipated regulatory-mandated levels but might present a cost effective first step for more concentrated effluents which could then be completed by chemical oxidation. It is noted in the case shown above, that cyanide seems to be converted to cyanate, the effect of which would have to be taken into account sooner or later. Meanwhile HSA Reactors Ltd. have gone out of business and are being liquidated.

Thiocyanates

According to a variety of sources, thiocyanates (CNS^-) are toxic to fish only at levels 1000-10,000 times higher than at which cyanide is lethal, i.e. 50-500 ppm CNS^-. More recent unconfirmed reports indicate that there may be cumulative toxicity problem associated with thiocyanate on fish. Some US tests have been talked about in which fish exposed to thiocyanate for an extended period had a low mortality rate until subjected to stress when there was a sudden high mortality. These tests were referred to in passing by Jim Kerrigan of AMAX ESI, Golden and by Jim Scott of Environment Canada, Hull, Quebec.

ENVIRONMENT CANADA, the EPA and State and Provincial Governments are evaluating the toxicity effects and whether and how CNS^- in mine and mill effluent discharges should be regulated, if at all.

In 1980, INTERNATIONAL ENVIRONMENTAL CONSULTANTS LTD. (IEC) undertook a literature review for ENVIRONMENT CANADA, on "The Fate of Thiocyanate in the Aquatic Environment". They concluded that thiocyanate is biologically degraded to sulfate, CO_2 and ammonia by several strains of bacteria. Unlike biodegradation of other sulfur containing species such as sulfide and thiosulfate, sulfuric acid is not a product. The bio-oxidation of thiocyanate is likely to be slow and no significant depletion of oxygen is expected to result from bio-decompostion of thiocyanates.

Photo-decompostion of thiocyanate is considered unlikely and little evidence of other chemical transformation of thiocyanate in nature were identified.

The IEC Report may be available from ENVIRONMENT CANADA (DSS Contract OSS79-00170) or possibly also from the author:-

IEC INTERNATIONAL ENVIRONMENTAL
CONSULTANTS LTD.
5233 Dundas Street West, #410
Islington, Ontario M9B 1A6
(416) 236-1077

It has been shown that alkaline chlorination decomposes thiocyanate readily before it attacks cyanide. It is also found that the SO_2 processes do not attack thiocyanates. Peggy Layne of Raleigh, North Carolina, completed a M.Sc thesis on CNS^--destruction by ozone. She may be reached at:

PEGGY LAYNE
Hazen and Sawyer
Box 30428
Raleigh, NC 27622
(919) 782-8333

DAN KAPPES and DON BAKER (1981 personal communication) both cite instances where alkaline chlorination of thiocyanate rich effluents resulted in an increase in the measured cyanide levels.

Thiocyanates interfere with the standard total cyanide determination procedure which distills cyanide in the presence of sulfuric acid, but this interference has been overcome by a modification proposed by CONN (1981).

The bacterial decomposition of cyanides developed by Homestake is said to destroy thiocyanate as well. It is rumored that at Homestake, effluent CNS levels of up to 250 ppm CNS^- are experienced before treatment, but this also should be confirmed.

BYERLEY & ENNS (1982) have described a process whereby cyanide can be regenerated from thiocyanate. More information can be obtained from:-

WATERLOO CENTRE FOR PROCESS
DEVELOPMENT
University of Waterloo
Waterloo, Ontario N2L 3G1
E.B. Cross, Executive Director
J.J. Byerley
(519) 885-1211 Ext. 3300
Telex: (069) 55259

The process described by BYERLEY & ENNS (1982) employs an electrolytic cell about which not too many details have been released until the patent position is resolved. The cell employs bipolar electrodes and some form of preconcentration of CNS^- using ion exchange may be required.

At the Homestake mill, thiocyanate formation is symptomatic of cyanide consumption as a result of the presence of sulfides such as pyrrhotite in the ore. Homestake controls this phenomenon by judicious use of oxidation and pH control.

HALBE et al (1979) showed that cyanide consumption at Homestake goes up in summer, which has now been identified as being almost completely due to increased formation of thiocyanate. The rate of this reaction increases sharply above 10°C. Since tailings pond water at 20°C in summer is recycled to the process, a greatly increased cyanide consumption was observed compared with the earlier system in which fresh process water at 4°C was added to the system. Spray cooling was practised in 1978 with some success and the spray cooling was to be expanded in 1979.

Clearly, one way to reduce cyanide consumption and thiocyanate levels in tails is to leach pulps that generate CNS at a reduced temperature where possible.

CYANIDE RECOVERY

Cyanide recovery processes have been employed in the past and are likely to have greater potential applicability where ores with very high cyanide soluble copper must be treated, or where cyanide is very expensive such as in Peru where cyanide costs $3.00/kg.

With the growing number of CIP plants, the need for cyanide recovery appears to be growing since, contrary to the MERRILL-CROWE process where barrens containing cyanide can be returned for the most part to the leach circuit, only very limited cyanide can be recovered from CIP tailings pulp, since the whole point of using CIP is usually to avoid using a solid/liquid separation step in most cases.

In South Africa there is some concern that as more CIP plants come on-line, the overall cyanide demand will increase to the extent that an additional cyanide production facility will be needed which could result in a higher price for cyanide. Consequently, there is renewed interest in recovering cyanide from pulps. Clearly most of the processes tried before and outlined below, will be less likely to be viable for treatment of pulps than they were for solutions.

DORR & BOSQUI (1950) reviewed several techniques for cyanide recovery from barren solutions and foul liquors, which were also reviewed with inclusion of more recent pilot testwork on cyanide recovery by ion exchange by GILMORE & GOW (1963), which was inserted in Volume 2 (Phase I) of the Randol report "Innovations in Gold & Silver." More detailed information is provided by MCQUISTON & SHOEMAKER (1975).

These techniques and installations include:-

1) Mills-Crowe Process

Acidification to form HCN which is driven from solution by aeration and readsorbed in an alkaline solution in an absorption tower.

2) Regeneration at Pachuca, Mexico

Acidification of solution with SO_2 to neutralize lime and convert cyanides to HCN. Volatilizing HCN with a large volume of air. Absorption of HCN in mill solution. Zinc dust addition to precipitate gold in the pregnant solution after cyanide has been driven off.

SO_2 gas was made in a rotary sulfide burner and brought into contact with the cyanide solutions in an acidifier. HCN formed in the acidifier remains in the acid

solution until removed by air dispersion. It is remarkable that no measurable HCN was lost from the acidified solution as it passed through an open weir box 6' long.

3) Flin Flon Mine, Manitoba

Recovery of cyanide at the Flin Flon Mine of Hudson Bay Mining & Smelting, as described by DORR & BOSQUI (1950), for a plant treating 2814 tpd of barrens.

Again this process consists of acidification and volatilization of HCN by aeration in a dispersing tower. Airborn HCN was redissolved in an alkaline solution in an absorbing duct. A total of 36,000 ft^3 of air at 4" water pressure was required for the process.

Material balance was as follows:-

Barrens to Regeneration	2814 tons/day
Regenerable Cyanide (NaCN)	2.23 lb/ton
Lime	0.25 lb/ton
Tailings from Regeneration	
Regenerable Cyanide (NaCN)	0.18 lb/ton
Residual Sulfuric Acid	1.91 lb/ton
Sulfuric Acid Consumption	4.58 lb/ton barrens
Recovery of Regenerable Cyanide	91.5 %

4) Leaver & Woolf Process, USBM

This process demonstrated on a lab scale, involved regeneration of cyanide tied up in solution as complexes with zinc and copper in fouled mill solutions.

A soluble sulfide is added to the solution followed by acidification in a closed reactor to pH 5 or 6, whereby Cu & Zn sulfides precipitate and up to 80% of the combined cyanides are regenerated in the solution and can be recovered by filtration. Only after filtration is lime added to the filtrate to 'fix' the cyanide again.

5) Electrolytic Regeneration of Cyanide from Metallic Cyanide Complexes

Electrolytic removal of metallic impurities as a means of cyanide regeneration combined with recovery of the base metals were developed as a process but found uneconomical owing to the high cost of installation and operation, according to DORR & BOSQUI (1950).

Electrolytic recovery of cyanide from foul bleed solutions appears more promising in the light of new high surface area electrolytic cells available from HSA Reactors Ltd.

Reference to pilot testing of HSA Reactors equipment at Pamour Porcupine Mines Ltd. is made by INGLES & SCOTT (1981) inserted in this chapter.

Since the previously mentioned paper appeared, HSA reactors Ltd. have secured patent protection and are actively seeking applications for their well engineered equipment. More details on availability and cost as well as test facilities could be requested from HSA Reactors Ltd. except that they have recently gone out of business and are currently being liquidated by Canada Development Corporation. It is not yet known who will acquire the rights to the technology.

It is believed that the HSA electrolytic cell employed in the tests at the Pamour Shumacher mill was not able to liberate cyanide from iron cyanides or cobalt cyanide, but this should be confirmed.

6) Electrolytic Regeneration of Cyanide from Thiocyanates

BYERLEY & ENNS (1982) referred to above, have developed an electrolytic cell employing bipolar electrodes which regenerate thiocyanate to cyanide. More information is available from:-

J. J. BYERLEY
Waterloo Centre for Process Development
Waterloo, Ontario N2L 3G1
(519) 885-1211

7) Ion Exchange Resins

Several IX resins have been shown to adsorb cyanide and several new IX products have been developed since GOLDBLATT (1959) evaluated the possibility of recovering cyanide from gold mill wastes by ion exchange.

GILMORE (1976) again reviewed the subject, which was also tested on a pilot scale at the Homestake Mine in South Dakota. More information is summarized by INGLES & SCOTT (1981) inserted in this chapter.

The RANDOL investigation did not identify any operating plants employing IX for cyanide recovery.

GILMORE (1976) of CANMET used static columns to investigate the suitability of ion exchange on barren solutions from 6 gold mines. Adsorption was accomplished using two columns in series containing Amberlite IRA 400 resin. The resin was in the $SO_4^{=}$ form in both columns. Contrary to GOLDBLATT's (1959) findings, it was not necessary to condition the second column with cuprous cyanide.

Ind. Eng. Chem. 51, 241-6 (1959)

Recovery of Cyanide from Waste Cyanide Solutions by Ion Exchange Pilot Plant Studies

Pilot plant work has confirmed laboratory work showing that recovery of cyanide from gold mine effluents by ion exchange is economically attractive. This recovery was accomplished with poisoned, discarded anion exchange resin (IRA-400) from a uranium plant.

With effluents containing 0.10 to 0.16 pound of sodium cyanide per 100 Imperial gallons, recovery in the pilot plant was about 95%. At the same time the resin was purged of temporary poisons, and base metals which were formerly cyanide complexes were recovered.

Thus for a gold and uranium producer, a combined unit could recover cyanide, water, and base metals, and could also regenerate uranium plant resin.

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The first column was desorbed with 1% H_2SO_4 which decomposed the metal cyanide complexes. The barren then flowed through a cationic exchanger IRA 400 which adsorbed the metals, while the HCN passed through the column and was collected in a caustic trap. The recovered cyanide was available for reuse in the gold cyanidation step. The second absorption column was also desorbed with 1% H_2SO_4. The metals were desorbed from the cation exchange resin by a brine solution.

The results indicated that ion exchange can remove cyanide from barren solutions to below 0.1 mg/l.

8. MNR Regeneration/Recovery of Cyanide from Effluent

The cost of removing a pound of cyanide from effluents by destructive processes is generally much more expensive than adding apound of cyanide to a leach process. What this means is that every pound of cyanide added in excess of that really needed will contribute not only the wasted cost of that pound of reagent, but an even greater cost of removing it in a subsequent effluent treatment step.

Some effluents contain relatively high concentrations of cyanide--particularly barren bleeds from plants treating ores containing high concentrations of cyanide soluble base metals. For example, to leach gold using a cyanide solution containing soluble copper, cyanide must be added in excess of 5 moles CN^- per mole Cu^{++} to efficiently leach gold. If an ore contains excessive amounts of cyanidej-soluble copper, the cyanide requirement may be so high as to render the ore uneconomic. One such example is the Centinella Mine ore from Punitaqui, Chile.

BERGMAN, et al. (1984) described a new approach to cyanide recovery in the processing of this ore using a process piiot tested at Mountain States Mineral Development Laboratories, Tucson.

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At the University of Arizona conference on "Cyanide and the Environment," December, 1984, George Potter reported on this process which has been developed through pilot plant stages. He advised that the cyanide recovery cost amounted to about $1.00 per ton ore, i.e., about U.S. $0.10/Kg cyanide recovered, which is remarkable.

He also indicated that although a high recovery of cyanide is achieved, residual levels would still be high enough to require some form of treatment before the final effluent would be suitable for discharge as an effluent.

This promising development is described by BERGMANN, et al. (1984) below.

Abstract Regeneration of Cyanide - A Case Study

Pilot Cyanidation of a High-Copper

Gold Ore from Punitaqui, Chile

Dr. Arthur Bergmann, Armando Guzman, and George M. Potter

Complex high-copper gold ores may present serious processing problems. The treatment of a 0.45 percent copper, 3 to 5 gram per ton gold ore, and flotation mill tailings (0.42 percent copper and 1.66 grams gold), largely oxidized, from Punitaqui, Chile is a case in point. This paper describes intensive laboratory studies of cyanidation, flotation, acid-pre-leaching, and combination methods tried in an effort to find a feasible gold-copper recovery process. For various reasons, only direct cyanidation with abnormally high cyanide strength solutions and consumption of cyanide provided technically acceptable results, but cyanide costs were not tolerable. Therefore, a special cyanide regeneration process was applied on pilot scale to recover at least 95 percent of the total cyanides in the regeneration plant solution feed and at the same time remove and recover the copper. Pilot plant metals and cyanide balance data are given. The significant advantages of the regeneration plant operation in improving the process economy and reducing environmental hazards through removal of a heavy metal (copper) and complex and simple cyanides from wastes are noted.

2. Introduction

The recovery of gold and copper from complex ores by non-smelting methods may present serious economic and technical problems. As an example, the MNR Reprocessing, Inc. Centinela Project in Chile is a case study of the process investigation of gold-copper stored mill tailings and mine reserves requiring the development of cyanide regeneration process to provide technically acceptable results.

The Centinela Project comprises several deposits of old flotation mill tailings and unmined ore reserves within a 100-km radius of the town of Punitaqui, Coquimbo Province, Chile. The major tailing deposit contains 2.1 million dry metric tons at a grade of 1.66 grams of gold per ton and 0.42 percent copper. Unmined reserves in the area may exceed 1 million tons at a grade of 3 to 5 grams of gold per metric ton and 0.45 percent copper.

Intensive laboratory studies of cyanidation, froth flotation, acid pre-leaching to remove oxide copper, and combination methods were tried in an effort to find a feasible gold-copper recovery process. Non-cyanide leaching, such as by thiourea and hypo methods, was considered but not applied, because of potentially high process costs or lack of sufficient process development. Of the methods tried, only direct cyanidation with abnormally high cyanide leaching solution strength and free cyanide consumption provided technically acceptable results. Therefore, a special cyanide regeneration process was applied on a pilot scale to recover more than 95 percent of the total cyanides in the regeneration plant solution feed and at the same time remove and recover the copper in solution.

This paper is considered to be a progress report, inasmuch as detailed pilot studies designed to outline optimum regeneration process variables are still in progress. Regeneration process detailed descriptions, reagent consumptions, and operating data are therefore not being reported here, but are deferred to a later paper. Meanwhile, the pilot regeneration plant operations and performance have been consistent and reliable so that gold-copper metallurgical data pertaining to the Centinela Project together with quantitative cyanide regeneration information are presented in some detail under separate headings, following.

3. General

3.1 Location

The Centinela Project includes several deposits of stored flotation mill tailings and potential reserves of unmined vein ore, all containing gold and copper values. The Punitaqui area in Coquimbo Province lies from about 250 to 350 km north of the Chilean capital Santiago de Chile. A major seaport, Coquimbo, is about 100 km to the northwest. A large part of the potential

reserves is near the village of Punitaqui, which has an altitude of 200 to 300 m above sea level, and the climate is relatively mild. The area is served by paved roads from Santiago de Chile, its seaport Valparaiso, and the port of Coquimbo.

3.2 Geology

The several geological areas involved in the Centinela Project contain gneisses, phyllites, greenstones and a wide variety of marine and continental sediments of (questionable) Pre-Cambrian, Paleozoic, Mesozoic, and Cenozoic ages, intensively mineralized in connection with the Andean Batholith intrusion. Major and local faults are key factors in the mineralization, characteristically copper sulfides with varying gold and silver content.

4. Nature of Ore

4.1 Chemical	Au gm/T	% Cu	Ag gm/T
Old Flotation tailings (approx. 2.1 M tons)	1.66	0.42	1.0
Gold ore reserves (inferred, 1. M tons)	3 to 5	0.3 to 0.6	

4.2 History and Mineralogical-physical nature

The Punitaqui area has been sporadically active for more than 100 years in producing gold-copper ores. In 1956 the Empresa Nacional de Mineria installed a 500 tpd froth flotation plant to process ores from the region; however, the actual average production has been considerably less. The Minero Cerro de Centinela S.A. concern acquired the property from government-owned CORFU in June 1983.

The flotation mill tailing reserves have a physical screen analysis of 3 percent plus 200 micrometers and 50 percent minus 36 micrometers. Both tailings and mine ore contain gold too closely associated with hematite, copper and/or gangue to determine the mode of mineralogical occurrence. Copper is largely present in oxidized copper minerals in the mill tailings and in the presently known mine ore reserves. Carbonates are present in amount high enough to preclude an economical acid pre-leaching step for copper removal. Other constituent minerals are quartz, iron oxides, copper silicates, and silicate gangue. Copper is quite uniformly distributed through the mill tailing sizes, whereas the gold is slightly enriched in the finer sized fractions.

5. Laboratory test results

Extensive laboratory test work to determine the amenability of the various Centinela Project gold-copper old mill tailing deposits and newly mined ores was done. Various leaching methods and froth flotation (to recover gold and copper or remove acid consuming gangue prior to leaching) were tried. Preliminary process testing and development was done at the Metallgesellschaft AG Mining Division Laboratory, in Meggen, West Germany. Special processes such as pressure leaching, chlorine leaching, and others were tested by Lurgi Chemie und Hüttentechnik, Frankfurt am Main, West Germany. The Mountain States Research and Development, Tucson, Arizona provided confirmatory flotation and leaching tests and participated in the laboratory-scale and pilot cyanide regeneration investigations. The response of the tailing material and the mine ore were similar, although of course the mine ore was higher grade in gold and copper. Individual process test comments follow.

5.1 Froth Flotation

Froth flotation tests were conducted on mine ore assaying 11.5 grams of gold and 6.1 grams of silver per metric ton and 0.24 percent copper. About 67 percent of the gold, 21 percent of the silver, and only 6 percent of the copper in the ore were recovered in a cleaned concentrate assaying 465 grams of gold, 75 grams of silver and 0.8 percent Cu, and representing 1.7 percent of the original weight. The flotation feed size was 80 percent minus 150-mesh (tyler). Unfortunately, the flotation tailing still consumed exorbitant amounts of cyanide upon leaching.

Similarly, disappointing flotation results were obtained from stored mill tailings. The feed assayed about 1.7 grams of gold and 0.4 percent copper. By refloating the material without regrinding, the gold in the tailings was reduced to only about 1.5 grams at the lowest and always more than 0.3 percent copper in the form of easily leachable copper oxides.

In other tests, attempts to remove carbonates by flotation so as to permit acid leaching for copper removal prior to cyanidation were not successful. Subsequent acid leaching tests still exhibited consumption in excess of 100 kg of H_2SO_4 per metric ton.

5.2 Leaching

5.2.1 Agitation Cyanidation

Exhaustive agitation cyanidation testing of the Centinela stored old flotation mill tailings was carried out by the several laboratories. The usual parameters such as pH, time of agitation, percent solids in the slurry, strength of the cyanide solution, and amount of regrinding, if any, were carefully outlined. In summary, a gold recovery of about 85 percent of the feed content could be

attained without regrinding, or 90 percent with regrinding. From 40 to 50 percent of the copper in the material also dissolved. The pH was 10.5 with lime (CaO) and the percent solids 40 to 45, while agitation time of 24 hours appeared to be sufficient. The apparent consumption of free cyanide was very high, ranging from 3.0 to 8.0 kg of NaCN/metric ton in various parts of the tailing deposit. An unusual and very significant requirement was the very high initial concentration of free NaCN essential to obtain satisfactory recoveries; at 45 percent solids, 11.5 kg of NaCN per ton of ore addition was needed. Of the 11.5 kg free NaCN feed to the leaching system, only from about 3 to 8 kg per ton of ore remained as free NaCN after leaching. To emphasize the importance of the high cyanide concentration required for satisfactory leaching, a slide is presented showing in a curve the interdependence of gold recovery and cyanide concentration.

Cyanide agitation leaching tests were made on mine ore from accessible areas of the Punitaqui mine. The ore was ground to 200-mesh prior to testing. The results indicated that up to 91.5 percent of the gold could be recovered from 8 gram gold, 1.6 gram silver, 0.24 percent copper feed in 48 hours time. As in the case of the retreatment of the old tailings, very strong initial free NaCN solutions were needed (11.25 kg NaCN per ton of ore) and 4.6 kg of free cyanide was consumed per ton of ore. Lime usage was 1.6 kg of CaO.

5.2.2 Percolation cyanide leaching

Cyanide percolation leaching tests were made on samples of Centinela tailing material after careful agglomeration. Indicated extractions of gold were virtually as good as those obtained by agitation leaching. However, unusual difficulty was found in making pellets for percolation leaching. Even with 7.5 kg per ton each of lime and portland cement and curing, only marginally leachable pellets could be made. The commercial handling of such pellets from the point of physical degradation is in doubt.

The mine ore also responded to percolation cyanidation (heap) leaching tests. Ore crushed to 1/2" yielded 80 percent extraction of the gold and 45 percent of the copper after 26 days of leaching. The ongoing solution strength was 9.3 kg NaCN per ton of solution. Indicated consumption of free cyanide was 2.2 kg per ton of ore.

5.2.3 Other leaching methods

Pressure leaching

Pressure leaching in a tube reactor (Lurgi Company is a patent licensee) may provide the same recoveries as in atmospheric conventional leaching in shorter time and with lower reagent consumption. However, in the case of the very refractory Centinela material, cyanidation testing in the pressure system apparently did not provide metallurgical advantages, in that reagent consumption was about the same as in conventional methods.

Chlorine leaching

Chlorine leaching of the Centinela ores and old tailings was studied, with and without NaCl and CaO Cl_2 additions, but recoveries were slightly lower than cyanidation. No cost or process advantages were inferred, and further work was not done on this approach.

H_2SO_4 Pre-Leach

Leaching of the Centinela ores and materials with sulfuric acid to remove copper prior to cyanidation did have the effect of considerably lowering the subsequent cyanide consumption. Nevertheless, the consumption of sulfuric acid (H_2SO_4) ranged from 120 to 143 kg per ton of ore, and the overall cost of cyanide plus sulfuric was estimated to be more than that of straight cyanidation. Thus the approach was not continued.

Additional leaching methods

Other leaching methods were considered but not tried. They included the ammonium thiosulfate (hypo) system and thiourea leaching. Because these processes are still in somewhat of a developmental stage, they were not tried on Centinela materials at this time.

5.3 Gravity methods

Because of the fine grain size and complex mineralogical association of the gold at Centinela, gravity methods were not incorporated.

6. Discussion of metallurgical testing

Of all the metallurgical methods tried, direct cyanidation by either percolation (heap) leaching or slurry agitation leaching appeared to be technically most efficient and lowest cost. Even so, the high consumption of free cyanide and the need for adding unusually strong feed solutions created an anti-economical process, unless the cyanide could be feasibly regenerated. Therefore, efforts were directed to development of a suitable regeneration process. The requirements were to recover almost all of the free and complex cyanide in the leach liquor at a reasonable cost and at the same time remove and recover dissolved copper and perhaps other impurities (metals). Prior art and tests on the Centinela leach solutions and slurries indicated that gold (and silver) could be removed and recovered by (preferably) activated carbon processes from the solutions or slurries before the regeneration step.

7. Cyanide regeneration

7.1 Background

Historically, cyanide regeneration has been practiced for many years. For example, the Cia. Real del Monte y Pachuca (Pachuca, Mexico) still uses a regeneration process in operation since the 1920's. A similar process is described in the literature.[1] At Pachuca a Merrill-Crowe precipitation system barren solution is acidified in packed towers with SO_2 gas. The resulting HCN solution is sparged with large volumes of air, in packed towers, and the effluent HCN-bearing gases are reabsorbed in lime (CaO) solution also in towers, to reconstitute calcium cyanide solution.

A similar process at Flin Flon, Canada formerly operated.[2] However, sulfuric acid was used for acidulation, and the displacement of the HCN and readsorption took place in chambers equipped with mechanical rotors for gas-solution contact.

The Michigan Technological University and the White Pine Copper Company successfully collaborated on a process to cyanide-leach copper from White Pine ores, recover the copper, and regenerate the cyanide in a cyclic process.[3]

7.2 Laboratory-scale regeneration process development

A laboratory bench-scale prototype regeneration system was developed, studied, and modified prior to scale-up. The cyanide materials balance was obtained for the agitation leaching of tailings and is shown on the following page.

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1. Lawr, C.W. "Cyanide Regeneration or Recovery as Practiced by the Compania Beneficiadora de Pachuca, Mexico" AIME San Francisco Meeting, October 1929.

2. The Mill Staff "Cyanide and Regeneration Pant and Practice at Flin Flon" CIMM 1946.

3. Clarkson, John F., and Virgil L. Lessels "Copper Recovery from Mill Tailings by Cyanidation" AIME SME Preprint 75-B-107.

	NaCN kg per metric ton of ore
NaCN added to leaching	11.25
Free NaCN in leach effluent, and	6.35
Complexed cyanide in leach effluent	4.70
Total free and complex cyanide in effluent	11.05
Cyanide content in solid tails	0.20
Free cyanide content after regeneration (97.5%)	10.57
Other (CN) in regenerated solution	.08
Unaccounted for (largely in safety scrubber)	0.40

These encouraging results led to the development of a pilot regeneration plant as described in a following section.

8. Pilot-scale tests and regeneration

8.1 Pilot regeneration plant

Based upon encouraging bench-scale regeneration tests and cyanide leaching tests of Centinela ores and products, a 5 gpm pilot cyanide regeneration plant was constructed at the Tucson facilities of Mountain States Research and Development. The plant incorporates the following essential stages:

- Storage of cyanide leaching pregnant solution to provide accurate accountability and steady flow to the plant.
- Extraction of gold and silver from the pregnant solution in a series of 5 expanded-bed activated carbon columns.
- Addition of reagents to the effluent solution from carbon columns.
- Thorough mixing of solution and reagents.
- Careful control of physical and chemical parameters.
- Removal by filtration of copper (and certain other heavy metals) that might be present.

-Adjustment of solution by addition of any necessary alkali (typically lime) and cyanide (usually NaCN) prior to reuse in the leaching cycle.

-A completely sealed system further monitored by electronic cyanide detectors interlocked with certain controls, to provide safe operation.

Depending upon conditions, testing of the pilot unit indicated that from 90 to 99.7 percent of the total cyanide fed to the plant was recovered as a suitable free cyanide solution for reuse in leaching. Copper recovery from the plant feed was as high as 98 percent of the feed solution content.

8.2 Pilot simulated heap leaching and regeneration

To provide suitable solution for further regeneration pilot tests and also confirm percolation cyanide leaching response of Centinela mine ore, an 18.1 metric ton column leaching test was made. A sample assaying 4.39 grams of gold, 2.40 grams of silver, and 0.95 percent copper was crushed to 21 percent plus 4 mesh and agglomerated with 1.5 kg/MT $Ca(OH)_2$ at 10 percent moisture in preparation for leaching. After 26 days of leaching and 3 days of draining and washing, gold recovery was 80.4 percent, silver 28.1, and copper 45.0. The estimated process loss of cyanide in the heap leaching and regeneration steps totaled 1.5 kg NaCN per metric ton of ore treated; this loss might be decreased by better washing. Metallurgical data for the subsequent regeneration plant operation are presented in Table 1, Metallurgical Data, Regeneration.

Regenerated cyanide solution was made up to 9.19 kg NaCN per metric ton strength by adding 1.19 kg/T NaCN and used to leach duplicate 1-ton samples of Centinela ore. The leaching recoveries were fully as good as if fresh NaCN solutions were used.

The data presented in Table 1 indicate that about 99.7 percent of the total cyanide (both free and complex) was recovered in regenerated free form as a combined solution containing the regeneration solution, gas scrubber solution, and filter wash. The copper product contained more than 99 percent of the original regeneration plant feed solution content and assayed 60.3 percent copper (dry basis).

The considerable dilution evident in the combined regeneration plant solution products is expected to be reduced markedly in longer continuous runs in practice. However, in order to maintain strict solution balance conditions in a cyclic leaching and regeneration circuit, an accessory conventional HCN sparging and reabsorption system has now been added to the pilot unit to treat a small part of the regeneration plant flow, as necessary to avoid any net dilution.

TABLE 1

SOLUTION REGENERATION

METALLURGICAL DATA

	Volume, liters	Assay CN, Reported as NaCN		Cu gm/L	CN Total Content, as NaCN	CN Distr. of Total	Content Cu	% Cu Recov.
		Free kg/T	Total kg/T		kg	%	kg	
Feed Solution	10209	7.1	9.15	2.77	93.41		28.28	
* Regen.Solution	12239	7.55	7.55	.02	92.40	98.3	.25	0.87
Copper Product	53.41 kg	0.44	4.42	60.3%	0.24	0.3	28.03	99.13
* Scrubber Sol.	114	2.57	2.57	(none)	0.29	0.3	-	-
* Filter wash	2380	.36	.45	(negligible)	1.07	1.1	-	-
Calc.Feed.Sol.	12239				94.0	100.0	28.28	100.00
* Regenerated Comb.Solution					93.76	99.7		

9. Conclusions and Discussion

Laboratory and experimental pilot leaching investigations show that the Punitaqui ores and old stored tailings tested respond well to cyanide leaching provided that an unusually high concentration of free cyanide on the order of 9 to 12 kg of NaCN per metric ton of leaching solution is used. The gold and silver dissolved are readily recovered in active carbon. Gold recoveries on the order of 85 percent from tailings and 90 percent from ores were achieved.

9.1 General

From the laboratory bench scale and pilot studies of the regeneration process under investigation, it was concluded that the system reliably removes and recovers heavy metals such as copper from the Centinela Project high-copper cyanide leaching pregnant solutions, following recovery of gold in active carbon. At the same time cyanide (both free and complex) in Centinela solutions largely reports in a regenerated solution form suitable for recycling to the leaching process.

9.2 Environment

The regeneration process studied is foreseen to have a favorable impact upon environmental operational factors as well as on the economy of treating gold-copper ores and products such as the Centinela. All of the water in the entire process except for moisture content of the final tailing is planned to be recycled. Inasmuch as soluble heavy metals cyanides (such as copper) are not recycled back to the ore leaching stage, waste solids should be relatively low in these compounds. Evidently there would be no extra process costs because of the neutralization of various waste liquids.

10. Future Work

Although reliable and consistent results have been achieved in process studies to date, "fine tuning" investigations to optimize reagent and other process variables continue. Thus, process details are being reserved for a subsequent report.

Study of the potential application of the process to a variety of other ores and products has been initiated.

Preliminary capital and operating cost estimates (U.S.A. basis) are under preparation, and if available in time will be discussed at this presentation period.

Recovery of Cyanide from Waste Cyanide Solutions by Ion Exchange

Pilot Plant Studies

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This system achieves the ultimate in efficient, economical plant operation. Permanently fouled ion exchange resin, which would otherwise be discarded from the uranium plant, is used to recover cyanide, water, and complexed base metals from the effluent of the gold works. Furthermore, this same effluent can substitute for caustic soda in removing temporary poisons from the uranium plant and thus reduce operational costs

Laboratory work at Stilfontein (*6*) has shown the feasibility of applying ion exchange for the recovery of cyanide from waste cyanide effluents, particularly those of the gold mining industry. The results were sufficiently encouraging to warrant further investigation on a pilot plant scale. However, until recently certain aspects of the investigation could not be disclosed for reasons of security under the South African Atomic Energy Act.

In 1954 the Stilfontein Gold Mining Co. became a joint uranium producer with several other smaller mines which pumped their ore pulp to the Stilfontein uranium plant for treatment (*7*). With the pulp there was a considerable amount of solution containing cyanide which had to be combined with Stilfontein's cyanide waste solution, complexed with iron(II) sulfate, and disposed of along with the pulp residue. Not only was there a loss of potentially recoverable cyanide with the additional expense of its neutralization, but also a loss of 500,000 gallons of water daily. It was the unsatisfactory economics of such a combined loss that initiated the original investigation into cyanide recovery by the use of ion exchange resins.

The recovery and concentration of uranium at Stilfontein requires the use of a strong base ion exchange resin (Rohm & Haas Amberlite IRA-400). While resin is in the uranium plant, its capacity for uranium is considerably reduced by the presence of certain compounds in the leach liquor from which the uranium is extracted which are poisonous to strong base anion exchange resins. Some of these poisons are temporary, such as silica and the polythionates which can be removed by a 5% caustic soda regenerant.

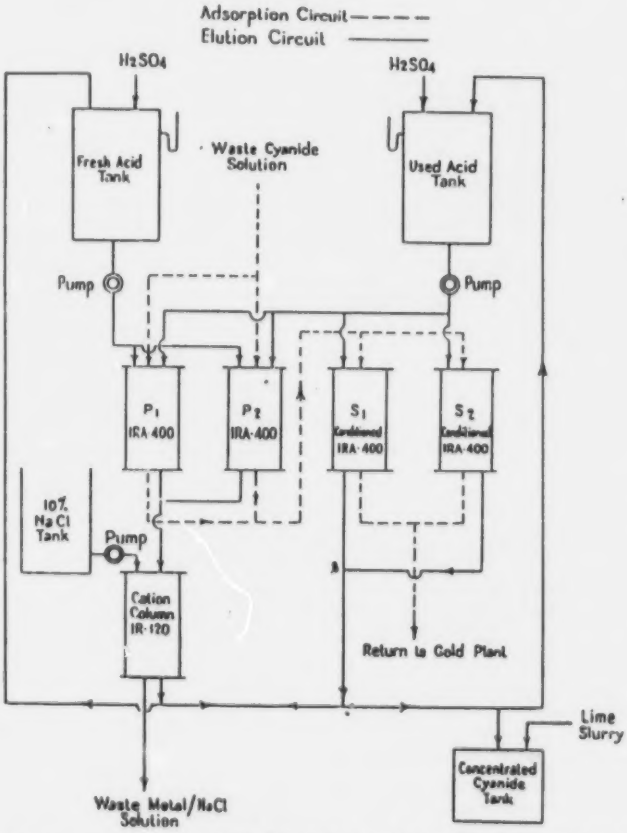

Figure 1. Free cyanide from the primary column effluent is complexed with deliberately precipitated copper(I) cyanide in the conditioned columns (S_1 and S_2), and effluent from them can then be returned to the gold plant as comparatively fresh water

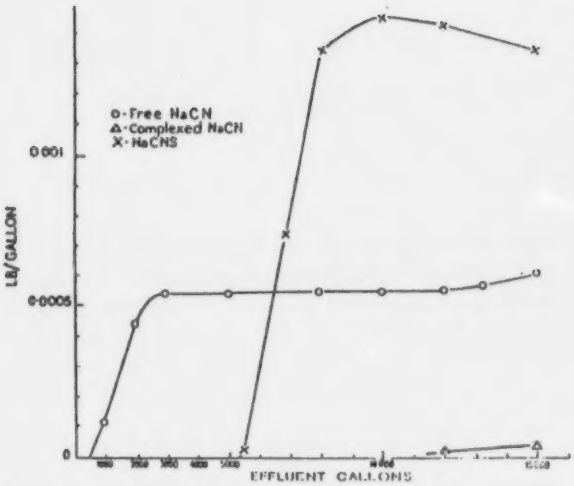

Figure 2. Adsorption of the primary column (as shown by these typical curves) is complete when thiocyanate in the effluent begins to drop with an accompanying increase in cyanide

Influent, 0.0010 pound of sodium cyanide and 0.0009 pound of sodium thiocyanate per gallon

However, one of the cobalt cyanide complexes, derived from the acidification of the original cyanided ore pulp, is a permanent poison to the resin (*3, 8*). Over a period of two years the resin's capacity for uranium is so reduced by gradual build-up of the cobalt complex that its further use in the plant is uneconomical and a large quantity of used resin becomes available for other uses.

Recovery Process

The pilot plant studies on cyanide recovery are based on work carried out on the used resin from the uranium plant. In compliance with gold plant practice, all references to cyanide, whether complexed or free, are sodium cyanide as NaCN. In addition, all gallons are in Imperial units, and weights are avoirdupois including that of gold.

The principle of ion exchange cyanide recovery is to absorb the metal cyanide complexes present in gold plant waste cyanide solution (Table I) on a column of the strong base anion exchange resin in the sulfate form. The effluent from this column is then passed to another column of similar dimensions where free cyanide is complexed with copper(I) cyanide that has deliberately been precipitated within the second columns' resin beads. A column of resin containing precipitated copper(I) cyanide is referred to as being "conditioned."

Effluent from this second column, which contains thiocyanate and carbonate anions but is otherwise free of deleterious substances, can be returned to the plant as comparatively fresh water.

The columns are eluted with 1.0% sulfuric acid solution which decomposes the metal complexes in the first column and the copper cyanide complex in the second conditioned column. During elution of the first column, the eluate containing various metal sulfates and hydrocyanic acid is passed directly through a column of cationic resin of the sulfonic acid type (Rohm & Haas IR-120) in the sodium form to remove metal ions. The eluate, free of metal ions, is then suitable for re-use in the gold plant.

If it is necessary to increase cyanide concentration further, the eluate is reacidified to its former 1.0% sulfuric acid strength and used to eluate the second copper(I) cyanide conditioned column. In the latter instance it is not necessary to pass the eluate again through the cation column, as copper(I) cyanide from the breakdown of the copper complex is reprecipitated within the resin beads.

Metals are eluted from the cation column by a 10% sodium chloride solution.

Table I. Composition of Waste Cyanide Solution from the Gold Reduction Plant

Components	Lb./100 Gal.
NaCN (total)	0.10–0.16
NaCNS	0.07–0.10
Zn	0.01–0.03
Ni	0.001–0.015
Cu	0.001–0.010
Co	0.0001–0.001
Au	0.00001–0.00004

Pilot Plant Construction

Columns for the pilot plant (Figure 1) were constructed from 17.5-inch rubber-lined piping and were 6.0 feet long, with 0.75-inch stainless steel outlets attached to the top and bottom rubber lined plates. These in turn were bolted to the flanges of the columns.

Inside each column over the bottom outlet, was a perforated, 4-inch-diameter plastic disk mounted on 0.25-inch legs so that a free flow of solution was achieved through and around its sides. The disk and the bottom of each column were covered to a depth of 3 inches with 1-inch stones, 3 inches with 0.5-inch stones, 3 inches with fine-screened gravel, and finally resin to a depth of 24 inches.

The fresh and used acid tanks had a capacity of 500 gallons each, and the 10% sodium chloride and concentrated cyanide tanks were of 200-gallon capacity. All tanks were rubber lined, with 0.75-inch stainless steel outlets at the base. Both the fresh and used acid tanks were sealed, except for U-trap vents at the top of each which contained a lime slurry to prevent loss of hydrogen cyanide by evaporation from the acidified contents.

Columns and tanks were interconnected with 0.5-inch polythene tubing. Elbows, T-pieces, and diaphragm valve connectors were of 0.5-inch Kralastic piping. Saunders diaphragm 0.5-inch valves of mild steel were used with the columns and tanks when 1.0% sulfuric acid was used. Diaphragm valves on the cation column, sodium chloride tank, and pump were Saunders plastic 0.5-inch valves.

Gorman-Rupp Mansfield Line 8B12 pumps were used for pumping sulfuric acid and sodium chloride eluriants. Each of the primary (P_1 and P_2) and secondary (S_1 and S_2) columns were loaded with used IRA-400 resin from the uranium plant; fresh IR-120 was used in the cation column. The resin depth of 24 inches allowed a volume of 3.3 cubic feet of resin or 20.6 gallons for each column. Adsorption flow rate was 3.5 gallons per minute (0.17 bed volume per minute); elution flow rate, which was also the adsorption flow rate of the cation column, was 1.0 gallon per minute (0.05 bed volume per minute).

Conditioning. Maximum conditioning of secondary columns S_1 and S_2 was achieved by the following procedure: Commercial copper sulfate was dissolved in water to give an approximately 2.5% solution, and a strong solution of commercial caustic soda was added to precipitate the hydroxide. The addition of caustic soda was continued until the cambridge-blue precipitate just turned to a deeper or oxford-blue color.

A strong solution of sodium cyanide was then added until the precipitate

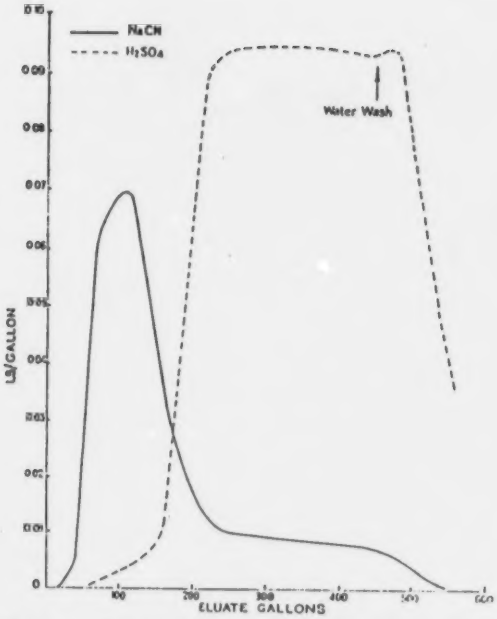

Figure 3. Elution of cyanide from primary column with 1.0% sulfuric acid

Effluent is passed directly to cation exchange column to remove metallic ions

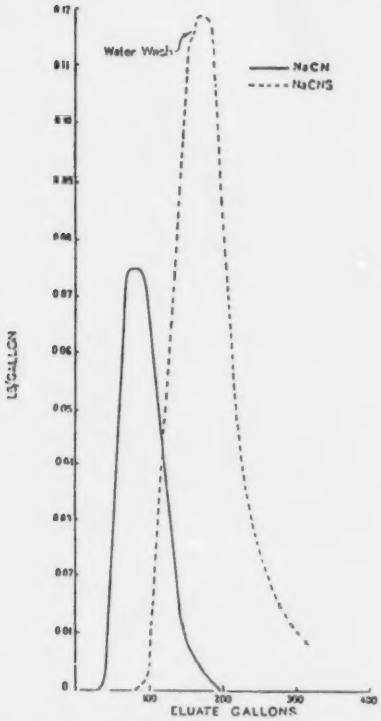

Figure 4. Elution of cyanide from secondary column with 1.0% sulfuric acid

First portion of effluent returned to gold plant. Second portion recycled to used and fresh elute tanks

dissolved. The cuprocyanide solution (approximately 30 gallons) was then pumped into a secondary column and allowed to percolate very slowly through the resin bed for a period of 12 to 18 hours.

The bed was then thoroughly washed with water and eluted with 1.0% sulfuric acid solution until the cyanide concentration of the eluate dropped to less than 1.0 gram per liter of sodium cyanide. The column, after washing by downflow, was ready for adsorption of free cyanide.

Plant Operational Procedure

The main objects of the investigation with the pilot plant were to recover and concentrate cyanide by ion exchange and to achieve this by the use of the uranium-plant used resin (Amberlite IRA-400). Procedure for operating this pilot plant was based on a previous report which continued a step by step procedure for continuous operation (*6*).

Adsorption curves determined with the pilot plant for the primary and secondary columns follow closely those obtained on the laboratory columns; Figure 2 illustrates the adsorption curve for a primary column. Exhaustion of the primary column was estimated to be complete when the thiocyanate content of the effluent began to drop with a corresponding increase of cyanide. This was an indication that the column was saturated with complexes, and thiocyanate was beginning to pass straight through the resin bed. Completion of a secondary column adsorption cycle was taken on the first trace of cyanide breakthrough.

In the original laboratory work, nickel was evident in the primary column effluent throughout the adsorption cycle. Since then the Stilfontein plant has adopted a fairly large water wash for its pulp filters, resulting in a higher dilution of the waste cyanide solution than previously experienced. At this lower concentration, nickel cyanide is completely adsorbed by the resin and only appears in the effluent when the resin bed is almost saturated with the metal complexes. Therefore, as a rapid means of determining column exhaustion it has been found preferable to estimate a spot test (*5*) the completion of the adsorption cycle by the appearance of nickel in the effluent.

Elution curves with 1.0% sulfuric acid are shown for the primary and secondary columns (Figures 3 and 4). As the eluates from the primary columns were passed directly into the cation resin column to prevent metals entering the used acid tank, a further curve (Figure 5) shows the eluate after passage through the cation column.

One cation resin column of 3.3 cubic feet of IR-120 had sufficient capacity for metals from the elution of two primary columns. Therefore, for calculation purposes, a "run" includes the adsorption and elution of two primary columns, one secondary column cycle that may have taken place during that period, and one cation column adsorption and elution cycle (Table II).

For studying the economics of the cyanide recovery process, it had been decided originally that metals adsorbed by the cation column were waste products to be removed from the column as economically as possible.

Elution of the cation column by the

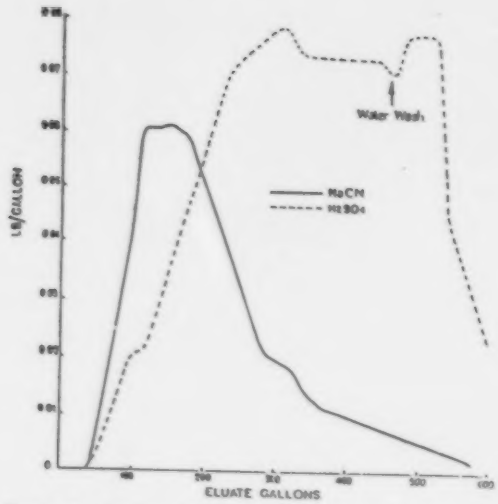

Figure 5. Primary column eluate after passage through cation exchange column

First portion of cyanide bearing effluent returned to used acid tank. Second portion is returned to fresh acid tank

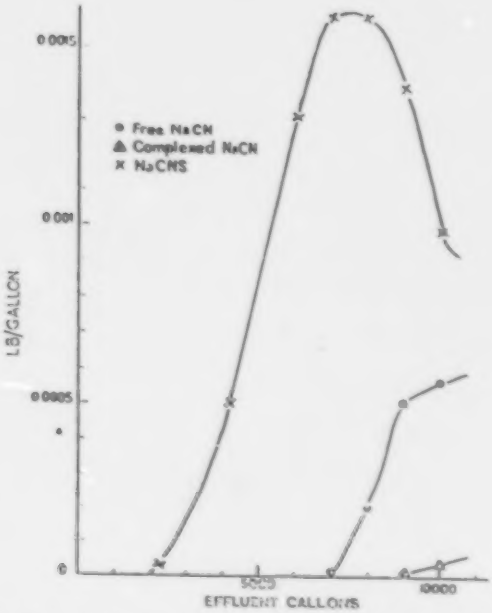

Figure 6. This primary column is fouled with copper(I) cyanide, and free cyanide breakthrough is delayed because of complexing as in a conditioned column. Treatment with iron(III) sulfate regenerates the primary column

conventional methods with 10% sodium chloride elutriant would not only require operational procedure equivalent to the rest of the pilot plant alone but also the quantity of elutriant to ensure maximum recovery would prove expensive. Therefore, a method similar to that used for regenerating resin columns for chromium recovery from plating solution was adopted (7). The cation column, upon exhaustion after the passage of the eluates from the two primary column elutions, was not required for a further 30 hours or so. Consequently, this period of time allowed a prolonged contact of elutriant with the resin.

Cation Column Elution. The column was drained of superfluous liquid equivalent to the volume above the resin bed, replaced with 30 gallons of 10% sodium chloride solution, and a further 10 gallons of column liquor was removed. The resin was allowed to stand overnight in contact with the brine solution, and on the following day it was slowly drained to waste.

Such lengthy contact time of the sodium chloride elutriant with the loaded resin effectively removed most of the metals with a minimum use of regenerant. The resin, after backwashing thoroughly with water, was prepared for the next cycle by draining the column until only six inches of water remained above the level of the resin bed.

Eluate Distribution. From the elution curves (Figures 4 and 5), the following procedure was adopted for the eluate distribution from the primary and secondary columns.

Primary Columns (from Figure 5)

Source	Gallons	Bed Vol.	Destination
Fresh acid tank	40	1.9	Waste
	200	9.7	Used acid tank via cation column
	220	10.7	Return to fresh acid tank
Water	120	5.8	Fresh acid tank
Total	380		

Figure 5 shows that water to fresh acid tank is quite high in acid because of the removal of bisulfate ion from the resin bed. This leaves most of the resin in the sulfate form, which at the same time recovers acid (2).

Secondary Columns (from Figure 4)

Source	Gallons	Bed Vol.	Destination
Used acid tank	40	1.9	Waste
	90	4.4	Concd. cyanide tank
	20	1.0	Return to used acid tank
Water	110	5.3	Fresh acid tank
Total	260		

As with elution of the primary column, acid recovery was high because of the removal of the bisulfate ion from the resin.

The above procedure does not allow for a complete solution balance, and

Table II. Cyanide Recovery

Resin capacity was lowered by the presence of copper(I) cyanide

Run No.	Influent, Gal.	Total NaCN Available, Lb.	NaCN Eluted per Run, Lb. P_1	P_2	S_1	S_2	Total NaCN Recovered, Lb.
27	35,280	39.1	13.3	12.5	6.1	...	31.9
28	25,200	28.9	12.5	11.5	...	5.8	29.8
29	21,420	29.4	11.6	11.0	...	...	22.6
30	17,850	24.0	10.9	10.5	6.0	...	27.4
31	15,540	20.7	10.0	9.0	...	5.9	24.9
		P_1 and P_2 regenerated with $Fe_2(SO_4)_3$					
32	32,970	35.3	13.4	13.0	6.2	...	32.6
33	27,500	31.0	12.0	12.0	...	5.9	30.3
34	20,000	28.1	10.5	13.8	5.8	...	30.1
35	20,580	32.3	10.7	14.0	...	5.9	30.6
36	19,000	33.1	12.1	14.3	6.2	...	32.6

contents of the used acid tank tended to build-up. This was alleviated by using, on occasions, a portion of the used acid for elution of the primary columns.

Source	Gallons	Rel Vol.	Destination
Used acid tank	40	1.9	Waste
	180	8.7	Concd. cyanide tank via cation column
	40	1.9	Return to used acid tank via cation column
Fresh acid tank	200	9.7	Return to fresh acid tank
Water	120	5.8	Fresh acid tank
Total	580		

Obviously, the procedure can be somewhat elastic in operation; this was most desirable as the distribution of the eluate was dependent on the amount of complexed and free cyanide in the gold plant effluent, which varied considerably. Therefore, to avoid build-up of solution in the used acid tank, the elution procedure was varied to suit conditions.

Depending on the amount of the nickel complex adsorbed on a primary column, some of the nickel cyanide was incompletely decomposed by the eluriant. However, back-elution with the last 200 gallons of fresh acid in the latter half of the elution cycle removed most of the residual nickel from the resin bed.

Cyanide Recovery

The majority of the cyanide recovered from the waste cyanide solution was that which had been complexed with the zinc, nickel, and copper. Practically all the cyanide was recovered from the decomposition of zinc and nickel but only a portion from the copper complex according to the following equation:

$$2R_4[Cu(CN)_4] + 3H_2SO_4 \rightarrow 2CuCN + 6HCN + 3R_2SO_4 \quad (1)$$

Therefore, after each adsorption and elution cycle more copper remained behind as copper(I) cyanide, until the resin was so fouled that only about a third of the other metal complexes were adsorbed. Figure 6 shows how free cyanide breakthrough had been delayed because of complexing with copper(I) cyanide in a manner similar to a conditioning column, to be followed shortly after by the zinc and nickel breakthrough. This resulted in a lowering of capacity as shown by the eluted columns for runs 27 to 31 of primary columns P_1 and P_2 in Table II.

However, copper(I) cyanide fouling the primary columns could be readily removed by treating the column with a strong solution of iron(III) sulfate, very much in the same manner as the cation column is eluted of the metals by sodium chloride solution. The reaction between insoluble copper(I) cyanide and iron(III) sulfate (*7*) is illustrated by Equation 2.

$$Fe_2(SO_4)_3 + 2CuCN \rightarrow 2FeSO_4 + Cu_2SO_4 + (CN)_2 \quad (2)$$

As the Stilfontein Uranium Plant uses the acid leach process, large quantities of waste dilute iron(III) sulfate solution [0.4% iron(III) ion] are available. This dilute iron(III) sulfate has been very effective for removing copper(I) cyanide by passing the solution through a column for a period of 12 hours at 3 to 4 gallons per minute. A thorough wash with water prepares the column for the next cycle.

Alternatively, a 10% solution of sodium cyanide removes copper(I) cyanide. The copper in the sodium cyanide eluate is removed by acidification to precipitate copper(I) cyanide, and the clear cyanide solution is decanted off and then made alkaline for re-use.

The number of runs obtained before the primary columns required regeneration by iron(III) sulfate varied from five to 11, depending on the amount of copper present in the waste cyanide solution. Comparison of the two series of runs in Table II shows that fouling was greater in the runs 27 to 31. The secondary conditioned column capacities remained constant maintained throughout six months' operation. No doubt some copper was lost from the secondaries during each elution, but it was replaced by the small leakage of copper complex which unavoidably occurred on occasions from the primary columns.

Water and Gold Recovery

At the same time that cyanide was recovered, water and gold was also recovered (Table III). The amount of water available for re-use in the gold plant would be theoretically equivalent to the influent introduced into a cyanide regeneration plant. By the time it emerges as the effluent it is comparatively free of deleterious substances, except for thiocyanate which is not known to be actively poisonous to gold precipitation. Nevertheless, it would be advisable to dispose of a quarter of the effluent to avoid too great a build-up of the thiocyanate in what would amount to a closed circuit between any proposed cyanide recovery unit and the gold plant (Table III).

The gold cyanide complex is not adsorbed to any great extent by the strong base resin in the presence of other metal cyanide complexes. Once the resin is saturated with respect to gold, leakage of gold will take place. The extent of gold leakage from the resin is a function of the composition of the influent solution. In the event of a closed circuit between cyanide recovery unit and gold plant, this leakage would be returned to the gold plant where this gold would be eventually recovered. In some instances effluent gold concentration was actually higher than influent concentration (Table III).

If fresh resin is used, the appearance of gold in the effluent is delayed for some time until equilibrium is reached, but with used resin from the uranium plant, where there has already been a considerable amount of gold adsorbed on the resin (amounting in some cases to as much as 0.45 ounce per cubic foot of wet settled resin) breakthrough

Table III. Gold and Water Are Recovered as Well as Cyanide

Run No.	H_2O, Gal. Influent	H_2O, Gal. Recovery (75% of influent)	Au, Ounce/100 Gal. In influent	Au, Ounce/100 Gal. In effluent	Au Recovery, Ounce/100 Gal. 75% of effluent	Au Recovery, Ounce/100 Gal. In concd. cyanide soln.	Au Recovery, Ounce/100 Gal. Total
27	35,290	26,460	0.000483	0.000575	0.152	0.006	0.158
28	25,200	18,900	0.000271	0.000483	0.088	0.007	0.095
29	21,420	16,065	0.000160	0.000155	0.025	0.006	0.031
30	17,850	13,388	0.000224	0.000218	0.029	0.005	0.034
31	15,540	11,655	0.000239	0.000182	0.021	0.004	0.025

Table IV. Comparison of Cyanide, Gold, and Water Recovery with Reagent Consumption

Run No.	NaCN Recovered, Lb.	Au Recovered, Ounce	H_2O Recovered, Gal.	H_2SO_4 Consumed, Lb.	NaCl Consumed, Lb.	H_2O Consumed, Gal.	$Fe_2(SO_4)_3$, Lb.
27	31.9	0.158	26,460	69.37	30	610	
28	29.8	0.095	18,900	56.63	30	562	
29	22.6	0.031	16,065	32.48	30	450	
30	27.4	0.034	13,388	43.82	30	485	
31	24.9	0.025	11,655	40.02	30	850	30*
Total	136.6	0.343	86,468	242.24	150	2,957	30

* The iron(III) sulfate consumed in run 31. This reagent needed once each 5 to 11 runs.

is immediate. In practice the amount of gold present on the resin before self elution begins to take place is approximately 0.35 ounce of gold per cubic foot.

From the given five runs 27 to 31, Table IV has been constructed for calculating the economics of reagent consumption under the poorest conditions for cyanide, gold, and water recovery. No attempt has been made to convert the economics to a cash basis as prices for materials in South Africa are different from those elsewhere. For instance, water recovery is an important factor in South African plant economics as the price charged to Stilfontein amounts to one shilling per thousand gallons [14 cents (U.S.A.) per 1000 Imperial gallons].

For ease of comparison however, the totaled values of Table IV have been converted to equivalents of recovery and consumption to 1.0 pound of sodium cyanide recovered as follows:

Recovered	Reagents Consumed
1.0 lb. NaCN	1.77 lb. H_2SO_4
0.0025 oz. Au	1.0 lb. NaCl
633 gal. H_2O	21.65 gal. H_2O
	0.22 lb. $Fe_2(SO_4)_3$

Under South African milling conditions and using uranium plant discarded resin, this would appear economically attractive for the treatment of 10 to 11 million gallons of gold plant effluent at present available from the Stilfontein gold plant each month.

Base Metal Solution Balance

The amount of zinc and nickel recovered as concentrates in the sodium eluate from the cation column is also given here. This should not be, at least for Stilfontein, construed in any way as a contribution to the lowering of operating costs.

Table V gives the balance for zinc and nickel, and there appear to be possibilities, after applying conventional chemical practices to the zinc-nickel-brine solution, of proving concentrates of each metal salt, with recovery of sodium chloride, sufficiently attractive for future application.

Table V. Zinc and Nickel Recovery Data Show Possibilities for Providing Concentrates of Each Metal Salt

30 gallons of 10% sodium chloride cation column eluriant was used for each run

Run No.	Metal Available for Recovery, Lb. Zn	Metal Available for Recovery, Lb. Ni	Metal Recovered, Lb. Zn	Metal Recovered, Lb. Ni
27	5.02	2.12	4.95	1.90
28	4.10	1.70	3.80	0.88
29	3.50	1.20	3.00	1.04
30	3.00	1.10	2.70	1.00
31	2.80	1.40	2.50	1.00

Contrary to expectation, cobalt as the cyanide complex did not pose any problems. Although the amount of cobalt in the effluent was less than that in the influent (0.00006% as compared with 0.00010%), this was balanced by amounts of cobalt found in the eluates and water washes. Analysis of the resin after several runs indicated no increase in cobalt content. Thus, the cobalticyanide complex found in the gold plant alkaline solution is not the same as that found in the ore pulp after acidification, and therefore it is not held so tenaciously by the resin exchange sites.

Resin Regeneration by Waste Cyanide Solution

During the investigation a considerable number of resin analyses were carried out to determine what effect the gold plant effluent had on the used resin itself. What was particularly noticeable was the resin beads regained their original color and appearance after one run and temporary poisons such as silica and polythionates adsorbed on the resin from the uranium pregnant solution had been almost entirely removed.

This immediately suggested the possibility of using the waste cyanide solution with its alkalinity of pH 11.0, as a regenerant in place of the somewhat expensive caustic soda at present used. Not only could a cyanide regeneration plant be used for cyanide recovery, but a double purpose would be achieved by regenerating the resin at the same time in the primary columns.

As this could be immediately applied in the plant, experiments were undertaken on the uranium plant itself, where gold plant effluent was led directly into a set of three uranium columns containing 200 cubic feet of IRA-400 each. Analysis of the resin before and after treatment is shown by Table VI, where percentage removal of silica and polythionates with 5% caustic soda is also compared. It is estimated that by using gold plant waste cyanide solution instead of caustic soda as a regenerant, there would be a saving of £5000 per annum to the Stilfontein uranium plant.

Table VI. Comparison of Waste Cyanide and 5.0% Caustic Soda for Regeneration of Uranium Plant Resin

Use of waste cyanide solution would result in a considerable saving

Regenerant	Removed, % Silica	Total sulfate	Polythionates	Cobalt
Waste cyanide	75.0	62.4	81.3	0.4
5% NaOH	96.3	21.2	30.0	Nil

Personnel Requirement

Because of the long adsorption times, only one skilled and one unskilled operator working a morning or afternoon shift and alternating weekends are all that would be required to operate manually the adsorptions and elutions of a full plant with a capacity for 3,000,000 gallons of waste cyanide solution daily.

Conclusions

Experimental work with the pilot plant has confirmed expectations for a satisfactory economical process to recover cyanide, water, and gold from the effluent of a gold reduction works by the use of a strong base ion exchange resin. In addition the resin formerly used in the uranium plant and discarded has been found suitable for use in the cyanide recovery process.

The gold plant effluent also exhibits a cleansing action on the uranium plant resin, in some respects superior to that of caustic soda used at present as a regenerant for removing temporary poisons from the resin. Therefore, any large plant for operation at Stilfontein will be designed so as to achieve the double purpose of recovering cyanide and regenerating resin for the uranium plant.

Acknowledgment

L. A. Krige assisted both on the original laboratory work and the present pilot plant, and F. X. McGarvey of the Rohm & Haas Co. reviewed and read proof in the U. S. The manager of Stilfontein Gold Mining Co., Ltd., and the consulting engineer, General Milling and Finance Corp., gave permission to publish this paper.

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MEMO

CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

TO Distribution

FROM W. D. Faulkner

DATE April 19, 1983

SUBJECT Cyanide and Activated Carbon

Here is the story on cyanide destruction with activated carbon as recalled to me by the Calgon man that did the work in the 1970's. Calgon received a patent on the process.

Granular carbon will promote air oxidation of cyanide to cyanate very effectively. Cyanate is about 1/200th as toxic as cyanide. But to destroy the cyanate and go all the way to NH_3 and CO_2 a catalyst is needed. Calgon used copper sulfate at about the same concentration as cyanide. The reaction products then hydrolyze as follows:

$$KCNO + 4\ H_2O \rightarrow KOH + NH_4OH + H_2CO_3$$

where upon these products reacted with the copper in solution to form

$$Cu\ (OH)_2 \bullet CaCO_3$$

which set-up like a blue cement in the carbon column. They didn't find a way to circumvent the problem at the pilot plant stage.

I understand that the E.L. Bateman Company of South Africa is promoting a cyanide recovery technique involving carbon.

I'm guessing as to the overall mechanism. Its possibly an adsorption of the cyanide complex followed by acidification of the carbon to release HCN and then caustic scrubbing to produce NaCN. I don't believe anyone is using the process commercially, but its also relatively recent development.

Bill

WDF:yeh

9) Carbon Adsorption of Cyanide

There is some talk of using carbon to recover cyanide from solution and even CIP tailings pulps. Since cyanide is destroyed by carbon in the CIP process especially at a reduced pH in the presence of copper ions, it remains to be seen just how such a process will work.

Carbon adsorbs species as ion pairs according to DR. RAY DAVIDSON of AARL and DR. GLORIA MCDOUGALL of Sentrachem Ltd. For good adsorption, the ionic charges on these pairs should be balanced. That is AuCN and CuCN will adsorb much more readily than $Au(CN)_3^{-2}$ or $Cu(CN)_3^{-2}$ for example. Iron cyanide complexes usually contain a large amount of cyanide per unit of iron because of the large number of cyanide ions around an ion atom - e.g. $Fe(CN)_6^{-4}$. However, since $Fe(CN)_6^{-4}$ has four negative charges, it probably would not load well. However, it is possible that species such as Prussian Blue might well be made to adsorb on carbon. Conceptually such species could possibly be eluted again to regenerate cyanide by changing the pH for example to drive off some cyanide rendering the species charged again, but this would have to be established. Bateman Uranium Corporation is reputed to be offering a process for cyanide recovery from pulps using a specially treated carbon. Details of their process were not revealed. Meanwhile, mining companies can probably get some information from:-

BATEMAN URANIUM CORPORATION
Suite 101, Irongate 1
777 South Wadsworth Boulevard
Lakewood, CO 80226
Peter Sutherland
(303) 989-4921

10) Resource Technology Associates

RTA has developed a cyanide recovery process which is currently being patented, and no details have yet been released.

RESOURCE TECHNOLOGY ASSOCIATES
11728 Highway 93
Boulder, CO 80303
(303) 499-1032
Mark Peters
Dr. John R. Larson
Executive Director

SOURCES OF EXPERTISE AND INFORMATION

Sources of expertise on the subject of cyanide in gold and silver mine and mill effluents are numerous. This list refers to consultants and organizations that offer information as a public service. There are also numerous individuals in mining companies who have expertise in this area that are not listed here.

MR. FREDERICK W. DEVRIES
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INCO METALS, INC.
J. Roy Gordon Research Laboratories
Sheridan Park
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Bruce R. Conard
Eric A. Devuyst
(416) 822-3322

HOMESTAKE MINING COMPANY
Post Office Box 875
Lead, SD 57754
Terry I. Mudder
James L. Whitlock
(605) 584-1020

DONALD R. BAKER
A Professional Corporation
Post Office Box 1404
Bethlehem, PA 18016
(215) 691-0279

REVIEW DOCUMENTS

Excellent review documents on cyanide and cyanidation effluent detoxification include the following:

1) Ed: HUIATT, JERRY L., KERRIGAN, JAMES E., OLSON, FERRON A., and POTTER, GARY L. (1982) Proceedings of NSF Workshop "Cyanide from Mineral Processing," February 2-3, 1982, Salt Lake City. Available from:

   UTAH MINING AND MINERAL RESOURCES
   RESEARCH INSTITUTE
   College of Mines and Mineral Industries
   209 W. C. Browning Building
   Salt Lake City, UT 84112

2) HUIATT, JERRY L. (1984) Synopsis of a Workshop on Cyanide from Mineral Processing TMS-AIME Annual Meeting, February 26-March 2, Los Angeles, California.

3) MILGRAM, DEENA K. (1984) "Cyanide Control in the Ontario Gold Mining Industry - Background Information," Ontario Ministry of the Environment document to be published in 1984. Available from:

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CHAPTER 41

FLUORIDE F

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OCCURRENCE OF F^-

Fluoride occurs in the groundwater supply in some granitic areas of the world. It also occurs in drainage from some coal mine waste piles and in the effluents from some base metal refinery-smelters.

Other industries that discharge fluorides in process waste streams include coke manufacturers, glass and ceramics producers, transistor manufacturers, electroplating operations, steel and aluminum processors, and pesticide and fertilizer manufacturers.

Glass and plating wastes contain fluoride as HF or F^- ions depending on pH. Fluoride from fertilizer plants is often in the form of SiF_4 as a result of processing phosphate rock. Aluminum producers use fluorides in cryolite Na_3AlF_6 as a catalyst in bauxite reduction. Wet scrubbing of process fumes results in high fluoride levels in effluents with typical levels of 100-150 ppm.

Wastewater from BOLIDEN METALL's Skelleftham works in Sweden contain 124 mg/l F according to BLYTHE, et al. (1981).

Fluoride occurs in a number of mining operations, notably the fluorspar deposits in dolomites of the Marico District in the western Transvaal. Fluoride levels of 4 mg/l and more are commonly found in groundwater in this area. Fluoride levels are generally enriched around fluorspar mining areas in the U.S.A.

At ROOIBERG MINERALS DEVELOPMENT CO., which mines tin in the Transvaal, the available water supply contains 6-12 ppm F^- as described in the Appendix I trip report. Levels of up to 3 mg/l occur naturally in the streams of the area.

ISCOR, a South African steel manufacturer, according to HEYNICKE and VON REICHE (1969), discharged two effluents of 1.0 and 2.5 Mgpd with 2-2.5 and 1.0 mg/l F^-.

In the gold mines of the Evander area of the eastern Witwatersrand, fluoride appears in underground water in concentrations up to 6 mg F/l according to KEMPE (1983). Fluoride also appears in coal mine effluents in the Vereeniging, Transvaal, area. Levels around the acceptable standard of 1.0 mg F/l are common, although isolated occurrences of 3 mg F/l are encountered.

In the U.S.A., municipal water supplies with high fluoride levels occur in several parts of the southwest. According to LETKIEWICZ (1983), there are more than 2,000 water supplies in the U.S.A. in which the fluoride MCL (maximum contaminant level) is exceeded. Of these, nearly all have fluoride levels between the MCL (1.4-2.4 mg/l) and 12 mg/l. There are also known water supplies with F^- levels as high as 30 mg/l but in

these, the concentration of other minerals is usually too high for the water to be used as a potable supply without desalination according to RUBEL (1984).

ENVIRONMENTAL AND HEALTH EFFECTS

Due to the natural affinity of fluoride ions for calcium and phosphates, there is a complex interaction between ingested fluoride and skeletal components. Results of many years of investigation into the health effects of fluoride on animals and humans have not been conclusive. One problem is that skeletal effects, except for dental fluorosis (mottled teeth) in children, develop over long periods of time. There are many documented cases of dairy animals and other animals that have experienced fluoride toxicosis (bone deterioraton due to excessive fluoride) from ingestion of water with fluoride levels from 6-12 mg/l. This affliction results in crippling and death.

Dental fluorosis in children is a direct result of water ingestion with fluoride exceeding MCL by children up to the age of twelve.

Crustaceans accumulate F^- in marine environments. There are believed to have been cases of crustacean accumulation of fluoride near a West German copper refinery due to effluent discharges to the North Sea, but details were not available. This was also a critical issue in licensing of a copper refinery proposed near the coast in South Africa.

REGULATORY LIMITATIONS ON FLUORIDE IN EFFLUENT DISCHARGES

Very few mine-mill permits list fluoride as a restricted contaminant.

	Permit Limit F (mg/l)
Climax - Molybdenum Mine, Climax Colorado, 24-Hour Maximum	3.0
South Africa	
General Standard	1.0
Special Standard	1.0
Drinking Water, Recommended Limit	1.0
Drinking Water, Maximum Allowable	1.5

	FLUORIDE Permit Limit F (mg/l)
Ontario Ministry of the Environment (1978)	
Recommended Maximum - Irrigation	1.0
Water Quality Criteria - Livestock Watering	2.0
Drinking Water, Recommended Maximum	1.2
Drinking Water, Rejection	2.4
U.S.A. Maximum Contaminant Level (MCL)	
12.0°C, 53.7°F	2.4
15.5°C, 60.0°F	2.0
26.6°C, 80.0°F	1.4
Brazil (States of Rio de Janeiro, Sao Paulo, and Minas Gerais)	10.0

TREATMENT FOR FLUORIDE

A variety of treatment methods have and are being used for fluoride removal. A summary of some of these is provided by PATTERSON (1975) in a table which is reproduced here. There are basically two categories of process--precipitation and adsorption.

Summary of Fluoride Treatment Processes and Levels of Treatment Achieved.

Treatment Process	Fluoride Concentration (mg/l) Initial	Final	Current Application	Ref.
Lime Addition	—	10	industrial	4
Lime Addition	1000–3000	20	industrial	1
Lime Addition	1000–3000	7–8 (after 24-hr settling)	industrial	1
Lime Addition	500–1000	20–40	industrial	5
Lime Addition	200–700	6 (16-hr settling)	industrial	6
Lime Addition	45	8	industrial	7
Lime Addition	4–20	5.8 (ave.)	industrial	8
Lime Addition	500	80	industrial	8
Lime + Calcium Chloride	—	12	industrial	9
Lime + Alum	—	1.5	industrial	10
Alum	3.6	0.6–1.5	municipal	11
Alum	80	2	lab scale	9
Hydroxylapatite Beds				
synthetic	12–13	0.5–0.7	municipal	12
synthetic	10	1.6	municipal	13
bone char	6.5	1.5	municipal	14
bone char	9–12	0.8	municipal	15
Alumina Contact Beds	8	1	municipal	14
Alumina Contact Beds	9	1.3	industrial (lab scale)	1
Alumina Contact Beds	20–40	2–3	industrial (pilot scale)	5

1 ZABBAN and JEWETT (1967)
4 SCHINK (1968)
5 PETROVA and BAKHUROV (1969)
6 ROHRER (1971)
8 TEER and RUSSEL (1972)
9 ZABBAN and HELWICK (1975)
10 SKRIPACH, et al. (1971)
11 CULP and SKOLTENBURG (1956)
12 WAMSLEY and JONES (1947)
13 CILLIE, et al. (1958)
14 MAIER (1953)
15 PUBLIC WORKS (1955)

Adsorption methods for fluoride removal are employed for water containing relatively low levels of fluoride, say in the 1-25 mg/l F^- range. The activated Alumina process described below is the most widely used process. Precipitation is used when the fluoride level is so high that the adsorbent would be exhausted too quickly resulting in excessive regeneration reagent requirement or cycles or as a rougher step followed by adsorption for polishing.

PRECIPITATION OF FLUORIDE

As mentioned above, precipitation is used for removal of fluoride from more concentrated streams, say over 50-100 ppm F^-.

Reagents that have been used for fluoride removal include lime, magnesium compounds (e.g., dolomite), and aluminum sulfate (alum).

In addition, at least one attempt has been made to use a combinaton of lime and phosphate to duplicate nature's Ca-fluorapatite.

LIME PRECIPITATION

According to PATTERSON (1975), direct addition of lime is the standard technique for reduction of high concentrations of fluoride ions. Lime reacts with fluoride to produce CaF_2 which has a theoretical minimum solubility of 8 mg/l F at stoichiometric concentrations of calcium (34 mg/l). Reported fluoride removal down to only 10-20 mg/l reflect the slow rate of precipitate formation according to ZABBAN and JEWETT (1967) and SCHINK (1968).

Twenty-four hour contact with lime, however, was reported to reduce fluoride to near the theoretical limit of 8 mg/l (ZABBAN and JEWETT, 1967). At very high lime concentrations, however, improved fluoride removal has been reported, but this may require lime addition of up to 4 g $Ca(OH)_2$ per l of water resulting in an effluent pH of 12 according to ROHRER (1971) and RABOSKY and MILLER (1974). Lime dosing at this level was reported to reduce fluoride from 200 mg/l to 3 mg/l F in 19 hours according to ROHRER (1971).

ZABBAN and HELWICK (1975) reported one case in which total fluoride was reduced to 12 mg/l by lime and $CaCl_2$ addition at pH 7-8.

ROHRER (1971) described an operation where lead and fluoride were precipitated sequentially by addition of trisodium fluoride lime and polyelectrolyte. F^- was reduced to 6 mg/l after 16 hours. Addition of excess lime further reduced the fluoride concentration. Recarbonation provided a way to remove excess Ca^{++} ions and adjust the pH. It is possible that the phosphate addition for lead also helped remove fluoride.

PATTERSON (1975) refers to two experiments in which the addition of sodium hexametaphosphate with alum enhanced fluoride removal (ZABBAN and HELWICK, 1975; MILLER, 1974). In one application of alum plus sodium hexametaphosphate (4:1 ratio), fluoride was dropped from 20 mg/l to below 2 mg/l at pH 7 according to ZABBAN and HELWICK (1975).

Lime addition for fluoride removal employs standard equipment as used in lime softening of municipal water. This includes a rapid mixing basin for chemical addition, a flocculating unit, and a settling basin for solids separation.

According to CILLIE, et al. (1958), the two South African steel mills (ISCOR) with effluent flows of 1 and 2.5 Mgpd were able to reduce fluoride levels to 2-2.5 and 1.0 mg/l F. The fluoride enters the system from electrolytic tinning units and is precipitated with lime prior to the effluent being diluted by combination with total plant effluent.

Normal ways of disposing of the precipitate sludges containing fluoride, according to PATTERSON (1975), is by laggooning, sand bed drying, or filtration.

BOLIDEN-SKELLEFTHAM

BLYTHE, et al. (1981) describe a treatment process for removal of arsenic, heavy metals, and fluoride from a metallurgical plant effluent of BOLIDEN METALL, Skellefthamn, Sweden, in which F is reduced from 124 ppm F at pH 3.5 to 33 ppm at pH 11.5 by lime addition and settling. In order to safely dispose of the gypsum precipitate containing fluoride, the metals and arsenic are first precipitated by sulfide addition at pH 3.8, and the precipitate is recovered by filtration because contamination of the calcium sulfate-fluoride precipitate with metals such as As, Cu, Pb, Zn, etc. would render it unfit for landfill disposal in Sweden.

Nonetheless, the removal of F^- from 124 ppm to 33 ppm also does not indicate a very useful fluoride removal process.

BOLIDEN-Skellefteham: Influent - pH 2.5, 124 ppm F^-
Outflow - pH 11.5, 33 ppm F^-

The BOLIDEN flowsheet and solution compositions at various stages is inserted in Chapter 29 on arsenic removal.

MAGNESIUM PRECIPITATION

PATTERSON (1975) notes that fluoride removal from waters in the lime-soda softening process was observed to be in direct proportion to the amount of magnesium hardness removed, and believed to be due to be due to adsorption of fluoride to the magnesium hydroxide flocs. CULP and SKOLTENBURG (1958) were able to reduce fluoride from 3-4 mg/l to 0.8-1.12 mg/l F. Fluoride reduction is achieved in conjunction with magnesium hardness removal at several municipal water treatment plants in the U.S.A. where fluoride is present at concentrations of 2-3 mg/l, according to SAVINELLI and BLACK (1958).

No plant was found in which $Mg(OH)_2$ or MgO is added specifically for fluoride removal.

ALUMINUM SULFATE (ALUM) PRECIPITATION OF F^-

CULP and SKOLTENBURG (1958) reported that for a water of low hardness containing 3.6 mg/l F^-, simple alum addition plus small quantities of lime for pH control resulted in fluoride reduction to 1 mg/l, but this method was less effective for hard waters.

Addition of alum results in co-precipitation of fluoride onto the aluminum hydroxide. The best removal appears to occur at pH 6-7 with fluoride dropped first from 100 mg/l to 5 mg/l by lime precipitation at pH 11.9 and then to 1.7 mg/l by alum coagulation at pH 5.9-7 according to RABOSKY and MILLER (1974).

ZABBAN and HELWICK (1975) found that fluoride removal from solutions containing up to 100 mg/l F is dependent only on alum dosage and pH with the best performance around pH 7. In one case, at 40 pounds alum per pound fluoride, F^- was reduced to 4.8 mg/l. At alum doses of 200 pounds per pound F^-, effluent levels of 2 mg/l were achieved.

SKRIPACH, et al. (1971) described fluoride and arsenic removal from rare earth processing effluents in which an effluent concentration of 1.5 mg/l F was achieved by adding lime in stages plus superphosphate and alum.

REVERSE OSMOSIS

RUBEL (1984) discusses the use of desalination for fluoride removal. Rejection of fluoride by R.O. is temperature and pH sensitive. At low pH, say 5.5, fluoride rejection is around 50%. At higher pH, CaF_2 precipitation has caused membrane fouling problems. Two possible solutions exist. First is the new seeded slurry reverse osmosis process which effectively avoids membrane fouling problems (when tubular cellulose acetate membranes are used, pH 5.5-6.0 is still the recommended operating range). Secondly, to select one of the new membranes which give a better fluoride rejection at low pH (and it is believed that up to 90% rejection at pH 5.5 has been demonstrated).

Desalting processes are relatively expensive; they cost around $\$0.50/m^3$ recovered water. This is about ten to twenty times the cost of adsorption processes. However, R.O. could nonetheless be useful for fluoride removal if a desalination process has to be used in any case to meet another parameter, e.g., reduction of TDS. If fluoride removal could be achieved, then there would be no extra cost.

ADSORPTION

Adsorption of fluoride from water as it passes through a bed of granular material is routinely practiced and, in fact, is the standard way of removing fluoride from municipal drinking water when the raw supply exceeds allowable limits.

PATTERSON (1975) concludes that adsorption methods are usually only applicable to low-level fluoride waters or for polishing processes after reduction of fluoride levels by previous treatment to the 10-20 mg/l level; otherwise, the need for frequent bed regeneration makes the process economically unfeasible.

Various adsorbents have been used for fluoride removal including hydroxylapatite (synthetic, processed bone and bone char), ion exchange resins, and activated alumina. Of these, activated alumina has now become established as the most reliable and economical process.

HYDROXYLAPATITE

Reduction of fluoride from 12-13 mg/l to 0.5-0.70 mg/l has been reported for a full scale plant by WAMSLEY and JONES (1947). Later reports by SAVINELLI and BLACK (1958) indicated that this unit and others like it were ultimately abandoned due to high chemical costs and bed attrition in which up to 42% of the adsorbent was lost per year. For a similar pilot plant operation in South Africa described by CILLIE, et al. (1958), 10 mg/l

fluoride could be reduced to 1.5 mg/l, but the presence of chlorides in the water reduced filter bed capacity and increased regeneration chemical requirements.

Natural bone char hydroxylapatite can be used but requires phosphoric acid and sodium hydroxide for regeneration which MAIER (1953) found to be too expensive.

ION EXCHANGE

Natural and synthetic zeolite ion exchangers have been examined and reported to be effective for fluoride removal. The exchangers were both pretreated and regenerated with aluminum salts, and it has been established by MAIER (1958 and 1971) that fluoride removal is attributable to aluminum oxide which precipitated in the column bed.

ROHM and HAAS have developed a strong anion exchange resin selective for fluoride, but overall treatment and chemical costs for regeneration were found to be excessive (MAIER, 1953).

ACTIVATED ALUMINA

Activated alumina has been used for many years for fluoride removal from municipal water. A wellknown unit at Bartlett, Texas, has been in successful operation since 1952 using a 500 cubic foot bed regenerated by sodium hydroxide and neutralized with sulfuric acid. Fluoride is reduced from 8 mg/l to 1 mg/l according to PATTERSON (1975) and MAIER (1971). In 1952, the cost of fluoride removal at this plant worked out to \$0.05/1,000 U.S. gal. (\$0.013/m^3). The Bartlett, Texas, plant is no longer in operation according to RUBEL (1984).

Since then, a host of fluoride removal plants have been installed throughout California, Arizona, and Texas. A definitive and comprehensive design manual by RUBEL (1984) has been released by the EPA. Total operating costs for fluoride removal in the U.S.A. today costs between \$0.085 and \$0.20/m^3 (\$0.02-\$0.05/m^3) according to this document which is referenced below.

RUBEL and WOOSLEY (1979) described cost effective operating practices developed at three water treatment plants for removing excess fluoride from drinking water by activated alumina. By the use of these methods, the fluoride removal capacity of alumina was increased by a factor of five. Their paper is also inserted below.

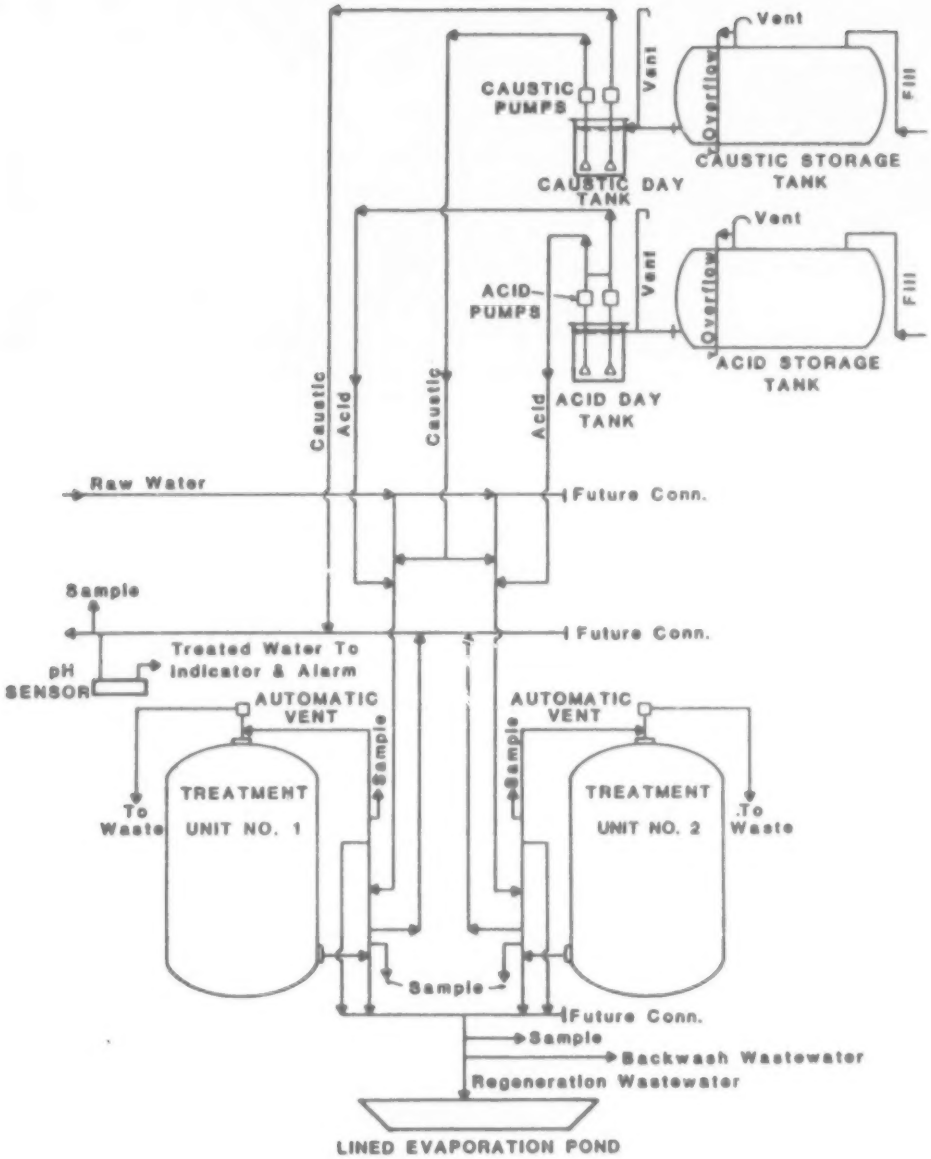


FIGURE 3-2 BASIC FLOW DIAGRAM

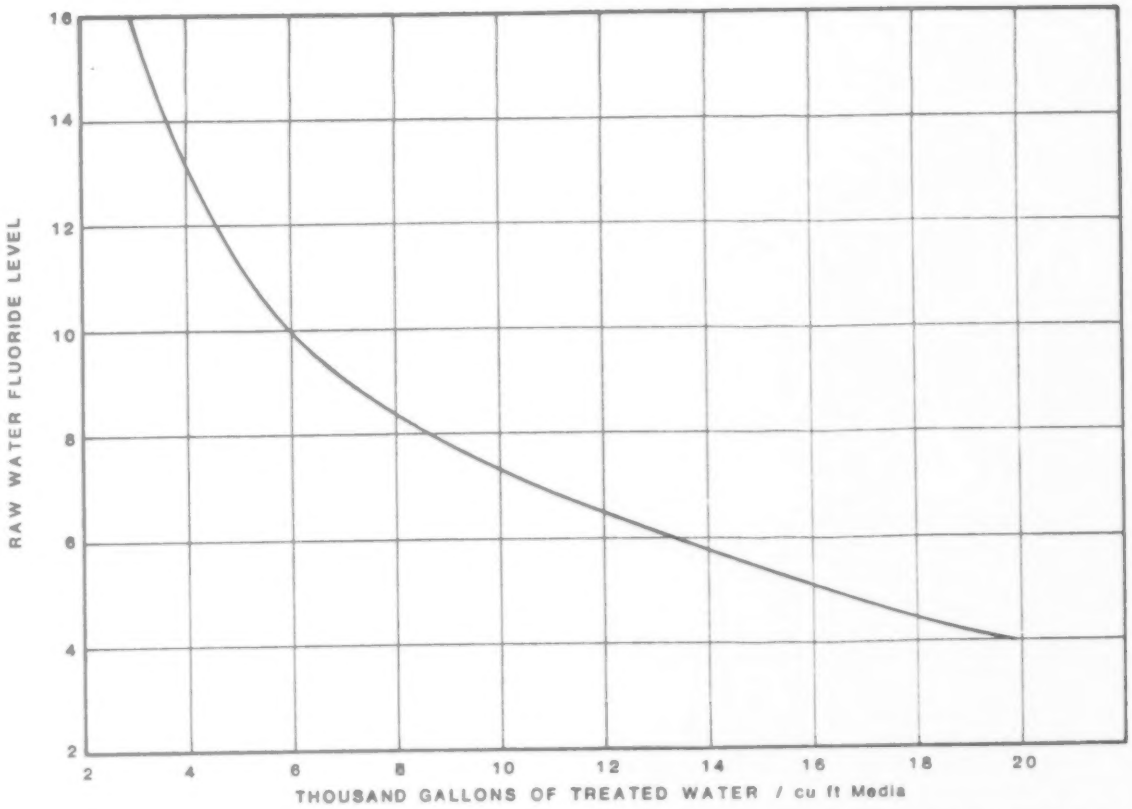


FIGURE 6-1 CURVE ILLUSTRATION RULE OF THUMB FOR VOLUME OF WATER TO BE TREATED PER CYCLE VS. RAW WATER FLUORIDE LEVEL

A granular activated alumina is used for fluoride adsorption. The material is a by-product of aluminum production. It is primarily an aluminum oxide which has been activated by exposure to high temperature and caustic soda. The material is highly porous, and the surface area per unit of weight is quite high.

RUBEL (1984) recommends the use of 28-48 mesh Alcoa F-1 grade alumina in defluoridation processes.

CAPACITY OF ACTIVATED ALUMINA FOR F^- REMOVAL

Capacity of activated alumina for F^- removal is very pH dependent as demonstrated by WU (1978) who first suggested that activated alumina capacity for fluoride uptake from water is much greater at pH 5.5 than at 7.0. He reported maximum removals of 4,200 grains/ft^3 at pH 5 with pure NaF solutions. Other investigatiors who have made bench, pilot, or commercial installation studies have reported much lower capacities because they have not understood or chosen to operate at optimum pH conditions.

RUBEL (1984) cites three plants which have operated routinely for years at a low cost meeting the municipal fluoride levels. These are listed below. By paying close attention to pH control, the three plants are able to routinely remove in excess of 2,000 grains/ft^3 (4,600 g/m^3). For higher fluoride concentrations, the activated alumina adsorption capacity increases. For a water with 22 mg/l F^-, the alumina capacity reaches 4,500 grains/ft^3 (10,400 g/m^3).

In this optimum pH range (5.0-6.0), other ions that compete with fluoride for the same adsorption sites are not adsorbed. Included are silica, which is adsorbed in the pH range 6-10, and some hardness ions which are removed in the pH range 7 through 10. Hardness removal occurs at the start of a treatment run. However, activated alumina preferentially adsorbs fluoride; therefore, as the run progresses, hardness removal ceases. At the optimum fluoride removal pH, some organic molecules and some trace heavy metal ions are also adsorbed. However, except for arsenic, these are completely regenerated along with the fluoride. Arsenic presents a problem as it is preferentially adsorbed over fluoride by the alumina at the same optimum pH. Arsenic is more difficult to regenerate than fluoride. Therefore, when excess fluoride and arsenic are present in a water supply, a special treatment technique is required as described by RUBEL and WOOSLEY (1978).

EXAMPLES OF PLANTS USING Al_2O_3 ADSORPTION OF F^-

	Startup Year	U.S. gpm	m^3/d
Lake Tamarisk, Desert Center, California	1970	1,100	6,000
Rincon Water Co., Vail, Arizona	1972	500	2,700
Town of Gila Bend, Arizona	1978	900	4,900
Rooiberg Tin Mine, Transvaal	1985	95	518

CONCEPTUAL DESIGN

Of the many configurations to choose from, i.e, gravity or pressure flow, single or multiple treatment beds, upflow or downflow treatment flow direction, and series or parallel treatment vessel arrangement, RUBEL (1984) reports that the most efficient, cost effective configuration is a parallel downflow multiple bed pressure system. Best cost effectiveness is achieved (for both capital and operating costs) with two treatment beds.

The two-bed series combination yields the highest fluoride loading on the media, and the lowest fluoride level in the treated water, but this is often too low to be desirable. The parallel system allows an opportunity to blend two streams.

REGENERATION OF ALUMINA

Alumina is regenerated using a 1% sodium hydroxide solution. Optimally, 50 percent NaOH solution is used which may require heating as it freezes at 55°F and is very viscous below 70°F. Fluoride ions are repelled from the alumina granules when the pH rises above 10.5.

0.4 gallons (5 lbs.) of 50% NaOH solution is required per ft^3 per regeneration. The caustic requirement for regeneration is a function of the raw water fluoride level which dictates the frequency of regeneration and the volume of water over which the cost must be distributed.

Use of too highly concentrated NaOH solution enhances comsumption of alumina granules.

MEDIA CONSUMPTION

Consumption of alumina should be close to zero in a well-operated activated alumina fluoride water treatment plant. Excessively long backwash periods cause excessive

alumina losses through attrition and elutriation. Monitoring of backwash fluids can help detect this.

During regeneration, excessively high and/or low pH exposure attacks the media. If the regeneration solution exceeds 1.5% NaOH, the solution is aggressive to activated alumina.

Also, if the pH of the post regeneration neutralizing solution (acid addition) is below pH 2.0, the alumina dissolves very rapidly with resulting losses.

Finally, alumina can be lost through the effluent underdrain collection system within the bed. If alumina grains ever appear in the treated effluent, this indicates that the collection system is in need of repair.

A conservative bed replacement estimate according to RUBEL (1984) is ten percent per year.

OPERATING SEQUENCE

1. Feed pH adjustment to Ph 5.0-6.0.
2. Adsorption mode - downflow.
3. Backwash mode.
4. Regeneration.
5. Neutralization after regeneration.

Raw water is used in each of these steps.

Details of the operation of an activated alumina plant for defluoridation are provided by RUBEL (1984) including several knowhow items which would prove helpful in optimizing results for a given plant.

Fines that accumulate on top of the alumina bed should be removed to avoid an unnecessarily high pressure drop across the bed when commencing a run.

BACKWASHING

Backwashing of the bed with raw water after each run prior to regeneration is important to remove suspended solids filtered from the feedwater. Upflow backwash expands the bed. Backwash at 8-9 gpm/ft^3 expands the bed about 50%, which is recommended. Normally, backwashing lasts ten minutes. RUBEL (1984) provides a valve operation chart for the backflush mode.

REGENERATION

Regeneration of the bed on completion of an adsorption run generally includes two discrete regeneration steps. First is upflow regeneration following draining of the bed after backflushing. Regeneration is followed by an upflow rinse. The unit is then drained to the top of the bed prior to the second regeneration step which is downflow. Both steps use 1% (by weight) NaOH solution.

A skilled operator can reduce the concentration of NaOH to 0.75% and achieve the same high regeneration efficiency; however, below 0.75%, the efficiency drops rapidly. At this lower caustic concentration, the saving in NaOH consumption amounts to 20%.

As a rule of thumb, fifteen gallons of 1% NaOH solution is needed per cubic foot of treatment media. The minimum time for the regenerant solution to flow through the bed is thirty minutes. Thirty-five minutes is recommended for a 5' bed. A flow of 2.5 gpm/ft^2 for thirty-five minutes per regeneration is usually sufficient, which equates to 0.2 gallons of 50% NaOH per cubic foot of treatment media for each regeneration step (upflow and downflow).

After backflush, prior to upflow regeneration, the bed must be drained to remove water which dilutes the caustic concentration. Upon completion of draining, the upflow regeneration starts. On completion of the upflow regeneration, the caustic feed pump is turned off and the day tank refilled. Raw water continues to flow for sixty minutes at 2.5 gpm/ft^2 upward through the bed to flush out the fluoride. After this rinse step is completed, the vessel is drained to the top of the treatment bed, again to remove dilution water. Then, downflow regeneration is followed by a draining period prior to the start of the neutralization mode.

NEUTRALIZATION

Neutralization is critical to the success of the following adsorption (treatment) run. The objective of this mode is to return the bed to the treatment mode as rapidly as possible without dissolving the activated alumina. The pH of the alumina upon completion of regeneration is 12 plus. It must be adjusted down to 5.5. Therefore, it must pass through pH ranges where ions that compete for adsorption sites on the alumina will be loaded into the bed. The minimum pH that can safely be reached is pH 2.5. A lower pH is too aggressive and is not recommended.

After 15 minutes of downflow regeneration, the flow is adjusted to the normal treatment mode rate. The acid pump is started, and the pH of the raw water adjusted to 2.5. Acid feed rate again varies with the alkalinity of the raw water. The raw water flow rate may have to be reduced to achieve pH 2.5 at the maximum acid pump feed rate.

As the neutralization mode proceeds, pH of the treated water gradually drops below 12. The rate of pH reduction increases at an increasing rate. As the treated water drops below ten, the treated water fluoride level begins to drop below that of the raw water. At that time, treatment begins. At the point where the fluoride level drops below the MCL, the water becomes usable and can be directed to storage even if the pH is still high (say pH 9.5).

When the treated water pH drops to 8.5, the raw water pH is adjusted up to 4.0 as the bed rapidly neutralizes. When the treated water drops to pH 6.5, the raw water is adjusted up to pH 5.5 where it remains through the duration of the run.

Volume of wastewater produced during the regeneration of the alumina bed varies with the physical and chemical characteristics of the raw water. A useful rule of thumb is 300 U.S. gallons per ft^3 of media, i.e., 40 m^3 wastewater per m^3 media per regeneration.

Typical volumes of wastewater generated during each regeneration cycle for a hypothetical plant as described by RUBEL (1984) are:

Backwash	60 U.S. Gal.
Upflow Regeneration	15 U.S. Gal.
Upflow Rinse	30 U.S. Gal.
Downflow Regeneration	15 U.S. Gal.
Neutralization	180 U.S. Gal.
TOTAL	300 U.S. Gal.

Operating experience for each given plant will soon come up with deviations from these quantities.

DISPOSING OF WASTEWATER

All the known fluoride treatment plants using activated alumina are located in areas with net evaporation climates and, as such, are suitable for disposal of the regeneration wastewater containing flouride into lined evaporation ponds.

LABORATORY REQUIREMENTS

RUBEL (1984) recommends that the operator of an activated alumina fluoride removal plant be equipped with the operations and maintenance (O&M) manual for the plant and also the latest edition of Standard Methods for the Examination of Water and Wastewater by AWWA-APHA and basic laboratory equipment. Primary analytical needs are to determine pH and fluoride. Fluoride measurement can be by ion-specific electrodes provided the

:t buffer (TISAB) is employed for the water to be treated. There are also two te wet chemistry methods using SPADNS and Alizarin. Distillation and/or correction terferring ions (e.g., alkalinity, aluminum, iron, sulfate, etc.) are required for te results.

,TING COSTS FOR DEFLUORIDATION BY ACTIVATED ALUMINA

include the following:

- Treatment chemicals.
- Operator labor costs.
- Utility costs.
- Replacement alumina.
- Replacement parts and miscellaneous materials.

L (1984) discusses each cost item in some detail.

ding to RUBEL (1984), the U.S. price for ALCOA F-1 28-48 mesh activated alumina s from $0.697/lb to $0.516/lb depending on quantity.

ıting costs (1984) vary as follows:

Operating Cost Items		U.S. Dollars per 1,000 U.S. Gallons Treated Min. $	Max. $	Ave.
Treatment Chemical -	Acid	0.02	0.08	0.05
	Caustic	0.02	0.12	0.05
Operating Labor		0.03	0.10	0.06
Utilities		0.005	0.05	0.01
Replacement Media		0.005	0.03	0.02
Replacement Parts, Etc.		0.05	0.10	0.01
TOTAL		0.085	0.39	0.20

FLUORIDE

	$/m³	Treated Water	
	Min.	Max.	Ave.
	$	$	$
Treatment Chemicals - Acid	0.005	0.020	0.013
Caustic	0.005	0.030	0.013
Operating Labor	0.008	0.030	0.016
Utilities	0.001	0.013	0.003
Replacement Media	0.001	0.008	0.005
Replacements Parts, Etc.	0.013	0.026	0.003
TOTAL	0.033	0.127	0.053

CAPITAL COST FOR ACTIVATED ALUMINA DEFLUORIDATION PLANT

RUBEL (1984) estimated costs for a 600 U.S. gpm (3300 m³/d) defluoridation plant in a warm Arizona climate at $347,000 of which $138,000 was for the lined wastewater evaporation pond. The cost breakdown was as follows:

Flowrate: 600 U.S. gpm, 3300 m³/d.

Process Equipment	
Treatment Vessels	$ 33,000
Treatment Media - Alumina	20,500
Process Piping, Valves, and Accessories	16,400
Instruments and Controls	8,300
Chemical Storage Tanks	21,000
Chemical Pumps, Piping and Accessories	6,300
Subtotal	$105,000
Process Equipment Installation	
Mechanical	$ 36,000
Electrical	7,000
Painting and Miscellaneous	4,500
Subtotal	$ 47,500
Miscellaneous Installed Items	
Wastewater Evaporation Pond - Lined	$138,000
Building and Concrete	28,000
Sitework, Fence, and Miscellaneous	11,000
Subtotal	$177,000
Contingency 4%	17,000
TOTAL	$347,000

The Removal of Excess Fluoride From Drinking Water by Activated Alumina

Frederick Rubel Jr. and R. Dale Woosley

Described here are cost-effective operating practices developed at three water treatment plants for removing excess fluoride from drinking water by activated alumina. By use of these methods the fluoride removal capacity of alumina was increased by a factor of five.

Under the national Interim Primary Drinking Water Regulations maximum contaminant levels (MCL) in potable water supplies have been established for ten inorganic chemicals, including fluoride. The MCL for fluoride varies from 1.4 to 2.4 mg/L depending upon the annual average of the maximum daily air temperatures (Table 1). If the prescribed maximum level is to be enforced, its achievement must be technically and economically feasible.

Since it became known that excess fluoride in drinking water caused mottled teeth in children,[1] many methods of removing fluoride have been developed. One of them employs activated alumina to defluoridate water supplies. Although many investigators have found that activated alumina is quite effective in reducing fluoride to very low levels in treated water, there is an abundance of confusion as to the useful capacity of activated alumina.

Churchill,[2] in his 1936 patent on the use of activated alumina for fluoride removal, states that a pH of 5 to 6.5 should be used during treatment for best results. There is no stated capacity in his patent. E.A. Savinelli and A.R. Black,[3] in their 1958 bench experiments, showed that a capacity of 7800 g/m³ (3400 grains/cu ft) was achieved when treated water pH was 5.6. Their studies were made with tap water to which sodium fluoride had been added. Yeun C. Wu,[4] in a recent article, again shows that treatment pH is quite important for high removal capacities. He reports maximum removals of 9600 g/m³ (4200 grains/cu ft) with treatment at pH 5.6 in pure sodium fluoride solutions. Other investigators[5-9] who have made bench, pilot, or commercial installation studies report much lower capacities because they have not understood or chosen to operate at optimum pH conditions.

Two plants that have had several years of low-cost experience in producing waters with fluoride concentrations reduced to acceptable levels are the Lake Tamarisk plant at Desert Center, Calif., with nine years of operation, and the Rincon Water Co. plant at Vail, Ariz., with six years of operation. A third plant began operation in Gila Bend, Ariz., in May 1978. By paying close attention to pH control, the three plants are able to operate routinely with removal capacities exceeding 4600 g/m³ (2000 grains/cu ft). Removal capacities exceeding 7000 g/m³ (3200 grains/cu ft) were observed during the pilot work done at Gila Bend, Ariz., to confirm that the developed operating practices would work on that water supply.

Development work with pilot-plant equipment on a continuing basis has perfected the water treatment and alumina regeneration processes at each of these locations. This article outlines the operating practices developed for removing fluoride to acceptable levels.

Fluoride Removal Technology

This article is based on pilot-plant experiments and plant data for which granular activated alumina[a] (mesh size 28 to 48) was used.

The basic principles of fluoride removal technology are

1. Optimizing the environment for sorbing of fluoride ions to activated alumina surfaces
2. Preventing competing ions from occupying alumina surfaces that should be reserved for fluoride ions
3. Upon regeneration of an expended treatment bed, taking all steps necessary to remove all fluoride ions from the bed before returning it to treatment.

There are also many "common sense" principles that apply to the process which, though important, are not as critical as the three listed.

There are four modes of operation: treatment, backwash, regeneration, and neutralization. Operating details for each mode are discussed here.

Treatment mode for virgin or regenerated treatment bed. The optimum environment for fluoride removal exists when raw water pH is adjusted to 5.0–6.0 by sulfuric acid injection. Because acid feed rates are a function of the raw water alkalinity, they vary from one water to another. The best results obtained to date have occurred when the raw water pH has been held carefully at 5.5. In this environment the attraction of the fluoride ion to the activated alumina surface is most favorable and interference by competing ions is minimal. Adsorption is the most probable mechanism for fluoride ion removal from water, but because work in this area is still in progress, discussion of mechanism is premature. In applications

[a] F.J. Akos, Pittsburgh, Pa.

TABLE 1
Maximum Contominant Levels For Fluoride

Average Maximum Daily Temperature °C	°F	Fluoride Level mg/L
≤12.0	≤53.7	2.4
12.1-14.6	53.8-58.3	2.2
14.7-17.6	58.4-63.8	2.0
17.7-21.4	63.9-70.6	1.8
21.5-26.2	70.7-79.2	1.6
26.3-32.5	79.3-90.5	1.4

TABLE 2
Water Analyses At Existing Operations

Parameter	Facility: Lake Tamarisk	Rincon Water Co.	Town of Gila Bend
Ca—mg/L	11	51	31
Mg—mg/L	0.5	5.0	<1
Na—mg/L	56	151	306
SO_4—mg/L	40	264	160
Cl—mg/L	67	22	540
Hardness (as $CaCO_3$)—mg/L	30	152	70
Total alkalinity (as $CaCO_3$)—mg/L	77	171	40
Phenolphthalein alkalinity (as $CaCO_3$)—mg/L	0	0	2
Fe—mg/L	0.2	<0.05	0.2
SiO_2—mg/L	22	55	21
F—mg/L	7.5	4.5	6.0
Total dissolved solids—mg/L	407	650	1121
pH	7.9	7.5	8.1

Year 1970 1973 1974

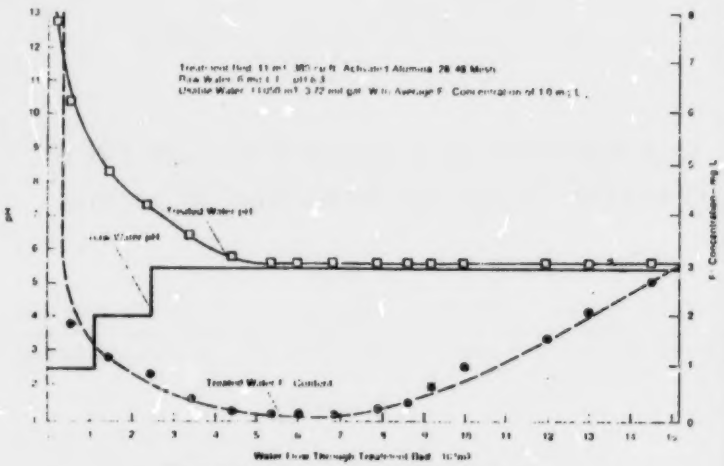


Fig. 1. Typical Operational Run at Gila Bend, Ariz.

to date, treatment bed capacities consistently have exceeded 4600 g/m³ (2000 grains/cu ft), and some runs have exceeded 9200 g/m³ (4000 grains/cu ft).

As raw water pH moves above 6.0 or below 5.0, fluoride removal capacity deteriorates at an increasing rate. For example, from previous experiments it has been shown that at pH 7.0 bed capacity is about 1100 g/m³ (500 grains/cu ft). Though efficiency might appear to be the same, breakthrough occurs earlier and treatment runs are shorter. Fluoride removal efficiency at optimal pH approaches 100 percent, as indicated by treated water fluoride concentration well below 0.1 mg/L during portions of the treatment run at each installation. This efficiency is achieved in waters with different chemistries including varying fluoride levels (Table 2). Superficial residence time (flow time through the bed neglecting the volume of bed material) is also a limiting factor: a 5-min minimum is a practical limit for maximum removal efficiency. Best results occur with flow directed down through the bed. Care must be taken to prevent a wall effect or channeling.

The initial effluent pH is high, with no fluoride removal, as explained in the discussion on neutralization mode. After a short period both pH level and residual fluoride drop to acceptable levels. At that point usable water can be directed to storage or distribution. Fluoride level drops rapidly to a very low level and remains there until breakthrough begins, at which point it increases gradually until the treatment run is terminated.

Treated water pH drops below 6. Because water of this pH is corrosive, the treated water pH must be adjusted to a desirable level (about 7.5) by injection of sodium hydroxide or by blending.

Backwash mode. For two reasons it is important that the bed be backwashed with raw water before each regeneration: first, any suspended solids that have been filtered from the raw water by the treatment bed tend to blind the bed and must be removed; second, even though filtration may not have taken place, the downward flow tends to pack the bed. Therefore, an upflow backwash expands the bed, breaking up any tendency toward wall effects or channeling. A backwash rate of 5–6 mm/s will expand the bed about 50 percent, which is adequate. Care must be taken to avoid backwashing granular bed material out of the treatment unit. Normally, backwash is completed within 10 min.

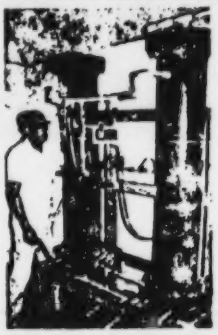
Regeneration mode. The object of regeneration is the removal of all fluoride ions from the bed before any part of the bed is returned to the treatment mode. The most successful regeneration is accomplished in two steps: the first is upflow immediately after backwash while the bed is still expanded, followed by an upflow rinse. The unit is then drained to the top of the treatment bed. The second regeneration step is downflow immediately followed by the neutralization mode. Regeneration steps employ 1 percent (by weight) sodium hydroxide solution flowing at a rate of 1.7 mm/s. With a standard treatment bed depth of 1.5 m, each regeneration step takes 35 min. Chemical consumption in each regeneration step is 27 L of 50 percent NaOH per cubic metre of treatment media (0.2 gal/cu ft). The intermediate upflow rinse flows at a rate of 3.4 mm/s for a period of 30 min. If the treatment bed depth varies from standard, flow rates and times must be adjusted. The regenerant solution is usually an in-line dilution of 50 percent sodium hydroxide with raw water, with the sodium hydroxide maintained at or above 21° C to prevent freezing.

Neutralization mode. The object of this step is to return the bed to the treatment mode as rapidly as possible without dissolving the treatment media. As soon as the second (downflow) regeneration step has been completed, all of the fluoride should have been removed from the bed. At this point the bed is drained again to the top of the treatment media. Raw water with pH adjusted to 2.5 is then fed downflow at the normal treatment flow rate (Fig. 1). Sulfuric acid concentrations again vary with the alkalinity of the specific raw water. The entire bed has a pH range from 12.5 to 13.0, and as the top of the bed begins to

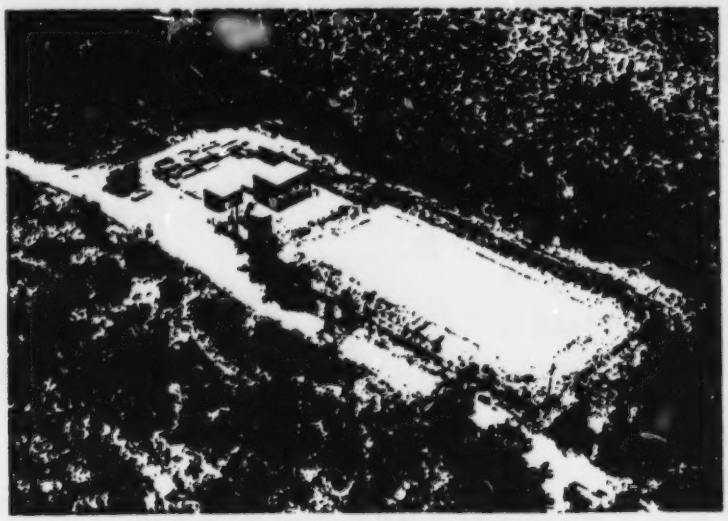
* This is ambiguous: 27 or (2x27 = 54L) ?

TABLE 5
Operating Costs At Existing Treatment Plants

Item	Location					
	Lake Tamarisk		Rincon Water Co.		Gila Bend	
	¢/1000 L	¢/1000 gal	¢/1000 L	¢/1000 gal	¢/1000 L	¢/1000 gal
Treatment chemicals	2.2	8.3	1.3	5.1	1.0	3.7
Operating labor	1.3	5.0	1.1	4.1	1.6	6.0
Electric utility	0.1	0.5	0.1	0.4	0.1	0.6
Media replacement	0.2	0.7	–	–	–	–
Spare parts & misc	0.1	0.3	0.2	0.8	0.2	0.8
Total	3.9	14.8	2.7	10.4	2.9	11.1



Pilot-Plant Equipment in Use at Gila Bend, Ariz.



Aerial View of Rincon Water Co. Treatment Plant, Vail, Ariz.

neutralize and enter a treatment mode, the fluoride level in the treated water starts to drop below that of the raw water. Treated water pH also begins to drop. As the fluoride level drops below the mandatory limit, the water becomes usable and can be directed to storage or distribution. pH may still be high (9.0–9.5) in the treated water; however, this water can be blended with treated water of lower pH from other treatment units. When the pH is 9.0 to 9.5, the raw water pH is adjusted to 4.0 as the bed rapidly neutralizes. When the treated water pH drops to 7.5, the raw water pH is adjusted to 5.5, where it is maintained throughout the remainder of the run.

Initial Start-Up Procedures

When the bed material is first placed into the treatment unit, the vessel should be half filled with water. As the activated alumina is poured into the bed from above, the water dissipates the heat generated by the heat of wetting of the activated alumina, thereby preventing cementing of the bed. The water also aids in separating fines from the granular material; protects the underdrain assembly from impact; and initiates stratification of bed material. Once the bed is in place, it must be backwashed for an extended period until all of the alumina fines are flushed from the virgin bed. The flow is then reversed and downflow treatment begins for the virgin run.

Blending of Treated Water

Blending can take place in either large reservoirs or the treated water main. During a treatment run there is a long period when the fluoride level of the treated water is well below desired levels. As breakthrough occurs there is a long period of slowly increasing fluoride concentration in the treated water. It has been found that treated water can continue to flow to storage or distribution until the fluoride concentration reaches one and one half to two times the maximum allowable level; the resulting total average fluoride level continues to meet the prescribed fluoride level (one half the maximum allowable level).

When there is a large reservoir in which the major portion of a treatment run can be stored, blending takes place there. At locations where the reservoir is not large and there are two or more treatment units, staggered regenerations accomplish the same result; that is, a regenerated treatment unit will produce water of very low fluoride content while a second unit in the later stages of its treatment run may be producing water of a higher fluoride level. By mixing the effluent from the two units in the treated water main, an average fluoride concentration near the prescribed level can be maintained. Similarly, the treated water of high pH occurring early in the run for one unit can be blended with the low pH effluent of another unit in a later stage. The benefit of this blending is short-lived; soon the pH of the blended streams requires adjustment.

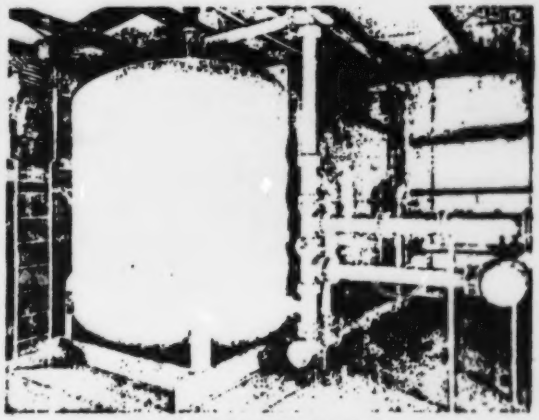
Disposal of Wastewater

The wastewaters resulting from backwash, regeneration, and the early part of neutralization are not suitable for consumption and must be discarded. The backwash water, which is only raw water, can be discharged to existing storm water disposal systems. The only objectionable feature of the regeneration waste is the high concentration of fluoride ions that cannot be returned to the groundwater aquifer. Its high pH can be neutralized. Disposal of waste of high fluoride concentration must comply with local wastewater discharge standards, which vary. Existing plants concentrate the waste in lined evaporation ponds; eventually the concentrated waste must be transferred to an acceptable disposal site or the fluoride must be reclaimed.

The volume of wastewater is approximately 4 percent of the total throughput.

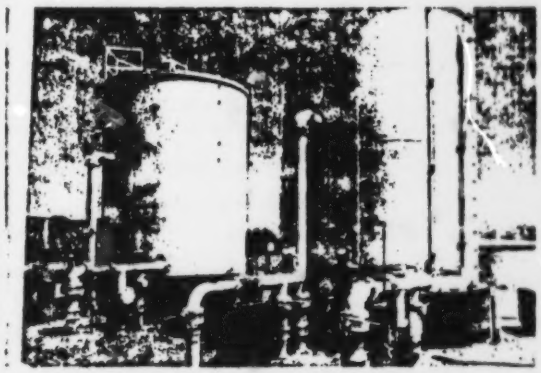
Materials of Construction

The cost of a treatment plant is a function of the quality of the construction materials in its design. Trouble-free, low-cost plant operation can be achieved only by proper selection of materials to meet the service requirements of the process. Without considering the materials for concentrated acid and caustic

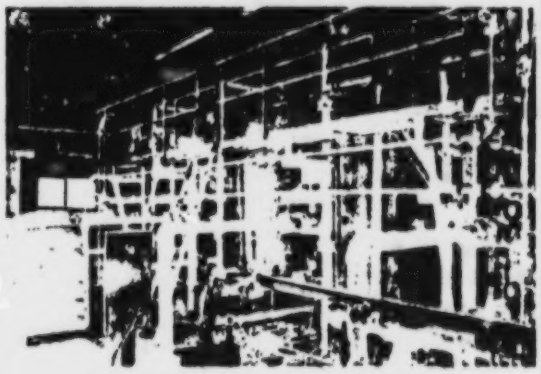


Treatment Units at Gila Bend, Ariz.

Treatment Plant at Gila Bend, Ariz.



Lake Tamarisk Treatment Plant at Desert Center, Calif



Rincon Treatment Unit Acid Line in Foreground

systems, treatment system materials must be suitable for service under the following conditions: (1) potable water system; (2) ambient temperatures (provision for thermal expansion); (3) exposure to sunlight (or protected); (4) pH 2-13; and (5) ease of maintenance (remove and replace with minimum logistics). Materials for the chemical storage and handling systems should comply with chemical manufacturers' guidelines.

Operator Requirements

A qualified operator for a fluoride removal water treatment plant requires thorough fluoride removal process training, preferably at an existing treatment plant. The operator must be able to service pumps, piping systems, instrumentation, and electrical accessories. The operator must be totally informed about the characteristics of sulfuric acid in all concentrations and sodium hydroxide in all concentrations. Safety requirements as to clothing, equipment, and antidotes must be thoroughly understood and executed. The operator must be trained to run routine water analyses including at least two methods for determining fluoride levels. He needs simple mathematics for record keeping during a treatment run and for operation cost accounting. Above all, the operator must be dependable and conscientious.

Cost of Operation

The cost of operating an alumina fluoride removal system including chemicals, electricity, bed replacement, replacement parts, and labor, currently falls in the range of 2-5¢/kL (8-20¢/1000 gal) of treated water. Individual plant operating costs vary as functions of raw water fluoride level, plant capacity, treated water consumption, electric utili-

ty rate, labor costs, delivered chemical costs, and so forth. The low operating costs at the three operational plants discussed in this article are shown in Table 3. The 1977-78 materials and construction costs for the plant at Gila Bend were less than $200 000. The plant was designed for 2.8×10^{3} m³/day (0.75-mgd) average production with peak capacity of 4.8×10^{3} m³/day (1.3 mgd).

Conclusion

Low operating costs for removing fluoride from potable water can be achieved with an activated alumina system. Reliability of plant equipment, materials, and operational costs have been documented through nine years of commercial field experience. Installation and operating costs are compatible with limited public budgets and funding programs. All materials and equipment are available, and there is existing technology to assist in designing a plant to meet fluoride MCLs.

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Not included in the capital costs are engineering, finance charges, real estate cost, and taxes.

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In 1984, two water defluoridation plants, each of 518 m^3/d, were installed to treat minewater containing 6-10 mg/l F as described in Appendix I.

In this case, the original testwork was carried out by the National Institute for Water Research. Final design and construction was by:

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Capital investment for the two plants including the reticulation system was R0.75 million. Operating costs are estimated at U.S. \$0.20/m^3 U.S. \$0.76/1000 U.S. gallons which is relatively high even taking into account that these are smaller plants with higher relative overhead, and the cost includes engineering and taxes.

In this case, the regeneration wastewater is used to pump tailings to the tailings dams.

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CHAPTER 42

IRON Fe

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INTRODUCTION

Iron occurs in solution as ferrous and/or ferric ions depending on pH and dissolved oxygen concentration. At neutral pH and in the presence of oxygen, soluble ferrous iron (Fe^{2+}) is rapidly oxidized to ferric iron (Fe^{3+}) which readily hydrolyzes to form the insoluble precipitate ferric hydroxide $Fe(OH)_3$.

Below pH 6, the rate of ferrous iron oxidation to ferric is extremely slow. Therefore, acid and/or anaerobic conditions are necessary for iron to exist in solution.

In addition, at pH values above 12, ferric hydroxide will redissolve due to the formation of the $[Fe(OH)_4]^-$ complex anion. Also, even in acidic, anaerobic conditions, if a source of sulfide ions is present, iron will be removed from solution as FeS or Fe_2S_3. Ferric and ferrous ions are also solubilized in the presence of cyanide due to the formation of ferri- and ferrocyanide complexes. Such complexes present considerable difficulties for both iron and cyanide removal. Since the sulfide precipitates are more stable than the cyanide complexes, however, addition of sulfide to polish solutions may offer one possible way to remove iron and to render any cyanide ions amenable to oxidation if necessary.

Ferrous ions and ferrous hydroxide are greenish in color. Ferric ions in solution are yellow, but when ferric hydroxide precipitates, the precipitate is red-brown and gelatinous. Acid mine drainage in contact with air turns red brown in color because of the suspension of colloidal ferric hydroxide particles.

Acid mine drainage, which includes water draining or pumped from both underground and open pit mines, seepage and runoff from mine wasterock, tailings ponds, and surface runoff from any area affected by mining (e.g., concentrate stockpile areas, mine-mill-smelter yards, roadbeds, and rail beds constructed with wasterock, etc.), usually contains iron often with minor amounts of other metals, e.g., Cu, Zn, Ni, and Mn.

Iron in acid mine drainage often helps in the removal of other metals because it acts as excellent co-precipitant. However, ferric hydroxide is a gelatinous, difficult to settle precipitate usually with a very low terminal solids density which requires large lagoons for disposal unless special measures are adopted.

OCCURRENCE OF IRON

Surprisingly, iron contamination of water occurs prolifically around mines other than iron mines. Acid mine drainage is one of the most formidable challenges facing the mining industry. It affects base metal mines, especially massive sulfide deposits, uranium mines particularly of the Elliot Lake and Witwatersrand type, gold and silver mines associated with sulfides and, of course, the enormous coal mining industry. It is the ubiquitous occurrence of iron sulfide minerals, e.g., pyrite, pyrrhotite, and marcasite, that generates acid mine drainage on oxidation.

Acid mine drainage inhibition and treatment has been discussed in separate chapters, and most of that discussion would be applicable to this discussion on iron removal.

Iron sulfide minerals may comprise only 1-3% of a mine tailing, or they may be as much as 95% of a tailing material. Both generate acid mine drainage.

In waters of low dissolved oxygen, iron may be reduced to the ferrous form, and some iron may be in solution as the ion. Ferrous iron may be released from lake sediments if the water above the sediments becomes totally anaerobic; the release of iron is the result of a shift in the redox potential below a critical level at the sediment surface according to ONTARIO MOE (1974).

ENVIRONMENTAL IMPACT OF IRON

Iron is an essential mineral constituent for just about all life forms.

In the public water supply, soluble iron at levels in excess of 0.3 mg/l Fe can cause staining of tile surfaces.

Excessive levels of iron in drinking water (around 0.5 ppm and more) start to impart a flavor to water, and 1.0 mg/l Fe is cause for rejection as drinking water.

Iron in receiving waters (lakes and streams) interferes with aquatic biota. It is the fouling properties of iron hydroxide that apparently does more damage than soluble iron in water. There are several types of impact:

1. Impairment of fish larvae respiration.
2. Impairment of gill action through fouling.
3. Impairment of streambed habitats by formation of ferricrete.
4. Fouling of streambed plants and algae.

It is concluded that iron released into the aquatic environment will almost always be precipitated. Fine flocs formed at low iron concentrations may sometimes do more damage than large flocs formed at higher iron concentrations.

The criteria for total iron levels in freshwater at which the environment is protected is 300 ug/l total iron in Canada, and 1,000 ug/l total iron in the U.S.A. U.S. EPA (1972), CANADA (1979).

In the marine environment, a criteria level of 300 ug/l has been set by U.S. EPA (1972). ONTARIO MOE (1979) provides a lengthy discussion on the effects of iron on several aquatic algae and organisms which was found to be highly variable. Below 300 ug/l Fe, it was concluded, all aquatic species would be protected since below this level iron flocs would be unlikely to form.

Another environmental effect of iron in solution is the pH reduction that occurs during the hydrolysis of ferrous to ferric iron.

REGULATORY LIMITS FOR IRON

In reviewing the permits for discharge of effluents encountered during the course of this investigation, it was found that iron is not very often included. The only cases found which limit iron levels in their discharge are as follows:

	Iron Total Limit (mg/l)
Mount Emmons, Colorado NPDES	1.0
NORANDA Grey Eagle Zero Discharge Except Excess Water Can Be "Irrigated" After Treatment	0.20
Climax Molybdenum, Climax, Colorado	0.60
Typical Arizona Copper Concentration	
25-Hour Max.	1.00
30-Day Ave., Max.	0.50
Public Water Supply, U.S. EPA (1976)	0.30
Public Water Supply, Canada (1979)	0.05
South African Drinking Water SABS (1971)	
Recommended Maximum	0.10
Rejection Limit	1.00

TREATMENT FOR IRON

The most usual treatment process for iron is oxidation to ferric and precipitation of ferric hydroxide near pH 7 where the solubility of iron is at a minimum. Often, when other metal ion contaminants must be removed as well, a somewhat higher pH is employed.

Fe (ug/L) IRON

Summary of North American Water Quality Criteria for Iron

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	1,000	--	<300 *	--	--	300	300-1,000	300	--
MAX. PERMISSIBLE LIMIT		--	--	--	--	300	10-300	--	--	--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<50	--	--	< 50 *	--	--	--	300-1,000	--	--
MAX. PERMISSIBLE LIMIT		300	--	--	<300 *	--	--	--	--	--	--
PUBLIC WATER SUPPLY		300	300	--	50	300	50-100 (obj) 300 (limit)	--	--	300	300
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	No upper Limit	(300)	--	--	--	--	--	--	--	--
	IRRIGATION	5,000	(300)	--	5,000	5,000	--	--	--	--	--

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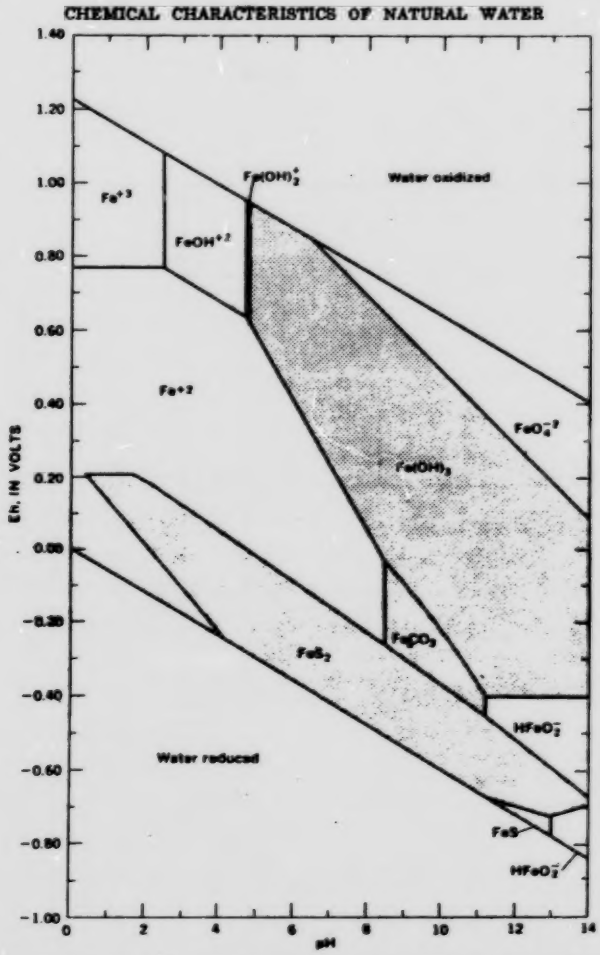

FIGURE 14.—Fields of stability for solid and dissolved forms of iron as function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of sulfur species 96 mg/l as SO_4^{-2}, carbon dioxide species 1,800 mg/l as HCO_3^-, and dissolved iron 0.0086 mg/l.

At pH 7.0-7.5 and above, conversion of ferrous to ferric iron occurs very rapidly as described in the section on acid mine drainage treatment. Spontaneous formation of ferric hydroxide then results in iron removal by precipitation.

JOBIN and SHOSH (1972) found that the rate of ferrous oxidation is dependent on pH, buffer intensity in bicarbonate systems, and upon the concentration of organic matter. Organic compounds containing hydroxyl and carboxyl functional groups seem to greatly reduce oxidation rates and can result in high soluble iron levels if the organic substances do not readily break down.

If iron is present in acid waters as the ferric ion, simply neutralizing the acid will precipitate the iron.

In some cases where there is a significant quantity of dissolved CO_2 in the water, this will be present as bicarbonate HCO_3^- in the acidic water. The bicarbonate/carbonate system buffers the water and consumes more lime than would otherwise be required to increase the pH over 7. By vigorous aeration of the water to remove CO_2 from solution, it is possible to reduce the amount of lime needed to modify the pH and precipitate iron. This process is applied at BETHLEHEM STEEL CORP.'s Panther Valley Division anthracite coal mine water treatment plant.

Iron removal from municipal water supplies has been practiced for many years. Iron levels in ground water supplies are characteristically 1-10 mg/l as ferrous iron. Ground waters are typically anoxic and weakly acid, usually high in CO_2. Aeration to remove CO_2 (and consequently increase pH) and to oxidize ferrous to ferric comprises the standard municipal water treatment. Lime is frequently employed for additional pH adjustment. The following table summarizes the treatment performance for some municipal iron treatment plants as reported by PATTERSON (1975).

SUMMARY OF MUNICIPAL PLANT PERFORMANCE FOR IRON

Process	Iron Concentration mg/l		
	Influent	Effluent	Reference
1. Chlorination, Alum-Lime-Sodium Silicate Precipitation and Sand Filtration	1.5	0.05	HANEY (1964)
2. Aeration, Lime, Sand Filtration	2.4	0.0	HANEY (1964)
3. Aeration, Sand Filtration	2.5	0.13	GARDNER and STIKA (1964)
4. Aeration, Coke Bed Filtration, Sedimentation, Sand Filtration	5.7	0.13	McCRACKEN (1961)
5. Lime, Aeration, Diatomite Filtration	10	1.10	KOLLIN (1962)

In the treatment of acid mine drainage, it is usually necessary to neutralize relatively high concentrations of acid and to precipitate considerably higher concentrations of iron;

this consumes much more lime and generates much larger volumes of precipitate sludges which must be disposed of.

TREATMENT OF IRON IN ACID MINE DRAINAGE

Treatment Chemical	pH	Initial Iron (mg/l)	Effluent Iron (mg/l)	Reference
Limestone Slurry		145	5	PATTERSON (1975)
Lime		157	1.6	PATTERSON (1975)
Soda Ash		126	2.3	PATTERSON (1975)

During the course of this investigation, the following iron removal results were idendified:

Operation	Reagent	Treatment pH	Iron in Influent (mg/l)	Iron in Effluent (mg/l)	Plant Capacity
AMAX, Mount Emmons	Lime, F_L, F	10.6	27-800	0.05-0.30	11,000 m^3/d
Brunswick Mining	Lime, D	9.03	951	2.35	
ERPM - Rand Mines	HDS	7.3	650	Nil	50,000 m^3/d
ERPM - Rand Mines	R.O. Pilot	4.5	6.0	0.06	5 m^3/d
Falconbridge, Onaping	Limestone, D	7.0	2-4	0.04-0.60	-
Gilman, Colorado	Lime, D	9.60	50-180	0.10-1.20	500-700 m^3/d
INCO, Copper Cliff	Lime, S	10.0	13.4	0.35	272,000 m^3/d
JABILUKA Uranium	Lime, S	8.0	2,000	1.0	-
Noranda, Waite-Amulet	Lime, HDS	9.80	254	1.40*	4300 m^3/d
Ontario Cu, Pb, Zn Mill G	Lime, HDS	8.9	676	0.77	4300 m^3/d
Ontario Cu, Pb, Zn Mill M	Lime, S	10.2	4.70	0.48	4000 m^3/d

* Drops to 0.30 mg Fe/l in polishing pond decant.

LIME: Lime Neutralization
FL: Precipitate Flotation
F: Multi-Media Filtration
D: Decantation

HDS: High Density Sludge Process
S: Settle in Thickener-Clarifer
R.O.: Reverse Osmosis

TREATMENT COSTS

Operation	Plant Size	Cost/m³	Capital
INCO Copper Cliff	272,000 m³/d	US $0.06/m³	C $4.1 Million (1975)
Eastern Canada Mine #6	2,900 m³/d	US $0.60/m³	
Falconbridge, Sudbury	16,000 m³/d	US $0.01/m³ (1979)	C $257,000 (1978)
R. Osmosis	Conceptual	US $0.50/m³	

DISCUSSION

1. The HDS process described in Appendix I in trip reports for:

   RAND MINES, ERPM
   KROMDRAAI COAL MINE
   NORANDA, GECO
   NORANDA, WAITE-AMULET

   The HDS process offers a significant advantage in the treatment of acid mine drainage containing high levels of iron in that a dense, stable sludge can be produced which is compact and safe to dispose of and non-amphoteric.

2. In the section on acid mine drainage, HDS application at several additional operations is discussed in which sludges with up to 50% solids are generated.

3. BETHLEHEM INTERNATIONAL ENGINEERING CORP., Bethlehem, Pennsylvania, has shown that HDS sludge from acid mine drainage yields a stable waste material when mixed with a pozzolan that is suitable for landfill disposal.

4. The Wannamaker Continuous Concentrator has been demonstrated for acid mine drainage treatment from the Argo tunnel. This is a form of cross-flow micro-filtration technology using sludge recycle which also achieves a relatively low iron value in the treated effluent and a precipitate with a higher percent of solids.

5. The USBM at Pittsburgh has shown the effect of a natural bog in raising the pH of acid mine drainage and precipitating iron as ferric hydroxide.

6. BARRET, HAENTJENS AND CO. of Hazelton, Pennsylvania, has developed a new jet pump which effectively flash-precipitates iron from acid mine drainage at a lower pH. This device is described in the section on AMD treatment.

7. Although various processes will be needed to polish effluents from mining and milling operations, the magnitude of the acid mine drainage problem is so great that attention will have to focus on prevention of the problem rather than treatment technology.

8. It was pointed out above that neutralization of acid mine drainage to a pH in excess of 7.0 at which ferrous ions oxidize rapidly to ferric ions can be quite expensive. An interesting innovation in this respect was proposed and described by MIHOK (1969) who found in laboratory batch flow tests conducted with high iron acid mine drainage treated with activated carbon that the iron was rapidly catalytically oxidized by the activated carbon. The ferrous iron content of an acid mine water flowing through an aspirated activated carbon column was reduced from around 700 to 10 ppm in less than one minute at pH around 2.5.

   The activated carbon was used repeatedly with little loss in efficiency and no discoloration or solids deposition. In the batch tests, about one-third of the iron was adsorbed by the carbon, but with continuous flow, little iron adsorption is expected. (No reasons were given.)

   It was proposed that a catalytic oxidation step in the treatment of acid mine waters containing ferrous iron would facilitate neutralization providing precise control of pH, lower reagent costs, and elimination of aeration equipment. Also, limestone might possibly then be suitable for acid mine drainage neutralization which would result in further cost savings compared with lime, provided ferruginous coatings that passify limestone can ve avoided.

   Although this revelation was made in 1969, no commercial application has been identified. No reasons for this were identified. In the original tests, a commercial type coal-base activated carbon 12 x 40 mesh was used.

9. At Jabiluka Uranium, LEVINS (1979) reported levels of 2,000-5,000 mg/l Fe in acidic uranium ore leach tailings/raffinate waste at the Alligator Rivers region of Northern Territory, Australia. After adjustment to pH 8, the iron level dropped to 1 ppm. Several other contaminants are precipitated when lime is added to pH 8, including Al, Ba, Cr, Cu, Mg, Mn, Pb, U, V, Zn, P, Si, and SO_4, which all would accumulate in the precipitate sludge.

10. <u>Biological Oxidation of Ferrous Iron Aids Precipitation</u>: WICHLACZ (1985) described the kinetics of ferrous iron Fe(II) oxidation by attached bacteria in bench-scale

rotating biological contactors (RBC). Oxidation efficiencies of better than 80% were obtained over the range of Fe(II) mass loadings tested (0.14-2.34 mg Fe(II)/ cm^2/hr.). The amount of oxidation and the rate depended on a combination of influent and bulk fluid Fe(II) concentration as well as flow rate. A model describing attached bacterial growth and oxidation rate as a saturation function of substrate utilization was developed and tested. The maximum oxidation rate constant was proportional to flow rate, and the substrate concentration in the reactor varied with influent substrate concentration. The model allowed prediction of metabolic constants and included terms for both constant and growth rate dependent maintenance energies.

Toward the end of Chapter 25 on "Removal of Contaminants," reference is made to additional testwork in which rotating biological contactors have been used to oxidize ferrous to ferric.

P. L. WICHLACZ
E. G. & G. Idaho, Inc.
Idaho Falls, ID

11. Dissolved Air Flotation: An expensive aspect of neutralization and precipitation plants is the removal of the iron hydroxide precipitate. Clarification plants are sized for the hydraulic flow rate pretty much regardless of the precipitate loading being removed from suspension. BOSMAN (1983) of the ANGLO AMERICAN RESEARCH LABORATORIES pointed out that for low precipitate loadings, dissolved air flotation can offer a much more compact clarification step. Since the volume of precipitate in such cases is small in any case, solids density of the floated concentrate is pretty much irrelevent.

    This aspect is also discussed in chapters 12 and 24 on removal of suspended solids and acid mine drainage treatment.

12. Reverse osmosis using the seeded slurry innovation has been successfully demonstrated at RAND MINES LTD. ERPM mine as described in the Appendix I trip report. At pH 4.5, a 95% plus water recovery was achieved, and the iron content was reduced from 6.0 ppm to 0.06 ppm. WILMOTH and SCOTT (1976) found that Fe^{2+} ions could be removed from 64 ppm to 0.5 ppm in their tests of R.O., also yielding a product water at pH 4.5.

    A summary of the results achieved by WILMOTH and SCOTT (1976) is provided in the following table:

Chemistry Analyses Illustrating Effluents from Various Processes to Treat AMD

Sample	*Cond*	*Acid*	*pH*	*Ca*	*Mg*	*Total iron*	*Fe^{2+}*	*Na*	*Al*	*Mn*	*SO_4*	*Alk*	*TDS*
Example One - Limestone Neutralization: Ferrous(A) versus Ferric(B) Using No Coagulants													
Raw feed A	4,000	610	5.2	360.	110.	270.	260.	480.	5.4	5.9	3,000	12.	4,200
Feed B (H_2O_2)	4,000	590	3.1	340.	95.	270.	0.	440.	8.2	5.9	2,500	0.	3,500
Effluent A	4,000	230	6.5	420.	90.	150.	150.	380.	1.0	5.8	2,400	88.	3,500
Effluent B	4,000	13	6.5	380.	70.	6.2	0.	370.	1.2	5.0	2,000	50.	2,900
Example Two - Limestone Neutralization with Extended Aeration, Sludge Recycle, and Coagulant Addition													
Raw feed	3,650	460	5.5	370.	110.	230.	220.	470.	12.	5.4	2,800	8.	4,000
Effluent	3,650	0	7.4	520.	110.	0.9	0.	440.	0.4	3.9	2,700	47.	3,700
Example Three - Lime Neutralization Comparing *p*H 8(A) versus *p*H 7(B) Using Coagulant Addition													
Raw feed	4,000	520	5.7	400.	130.	280.	260.	510.	9.8	6.4	3,200	23.	4,500
Effluent A	4,100	0	7.9	600.	120.	2.1	0.	500.	0.4	1.6	3,300	88.	4,700
Effluent B	4,100	0	7.0	620.	120.	10.	0.7	490.	0.6	4.9	3,300	50.	4,400
Example Four - Combination Limestone-Lime Treatment(A) versus Lime Treatment(B) Using Coagulants													
Raw feed	3,600	630	5.2	340.	100.	290.	270.	380.	15.	5.4	2,700	4.4	3,800
Effluent A	3,500	0	8.0	560.	83.	2.3	0.	370.	0.5	2.2	2,500	100.	3,500
Effluent B	3,500	0	8.0	560.	95.	1.4	0.	360.	0.2	1.2	2,500	110.	3,500
Example Five - Lime-Soda Treatment Where Effluent Hardness Is Less Than 100 mg/liter													
Raw feed	820	170	3.0	28.	18.	17.	—	1.8	13.	4.5	270	0.	350
Sed. eff.	930	0	11.	140.	1.1	0.8	—	1.8	2.7	0.2	240	100.	500
Softener eff.	1,000	0	10.8	41.	0.4	0.3	—	140.	2.5	0.05	220	110.	510
Recarb. eff.	790	0	9.2	33.	0.4	0.3		140.	2.4	0.06	220	74.	470
Example Six - Alumina-Lime-Soda Treatment													
Raw feed		700	2.8	8.	25.	100.	—	2.	40.	4.0	750	0.	950
Effluent		0	7.5	20.	10.	0.3	—	150.	0.2	0.04	250	—	450
Example Seven—Reverse Osmosis Treatment													
Raw feed	1,000	240	3.4	130.	90.	77.	64.	—	12.	12.	750.	0.	1,300
Waste brine	3,600	810	2.9	490.	310.	330.	250.	—	44.	24.	2,800.	0.	4,500
Effluent	17	32	4.5	0.5	0.6	0.5	0.5	—	0.2	0.08	2.2	0.	5
Example Eight - Ion Exchange Treatment (Design Values)													
Raw feed	—	240	3.4	130.	90.	77.	64.	1.0	12.	12.	750	0.	1,300
Cation eff.	—	800	1.9	13.	5.	6.	5.	3.	0.2	0.6	750	0.	800
Anion eff.		0	8.0	13.	1.5	1.2	1.0	20.	0.2	0.3	40	20.	110
Neu. eff.	—	0	7.5	20.	1.5	0.1	0.1	20.	0.2	0.04	50	30.	120

Note: All units are mg/liter except for conductivity (micromhos/cm) and *p*H. Alkalinity and acidity are expressed as $CaCO_3$.

It is noted in the above table that ferrous iron could be reduced using H_2O_2 as an oxidant and limestone from 270 mg/l to 6.2 mg/l, although the same solution with limestone addition and extended aeration reached pH 7.4 and iron was reduced to 0.9 mg/l.

CATALYTIC OXIDATION OF IRON

In Chapter 39 where removal of copper is discussed, a paper by FAULKNER (undated) describes how iron can be catalytically oxidized from ferrous to ferric with the use of SO_2 and activated carbon, even at an acid pH.

CALGON CORPORATION
Activated Carbon Division
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
William D. Faulkner

KAIDA, et al. (1978) described a bench scale treatment of mine effluent containing iron, copper, Cd, and zinc. The process employs catalytic air oxidation of ferrous to ferric ions using $NaNO_2$, allowing fractional precipitation of ferric hydroxide prior to removal of other metals.

Both of these processes are petentially useful.

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CHAPTER 43

MANGANESE Mn

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OCCURRENCE OF MANGANESE IN THE MINE-MILL ENVIRONMENT

Manganese, although not nearly as abundant as iron in rocks and soils, is nonetheless very abundant. Manganese frequently occurs in mine drainage and is often associated with zinc, copper, and silver ores. In South Africa, MnO_2 is used as an oxidant in uranium leaching with the consequence that Mn^{2+} can occur at high levels in uranium plant tailings and raffinates.

The PEDCO (1983) report which lists the findings of analyses of thousands of mine waste, mill tailings, and mine water samples from mines in the U.S.A., leads to the conclusion that manganese is relatively susceptible to the acetic acid leach tests from mined materials used in the EPA's EP leach test criterion for "hazardous waste."

MAREE and DEWET (1980) showed how manganese in the Vaal River suddenly increased in acidified river water from 140 mg/l to 4400 mg/l at Orkney, Transvaal, where it caused a problem in treatment for use as municipal service water. It was suspected at the time that seepage of gold-uranium mill effluents and runoff from manganiferous soils could have been responsible. Since then, manganese levels have dropped to much less than 1 mg/l as a result of advanced, yet simple, water management and practices by mines from which effluents drain into the Vaal River in that area. (Drainage from several mining companies enters the Vaal River upstream of Orkney.)

HILL (1972) reported manganese in mine waters at 1.2-8.0 mg/l, and KUNIN and DOWNING (1971) reported one acid mine drainage flow with 50 mg/l Mn.

At ENOXY COAL, INC., Buckhannon, West Virginia, coal waste is mixed with a carbonate rock to avoid the generation of acid mine drainage. Although the carbonate rock does inhibit the generation of acid, manganese in the carbonate waste rock goes into solution and reaches 30-150 ppm. This manganese is difficult to remove. To precipitate manganese, at a pH of over ten is needed; then the treated water must be pH adjusted to meet effluent pH limits, all of which require expensive reagents according to:

ENOXY COAL, INC.
Post Office Box 710
Buckhannon, WV 26201
(301) 447-9272
Allan Meek

SUMMARY OF PEDCO (1983) DATA (mg/l or ug/g)

	Surface Mine Waste T	Surface Mine Waste A	Surface Mine Waste W	Underground Mine Waste T	Underground Mine Waste A	Underground Mine Waste W	Untreated Mine Water	Mine Water Pond Settled Solids T	Mine Water Pond Settled Solids A	Mine Water Pond Settled Solids W	Tailings Pond Solids T	Tailings Pond Solids A	Tailings Pond Solids W	Tailings Pond Liquid	Leach Liquors
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
URANIUM-OTHER															
Ave.	570	2.4	0.23	84.6	4	0.01	0.63	180	4.53	L	-			-	
No. of Samples	6	6	5	8	8	6	3	3	3	L	-			-	
Minimum	123	0.03	0.10	93.6	1.34	0.01	0.19	108	3.8	L	-			-	
Max.	1090	8	0.42	3510	7.5	0.01	1.22	250	8.6	L	-			-	
SOUTHWESTERN COPPER															
Ave.	225	1.49	4.36								268	3.2	0.06	0.30	640
No. of Samples	14	1.3	8								6	6	1	6	3
Minimum	35.7	0.09	0.02								57.3	0.05	-	0.01	550
Max.	373	5.10	34								687	10.7	-	1.40	710
COPPER-OTHER															
Ave.	938	2.15	0.80	-	-	-	-	-	-	-	369	5.5	0.68	100	110
No. of Samples	7	7	6								7	6	7	3	1
Minimum	93.4	0.53	0.04								10	1.29	0.03	0.09	
Max.	2640	7.3	1.5								1050	9.8	2.65	300	
WESTERN LEAD-ZINC															
Ave.	10400	4.2	0.76				78				1610	18	3.3	1.5	
No. of Samples	2	2	2				1				1	1	1	1	
Minimum	7950	2.6	0.63												
Max.	12900	5.8	0.88												
MISSOURI LEAD-ZINC															
Ave.				1310	1.6	0.4					1030	2.13	0.07		-
No. of Samples				1	1	1					3	4	4		
Minimum											411	0.84	0.03		
Maximum											2100	4.01	0.12		
MOLYBDENUM															
Ave.	369	1.10	0.32	846	7.35	0.08	23	-	-	-	715	5.25	0.54	4.26	-
No. of Samples	2	2	2	2	2	2	3				3	3	3	3	
Minimum	169	0.24	0.22	615	6.5	0.05	12				212	0.74	0.16	0.29	
Maximum	568	2.00	0.42	1080	8.2	0.12	41				1380	9.6	0.77	9.50	

SUMMARY OF PEDCO (1983) DATA (mg/l or ug/g) (Continued)

	Surface Mine Waste T	Surface Mine Waste A	Surface Mine Waste W	Underground Mine Waste T	Underground Mine Waste A	Underground Mine Waste W	Untreated Mine Water	Mine Water Pond Settled Solids T	Mine Water Pond Settled Solids A	Mine Water Pond Settled Solids W	Tailings Pond Solids T	Tailings Pond Solids A	Tailings Pond Solids W	Tailings Pond Liquid	Leach Liquors
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
NEVADA GOLD-SILVER															
Ave.	239	1.61	0.03	-	-	-	-	-	-	-	337	2.34	0.009	0.55	-
No. of Samples	5	5	3								4	4	3	2	
Minimum	126	1.23	0.01								71.8	0.99	0.001	0.008	
Maximum	325	2.10	0.07								635	4.35	0.02	1.1	
OTHER GOLD-SILVER															
Ave.	18.4	0.04	0.23	3960	10.3	3.63	-	-	-	-	6110	72.2	2.97	0.12	-
No. of Samples	2	2	2	3	3	3					5	5	4	4	
Minimum	13.4	0.02	0.05	3190	0.01	0.19					25.4	0.01	0.01	0.02	
Maximum	23.4	0.07	0.40	4910	16	7.80					19500	201	10.8	0.20	
TACONITE															
Ave.	3830	3.35	0.23	-	-	-	0.47	-	-	-	4340	19.3	0.17	3.89	-
No. of Samples	13	13	6				2				8	8	6	4	
Minimum	261	0.42	0.01				0.43				433	0.016	0.008	0.03	
Maximum	19300	9.9	0.99				0.51				7340	76	0.36	15	

T = Total A = Acetic Acid Leach W = Water Leachate

Mn (ug/L) MANGANESE

Summary of North American Water Quality Criteria for Manganese

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	--	--	--	Undefined Tolerance Limits	10-50	50	100-1,000	50	--
MAX. PERMISSIBLE LIMIT		--	--	--	--		50	--	--	--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<20 .02 (96-hr LC50)	100	--	<100 *	--	--	--	100-1,000	--	--
MAX. PERMISSIBLE LIMIT		100	--	--	100 *	--	--	--	--	--	--
PUBLIC WATER SUPPLY		50	50	--	<10	50	50 (limit)	(50)	--	50	50
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	-- Only few notes	(50)	--	--	--	--	(50)	--	--	--
	IRRIGATION	200	(50)	--	200	200	--	(50)	--	--	--

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ENVIRONMENTAL SENSITIVITY OF MANGANESE

Manganese is undesirable in the public water supply. Even very low levels, manganese causes staining of plumbing fixtures and ceramic tilework.

The U.S. EPA (1972, 1976) shows a public water limit for manganese of 0.05 mg/l manganese. CANADA (1979a, b) has set a limit for manganese in the public water supply of 0.01 mg/l.

At 1.0 ppm Mn and more, the hatchability of trout eggs has been found to be affected.

The ONTARIO MOE (1979) discussion of the rationale for establishment of Ontario's Provincial Water Quality Objectives does not review manganese. The U.S. EPA and Canada do not define criteria for manganese at which the environment is considered protected. In U.S. EPA (1976), an objective of 100 ug/l Mn is established for marine water. The U.S. EPA does not state whether this is total manganese or soluble Mn.

Information on the toxicity of manganese to aquatic life (both freshwater and marine) is very limited. DAVIES (1981) found that the LC_{50} of manganese for trout in soft water ranged between 14.5 and 30.0 ug/l. The hardwater LC_{50} for 20 cm fish was 116 ug/l.

REGULATORY LIMITS FOR MANGANESE

Quebec has set a maximum limit of 0.05 mg/l for manganese in receiving waters. There does not seem to be any factual substantiation for this limit other than the fact that this limit is the same as for drinking water.

The U.S. EPA maximum permissible limit in marine waters is 0.10 mg/l Mn.

The U.S. EPA (1972, 1976) limit for the public water supply is 50 ug/l.

The South African Bureau of Standards (1971) standard for manganese in drinking water is 0.1 mg/l recommended and 0.4 mg/l maximum allowable.

The SOUTH AFRICAN GOVERNMENT GAZETTE (1962) does not list a limit for manganese in the General Limit for Effluents. However, in the SPECIAL LIMIT which was designed for effluents discharging into a list of specific creeks and rivers (supposedly those that are capable of supporting trout), a limit of 0.01 mg/l Mn was imposed.

During the course of this investigation, the only examples of Mn limits in effluents found were as follows:

MANGANESE-SOLUBILITY CONTROLS

The solubility of manganese in natural water and the predominant dissolved forms to be expected can be effectively summarized by means of Eh-pH diagrams.

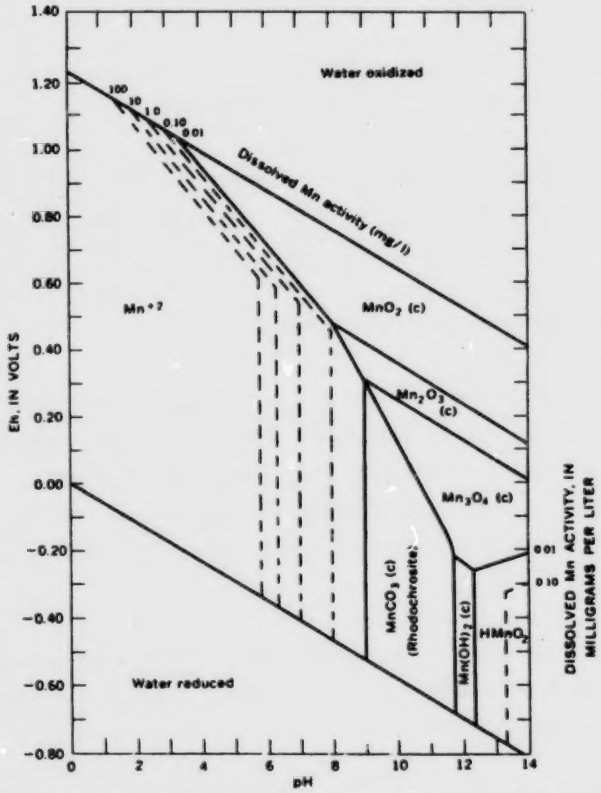


FIGURE 16.—Fields of stability of solids and solubility of manganese as a function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of dissolved carbon dioxide species 100 mg/l as HCO_3^-. Sulfur species absent.

	MANGANESE
	Mn_T (mg/l)
Mount Emmons	1.0
Climax Molybdenum Co.	
25-Hour Max., 30d Ave.	1.0
New Mexico Water Quality Control	
Commission, August 27, 1971	0.10
Gilman, Colorado	1.0

TREATMENT FOR MANGANESE

The solubility diagram for manganese in water inserted above was provided by HEM (1970) and indicates that to precipitate Mn^{+2} as a hydroxide, a pH of close to 12 is needed.

Of the various oxidation states of manganese, only the strongly oxidizing form permanganate and the divalent manganese in manganous ions are soluble in water.

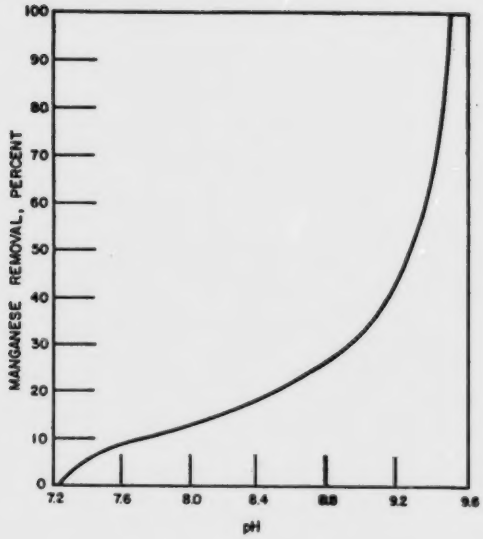
Removal of soluble manganese has been practiced for many years in the treatment of municipal water supplies and industrial process waters.

Treatment technology basically involves the conversion of the soluble manganous ion to an insoluble precipitate. In water treatment, this generally means simultaneous removal of iron since conditions under which high iron levels occur in water supplies are essentially the same as for soluble manganese. Removal of manganese is achieved by oxidation of the manganous ion and by separation of the resulting insoluble oxides and hydroxides of manganese.

Because of the low reactivity of manganous ions with oxygen, simple aeration is not an effective oxidation technique below pH 9, and even above pH 9, the air oxidation reaction is slow according to WELCH (1963).

BORGREN (1962) found that organic matter in solution can combine with manganese and prevent its oxidation by simple aeration, even at a high pH.

OWENS (1963) showed the effect of pH on manganese removal by lime. A reaction above pH 9.4 is required to achieve significant manganese reduction.



Effect of pH on efficiency of manganese removal using lime.
[From Owens (7), courtesy of *Water and Sewage Works.*]

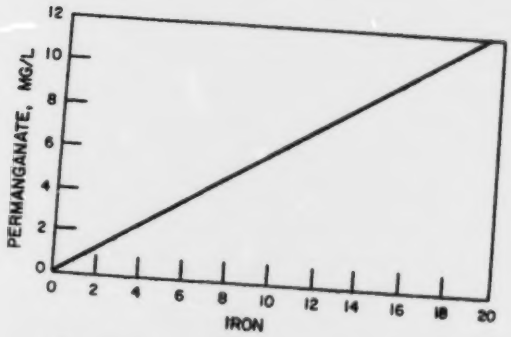
HILL (1972) reported that manganese can be reduced to less than 0.5 mg/l by simple neutralization and precipitation, but no pH values were mentioned. The use of calcium carbonate plus lime for iron and manganese removal from Japanese acid mine waters had proven successful.

The use of chemical oxidants to convey manganous ions to insoluble manganese dioxide in conjunction with coagulation and filtration has been recommended, although BORGREN (1962) reported that this may cause filtration problems. Apparently, the type of manganese flocs produced when strong oxidants are used tends to clog sand filters.

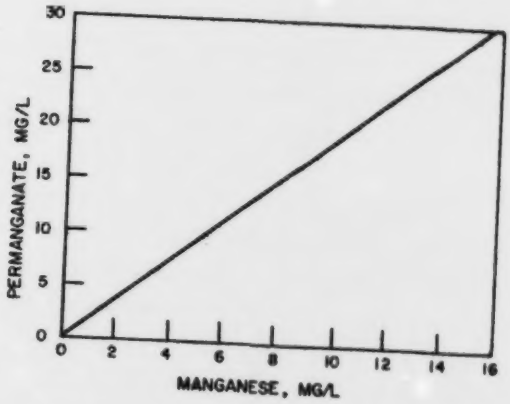
WELCH (1963) reported that manganese oxidation by chlorination may not be effective. OWENS (1963), on the other hand, reported removal of manganese at concentrations as high as 5.7 mg/l with chlorination followed by lime coagulation and rapid sand filtration. Sodium silicate was used as a coagulant aid. This is similar to the process currently in use by the Rand Water Board at their regional water supply treatment plant at Vereeniging, South Africa, which treats Vaal Dam water.

According to HARRIS (1962), effective manganese oxidation by chlorination requires a free chlorine residual of 0.5 mg/l and a dosage of 1.29 mg chlorine per mg manganese oxidized.

The successful use of potassium permanganate as a chemical oxidant has been reported. Addition of 1.5-2.0 mg/l of potassium permanganate reduced 1.0 mg/l of manganese to less than 0.05 mg/l according to HANEY (1964).



Permanganate requirement for oxidation of ferrous iron. [From Willey and Jennings (10), courtesy of American Water Works Association.]



Permanganate requirement for oxidation of manganeous manganese. [From Willey and Jennings (10), courtesy of American Water Works Association.]

$KMnO_4$ was added 30 minutes upstream from the prechlorination point which was followed by lime-alum-sodium silicate coagulation (4-10 hours retention) and rapid sand filtration.

Since iron is generally present, the quantity of permanganate used must include that needed for oxidation of the iron content. The stoichiometric relationship between permanganate required and the quantity of iron and manganese present is shown in diagrams reproduced from PATTERSON (1975) above.

HOLLAND (1964) demonstrated the ability to remove manganese at lower pH with simultaneous removal of iron by permanganate oxidation. The addition of 0.04 mg/l sodium alginate reduced 0.35 mg/l manganese to less than 0.02 mg/l in the filtered supernatant. BORGREN (1962) further pointed out an additional advantage of permanganate over chlorination as the absence of residual taste or odor.

CONSTABILE and PERRON (1971) described the use of a vacuum diatomite filter in conjunction with permanganate oxidation for manganese removal from a municipal water supply. Manganese was reduced from 1.23 mg/l to 0.05 mg/l or less. The unit required 250 lbs. diatomite per million gallons filtered (30g diatomite/m^3).

Permanganate may be used indirectly for manganese removal in the manganese greensand filter method. The filter is a combination of New Jersey glauconite (greensand), manganese sulfate, and potassium sulfate which results in a filter bed of sand grains containing high oxides of manganese as described by WILLEY and JENNINGS (1963). Upon contact with manganous ions, an oxidation-reduction reaction occurs resulting in the formation of insoluble manganese dioxide which remains in the filter bed. The bed is periodically reoxidized with permanganate, and solids are backwashed from the bed. With this system, manganese was reduced from 1.7 mg/l to zero at pH 7.2 using a pressure greensand system (ALLING, 1963). This plant, with 500-700 gpm (2,700-3,800 m^3/d), cost only a third in capital compared with a conventional aeration, lime coagulation-clarifer-filter-recarbonation system. A permanganate dosage of 13 mg/l was used. The water had a manganese concentration of 13 mg/l manganese. Treatment costs in absolute terms are meaningless because it was so long ago, but these were comparable with lime costs for conventional treatment. This plant was continuously regenerated with periodic backwashing of the greensand filter. Generalized removal capacities for greensand filters are given as 0.09 pounds manganese per ft^3 of filter volume with regeneration requirements of 0.18 lb/ft^3 of $KMnO_4$.

Flow rates of 3 gpm/ft^2 are considered normal by ALZENTER (?).

NETZER, et al. (1975) investigated the use of ozone in conjunction with lime as a manganese removal technique in laboratory studies. The following results were reported by PATTERSON (1975) for solutions of manganous chloride initially containing 94 mg/l manganese:

See Chloride Removal

United States Patent [19]

Bolton et al.

[11] **4,379,037**

[45] *** Apr. 5, 1983**

[54] **REMOVAL OF MANGANESE AND CHLORIDE IONS FROM AQUEOUS ACIDIC ZINC SULPHATE SOLUTIONS**

[75] Inventors: **Gerald L. Bolton, Fort Saskatchewan; Verner B. Sefton; Nicolaus Zabryckyj, both of Edmonton, all of Canada**

[73] Assignee: **Sherritt Gordon Mines Limited, Toronto, Canada**

[*] Notice: The portion of the term of this patent subsequent to Sep. 22, 1998, has been disclaimed.

[21] Appl. No.: **271,723**

[22] Filed: **Jun. 8, 1981**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 86,877, Oct. 22, 1979, Pat. No. 4,290,866

[30] **Foreign Application Priority Data**

Dec. 20, 1978 [GB] United Kingdom 49267/78

[51] Int. Cl.[3] C25C 1/16; C25B 1/26

[52] U.S. Cl. 204/119; 204/114, 204/128; 423/50; 423/500

[58] Field of Search 423/50, 500, 502; 204/114, 119, 128

[56] **References Cited**

U.S. PATENT DOCUMENTS

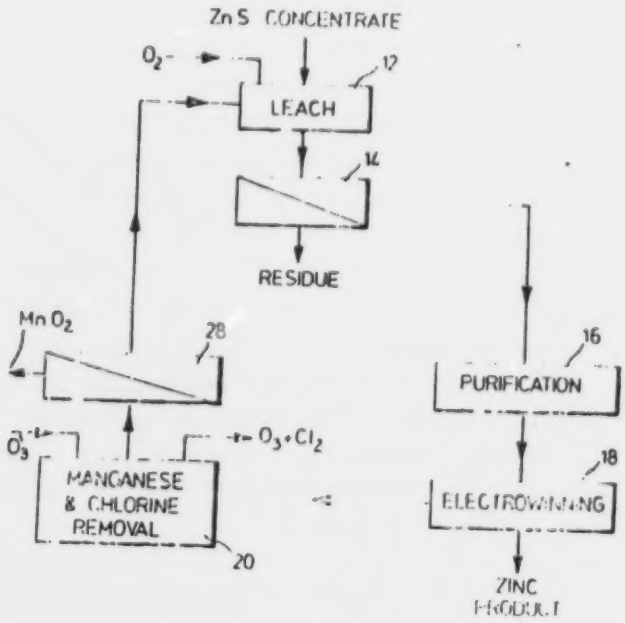
2,577,808	12/1951	Pye et al	423/502
4,120,941	10/1978	Nowak et al.	423/500
4,290,866	9/1981	Bolton et al.	204/119

Primary Examiner R. L. Andrews
Attorney, Agent, or Firm Robert F. Delbridge; Arne I. Fors

[57] **ABSTRACT**

A process for removing manganese and chloride ions from an aqueous acidic sulphate solution containing zinc, manganese and chloride ions without removing a substantial amount of zinc ions from the solution includes adjusting the free acidity of the solution if necessary to at least about 0.1 molar. The solution is then treated with ozone to oxidize manganese ions to manganese dioxide, and the ozone treatment is continued after the manganese concentration has fallen to a low level to oxidize chloride ions to chlorine gas. The precipitated manganese dioxide is removed from the solution.

11 Claims, 2 Drawing Figures



FINAL MANGANESE CONC. (mg/l)

pH	Lime Only	Lime Followed By Ozone
7.0	-	0.8
8.0	90	0.3
9.0	17	LT 0.1
10.0	0.15	LT 0.1
11.0	LT 0.10	-

Ion exchange has been used for manganese removal, and many advantages are claimed by ALZENTER (?). PATTERSON (1975) pointed out one drawback of ion exchange as its non-selective removal of manganese with other ions. ALZENTER mentions performance of the IX plant over three years during which manganese in feedwater was routinely reduced from 1.7 ppm to 0.10 ppm Mn and less on a regular basis with iron removal from about 50 mg/l to 0.3 ppm Fe.

Brine was used for regeneration of the resin, and manganese remained in solution in the brine presenting a disposal problem. An anaerobic waste stream is necessary for the ion exchange system to avoid air oxidation of manganese in the feedwater with resultant precipitation and clogging of the ion exchange bed.

PATTERSON (1975) points out that the cost of the above processes for manganese removal from wastewaters may be increased by the presence of acids, other oxidizable metals, or organics in the waste stream. He points out that the unit operation costs for coagulation-sedimentation-filtration should be similar to those for iron removal systems. Additional costs are attributable for chlorine (or chlorine dioxide) and chlorination equipment plus lime needed to meet the higher pH.

MANGANESE (TOTAL) IN TREATED MINE MILL WATER EFFLUENTS

	Inflow	Outflow	Treatment
Gilman, Colorado AMC	80-453	1.12	Lime pH 9.6
Denison Mines, Mine Water	1.9	0.44	Neutralization pH8 and dilution.

MANGANESE (TOTAL) IN TREATED MINE-MILL EFFLUENTS (Continued)

	Inflow	Outflow	Treatment
Mount Emmons			
Mine Water	6.5-80	0.05	pH 10.6 and
Tailings Seepage	400-500	0.05	Lectroclear flotation and filtration.
Noranda, Waite-Amulet	5.12	0.02	Lime HDS pH 9.80
Vaal Reefs, Raffinate	1670 ppm	LT 1.0 ppm	Lime pH 9.5; settle mix with tailings.
Rand Mines ERPM			
Mine Water	8.0	0.50	Pilot R.O. slurry seeded.
Rössing Uranium			
Tailings Decant	1900-2500		Geochemical adsorption and natural neutralization to pH 6.7.
Collected Tailings Seepage		1100	

During the course of this investigation, it was interesting that manganese was not monitored much of the time in effluents. In other cases, manganese removal required special conditions in water treatment.

MOUNT EMMONS, COLORADO

Manganese occurs in the old zinc mine water at 6.5-80 mg/l and in seepage from the stabilized tailings ponds at 400-500 mg/l. Through pH adjustment to pH 10.6, Lectroclear flotation of the precipitate, and multi-media filtration, Mn is reduced to 0.05 mg/l in the treated effluent.

Manganese removal requires a higher pH in the treatment plant than would otherwise have been needed.

Capital costs of this plant were $10 million, and operating costs for the 2000 U.S. gpm capacity plant run $700,000-1,000,000 per year operating at partial capacity.

An alternative means of removing precipitated metals that has been tested with promising results is dissolved air flotation.

GILMAN, COLORADO

Mine drainage from the underground zinc-silver mine located on the mountainside above the Eagle River runs 80-453 mg/l Mn. Originally, the ore was milled underground, and the tailings deposited to a tailings dam alongside the river in the valley below.

For years mine water has been segregated into a stream which requires treatment and one which does not. Treatment comprised raising the pH to 9.6 and settling in underground chambers to decant the water. However, during the 1970's, the Colorado Dept. of Health imposed an NPDES permit in which the maximum allowable manganese discharge is a level of 1 ppm.

The trip report in Appendix I includes reference to testwork by The New Jersey Zinc Company and the Colorado School of Mines Research Institute in which various oxidants were tested.

Although NaOCl was selected as the best oxidant from among $NaClO_3$, $K_2S_2O_8$, and H_2O_2, the amounts required were considered uneconomical in 1973. At that time, the addition of 1 lb. lime per 1,000 U.S. gallons of tailings effluent was deemed to be the best solution if operation of the mine seepage pumps were carefully synchronized with lime addition.

When 64 lbs. $Ca(OCl)_2$ equivalent were added per 1,000 U.S. gallons, manganese was dropped to 0.5 ppm Mn at pH 8.2. The addition of 22 lbs. of $Ca(COCl)_2$ equivalent and 23 mg lime per liter, reduced Mn to 0.9 ppm. Because $Ca(OCl)_2$ costs around $1.43/lb, it was concluded that this reagent would be uneconomical. Addition of 0.56 lbs. lime per 1,000 gal. resulted in a pH of 9.5 and reduced Mn to 1.1 ppm Mn, resulting in the conclusion that lime addition of 1.0-1.5 lbs. per 1,000 gal. would be the logical answer to reduce Mn to below 1.0 ppm Mn--cheap at 1.9 cents/lb lime at that time.

The Colorado School of Mines Research Institute showed that by passing the mine water through a column of crushed pyrolusite--which occurred in a vein in the mine--manganese levels could be dropped from 5 mg/l Mn to below 1.0 mg/l. The adsorption rate was shown to be a function of the manganese content of the feed solution and the retention time in the column. pH did not influence the adsorption rate in the range tested (pH 7.8-8.8). The pyrolusite adsorption of manganese II was found to be self-regerative to a degree. Mn II is adsorbed and in time oxidizes to $MnO_{1.3}$ and then to $MNO_{1.9}$ which is an adsorbent for incoming Mn II in solution. The granules in the column must be treated to restore permeability.

It was found that 1,000 gallons per minute of mine water containing 5 mg/l Mn II, a total of 5,407 m^2 of surface area would be required, or 32.8 tons of 1/2" x 1/4" pyrolusite. Assuming 120 lbs. per ft^3, this would require two 12 ft Ø tanks with 5' high beds of crushed pyrolusite.

It is believed that the pyrolusite adsorption tanks were never installed at the Gilman Mine. It is nonetheless of interest that the laboratory scale tests demonstrated the effectiveness of pyrolusite for Mn II removal from mine water at lower pH without the need for oxidation.

ENOXY COAL, INC.

At ENOXY COAL, INC., coal waste acid mine drainage is inhibited by adding a calcerous carbonate rock waste to the coal waste. This neutralizes any acid that is generated. However, although the AMD is neutralized and iron precipitated, manganese contained in the high $CaCO_3$ neutralizing waste goes into solution.

It was found that in solutions containing low levels of iron and up to 100-130 mg/l Mn II, it is very difficult and expensive to precipitate manganese. Randol International Ltd. recommended to ENOXY COAL that they test the HDS process.

THE HDS PROCESS

HERMAN (1984) of the BETHLEHEM STEEL CORP. showed at the Randol Workshop on Water Management that manganese can effectively be precipitated from acid mine drainage at a pH around 6.8 through the use of the high density sludge HDS process. In this process, lime is mixed with recycled sludge prior to being added to incoming acid mine drainage.

Manganese can be precipitated in this way even in the absence of iron.

A precipitate sludge is generated which lends itself to stabilization for landfill disposal by addition of a pozzolon. Apparently, if precipitated in the absence of iron, manganese redissolves readily unless stabilized in this manner.

More details on this process are available from:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18106
(215) 694-2424
Stewart T. Herman

RØSSING URANIUM LTD.

Manganese dioxide is used as an oxidant to dissolve uranium from RØSSING ore using a sulfuric acid leach at elevated temperature. Solution in the uranium tailings contains

2,000-2,500 mg Mn II/l at pH around 2. The tailings impoundment is porous, and seepage is collected by interceptor trenches. The natural rock and sediments contain carbonates which help to neutralize seepage solution. It is of interest that the seepage collected has pH 6.7, and the manganese level has dropped to 1100 ppm Mn.

In inspecting the trench faces, it is interesting to observe manganese oxide precipitating in the strata. Clearly, manganese oxides and hydroxides act as an excellent adsorbent for manganese from solution, even at relatively low pH.

Natural soils form good geochemical adsorbents for manganese: this property could undoubtably be exploited in special cases.

ORKNEY MUNICIPALITY, SOUTH AFRICA

River water from the Vaal River, when treated for use as municipal water by the municipal water treatment plant at Orkney (or Klerksdorp), Transvaal, was found in 1976 to be higher in manganese than the drinking water standard.

The National Institute for Water Research of the CSIR investigated various ways to remove manganese from this water. Their investigation concluded that:

1. The oxidation rate of Mn II is pH dependent.

2. The reaction Mn II and O_2 = MnO_2 is autocatalytic.

3. Measurable oxidation of Mn (II) by O_2 occurs only at pH in excess of 8.5.

4. Manganese is effectively removed from solution by adsorption on MnO_2. This adsorption is also pH dependent, requiring a pH of at least 7.7 to proceed at any pace.

5. Adsorbed metal ions on hydrated oxides are released when the pH is dropped.

6. The higher the amount of Cl_2 added, the faster the removal of manganese at around pH 7.

7. At 15 mg/l Cl_2 addition, the rate of Mn (II) removal is enhanced by increasing pH just one unit from 7 to 8.

8. Addition of 500 mg/l MnO_2 at pH 7.5 has a dramatic increase on removal of Mn (II) ions from solution.

9. In the presence of Cl_2, just 0.66 ppm $Mn^{+/}$ increases the rate of Mn II removal by 100%.

Eventually, it was found that allowing MnO_2 to coat filtersand in the filtration plant makes it possible to effectively precipitate manganese from the raw municipal water when it is filtered. The NIWR report with details has not been published. However, industry can approach the NIWR for help on manganese removal problems.

NATIONAL INSTITUTE FOR WATER
RESEARCH (NIWR)
Post Office Box 395
Pretoria 0001
(012) 86-9211
Telex: 3-630
G. R. Botha
Assistant Director
J. P. Maree

High manganese has been found in several other South African raw municipal water supplies.

VAAL REEFS EXPLORATION AND MINING CO. LTD., ORKNEY, TRANSVAAL

Manganese is used as an oxidant in acid uranium leaching on the Witwatersrand including Vaal Reefs. Typical uranium plant raffinates contain 1670 ppm Mn. Effluents from various Vaal Reefs plants are currently treated by mixing them with tailings pulps and adding lime to raise the pH to 9.5. A considerable amount of iron in the form of raffinate (730 ppm Fe^{2+}, 500 ppm Fe^{3+}) is added. This requires 10-12 Kg lime per ton which, at Vaal Reefs, costs R7.76 million/year in lime costs alone to yield a tailings dam decant solution with less than 1 ppm Mn.

Effluent neutralization in this way costs R0.80-R1.00 per ton ore treated which is a sizable percentage of total metallurgical costs, but allows zero discharge and recycle of all water that can be reclaimed.

Since the implementation of effluent neutralization at Vaal Reefs, the manganese level in the Vaal River water has been reduced to less than 1 ppm in the vicinity of the huge metallurgical complex.

RAND MINES LTD., ERPM SEEDED SLURRY R.O.

At the Hercules shaft of the ERPM Mine on the eastern Witwatersrand, a mine water was desalinated on a test basis in 1984 to demonstrate the seeded slurry reverse osmosis process.

Manganese levels were reduced from 8 mg/l in feedwater at pH 4.5 to 0.5 ppm Mn in the product water. This demonstrated a much higher tolerance to manganese than can normally be tolerated by membrane desalination processes, and a high water recovery in excess of 95%. More information on seeded slurry reverse osmosis is available from:

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Reams Goodloe
Tom Wolfe

Fundamental to the success of seeded slurry reverse osmosis is the availability of a new cost effective tubular R.O. unit referred to in the chapter on reverse osmosis.

BUREAU OF MINES, PITTSBURGH, JET AERATOR

ACKMAN and KLEINMANN (1984) described a new in-line aeration and treatment system for acid mine drainage. The principle is to add NaOH solution via a nozzle to the acid mine drainage via a jet pump followed by a static mixer ahead of discharge to a settling pond.

Although NaOH is more expensive than lime, in this case the equipment simplicity would enable significant capital cost savings.

Manganese was dropped in demonstration runs by 50% from a level of around 70 mg/l, at pH 4-6, and almost quantitatively from the same solution at pH 7-9.

Commercial jet pumps for the purpose are now available as described in Chapter 24 on acid mine drainage treatment. More information is available from:

BUREAU OF MINES
U.S. DEPT. OF THE INTERIOR
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Terry Ackman
Robert L.P. Kleinmann

ARGO TUNNEL TEST, WANNAMAKER CONTINUOUS CONCENTRATOR

The Colorado Dept. of Natural Resources, Dept. of Mine Land Reclamation, demonstrated a device known as the Wannamaker Continuous Concentrator in 1981 to treat ARGO TUNNEL acid mine drainage containing 108 ppm Mn.

The precipitate was recirculated through the Wannamaker Continuous Concentrator as described by HOLM and SIMPSON (1981).

In this test, manganese was reduced to 0.65 ppm at pH 9.2 and to 0.005 ppm at pH 9.8. The proposed water standard was 1.1 ppm Mn.

More information is available from:

COLORADO DEPT. OF NATURAL RESOURCES
Mined Land Reclamation Division
1313 Sherman Street
Denver, CO 80203-2273
(303) 866-3567
J. David Holm

Randol International Ltd. believes that the effectiveness of manganese removal would be enhanced if the cross-flow filter were to be used in an HDS mode--ie., mixing the filtercake slurry with lime before it contacts the influent water to be treated.

DRY MGO PRECIPITATION OF METALS

SCHILLER and KHALAFALLA (1983) describe a patented process for removal of heavy metals and manganese from wastewater employing a substantial excess of essentially dry powdered reactive MgO as the precipitant. The resulting precipitant settles rapidly to a small volume of solids which is not readily redispersed or redissolved. A water product with low suspended solids can readily be recovered by decantation. More information can be requested from:

S. E. KHALAFALLA
U.S. Bureau of Mines
Twin Cities Research Center
5629 Minnehaha Avenue South
Minneapolis, MN 55417

SULFIDE PRECIPITATION

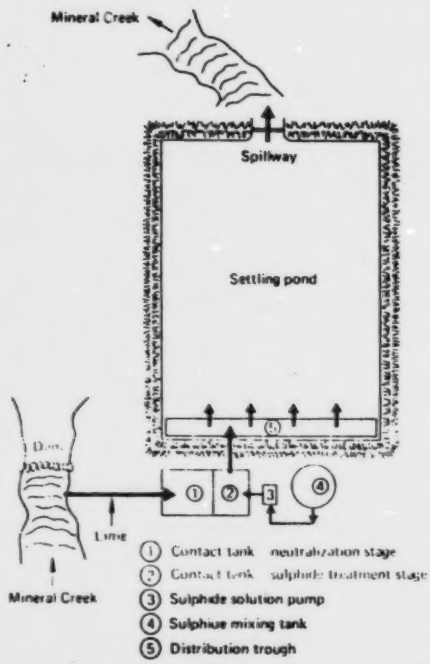
LARSEN and ROSS (1976) showed the effect of addition of lime and then Na_2S to acid mine drainage containing various metals including manganese.

It is of interest that manganese is one of the last metals to be precipitated in this way, and, even after 700 ml solution containing 0.1M Na_2S was added to an AMD sample containing 126.3 mg Mn/l, all manganese had still not been precipitated.

Two-stage process chemically treats mine drainage to remove dissolved metals

H. Peter Larsen and Laurence W. Ross, University of Denver

Fig. 1—Field treatment system for mine drainage



TREATMENT OF MINE DRAINAGE WATERS has fast become a necessity for all mining operations, and regulations governing discharge into local waterways can be expected to become even more stringent. One aspect of mine water treatment—removal of dissolved metals—can be accomplished by a two-stage process developed at the Denver Research Institute (DRI). The first stage of the process treats the waters by lime neutralization to eliminate Fe and Al. A second stage then removes Cu, Zn, Mn, and heavy toxic metals (Hg, Cd, As) by adding sulphide to the waters.

The quantitative effect of both stages of treatment can be predicted by a mathematical description based on the equilibrium relations involved:

$$mM^{+d} + dD^{-m} \rightarrow M_m D_d \downarrow \qquad (1)$$

where M is the metallic cation of charge $(+d)$ and D is the anion of charge $(-m)$.

The removal of dissolved metals by neutralization (stage 1) is predicted quantitatively. Total sulphide addition to achieve removal of specific metals is predicted for stage 2.

Table 1 provides the set of numerical constants used to describe the system mathematically. These values were selected from the literature as yielding the best approximation to measured results. Butler[1] has pointed out that K_{sp} values are often so small that they are outside the realm of realistic measurement. Therefore, a set of values that gives consistent results is all that is needed.

DRI process successful in field studies

Field investigation for the DRI process included erection of a treatment pond beside Mineral Creek in the

Fig. 2—Results of sulphide addition to Idaho drainage sample

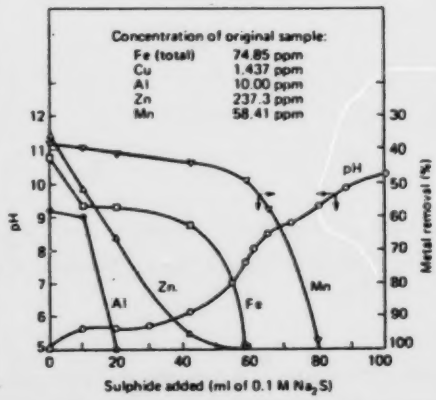
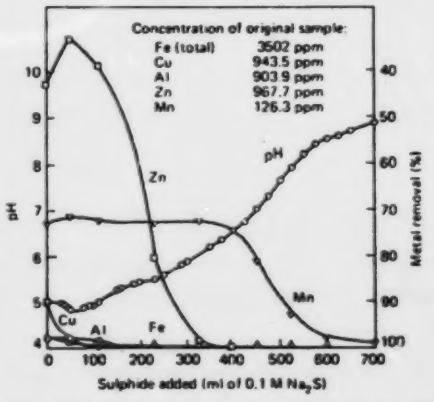


Fig. 3—Results of sulphide addition to Montana drainage sample



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CHAPTER 44

MERCURY Hg

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Regulatory authorities in most industry centers are "paranoid" about mercury and not without some justification. Mercury poisoning has resulted in an extremely unpleasant and even fatal illness in some of the people who worked with mercury in the past and also to people who ingested mercury via the food chain. Memories of contaminated tuna and the tragic Minamata Bay accident in Japan which resulted from an industrial discharge of an effluent containing mercury are still fresh in our minds.

Mercury can be a problem in the workplace when allowed to build up in recirculating metallurgical process solutions; for example, in zero discharge gold and silver recovery operations. Restrictions on mercury in mine-mill effluents are very strict indeed to protect aquatic life.

Mercury occurrences in nature are common especially in and around mineralized zones, particularly of volcanic origin (epithermal), gold and silver deposits and base metal deposits. Mercury also occurs as a primary resource and is often enriched in soils around mineralized zones even where base metals may be only weakly enriched.

During the late 1960's and early 1970's, mercury was considered to be a likely pathfinder element in mineral exploration. Numerous techniques were developed to analyze mercury in soils and soil gas, but the ultimate result was that mercury anomalies occur so much more frequently than mineral deposits that this technique has not become widely applicable.

Mercury probably occurs more often than it has been recognized in the effluents of mine-mill complexes. There are reliable quantitative ways to monitor the air in the work environment, but the EPA limits for mercury in water are so low that they are well below the best analytical techniques.

OCCURRENCE OF MERCURY IN THE MINE-MILL ENVIRONMENT

Based on data contained in the PEDCO (1983) report to the EPA, mercury levels in mine and mill effluents and leachates seldom exceed one ppm and are usually in the ppb range or less. A summary of their data for mercury has included below.

Historically, mercury was extensively employed for amalgamation recovery of gold from both placer and lode deposits but its use has now been almost entirely replaced by other processing methods. Mercury poisoning was apparently not all that uncommon among workers who operated amalgamation plants or amalgam treatment facilities. Even in recent times, amalgamation was used at the DUVAL CORP.'s Battle Mountain operation and at HOMESTAKE's Lead operation. At Lead, amalgamation of slimes has been entirely replaced by cyanidation leaching and carbon in pulp. At Battle Mountain, amalgamation has been replaced by the installation of jigs ahead of cyanidation to catch coarse gold. There are

still numerous plants in South America and South Africa which employ amalgamation to treat gravity concentrates as do small placer operations in Alaska, although in South Africa the trend is increasingly toward intensive cyanidation and electrowinning.

Mercury dissolves in alkaline cyanide solution with the result that if solutions are to be recycled, mercury levels can build up despite the fact that it generally follows gold through zinc dust precipitation into the precipitate or also through carbon adsorption and electrowinning.

Mercury is consequently recovered as a minor by-product at several gold mining operations including the CARLIN GOLD MINING CO., Nevada; PUEBLO VIEJO, Dominican Republic; PINSON GOLD MINING CO., Winnemucca, Nevada; and at FREEPORT GOLD, Elko, Nevada, to name a few.

When mercury is present in a milled ore, it may build up in solution as process water is recycled. If zinc precipitation is used, then mercury must be retorted from the precipitate and recovered prior to smelting. If carbon adsorption processes (either carbon columns for solution or CIP for slurries) are to be used, then mercury can report in the plant around the carbon regeneration kiln, the electrowinning cells, and over the elution vessels, as well as around the steel wool cathode smelting operation. In metallurgical solutions, mercury levels are likely to increase until an equilibrium level is reached and maintained. Interestingly enough, it is not only epithermal deposits that contain mercury. The Witwatersrand fossilized placer deposits also contain low levels of mercury along with other metals, but studies by the Chamber of Mines of South Africa have concluded that these present no cause for alarm from a safety or environmental standpoint.

In California, where PLACER SERVICES, INC. employs a dredge to rework an old placer deposit by digging deeper, amalgamation is used for gold recovery. However, more mercury is recovered than lost in the process. In this case, previous operations left mercury in their tailings which is now being recovered in PLACER SERVICES' more efficient gravity process.

Based on the PEDCO (1983) report data, mercury in copper, lead, zinc and other operations is generally present at very low levels. This data is relatively "spotty," but it is the best currently available. In some gold cyanidation operatons, the mercury levels undoubtably reach levels in the tens and likely in the hundreds of ppm.

PEDCO (1983) DATA SUMMARY - MERCURY

URANIUM - NEW MEXICO

All minewater and both acetic acid and water leach of solids are reported as less than 0.0005 mg/l Hg.

URANIUM - WYOMING

Surface mine waste acid leachate reached a maximum of 0.046 mg/l and a minimum of less than 0.0001 mg/l Hg. Acid leaching of low grade ore containing 0.046 mg Hg/Kg ranged between a maximum of 0.014 mg/l and a minimum of 0.0001 mg/l. All other leachates ranged between 0.0008 mg/l and less than 0.0001 mg/l Hg.

URANIUM - OTHER

Mercury levels are somewhat higher in this district as illustrated by the following summary although still well below the criterion of 0.2 mg/l.

Levels of up to 0.027 mg/l Hg were encountered in the aqueous leachate from surface mine waste and 0.046 mg/l Hg in the acid leachate from underground mine waste, and minewater pond liquid and untreated mine water are shown at less than 0.0076 mg/l or 8 ppb Hg.

WESTERN LEAD/ZINC DISTRICT

The average mercury in underground mine waste is shown as 0.34 mg/Kg with less than 0.00005 mg/l Hg in the acid leachate and an average of less than 0.0051 mg/l in the aqueous leachate. The maximum level in mine backfilled tailings aqueous leachate was 0.048 mg/l.

EASTERN LEAD/ZINC DISTRICT

Tailings pond liquid varied from less than 0.0002 mg/l to 0.0018 mg/l Hg. Tailings pond settled solids ranged from 0.01 g/t Hg but maximum acid leachate and water leachate reached 0.032 and 0.102 mg/l respectively. Averages were 0.0077 mg/l and 0.0303 mg/l.

MISSOURI LEAD/ZINC

Only one leachate, the aqueous leachate from tailings pond settled solids, exceeded 1.0 ppb at 0.0011 mg/l Hg. All the rest were very low, in the range 0.0002-0.0008 mg/l.

MOLYBDENUM

Tailings pond liquid and untreated mine water are listed at less than 0.0076 mg/l Hg, but the report does not specify how low.

NEVADA GOLD/SILVER DISTRICT

Not surprisingly, mercury reaches somewhat higher levels in leachates from gold and silver milling operations, but considering the known association between mercury and gold-silver orebodies, it was surprising that the leachable levels were not even higher.

Aqueous leachate from surface mine waste ran 0.022 mg/l Hg. Tailings pond liquid interestingly enough varied between 0.358 and 0.526 mg Hg/l, probably reflecting mercury leached in the cyanidation process. Even tailings pond solids run between 0.0025 mg/l and 0.0415 mg/l Hg.

Even though the EP toxicity test criteria were not exceeded by the leach test, decanted tailings pond liquid exceeded the EP leach test criteria for mercury in some cases.

OTHER GOLD/SILVER DISTRICTS

In this area, leach test results for three samples yielded less than 0.0011 mg/l Hg, but tailings pond liquid ran 0.0423 mg/l, and the acid EP leach test with acid from settled solids in the tailings pond exceed 5.7 mg/l. It is clear that from one gold mining district to another, there are major changes in mercury levels and also in the amount of mercury that is acid and water soluble.

TACONITE DISTRICT

Even in the taconite district, mercury levels in ore are higher than one might expect at 0.0013 mg/l in acid leachate. Although not a high level in itself, the acid leachate exceeds 1 ppb.

In the course of this investigation, it was surprising how seldom mercury is monitored on a regular basis; it having been determined in the past (it is assumed) that mercury levels are of no consequence in the effluents. The only references to mercury monitoring in mine and mill effluents encountered are as follows:

	Effluent Hg (ppb)	Permitted Hg (ppb)
Kidd Creek Mines, Timmins		
- Underground Mine Drainage	LT 1	
- Treated Mine Drainage in Holding Pond	LT 1	
- Recycled Minewater	LT 1	
- Kidd Creek Water After Mixing with Treated Water	LT 1	
Mount Emmons Operation, Climax Molybdenum Division		
- Maximum Permissible Limit (Daily)	0.05	0.05
- Measured in Treated Water Discharge	LT 0.20*	

	MERCURY	
	Effluent Hg (ppb)	Permitted Hg (ppb)
Kidd Creek Concentrator, Timmins		
- Tailings Decant After Lime Treatment	LT 1.0 ppm	

* Detection Limit

Most gold and silver recovery operations located in the western U.S.A. are "zero discharge" operations and consequently, effluent limitations do not apply as there is no effluent. These operations would be expected to have somewhat higher mercury levels in their recycled process solutions.

BYCROFT, et al. (1982) reported on mercury contamination of the Lerderberg River, Victoria, Australia, from an abandoned gold field. This paper was not obtained but could be requested from the authors at Monash University, Clayton.

PATTERSON (1975) refers to observations that caustic soda manufactured by chloralkali processes that use mercury may contain "very high" levels of mercury. Literature references report mercury levels of 0.2-150 mg/l in caustic solutions. Caustic from Swedish chloralkali plants contained an average of 3.26 mg/l Hg. Considering the very low levels of mercury allowed in effluents, even the possibility of levels of this magnitude in caustic soda reagents must be taken into account where caustic soda is used for pH adjustment. The addition of 0.3 lb. caustic per ton of solution, for example (150g/t), would add 1 ppb Hg to the effluent which is of the order of the maximum level permitted in mill effluents.

It is possible, but not confirmed, that environmental concerns about mercury losses in chloralkali plants may well have resulted in steps to reduce levels in caustic soda product since PATTERSON (1975) reported the results.

REGULATORY LIMITS FOR MERCURY IN EFFLUENTS

Objectives and maximum permissible limits for mercury in receiving waters are listed below. It is interesting that the MINISTRY OF THE ENVIRONMENT OF ONTARIO (1979) has set two objectives. First is a concentration of 0.2 ug/l Hg of total mercury in filtered water and second, a maximum level of 0.5 ug/g Hg in whole fish (wet basis) for the protection of aquatic life and fish-consuming birds as well as the human consumer.

Compiled by NORANDA

Hg (ug/L) MERCURY

Summary of North American Water Quality Criteria for Mercury

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9,**] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE				24-hr mean	0.1						
OBJECTIVE		0.05	0.05	0.57 x 10⁻⁶	0.2	.2	N.D.	--	NIL-5.0	--	--
MAX. PERMISSIBLE LIMIT		0.2	--	0.0017	--	0.2	0.2	0.1	--	0.1	--
PROTECTION OF MARINE LIFE				24-hr mean							
OBJECTIVE		--	0.1	0.075	.10 *	--	--	--	NIL-5.0	--	--
MAX. PERMISSIBLE LIMIT		0.10 ug/L	--	3.7	.10 *	--	--	--	--	--	--
PUBLIC WATER SUPPLY		2.0	2.0	0.144	1.0	--	N.D. (obj) 1,2,5 (limit)	(0.1)	--	--	2.0
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	10	(2.0)	--	3.0	10	--	(0.1)	--	--	10
	IRRIGATION	--	(2.0)	--	No limit Recommended	--	--	(0.1)	--	--	<.02

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.

2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.

3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Mercury, EPA 440/5-80-058.

4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).

5. Environment Canada. 1979. Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances, Mercury.

6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.

7. Gouin, D. et Malo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'Étude sur le Fleuve St. Laurent.

8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.

9.** British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries. (Receiving water objectives not available)

10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.

11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

TABLE

MERCURY

The U.S. EPA criteria objective for mercury in receiving waters for the protection of the environment has been set by the U.S. EPA (1980) at 0.00057 ug/l with a maximum permissible concentration of 0.0017 ug/l.

Since the detection limit of most commonly used analytical measuring instruments is much higher than this, the U.S. freshwater criteria are considered unrealistic. The U.S. objective and maximum permissible concentration are also well below background levels in many streams and lakes. The most sensitive detection equipment in common use is the U.V. detection system employed in the flameless atomic absorption cold vapor technique. This method has an accepted detection limit of 0.01 ug/l as Hg. Although the detection limit can be decreased to 0.001 ug/l, accuracy at this level is poor, and at such extremely low levels, there is no way of knowing whether the mercury measured is in fact in the water or introduced from other sources, e.g., adsorption on the walls of the laboratory glassware. Possibly the objective is meant to be regarded as a target with no serious intention of ever meeting it; the basis for the U.S. mercury objective and maximum permissible concentration is not known.

WATER QUALITY CRITERIA FOR MERCURY

Freshwater	Hg (ppb)
U.S. EPA (1980) Max. 24-Hour Average Hg Objective	0.00057
U.S. EPA (1980) 24-Hour Mean Max. Permissible	0.0017
NEW MEXICO (1971)	1.0
CANADA (1979) 24-Hour Mean Objective	0.10
CANADA (1979) Max. Permissible Objective	0.20
ONTARIO (1979) 24-Hour Mean Objective	0.20
ONTARIO (1979) Max. Permissible Limit	0.20
ALBERTA (1977) Max. Permissible Limit	0.10
SASKATCHEWAN (1975) Max. Permissible Limit	0.10
BRITISH COLUMBIA (1979) Objective	Nil-5.0
SOUTH AFRICA (1983) Proposed Limit for Effluents	20
Marine	
EPA (1980) Objective 24-Hour Mean	0.025
EPA (1980) Max. Permissible Limit	3.70
CANADA (1979a) Objective	LT 0.10
CANADA (1979a) Max. Permissible Limit	0.10
BRITISH COLUMBIA (1979) Final Effluent	Nil-5.0

Public Water Supply

U.S. EPA (1980)	0.144
CANADA (1979)	1.0
MANITOBA (1979)	2.0
SOUTH AFRICA (1971) Drinking Water Recommended Limit	5
SOUTH AFRICA (1971) Drinking Water Max. Allowable	10

MERCURY LIMITS IN MINE-MILL OPERATING PERMITS

Most of the operations visited did not have a stipulated mercury limit in their effluents because, in most cases, mercury was not deemed to be a problem. The few cases where mercury limits were included in the permit are as follows:

	Hg (ppb)
HOMESTAKE MINING COMPANY, Lead	
- Final Effluent (NPDES)	1.0
HOMESTAKE - McLaughlin Project	
- Treated Runoff Water, 30-Day Ave.	1.0
- Treated Runoff Water, Daily Max.	2.0
AMAX, INC., Mount Emmons	
- Final Effluent After Treatment (NPDES)	0.5

EFFECTS OF MERCURY ON METALLURGICAL EFFICIENCY

RENCO MINES LTD. in Zimbabwe recovers gold by cyanidation and CIP from an ore containing undersirable contaminants which interfere with the process. One of these (MENNE, 1984, personal communication) is bismuth which is believed to interfere with gold adsorption on carbon.

RENCO MINES LTD. adds 200g $HgCl_2$ to the pulp just before it reaches the first agitator. The $HgCl_2$ is added with the cyanide solution at the pump sump between the pulp pre-aeration tanks and the first leach agitator.

The 200g $HgCl_2$ dose was found to be critical. Any less than that, and gold recovery drops off. Any more does not help recovery but adds to expenses.

RENCO MINES LTD. made the fascinating observation that within minutes of being added, the mercury which was added in soluble form cannot be detected in the pulp solution. Of 200g $HgCl_2$ added in the circuit, only 50-70% can be found in the final tails.

Although the precise role of the mercury in gold leach and CIP enhancement is not yet understood, more information may be available from:

MR. H.G. BURKS
Consultant
19 Sable Way
Mshumavale - Gatooma
Zimbabwe
Telephone: Gatooma 2310

DAVID MENNE
Edward L. Bateman (Pty) Ltd.
Post Office Box 7028
Cloisters Square
Perth, WA 6000
(09) 322-4740
Telex: AA95066

A second effect of mercury on gold leaching was referred to at a verbal presentation on gold recovery on the Witwatersrand by P.J.D. Lloyd (recollection only) who then was Research Director of the Chamber of Mines Research Laboratories in South Africa. He presented data which supported his view that gold dissolution by cyanide from Witwatersrand ores was inhibited by the presence of small amounts of mercury in the ore which necessitated a leach residence time long enough to dissolve the mercury before the last of the gold could be brought into solution. Information may be requested from:

DR. P.J.D. LLOYD
Managing Director
EMS Minerals
Post Office Box 585
Bedfordview - Johannesburg
South Africa

The above indicates that the addition of mercury in soluble form may enhance gold extraction, but mercury in mineral form may retard leach kinetics. It must be stated that the latter observation was presented more as a tentative hypothesis than a fact.

ENVIRONMENTAL SENSITIVITY - MERCURY

The biologically significant form of mercury is methyl mercury which is very much more toxic to aquatic organisms than inorganic mercury. According to JOHNELS, et al. (1967) and KAMPS, et al. (1972), the bulk of mercury found in fresh water fish occurs in the form of methyl mercury. Methyl mercury may also be demethylated by bacteria in sediments according to SPANGLER, et al (1973).

Methylation of mercury in the environment occurs by at least two mechanisms as described by WOOD, et al. (1968) and LADNER (1971).

Administrative guidelines for fish for human consumption promulgated by the U.S. Food and Drug Administration and the Canadian Food and Drug Directorate are set a 0.5 ug/g mercury in edible portions. There is no evidence according to ONTARIO (1979) that concentrations of 0.5 ug/g mercury in fish have any effect on the fish themselves. Concentrations of mercury in fish that have been killed by chronic exposure to methyl mercury ranged from 9.5 to 23.5 ug/g Hg according to ONTARIO (1979).

ONTARIO (1979) provides a table showing the results of a series of toxicity studies which demonstrate that most organic mercury compounds are more toxic than inorganic mercury salts.

ONTARIO (1979) concluded that fish-eating birds should be protected if the concentration of total mercury in whole fish does not exceed 0.5 ug/g.

Bioaccumulation of mercury occurs in many fish, bird, and other aquatic species, and some examples are cited in ONTARIO (1979).

With the exception of some of the most severe cases of mercury pollution, aqueous mercury concentrations, U.S. EPA (1980) and NRCC (1979), are generally well below levels which would affect the wellbeing of aquatic and marine life.

According to HEIT and FINGERMAN (1977), the method used by the EPA to extrapolate to the objective figure and the MPC provided an erroneous result. The figures must be erroneous considering the bountiful fish populations that thrive in water with significantly higher mercury background levels.

Crayfish are apparently particularly sensitive to mercury with LC-50 of 50 ug/l and LC-50 of 250-1,000 ug/l reported by two papers which is about 2,500 times higher than that reported by another worker.

The second most sensitive species listed by the U.S. EPA is Daphnia magna which was observed to have a 48-h LC-50 of 5 ug/l as Hg_2Cl_2 (data from BEISINGER and CHRISTENSEN (1972)). The LC-50 value found in their study is 2,940 times greater than the MPC.

Rainbow trout LC-50 value of 250 ug/l Hg is tested as Hg_2Cl_2 compared with 20 ug/l for methylmercuric chloride according to the U.S. EPA (1980). Rainbow trout are generally considered to be one of the most sensitive fish species, and their LC-50 values are 147,000 and 17,000 greater than the MPC which suggests that the MPC derived by the EPA (0.0017 ug/l) is unrealistic.

Several studies showed that no toxic effects were observed at the Environment Canada 0.1-0.2 ug/l total mercury objective level, but if 10-20% of the total mercury is in a methylated form, then bioaccumulation could potentially occur. However, methylmercuric chloride concentrations of less than 0.01 ug/l Hg do not appear to cause great increases in fish mercury concentrations over background levels.

It is concluded that in arid regions where metallurgical operations can be operated on a zero discharge basis, mercury is of less concern environmentally than worker exposure to mercury vapor derived from processing solutions containing levels of mercury that have become elevated due to water recycling.

In areas where effluents must be discharged, the Canadian MPC and objective for 24-hour average levels of mercury are reasonable, whereas the U.S. EPA objective is both unenforceable for lack of suitable analytical equipment and unrealistic, being not supported by environmental evidence.

Even if methods could be devised to detect mercury at the EPA objective levels, there are no known processes that can reliably remove mercury from water to the levels cited.

The U.S. EPA marine criteria for MPC and 24-hour average concentration (3.7 and 0.025 ug/l) are based on the results of toxicity tests rather than bioaccumulation potential. Industry observers find these limits scientifically defensible as opposed to the freshwater criteria.

Generally, the 24-hour average objective of 0.025 ug/l is close to typical background levels which suggests that little if any addition to the environment over a long period of time would be permitted although, of course, the oceans have such a large volume that they can tolerate significant additions before the average background level would be impacted.

The U.S. Marine MPC of 3.7 ug/l is in line with toxicity test results and should not be exceeded.

Ultimately, objectives may have to distinguish between methylated and inorganic mercury levels in effluents.

TREATMENT FOR MERCURY REMOVAL

1) Selective Leaching: Gold and Silver Cyanidation

The Bureau of Mines of the U.S. Dept. of the Interior has conducted research into the question of mercury in gold and silver cyanidation solutions and pulps. STAKER, et al. (1983) investigated selective extraction of Au and Ag from a

low-grade Au ore containing Hg. Gold and silver were extracted from the ore in cyanide slurries, and mercury extraction was suppressed with sodium or calcium sulfide. Maximum Au extraction and minimum Hg extraction were obtained using solutions containing 0.34 lb. NaCN/ton solution. Increasing the cyanide concentration increased the mercury extraction without increasing gold extraction. Mercury extraction from the ore was suppressed with 0.5-2.9 lb. CaS/lb. Hg in the ore. Gold to mercury ratios of 100:1 to 400:1 were obtained in the leach solution and on the activated carbon in a CIP circuit.

The above is potentially very significant, especially in low-grade ores in the western U.S.A. which may contain, for example, 2-3 g Au/t with 5-15 g Hg/t. During cyanidation, 10-30 percent of the mercury is extracted along with Au and Ag, and once in solution, mercury follows gold or silver through the process requiring extra precautions in the plant.

Mercury vapor may cause health hazards in the electrowinning, retorting, and carbon reactivation as well as carbon elution steps.

The USBM process to inhibit mercury dissolution is potentially useful in that mercury then stays in the tailing solids. However, careful scrutiny of the effect of CaS addition on cyanide consumption, gold and silver leach rates and efficiency, and adsorption characteristics on activated carbon would be necessary before employing this process.

Further information on progress in this direction and reference to commercial plants that employ this process would be available from:

W. L. STAKER
Salt Lake City Research Center
Bureau of Mines
U.S. Dept. of the Interior
Salt Lake City, UT 84108
(801) 524-6100

For applications where effluents must be discharged for water balance considerations, the question remains whether inhibition of mercury leaching would be adequate to keep mercury in effluents down to levels that would meet the regulatory requirements.

MERCURY REMOVAL FROM GOLD MILL SOLUTION/EFFLUENTS

In the course of this investigation, not one case was encountered where mercury is deliberately removed from a process solution stream or an effluent prior to discharge.

However, mercury is involuntarily recovered as a byproduct by the same extraction process as is used for gold and silver recovery. Examples of such operations are:

Zinc Precipitation - Retorting
Rosario Dominicana, Pueblo Viejo, Dominican Republic
Carlin Gold Mines, Carlin Nevada

Carbon-in-Pulp - Elution - Zinc Precipitation Retorting
Freeport Gold Company, Elko, Nevada

Carbon in Pulp - Elution - Electrowinning - Retorting of Steel Wool
Pinson Gold Mining Co., Winnemucca, Nevada
Getty Mercur Gold Co., Toelle, Utah

It is believed that Harrison B. Salisbury of the Dawson Metallurgical Laboratories has conducted research into ways to remove metals such as mercury and thallium from gold leach solutions.

DAWSON METALLURGICAL LABORATORIES
5217 Major Street
Murray, UT 84107
(801) 262-0922
Harrison B. Salisbury

Several other methods have been employed or are under development to remove mercury from industrial effluents, mostly on a smaller scale:

Precipitation
Ion Exchange
Chelating Compounds
The Devoe-Holbein Process
Coagulation
Reduction to Metallic Mercury and Filtration

PRECIPITATION

In industrial applications, sulfide addition to precipitate mercury sulfide is commonly used. This may be combined with flocculation and separation by gravity settling, filtration, or dissolved air flotation and is also the basis for keeping mercury out of cyanide solution in the leaching of gold and silver from mercury-rich ores. Sulfide precipitation was discussed by BOUVENC (Undated).

PATTERSON (1975) points out that for high initial mercury levels, sulfide precipitation will achieve 99.9% removal at alkaline pH but even with filtration or activated carbon polishing, minimum effluent mercury achievable by sulfide precipitation appears to be 10-20 ug/l. Most effective precipitation appears to be in the near neutral pH range as far as minimizing sulfide dosages according to PERRY (1974).

In addition to the lack of capability to reduce mercury below 10 ug/l, other drawbacks of this method include: 1) formation of soluble mercury sulfide complexes at high levels of excess sulfide; 2) the difficulty of monitoring excess sulfide levels; and 3) the problem of toxic sulfide residual in the treated effluent according to PERRY (1974).

Although the last two of these obstacles have now largely been overcome, the inability to reduce mercury levels to below 10-20 ug/l does not meet the EPA or Canadian ambient water criteria for protection of the environment.

SULFEX PROCESS

Mercury sulfide solubility in pure water is reported to be 1×10^{-21} by YELIGAR, et al. (1981) making it one of the least soluble sulfides. The Sulfex process, described by YELIGAR, et al. (1981) and SCOTT (Undated), employs an iron sulfide sludge bed in a sludge blanket-type clarifier to precipitate mercury and other metals. In this way, sulfide levels are maintained at a constant concentration regardless of the rate of sulfide demand.

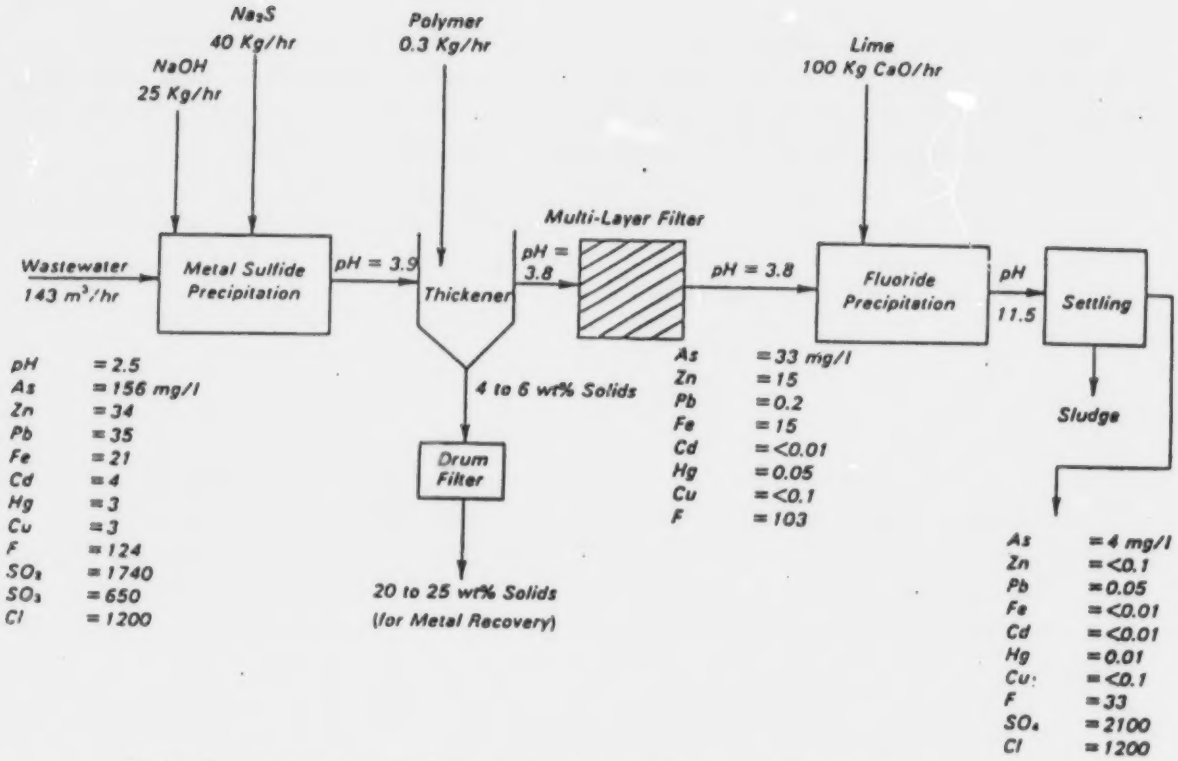
The Sulfex process is patented and, together with the sludge blanket reactor clarifier, is offered by:

THE PERMUTIT CO., INC.
Post Office Box 355
E49 Midland Avenue
Paramus, NJ 07652
(201) 967-6000

To date, the Sulfex process has been employed primarily to treat metal finishing and plating effluents, and no operations are known where it is used to treat metallurgical plant effluents although in principle there are no reasons for it not to work.

BOLIDEN METALL, SKELLEFTHAM PLANT, SWEDEN

Sulfide precipitation is employed by BOLIDEN METALL at their Skellefthamn plant in Sweden to remove arsenic at low pH 3.9 followed by filtration to remove the precipitate and lime addition to the filtrate to precipitate fluoride as CaF_2 followed by settling and decantation. This process is described by BLYTHE, et al. (1981) from which the following schematic diagram is taken showing that mercury in feed solution is dropped by sulfide precipitation from 3 ppm to 50 ppb and further to 10 ppb by lime addition and settling.



Typical residual metal concentrations obtained by full-scale test run (Boliden Metall).

SOURCE: BLYTHE, et al. (1981)

More information on this process, as well as the pitfalls to be guarded against when a complex solution is to be treated, is contained in the project summary by BLYTHE, et al. (1981). Additional insight may be possible from:

BOLIDEN METALL AB
Skellefteham
Sweden
Rolf Sevedberg

D. BHATTACHARYYA
Chemical Engineering Dept.
University of Kentucky
773 Anderson Hall
Lexington, KY 40506-0046
(606) 257-2798

According to BHATTACHARYYA (1985, personal communication), one of the problems is excessive cost at low pH when $SO_3^=$ is present because it consumes expensive sulfide reagent. A second problem is the efficient removal of finely divided sulfide precipitates. It is noted that at the low pH, mercury is removed only to 50 ppb and with subsequent

lime addition, to 10 ppb which more or less confirms the performance noted above for sulfide precipitation.

ION EXCHANGE

Most ion exchange treatments of inorganic mercury involve formation of a negatively charged mercuric chloride complex by adding chlorine to oxidize metallic mercury or chloride salts and removal of the mercuric chloride complex on an anion exchange resin. Most experience, according to PATTERSON (1975), has been with chloralkali plant wastes which contain high background chloride levels. There is some evidence, (PERRY, 1974, and GARDINER and MUNOZ, 1971), to indicate that the best ion exchange results are achieved in two stages with a roughing and a polishing step. Table 56 below from PATTERSON (1975) shows that anion exchange reduced mercury to 1 ppb in some cases.

Ion Exchange Treatment for Mercury.

Resin Type	Mercury Form	Treatment pH	Mercury (μg/l) Initial	Mercury (μg/l) Final	Additional Treatment	Reference
Mtylon-T	Inorganic	5–6	5,000–25,000	1	—	22
Lewatit	Inorganic	na	na	15	—	23
Anion[a]	Inorganic	7	850	2.5	—	24
Macroreticular	Inorganic	na	10,000	<10	—	25
Anion[a]	Inorganic	na	470	30	—	26
Osaka IE[a]	Inorganic	"acidic"	3,000–10,000	100–150	Prefilter	21
Osaka MR[a]	Inorganic	na	100–150	2–5	Osaka IE Resin	21
Imac-TMR	Inorganic	3	na	5	Carbon Prefilter	27
Anion[a]	Inorganic	5–7	na	100	—	18
Activex	Inorganic	na	10	<5	—	28
Ajinomoto	Inorganic	1.5	60	5	—	20
		6.0	87	3	—	
		11.0	1,800	990	—	
Billingsfors-	Inorganic	6.5	35	1	—	20
Langed Q13		na	na	10–20	absorption filter	19

[a] Mercury removed as mercuric chloride complex, $HgCl_x^{(x-2)}$

22 FEDONINA (1972)
23 OEHME (1971)
24 YOKOTA (1972)
25 EGAWA (1971)
26 OEHME, et al. (1972)
21 GARDINER and MUNOZ (1971)
27 ROSENZWEIG (1975)
18 CHEREMISINOFF and HABIB (1972)
28 LOGSDON, et al. (1974)
20 PERRY (1974)
19 U.S. EPA (1971)

Where chloride levels are low, cation exchange resins are effective. Although information on the cation exchange behavoir of mercury is scarce, Amberlite IRA-120 and Dowex-50W-X8 are both reported by ROESMER (1970) to be effective. Since then, of course, resin manufacturers have undoubtably developed improved resins for mercury removal, and it is recommended that sponsors get in touch with their local ion exchange salesmen for more information.

Resins that contain mercapto groups R-S-H such as polythiostyrene are highly specific for mercuric ions according to ROESMER (1970).

PATTERSON points out that regardless of whether anionic resins are used for mercuric chloride complex removal or cationic resins for mercuric ion removal, the best ion exchange treatment for inorganic mercury appears to yield an effluent with 1-5 ug/l. Most effective treatment results from two-stage treatment at neutral to slightly acidic pH.

Most available data relates to the treatment of inorganic mercury, and there is relatively little information on organic mercurials. However, efficient treatment of methyl mercury acetate has been reported with Dowex A-1 Chelate by MUZZARELLI and ISOLATI (1971) and Ionac SRXL resins by LAW (1971) whose paper is inserted below along with one by FREELAND, et al. (1974) who showed how polyethylamine-modified wool fibers can adsorb mercury as Hg^{2+} from solution. The process is said to be effective on 1 ppm Hg solutions, and effluents with only 0.02 ppm were achieved. Additional information on further progress in this field may be available from:

CSIRO
Division of Textile Industry
Post Office Box 21
Belmont, Victoria 3216
Australia

PATTERSON (1975) refers to the Osaka ion exchange process for mercury removal from acid solution which is available under license using an Osaka resin which achieves, according to GARDINER and MUNOZ (1971), levels as low as 5 ppb Hg. This reference may also include the address of the Osaka Company that markets this process and the resin.

A Swedish company (AKTIEBOLAC BILLINGSFORS-LANGED) has developed an ion exchange system which is similar in concept to the Osaka process. A strong base first stage exchanger is regenerable while the second stage polisher is not. Removal is as the mercuric chloride complex anion, thus requiring pretreatment of mercurous and organic mercury. More information is reported by CHEREMISINOFF and HABIB (1972) and ROSENZWEIG (1971).

WILMOTH, et al. (1979) tested lime neutralization, reverse osmosis, and ion exchange for their effectiveness in removing mg/l levels of ten trace elements from acid mine drainage under typical operating conditions. The contaminants were As, B, Cd, Cr, Cu, Hg, Ni, P, Se, and Zn. Treatment by lime neutralization was very effective in removing As, Cd, Ni, and Zn and ineffective for B removal. Dual-bed (strong acid-weak base) ion exchange was very effective in removing all the trace elements except P and B but including mercury.

Methyl Mercury and Inorganic Mercury Collection by a Selective Chelating Resin

Abstract. *A commercially available chelating resin selectively and quantitatively collects methyl mercuric and inorganic mercuric forms of mercury to the exclusion of all other metals studied, except the noble metals. Both forms of mercury can be collected from pH 1 to 9. Collected mercury is readily eluted with a slightly acid, 5 percent solution of thiourea, and the resin can be reused for many cycles. Selectivity, pH effects, capacity, and elution characteristics of the resin are described. A resin-loaded paper composed of 50 percent resin and 50 percent cellulose shows properties similar to those of the loose resin.*

The purpose of this report is to summarize available tests on a chelating resin, Ionac SRXL (*1*), which should provide new opportunities for analysis and for recovery of mercury from industrial and natural aqueous solutions. Previous studies have shown that the resin is highly selective for gold and platinum metals, but its usefulness for mercury had not been considered (*2–4*). My results indicate that the resin has a high affinity for dissolved mercury in both the methyl mercury and the inorganic forms.

Kuster and Schmuckler, original developers of the resin (*2*), explain the selectivity for noble metals by stating that it will "... bind only ions with the d^8 electronic configuration forming square planar complexes. ... ." They further explain that the resin has redox properties because of double bonds, enabling it to collect a species such as Pt^{4+} which is reduced to the Pt^{2+} and then bound as a square planar complex. The mechanism for Hg^{2+} and CH_3Hg^+ collection has yet to be determined.

The properties of SRXL resin were studied in two ways. Data were obtained with resin as received from the manufacturer and with resin-loaded paper, consisting of 50 percent SRXL resin (−325 mesh) and 50 percent cellulose (*4*). Comparisons were made between the resin behavior in a column and its behavior in the resin paper. All solutions were prepared with reagent-grade chemicals, and tracer studies were performed with the ^{203}Hg radioactive isotope and a NaI(Tl) detector.

Selective collection of noble metals, especially gold, from solutions containing high concentrations of more common metals has been reported (*2–4*). I have found also that the resin quantitatively collects dissolved mercury as methyl mercury or as inorganic mercury from solutions of high common metal concentration. A column of resin, 30 by 15 mm, quantitatively collected 100 μg of Hg^{2+} from 250 ml of chloride solutions of iron, nickel, copper, and zinc in amounts up to 10 g/liter. Radioactive ^{203}Hg was used to determine the completeness of collection (Table 1).

Selectivity tests for mercury in the CH_3HgCl, $HgCl_2$, and $Hg(NO_3)_2$ forms were conducted by filtering solutions containing a mercury salt mixed with various metals through paper disks (3.5 cm in diameter) containing SRXL resin; the solution was passed six times through each disk. The disks were rinsed with dilute HCl solution, dried, and analyzed by fluorescent x-ray spectrography. From solutions containing Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} or CH_3Hg^+, only the mercury was detected on the disks; the instrument conditions were sensitive to less than 5 μg for any one of the metals. Neutron activation analysis of SRXL paper disks which were used to collect gold from solutions containing nitrate or chloride salts of metals failed to show any common metal collection (*4*).

Comparisons with another resin, Chelex 100, reported to have a high affinity for Hg^{2+}, show that the Chelex 100 resin fails to collect the methyl mercury form although it does quantitatively collect Hg^{2+}. A paper specially prepared (H. Reeve Angel & Co.) with the Chelex 100 resin, was compared chromatographically with the SRXL

Table 1. Mercury ion (Hg^{2+}) collection from solutions of high metal concentration.

Conc. of Fe, Ni, Cu, and Zn mixture (g/liter)	^{203}Hg (count/min)[a]			Hg collected (%)
	Before	After	Background	
0.5	5202	217	224	~ 100
1.0	5318	214	213	~ 100
5.0	5498	225	209	~ 100
10.0	5510	225	209	~ 100

[a] Average of four or more 1-minute counts.

References and Notes

1. The SRXL resin, used to obtain the data for this report, is no longer commercially available from the Ionac Chemical Co., Birmingham, N.J. A resin reportedly identical is available from the Ayalon Water Conditioning Co., Ltd., P.O. Box 586, Haifa, Israel, under the trade designation of Srafion NMRR. Trade names and company names are used in this report for identification only and do not imply endorsement by the Bureau of Mines.
2. G. Kuster and G. Schmuckler, *Anal. Chim. Acta* 38, 179 (1967).
3. T. E. Green and S. L. Law, *U.S. Bur. Mines Rep. Invest. No. 7338* (1970).
4. ——, W. J. Campbell, *Anal. Chem.* 42, 1749 (1970).
5. Ayalon Product Information Bulletin, Srafion NMRR, Ayalon Water Conditioning Co., Ltd.
6. I thank T. E. Green and W. J. Campbell, College Park Metallurgy Research Center, College Park, Md., for suggestions and advice.

10 June 1971; revised 24 August 1971

paper. Metal mixtures including Hg^{2+} and CH_3Hg^+ were placed on both papers and developed under identical conditions. The SRXL paper showed complete separation of all metals examined (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}) from the Hg^{2+} and CH_3Hg^+ spot, which always had an R_f value of 0. The common metals showed no tendency to be retained by the paper. The Chelex 100 paper showed some affinity for most of the metals. Some spreading of the Hg^{2+} was also noticed. This comparison emphasizes the fact that the SRXL resin has the ability to discriminate between mercury and base metals instead of merely exhibiting varying degrees of affinity for the different ions as is more commonly observed in ion exchange.

The effect of *p*H on the collection of mercuric chloride, mercuric nitrate, and dissolved methyl mercury by the resin and the resin paper was examined over the *p*H range of 0.1 to 9. The results (Fig. 1) suggest the possibility of separating the forms of mercury in solution by *p*H adjustment. The trends and not the magnitudes are significant because different experimental procedures were necessary depending on whether the resin or the paper was used. Collection times were restricted to avoid quantitative collection as the purpose of this study was to observe differences in diffusion and absorption kinetics.

For the loose resin (Fig. 1A), a 200-ml solution, adjusted to the desired *p*H with dilute HCl and NaOH and containing ^{203}Hg radioactive tracer and 1000 μg of Hg^{2+}, or $CH_3{}^{203}Hg^+$ tracer and 990 μg of Hg as CH_3Hg^+, was shaken with 0.33 g of resin on a mechanical shaker for 2 hours. Portions (3 ml) were taken for the determination of radioactivity before resin addition and after shaking, in each case, to determine the amount of mercury collected by the resin. Although mercury is collected at *p*H > 7, use of the resin is probably best confined to *p*H < 7 as recommended by Koster and Schmuckler (*2*). The lowest collection of inorganic mercury is at *p*H 6. One liter of a *p*H 6 solution containing ^{203}Hg tracer and 100 ppm of Hg^{2+} as the chloride was prepared and passed through a small column (1 by 1.5 cm; 0.75 g) of the resin. The effluent from the column was periodically checked for ^{203}Hg activity. After about 600 ml of the solution had passed through the resin at an initial flow rate of 3 ml/min, a small amount (about 2 percent) of

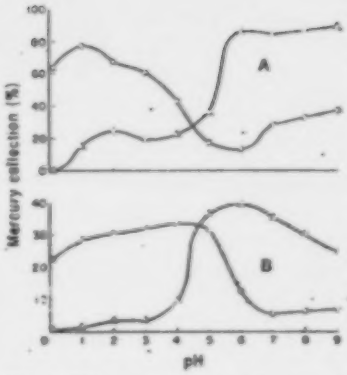


Fig. 1. Effect of *p*H on the collection of inorganic mercury (○) and dissolved methyl mercury (△), by SRXL resin (A) and SRXL resin-loaded paper (B).

mercury tracer began to come through the column. When the flow rate was reduced to approximately 1.5 ml/min, the mercury collection was again quantitative, and no further escape of mercury from the column was observed for the remainder of the 1000 ml of solution. These observations indicate that the total capacity of the resin is probably the same at *p*H 6 as at the lower *p*H values, but the rate of collection of Hg^{2+} is slower at *p*H 6. Therefore, a slower flow rate will be all that is required for quantitative recovery of inorganic mercury at this *p*H.

For the SRXL paper (Fig. 1B), small disks (1.3 cm in diameter) of the paper were suspended by thread for 24 hours in solutions of various *p*H, each solution containing 1000 μg of Hg as $HgCl_2$ or 930 μg of Hg as the methyl mercuric chloride. The disks were dried, and the mercury content was determined by fluorescent x-ray spectrography.

The sudden decrease in collection of the inorganic mercury at *p*H 6 is apparently the result of a reduction-precipitation reaction occurring on the surface of the suspended disks. The surface of the paper disk turns dark, and a white precipitate forms in the solution around the disk, suggesting the reduction of the Hg^{2+} to Hg^0 and $Hg_2{}^{2+}$ followed by precipitation. An essentially identical curve of the effect of *p*H on behavior, with darkening of the disks and formation of a white precipitate, is also observed in the collection of $Hg(NO_3)_2$ from nitrate solutions containing no chlorides. Filtering solutions of *p*H 6 or greater through SRXL resin-loaded paper results in quantitative recovery of the inorganic mercury. No precipitate formation or darkening of the disks was noticed in the solutions containing the methyl mercury.

The capacity of the SRXL resin for Hg^{2+} was determined by shaking 1-g portions of the resin with chloride solutions at *p*H 1.5 containing 2 g of $HgCl_2$ and 10 μc of ^{203}Hg. Portions were taken at intervals for the determination of radioactivity until no further loss of tracer from solution was observed. The capacity of the resin under these conditions was 540 to 550 mg of Hg^{2+} per gram of dry resin. This compares well with the 488 mg per gram of dry resin found by Koster and Schmuckler for Pt^{4+} (*2*).

A 5 percent aqueous solution of thiourea containing 5 ml of hydrochloric acid per liter will elute gold and platinum metals from the resin, permitting its reuse for many cycles (*5*), therefore this eluent was investigated for the removal of mercury from the SRXL resin. A series of eight cycles of mercury collection and elution were performed with the same 2-g portion of resin. For each cycle, mercury was collected from 100 ml of solution containing ^{203}Hg tracer, and each cycle contained the same amount or more mercury than the one preceding. The 100-ml volumes contained from 100 μg to 1 g of Hg. Tracer activity of 3-ml portions of each effluent showed that the collection was 100 percent at all concentrations. Mercury was then eluted from the resin with 10-ml portions of the 5 percent thiourea solution. More than 90 percent of the mercury was removed with the first 10 ml of eluent in each case, and elution was essentially complete after passing 30 ml through the resin. A rate of approximately 3 ml/min was used for the elution and the collection. After elution of the mercury, the excess thiourea was washed from the resin with distilled water, and the next 100 ml of solution were passed through the resin, starting the next cycle.

Thus the ability to selectively and quantitatively collect the highly toxic methyl mercury as well as inorganic mercuric salts, and the ability to be reused for many cycles, make this resin a very promising tool for attacking both the analytical and the industrial problems of mercury pollution.

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Adsorption of Mercury from Aqueous Solutions by Polyethylenimine-Modified Wool Fibers

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CSIRO, Division of Textile Industry, P.O. Box 21, Belmont, Victoria, 3216, Australia

■ When used in a packed column or a standing bath, polyethylenimine-modified wool (PEI-wool) had a substantially greater ability to adsorb mercury (Hg^2) from aqueous solution than unmodified keratin. A capacity of 3.3 meq/g was achieved within 30 min using solutions of 1000 ppm (Hg^2). Sorption from liquours passing through a column was rapid and effective at the 1-ppm level. The sorbed mercury was readily desorbed and the PEI-wool used repeatedly.

There have been several recent reports of the ability of protein fibers to adsorb mercury from aqueous solution (*1–4*), and the possibility of using them in effluent purification processes or for clinical purposes (*5*) has been discussed. Likewise, amine-modified cotton could adsorb mercury from solutions (*6, 7*). Here we report that the adsorptive capacity of wool for mercury (Hg^2) is substantially increased by polymerization of ethylenimine onto the fibers.

Experimental

PEI-Wool. Commercially scoured 64's quality Australian merino wool fibers (40 grams) were immersed (2 hr) in a 0.2% solution of ferrous ammonium sulfate (800 ml) and then squeezed before allowing to dry (48 hr) at 20°C. To the wool was added 0.25% hydrogen peroxide solution (600 ml) and ethylenimine (30 ml) (*8*). [Because of potential hazards from exposure to ethylenimine, it has been recommended (*9*) that protective gloves and goggles be used and that all operations be performed in a fume hood.] The fibers were heated (19 hr) at 50°C under nitrogen, rinsed under running tap water (2 hr), dried as before, and chopped to 1–3 mm lengths in a rotary mill. The uptake of ethylenimine (as bound PEI) was 10% w/w.

PEI-Reduced Wool. Unmodified wool (10 grams) was chemically reduced with 0.5M thioglycollic acid (300 ml) at 50°C for 3 hr, washed with distilled water, dried (100°C, 5 min), and converted to PEI-reduced wool as above. The uptake of ethylenimine (as bound PEI) was 20.2% (w/w).

Adsorption onto Columns of Chopped Wool Fibers. The wool (5 grams) was wet out in water containing 0.01% Antarox C0630 (a polyoxyethylated nonylphenol, GAF Corp.) and the resulting slurry poured into a glass column fitted with a porous plug and stopcock. When the fibers had settled they were equilibrated with solutions at the pH of the test solutions. The test solutions contained 1000 ppm Hg^2 (as $HgCl_2$ or a combination of $HgCl_2$–NaCl, Table I) and adjusted to various pH values with NaOH or HCl. Test solutions were admitted at the rate of one bed volume/min. The column effluent was collected in fractions and their mercury concentration measured.

Adsorption onto Wool in Standing Bath. The wool (5 grams) was stirred in a glass beaker with a solution (1 liter) adjusted to the required pH, containing 1000 ppm Hg^2 (as $HgCl_2$ or $HgCl_2$–NaCl, Table I) for prescribed periods.

Capacity of Wool Fiber Beds. Here the capacity of the beds has been expressed as milliequivalents of mercury per gram of wool (meq/g). For adsorption onto columns it was the amount of mercury adsorbed by the bed when its concentration in the column effluent reached 1% of the influent concentration. For adsorption onto wool in standing baths it was the amount adsorbed from the liquors after the prescribed period, and the value was calculated from the decrease in mercury concentration of the bath liquor. All adsorption measurements were made at 20°C.

Mercury Analysis. This was by atomic absorption spectrophotometry. Separate procedures used for solutions containing 1–1000 ppm (*10*) and up to 1 ppm Hg^2 (*11*) were essentially as described.

Results and Discussion

PEI-Wool. Protein fibers will bind approximately 1% of polyethylenimine irreversibly (*12*). This quantity will increase slightly if the fibers are pretreated with chlorine. By polymerization of ethylenimine monomer onto wool fibers, as reported here, irreversible binding of 10–20% PEI can be achieved. It is not known whether the PEI-wool composite so formed contains the PEI as a physically occluded or chemically grafted component. In the present work, wool treated by the last method has been used as packed beds in columns and in stirred standing baths to examine its potential in both continuous and batchwise mercury recovery processes.

Table I shows that maximum adsorption occurred in standing baths where, within 30 min, equilibrium was established. The capacity of 3.3 meq/g is of the same order as that of many granular ion exchangers. Even in solutions containing 10% NaCl, the adsorption of 1 meq Hg^2/g was still significant and may indicate that PEI-wool could

Table I. Mercury Adsorption by Polyethylenimine-Modified Wool

Liquor pH	Experimental method[a]	NaCl concn., %	Capacity, meq Hg^2/g wool
	PEI-Wool		
6	S_{30}		3.3
6	S_{30}		3.3
6	S_{15}	10	1.0
6	S_{30}	10	1.1
6	S_{15}	25	0.6
6	S_{30}	25	0.6
2	C		1.4
7	C		2.4
6	C	25	0.2
	PEI-Reduced Wool		
6	S_{30}		3.6
6	S_{30}		3.6
6	S_{15}	3	2.0
6	S_{30}	10	1.1
6	S_{30}	25	0.9
7	C		2.8
6	C	3	1.6
	Unmodified Wool[b]		
6	S_{30}	25	0
2	C		0.58
7	C		0.29

[a] S with a numerical subscript refers to adsorption in a standing bath for the indicated period (min); C refers to a column adsorption. [b] From (*1*).

have practical advantages in adsorbing mercury from electrolyte solutions (*13*).

In column adsorption tests, where the contact time was 1 min, the capacity was lowered slightly to 2.4 meq Hg^2/g at pH 7, indicating that adsorption was a rapid process. Sorbed mercury was quantitatively recovered by extracting the PEI-wool with *N* HCl (50°C, 15 min) or with citric acid solution (1%, pH2, 40°C, 15 min). The wool that was stripped in this way could be reused, an adsorption capacity of 2 meq/g persisting after 15 cycles.

Adsorption onto columns was effective when low concentrations of mercury were used. When 500-bed volumes of liquor containing 1 ppm Hg^2 (pH 6) were passed through the column (1 bed vol/min), the concentration in the effluent did not exceed 0.02 ppm. Greater efficiency could be expected from longer contact times in the column.

When we consider the pH range 2–7, we note that modification of wool with PEI changes the pH of maximum adsorption from 2 to 7; corresponding differences in the adsorption mechanisms might be inferred. Probably, at pH 2, the association of protonated amino groups with anionic mercuric complexes such as $HgCl_3^-$ or $HgCl_4^{2-}$ occurs (*1*). At pH 7, the adsorption probably involves chelation of Hg^2 with ligands located in both the PEI (*14*) and the wool.

PEI-wool appears to have a mercury adsorbing capacity exceeding cross-linked PEI-cotton (*6*) by a factor of 100. Although strict comparisons have not been made its rate of adsorbing mercury seems substantially greater than that reported for the modified cotton (*7*).

PEI-Reduced Wool. Ethylenimine was polymerized onto thioglycollate-reduced wool in the expectation that the chemically modified fibers, released from the restraint of protein disulfide bonds, would swell more readily in aqueous media. An increased PEI add-on and correspondingly improved mercury adsorption might then have resulted.

Practically, the amount of PEI formed in reduced wool was double that formed in native wool. Only minor increases were observed in the mercury-adsorbing capacity of PEI-reduced wool, consequently no advantage can be seen in using wool in the reduced form.

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Removal of Mercury from Aqueous Solutions by *N*-(2-Aminoethyl)aminodeoxycellulose Cotton

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■ *N*-(2-Aminoethyl)aminodeoxycellulose cotton (AEAC) was prepared in yarn form by reaction of ethylenediamine with chlorodeoxycellulose. The adsorption of mercuric ion by AEAC (degree of substitution 0.4) was studied over a wide range of concentrations. In the concentration range 0.5–43 g/l., the adsorption of mercuric chloride follows the Freundlich relationship, $\log_{10} x = 0.21 \log_{10} C + 2.7$, where x is the mg of mercuric chloride bound per gram of AEAC and C is the residual concentration in g/l. At concentrations in the range of 3.1–0.6 ppm, 100 mg of AEAC removed about 90% of the mercury present in 200 ml of solution, in a single equilibration. The results of this study suggest the possible use of AEAC as an agent for the collection of mercury in industrial processes.

The possibility of employing ion exchange or chelating resins as a means of removing heavy metal ions from solution has been explored by a number of workers (*1–5*). However, cost considerations have prohibited the widespread application of this technique on an industrial scale. A possible solution to the cost problem might be to use naturally occurring polymers or agricultural by-products as the basis for the exchange resin. In this regard, Friedman and coworkers (*6, 7*) have shown that mercuric ion is bound in large amounts by certain agricultural by-products and polyamine derivatives.

This investigation concerns the use of cotton cellulose as the insoluble support matrix; however, the same techniques could be readily applied to other celluloses or synthetic polyalcohols. In the study reported here, we have attached an ethylenediamine group to the anhydroglucose unit of the cellulose backbone via chlorodeoxycellulose (CDC) cotton yarn to give *N*-(2-aminoethyl)aminocellulose cotton (AEAC). AEAC very efficiently adsorbs mercury over a broad range of concentrations. Suprisingly, we observed that at very low concentrations (approximately 100 ppb), untreated cotton yarn also removes significant amounts of mercury. This adsorption may be due to carboxyl end groups and trace materials present in native cotton.

Experimental

Materials. Cotton was loose twist 12/3 (tex-151) Pima kier-boiled yarn unless otherwise specified. The phosphorus oxychloride ($POCl_3$), dimethylformamide (DMF), and

CHELATING COMPOUNDS - INSOLUBLE STARCH XANTHATE

Recently a company in Texas, POLLUTION TECHNOLOGY SYSTEMS, INC., has offered a process and a chelating organic product which removes metals including mercury from solution.

The product, DX-2000, is a buffered forty percent active organic material that effectively precipitates complexed or chelated cationic heavy metals from difficult to treat process waters. The vendors claim that the product is effective over a pH range of 3 to 11. Residual heavy metals are claimed to usually be well below local, state, and EPA-NPDES discharge limit permit requirements.

DX-2000 is claimed to be effective in removing metals also in the presence of complexing agents which would normally interfere with most other removal processes. The metal-DX-2000 sludge cake containing 40% solids is claimed to be more stable than metal hydroxide sludges.

Dosages of DX-2000 for metal removal vary from metal to metal as the loading ability of a liter of DX-2000 varies from metal to metal. For example, Mn^{+2} loads 77 g per liter of DX-2000 whereas gold loads to 550 g Au^{+1}, and silver loads to 300 g Ag^{+1} per liter of DX-2000. Mercury loads to 280 g Hg^{+2} per liter of DX-2000.

The manufacturer-vendor does not make claims regarding the level of mercury that can be achieved using DX-2000. In a pamphlet by the same vendor describing the use of insoluble starch xanthate, it is claimed that mercury levels were reduced to 0.7 and 1.0 ppb in two test solutions.

It is not known what the nature of the DX-2000 product is although the same vendor is known also to manufacture insoluble starch xanthate based on technology developed by the U.S. Dept. of Agriculture.

NORTHERN REGIONAL RESEARCH LABORATORY
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The insoluble starch xanthate is claimed to have removed mercury from 100 ppm to 1 ppb in one case and from a second solution containing 10 ppm to 0.7 ppb Hg.

The development of insoluble starch xanthate for heavy metal removal (including mercury) has been described by SWANSON, et al. (1973), WING, et al. (1974), GREENBERG and WING (1983), and WING (1983).

The vendor does not release much detail about how its process works as they wish to sell consulting and engineering services as well as product. More information can be obtained from:

POLLUTION TECHNOLOGY SYSTEMS, INC.
3015 Benton Street
Garland, TX 75042
(214) 272-4010
Mike Coward
Manager, Systems Engineering

IKEBE (1974) of SUMITOMO CHEMICAL CO. LTD., Japan, described a process whereby heavy metal ions, especially Cu^{2+} and Hg^{2+}, are sequestered with a dialkyldithiocarbamic acid and are treated with NaOH and Na_2S to produce a scum of CuS and PbS separating the sulfide scum by either precipitation or flotation and regenerating the dialkyldithiocarbamate ion which is then recycled "quantitatively." The use of NaOH in this process improves the efficiency of separation by preventing the formation of colloidal CuS. Thus, $Cu[S(S)CNEt_2]_2$ was suspended in one litre water, and two equivalents of NaOH was added and stirred. One mole Na_2S/l was added, and the CuS formed was removed by precipitation.

When one equiv. of Na_2S was added, approximately 100% of the $NaS(S)CNEt_2$ was recovered. The light yellow liquor recovered had a pH of 12.8 and contained only 1-2 ppm Cu. When NaOH was not used, the recovered $NaS(S)CNEt_2$ contained about 35% of the colloidal CuS in suspension.

DEVOE-HOLBEIN

Devoe-Holbein has also developed a metal removing process which relies on a "composition" or solid adsorbent to precipitate and remove metals. Examples are cited in their literature in which mercury was removed from 12.0 ppm to 4.8 ppb in one case and from 120 ppm Hg to 1.2 ppb in another. A schematic flowsheet for a process employing Devoe-Holvein compositions has been developed and an association formed with an engineering company to develop a practical process.

More information can be requested from:

DEVOE-HOLBEIN (CANADA), INC.
175 Bouchard Avenue
Dorval, Quebec H9S 1A9
(514) 636-6042
Telex: 05-821538
Bruce Holbein

Devoe-Holbein has not released data on the costs of the process or their "compositions." It was stated that in experimental quantities, the composition would be expensive. Prices

would be much, much lower if the product were in such demand as to justify mass production.

COAGULATION TREATMENT

Removal of mercury by coagulation has been reported for a variety of mercury-containing wastewaters. Coagulants employed include aluminum sulfate (alum), iron salts, and lime. The process has been applied successfully to both organic and inorganic mercury. In pilot plant tests of alum and iron treatment of inorganic and methyl mercury, inorganic mercury was removed effectively only by iron while neither coagulant provided effective methyl mercury removal according to O'CONNOR (1974).

Treatment data for alum and iron coagulation are summarized in the following table . Effluent levels of mercury achieved by alum treatment range from 1.5-102 mg/l and by iron treatment from 0.5-12.8 mg/l. Iron appears to be better than alum for the purpose achieving a lower effluent limit.

Alum and Iron Coagulation Treatment for Mercury.

Coagulant Salt	Dosage (mg/l)	Treatment pH	Mercury (μg/l) Initial	Mercury (μg/l) Final	Additional Treatment	Ref.
Alum	1000	3	11,300	102	Filtration	37
Alum	100	na	90	11	—	38
Alum	100	na	na[a]	10	—	38
Alum	21-41	6.7-7.2	5.9-8.0	5.3-7.4	Filtration	28
Alum	na	7.0	50	26.5	Filtration	35
Alum	20-30	na	3-8	1.5-6.4	—	36
Alum	20-30	na	3-16[a]	2.3-21.3	—	36
Iron	34-72	6.9-7.4	4.0-5.0	1.5-2.5	Filtration	28
Iron	na	8.0	50	3.5	Filtration	35
Iron	20-30	na	1-17	0.5-6.8	—	36
Iron	20-30	na	2-17[a]	1.2-12.8	—	36

[a] Organic mercury.

37 HONDA, et al. (1973)
38 HELLESTAN, et al. (1972)
28 LOGSDON, et al. (1974)
35 O'CONNOR (1974)
36 LOGSDON and SYMONS (1973)

ACTIVATED CARBON

The effectiveness of carbon treatment is dependent on several factors according to PATTERSON (1975). These include the chemical form of mercury in solution, concentration of mercury, dosage and type of activated carbon, as well as contact period. Increasing carbon dosage and contact times improves removal of both inorganic and organic mercury as would be expected and as described by LOGSDON and SYMONS (1973). Organic mercury is more effectively removed than inorganic mercury, and a

review of available treatment data by PATTERSON (1975) and shown below in tabular form indicates that the highest percentage removals (85-90%) result from carbon treatment of more concentrated mercury solutions. However, the lowest effluent mercury results from the treatment of lower initial mercury concentrations although the relative efficiency is less. Thus, carbon treatment of initial mercury levels of below 1 mg/l yields an efficiency of removal of less than 70%, but an effluent mercury of less than 0.25 mg/l. Carbon treatment of initial mercury of 10-100 mg/l yields 90 or more percent efficiency but effluent levels of 1-10 mg/l.

Activated Carbon Treatment for Mercury.

Mercury (μg/l)		Additional	
Initial	Final	Treatment	Reference
na	<100	Presettling	39
12–46	<0.5	—	
5.8	0.9	Iron Coagulation	35
9.3	1.6	Alum Coagulation	28
na	0.8	—	36
na	0.2	—	36
100	10–20	Precipitation	19
60–67	4.5–6.0	—	20
0.40–0.81	0.13–0.19	Polymer Added	40
0.5	0.21	Polymer Added	40

Source: PATTERSON (1975)

39 SUZUKI, et al. (1973)
35 O'CONNOR (1974)
28 LOGSDON, et al. (1974)
36 LOGSDON and SYMONS (1973)
19 U.S. EPA Report 805-25 (1971)
20 PERRY (1974)
40 SAN SCI DIV. (1974)

REDUCTION PROCESSES

Inorganic ionic mercury can be converted to the metallic form by reduction and separation by filtration or other solids separation methods. Several reducing agents are available including aluminum, zinc, hydrazine, stannous chloride, and sodium borohydride. PATTERSON (1975) references the use of reductive processes to treat solutions with initial mercury concentrations of 1.8-26 ppm Hg which resulted in final mercury levels in the effluents of 5-830 ug Hg/l.

In gold and silver recovery processes using the Merrill-Crowe process (zinc precipitation), mercury will be reduced as well as gold and silver and ends up in the zinc precipitate. If there is enough mercury present, this necessitates an additional step to retort the zinc precipitated metals to remove the mercury before the gold and silver can be smelted to a dore.

The data provided by PATTERSON indicates that in order to achieve mercury levels below 100 g/l, the use of reductants would have to be supplemented by a second polishing step by one of the other treatment steps discussed in this chapter. For example, where gold plant effluents are treated by ferrous sulfide addition and settling to remove cyanide, chances are excellent that mercury will also be precipitated as a sulfide. If carbon columns are used to recover incremental gold from effluents or recirculating solutions, the likelihood of further mercury removal is also excellent by carbon adsorption. If, in future, anionic ion exchange resins are used to recover gold as a cyanide complex, then possibly a pretreatment with chlorine to destroy cyanide will render the mercury in the chloride complex form suitable for loading onto the resin as well, or mercury may load as the anionic mercury cyanide complex.

Performance of Reduction Processes for Mercury Treatment.

Reductant Used	Mercury (μg/l) Initial	Mercury (μg/l) Final	Additional Treatment	Reference
Zinc	5,000–10,000	5–10	—	41
Zinc	1,800	140	(pH 11.5)	20
	12,500	830	(pH 10.0)	
	12,500	750	(pH 6.0)	
	12,500	470	(pH 2.5)	
Zinc	na	600	—	19
Stannous Chloride	2,800	500	—	20
Sodium Borohydride	10,000	220	—	20
	4,000	420		
	26,000	820		
Sodium Borohydride	4,700	200		42
Sodium Borohydride	na	<10	(pH 9–11)	18

Source: PATTERSON (1975)

41 WALTRICH (1973)
20 PERRY (1974)
19 U.S. EPA (1971)
42 COULTER (1973)
18 CHEREMISINOFF and HABIB (1972)

A full-scale commercial process based on the reduction of mercury by sodium borohydride is marketed as the Ventron process and is described by CHEREMISINOFF and HABIB (1972) and ROSENZWEIG (1971).

ADSORPTION PROCESSES

RANDALL (1974) tested the adsorptive properties of a wide range of agricultural wastes for the removal of toxic metal cations from synthetic solutions as well as mining and industrial effluent streams with a view to recovering metal values. Several of these wastes were reported to remove metals effectively to "below the levels prescribed by local or federal standards." Rate, selectivity, and capacity of the agricultural substrates for heavy metal cations were measured in the laboratory, and the authors claim very effective

removal of Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}. As with several of the processes mentioned above, this approach was not observed in commercial application although it may be worth further evaluation.

OTHER TECHNOLOGY

PATTERSON (1975) refers to a variety of other processes that are mentioned in the literature. These include solvent extraction with high molecular weight amines, the use of silicon alloys for reduction to elemental mercury (McKAVENEY, 1972), removal by insoluble starch xanthate-cationic polymer complexation (SWANSON, 1973; WINZ, et al. 1974), adsorption onto ground rubber and onto wool at sulfhydryl sites (FREELAND, et al., 1974).

Several of these processes appear promising yet in the course of this investigation, none were found in commercial application ten years after they were announced. It is emphasized that such experimental processes require considerable further development and pilot-scale testing before they could be considered suitable for commercial-scale application.

CONCLUSIONS

There are many treatment technologies available for mercury control. The more effective are summarized in the following table which was assembled by PATTERSON (1975). Among the processes listed, ion exchange, iron or alum coagulation, and activated carbon adsorption have the capability to reduce mercury below 10 ug/l, but the effects of cyanide on performance needs to be determined. The trip report on COTTER CORP.'s Schwarzwalder Mine in Appendix I describes an innovative new ion exchange process that reduces uranium and base metals to extremely low levels. Possibly this system would make further improvement possible in the performance of IX for mercury removal.

Conventional precipitation systems employing sulfide and flocculating aids seem capable of achieving mercury levels of 10-20 ug/l. However, RANDOL INTERNATIONAL suggests that combining the HDS process with ferrous sulfide or Na_2S addition may make it possbile to improve this when treating acid solutions.

Other methods, particularly the reduction process for small-scale use, are capable of producing very low-effluent concentrations of mercury. Many of these methods have not been tested in full-scale operation.

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By Richard T. McNerney

Analysis of mercury using a gold film detector

ATOMIC ABSORPTION (AA) flameless spectrophotometry is currently the most commonly used method for the determination of mercury in liquid matrices. However, serious limitations of the technique, including inconsistencies in the liquid calibration standard, interferences, and poor reproducibility, have raised questions regarding the accuracy of the AA method. The thin gold film (gf) technique described in this paper overcomes these limitations and at the same time reduces the complexity of mercury analysis.

The detection of elemental mercury vapor by thin gf sensors is a technique developed and patented by the Jerome Instrument Corporation.[1] The adsorption of elemental mercury vapor on a gold film approximately 200 Å in thickness produces a pronounced resistance change in the film; this resistance change is linear in the range of 1–100 ng of mercury.[2]

Dedicated, portable instruments utilizing the thin gf sensor for the analysis of mercury in dry soils by direct combustion and in air by direct sampling have been in use for several years. Recently a thin gf mercury analyzer and sample delivery system, the Jerome Instrument model 511, has been designed for the analysis of mercury in liquid matrices.

Mercury vapor, released in an air stream from aqueous solutions using wet-chemical procedures described later, is drawn into the instrument by an internal pump. The elemental mercury passes over, and is adsorbed and integrated by, the thin gf sensor. This integrated electronic signal is converted by a microprocessor to the mass of mercury per unit volume of sample. Data presentation by direct digital readout is in nanograms of mercury. Saturation of the sensor occurs after 500 ng of mercury has been accumulated; full sensitivity is reestablished in 10 min by thermal desorption of the mercury from the sensor.

Mercury concentrations normally found in liquid matrices such as water, urine, and blood are in the low nanograms per milliliter range. But quantitative analysis depends on a system that is not only sensitive to mercury, but is also selective for the element. A serious limitation to the AA technique for mercury analysis is the presence of interfering substances such as H_2O, SO_2, O_3, and a variety of organic and inorganic compounds.[1–6] The complexity of the techniques developed for the preparation and analysis of liquid samples for mercury are a result of the efforts to overcome these interferences.

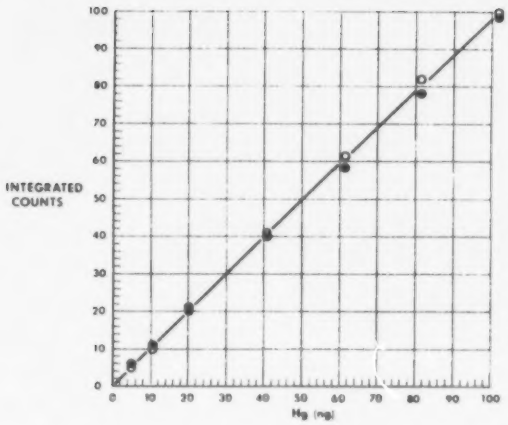
The thin gf sensor's specificity for mercury eliminates most interferences common to the AA technique,[7,8] and its design has resulted in significant improvements in signal reproducibility, calibration technique, and full-range linear response. The glassware system for sample preparation and delivery eliminates potential mercury loss from the sample. Microprocessor control reduces the complexity of the instrument's operation to a single manual control. With a minimum detection limit of 1.0 ng of mercury, the volume of sample necessary for analysis is usually less than 5 mL. Thus, the amount of reagent used in sample preparation is significantly reduced, minimizing the reagent blank. The system is field portable for on-site analysis where degradation of the sample due to transportation and long storage is a concern.[8]

Calibration

The thin gf technique determines the mass of mercury per unit volume of sample; thus, calibration can be performed using the most basic standard possible—the vapor pressure of mercury.[9] A small drop of liquid mercury in a closed container, e.g., a 300-mL polyethylene bottle, will saturate the enclosed air at a value which depends only on temperature. The effect of total pressure on the vapor pressure of mercury is negligible. The relationship of mercury concentration in ng/cm^3 to temperature is shown in *Table 1*.

With the saturated mercury vapor maintained at a constant temperature, a known mass of elemental mercury is injected directly into the flow path of the thin gf sensor using a gas-tight syringe. The ana-

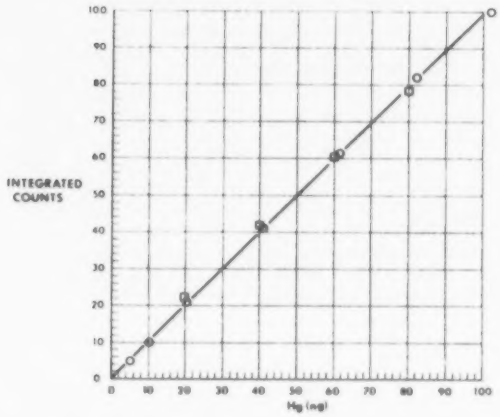
Mr. McNerney is Sales Manager, Jerome Instrument Corporation.



CALIBRATION RESPONSE

Hg	○ BEFORE	● AFTER
0	0	0
5.2	5	6
10.3	10	11
20.6	21	20
41.2	41	40
61.8	62	57
82.4	83	77
103.0	100	98

Figure 1 *Vapor standardization.*



□ AQUEOUS Hg	RESPONSE
0	0
20	22
40	41
60	61
80	78

○ VAPOR Hg	RESPONSE
0	0
5.2	5
10.3	10
20.6	21
41.2	41
61.8	62
82.4	83
103.0	100

Figure 2 *Aqueous vs vapor standardization.*

lyzer responds linearly to a series of mercury vapor standards. After a 10-min film heat which thermally desorbs the accumulated mercury, sensitivity and full range linearity are restored. This is illustrated in *Figure 1*.

Figure 2 shows the excellent correlation that exists between the vapor phase and aqueous mercury standards. However, the correlation will suffer due to the instability of liquid standards and the errors that occur in the preparation of the stock and working liquid solutions.

An accurate vapor standard depends on maintenance of the calibration vessel at a constant temperature and withdrawal of a precise volume of the standard. Dilution is not necessary since the vapor standard is within the working range of the instrument. Oxidation of the mercury droplet, which could reduce the vapor pressure of mercury, is prevented by periodic light shaking of the calibration vessel.

However, liquid standards for mercury, both stock and working solutions, have shown varying degrees of instability. For example, a 1000-ppm ± 1% mercury reference solution (certified AA standard), with an expiration date sixteen months from the date of initial use, over a period of four months decreased in mercury concentration by more than 20%. Working solutions of 20 ppb prepared from a liquid standard according to well-documented procedures will, when shaken slightly, evolve elemental mercury in significant quantities in the head space

Table 1

Temperature conversion table

Temp., °C	Ng/cm³
16	9.4
16.5	9.8
17	10.2
17.5	10.6
18	11.1
18.5	11.6
19	12.1
19.5	12.6
20	13.2
20.5	13.7
21	14.3
21.5	14.9
22	15.5
22.5	16.2
23	16.9

above the solution. As a result, the linear correlation that is observed for the vapor versus aqueous standards immediately after preparation of the working solution can deteriorate significantly over several hours.

Mercury reference standards for mercury in solution are prepared by weighing out and dissolving crystals of $HgCl_2$ in distilled water that has been slightly acidified. The significant sources of error in this technique are the weighing of the $HgCl_2$, the purity of the $HgCl_2$, and the possible mercury contamination of the labware used. The solution is then subject to decomposition as noted previously.

Whether the reference standard is purchased in liquid form or prepared by dissolving $HgCl_2$ in distilled water, concentrated stock solution must be diluted from one million ng/mL to a working solution containing 20 to 100 ng/mL. Possible sources of error include the dilution process itself, and the possibility exists for mercury contamination or the loss of mercury to the glassware used in the dilution process.

Inteferences

Independent studies regarding the lack of response of the thin gf sensors to interferences common to AA have been published,[6,7] and some of the results are shown in *Table 2*. Murphy[6] considers the chemicals listed in Table 2 to be some typical examples of the troublesome types of samples that cause interference in the direct determination of mercury. The gold film system permits each of these samples to be analyzed directly and accurately without interferences from possible gaseous emissions that may be interpreted as mercury.

SO_2, ozone, organic and inorganic compounds, and fine particulates do not cause a response of the thin gf sensor; the gf sensor also does not respond to water vapor. As a result, drying agents such as magnesium perchlorate, which have been shown to be a negative interference with AA instruments, are not necessary with the gold film detector.[4]

Also noteworthy is that several wet chemical preparations include two or three additional reagents to eliminate potential AA interferences such as sulfides and chlorine. The lack of response by the gf method to these interferences can thus simplify the chemical preparation of a sample.

Reproducibility, precision, and accuracy

In AA analysis, reproducibility is dependent on the rate at which mercury is liberated from solution. Factors which affect this rate of release are pump rate, bubbler characteristics, sample matrix, sample volume, and relative strength of the reducing agent.[10,11]

In contrast, the integration of the mercury signal by the thin gf sensor makes the analyzer relatively independent of the factors which affect the rate of release.

The precision of the analyzer was demonstrated in an independent evaluation comparing the model 511 to a flameless AA spectrophotometer.[12] Forty-five urine samples were analyzed in triplicate with each instrument. The sample size analyzed by the gold film detector was 0.2 mL, as compared to a 2.0-mL sample required by the AA spectrophotometer. The results listed in *Table 3* gave a coefficient of correlation of 0.985 between the two instruments. The relative standard deviation of the results

Table 2

Interference study, cold vapor AA (CVAA) vs gf mercury detector (GFMD)*

	CVAA		GFMD	
Sample (in water)	Hg added, ng	Hg measured, ng	Hg added, ng	Hg, measured, ng
Acetone (20%)	100	>1000	100	95
Sodium sulfite (10%)	100	220	100	100
Sodium thiosulfate (10%)	100	750	100	102
Pyridine (5%)	100	>1000	100	91
Ammonium hydroxide (20%)	100	>1000	100	96

*Source: Murphy, P.J., "Determination of nanogram quantities of mercury in liquid matrices by a gold film mercury detector," *Anal. Chem. 51*, 1599 (Aug. 1979).

Table 3

Comparison of gf detector with AA method for Hg in urine*

Sample no.	Thin gf method 8-20	8-24	9-1	AA 8-20	8-24	9-1
2	272	275	273	295	275	267
41	35	28	30	12	19	24
30	99	100	101	128	97	101
13	22	17	17	14	15	29

*All results are reported in micrograms mercury per liter.

obtained with the gold film detector was 2.4%, as compared to 6.8% for the AA instrument.

As mentioned previously, the linear range of the gold film detector is 1 to 100 ng with gf saturation occurring at 500 ng. At levels above 100 ng, the microprocessor automatically corrects for nonlinear response. A series of 2-mL injections of mercury-saturated vapor gave responses of between 21 and 26 ng, totaling 470 ng, 94% of film saturation. The vapor reference was maintained at 18.5°C. The RSD for this set of data was 5.7%.

Suggested analytical procedure for mercury in solution

Gold film technology coupled with microprocessor control and an improved glassware delivery system have enhanced the quantitative analysis of mercury in liquid matrices, while at the same time reducing its complexity.

An illustration of this is the recommended procedure for the preparation and subsequent analysis of mercury in urine. The sample preparation is a modification of the American Congress of Government Industrial Hygienists (ACGIH) method No. 165, published in the ACGIH *Analytical Methods Manual*.

It is extremely important to immerse new glassware in concentrated HNO_3 for at least 8 hr. After this initial mercury decontamination, normal rinsing in acid is required to ensure mercury-free glassware. To prevent contamination of the stored glassware, continuous immersion in distilled water is recommended.

It is important that the sample preparation glassware *never* come into contact with reducing agents such as stannous chloride or sodium borohydride, because mercury in the sample can be lost due to carry-over of these reagents.

The detailed procedure is as follows: Under a fume-hood, add 1 mL of concentrated HNO_3 to a 30-mL Pyrex test tube. Pipet 0.25 mL of a urine sample into the test tube; allow 5 min for the digestion of the sample at room temperature. Add enough distilled water to bring the final volume to approximately 30 mL; the final volume is not critical.

Transfer the diluted sample to the reaction vessel. Attach the vessel to the bubbler. Inject 0.5 mL of 10% stannous chloride solution into the reaction vessel. This closed system eliminates the possibility of mercury loss from the sample to the atmosphere.

Immediately press SAMPLE START—the system automatically rezeroes and aeration commences. The 60-sec cycle will automatically go to completion, and the mercury value will be displayed in nanograms with the reading held until the next sample cycle. Data can also be displayed on a chart recorder or entered into a computer.

Forty urine specimens with an average mercury concentration of 50 μg/L can be analyzed before film saturation occurs.

Summary

The incorporation of thin gf sensors into an analytical system designed for the determination of total mercury in an aqueous matrix represents a distinct improvement over the AA method. The integrating characteristics and the selectivity of the gf sensor to a mercury signal are the major reasons for this improvement.

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Determination of Nanogram Quantities of Mercury in Liquid Matrices by a Gold Film Mercury Detector

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Many papers have been published in recent years dealing with mercury analysis. One of the most significant mercury methods was developed by Hatch and Ott (*1*), who reported that mercury could be directly reduced to the elemental state in an aqueous medium and the mercury vapor measured by atomic absorption spectrometry. Another important technique was developed by Anderson (*2*), who demonstrated that mercury could be collected on gold for subsequent determination by atomic absorption. McNerney (*3*) and Ohkawa (*4*) have taken advantage of the amalgamation properties of mercury and gold and utilized a sophisticated instrument based on a change in the resistivity of a gold film detector. However, while this instrument has improved sensitivity (*4*) and analytical versatility, the technology developed using this important nonatomic absorption technique was limited to air samples or those samples decomposed by combustion.

It is the purpose of this paper to describe the use of a gold-film mercury detector coupled with a direct reduction technique to determine mercury in aqueous media. The system allows analysis of a wide variety of samples while eliminating most of the interferences usually associated with cold vapor atomic absorption techniques.

EXPERIMENTAL

The instruments used in this study were a Gold Film Mercury Detector, Jerome Instrument Corporation, and a Coleman MAS-50, Coleman Instruments. Additional equipment included Coleman MAS-50 aerators and Standard 500-mL BOD bottles.

Two reducing agents were employed: tin(II) chloride solution (10% in 10% HCl) and sodium borohydride solution (0.2% in 40% NaOH). The standard solution used was prepared using reagent-grade mercury sulfate.

All other chemicals used were reagent-grade and "mercury-free" and included acetone, sodium sulfite, sodium thiosulfate, pyridine, ammonium hydroxide, hydrochloric, nitric, and sulfuric acids.

RESULTS AND DISCUSSION

Figure 1 shows the adaptation of a gold film mercury detector set up to monitor mercury in aqueous solutions. In this system, mercury vapor is volatilized from solution onto the gold collector coil by means of a suitable reducing agent. The collected mercury is then thermally volatilized and collected on the gold films located internally in the instrument. Mercury adsorption onto these films causes an increase in resistance (displayed on the digital galvanometer) and that increase is proportional to mercury content. The instrument is calibrated after each determination using standard addition techniques.

Since the proposed system involves quantitative collection of the volatilized mercury, a time study was needed to determine the optimum collection conditions. Table I shows that 2 min are necessary to complete the collection cycle. The remainder of the data were obtained using the 2-min collection cycle, which begins after introduction of the reducing agent.

Table II shows comparative data of the proposed system and a conventional cold vapor atomic absorption analyzer. The different sample preparations included: Group 1, direct dissolution in water; Group 2, wet digestion with nitric and sulfuric acids; Group 3, direct dissolution in water plus addition of hydroxide (since acidification of sodium thiocyanate with nitric acid is potentially hazardous, hydroxide is added before the addition of the reducing agent. Hydroxide effectively competes with thiocyanate and allows for direct reduction of the mercury); Group 4, use of 0.2% sodium borohydride solution as the reducing agent (mercury forms a strong complex with iodide (HgI_4^{2-}) which keeps the mercury from becoming completely reduced on the acid side with tin(II)

Table I. Aeration (Collection) Time Study (50 ng Hg added in each case)

aeration (collection), s	mercury measured,[a] ng
5	6
15	13
30	22
60	35
120	50
300	52
600	51

[a] Average of triplicate determinations.

Table II. Comparison Study—Conventional Cold Vapor Atomic Absorption vs. Gold Film Mercury Detector

sample	CVAA[a]	GFMD[a]
Group 1		
KCl	1000	900
HNO_3	<1	<0.1
KOH (40%)	21	19
CH_2OHCH_2OH	<1	<0.1
Group 2		
ground bone-1	3900	4300
ground bone-2	285	284
EK11628, gelatin Hg ref. (*6*)	2200	2300
organic dye	410	390
Group 3		
NaCNS-1	1	1
NaCNS-2	<1	<0.1
Group 4		
KI	6	7
NaBr	37	40
Group 5		
waste water-1	5.2	5.5
waste water-2	0.3	0.3
Group 6		
$AgNO_3$-1	<10	<1
$AgNO_3$-2	95	94

[a] Average of duplicate determinations expressed as ng/g or ng/mL.

Table III. Interference Study—Cold Vapor Atomic Absorption vs. Gold Film Mercury Detector

	CVAA		GFMD	
sample (in water)	mercury added, ng	mercury measured, ng	mercury added, ng	mercury measured, ng
acetone (20%)	100	>1000	100	95
sodium sulfite (10%)	100	220	100	100
sodium thiosulfate (10%)	100	750	100	102
pyridine (5%)	100	>1000	100	91
ammonium hydroxide (20%)	100	>1000	100	96

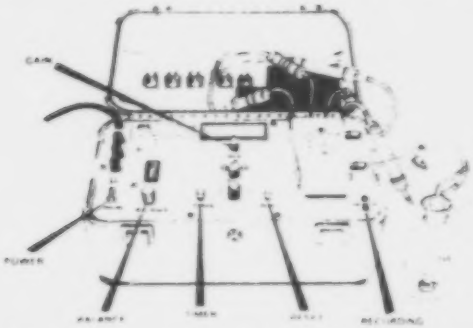

Figure 1. Adaptation of a gold film mercury detector using a direct reductino technique

chloride. Therefore, it is desirable to use a stronger reducing agent such as sodium borohydride in alkaline medium to quantitatively produce atomic mercury. All other data in this paper were obtained utilizing tin(II) chloride as the reducing agent); Group 5, addition of nitric acid followed by boiling (nitric acid addition and boiling allows for degradation of any organic mercury to the ionic state. It also might be noted that the proposed system allows for mercury analysis in water samples at the nanogram per liter level); and Group 6, precipitation of silver with a potassium bromide solution (5). There were no significant differences between the results obtained by the analyzers (correlation coefficient, r_{xy} = 0.9995), except that the gold film system offers lower detection levels (see Groups 1, 3, and 6, Table II).

The chemicals in Table III represent an interference study to show the advantages of the proposed system over cold vapor atomic absorption. Each chemical was dissolved in distilled water and diluted to 100 mL to give the indicated percentage by weight. Mercury and tin(II) chloride were added to the diverse matrices and the element was monitored by both techniques. In each case, erroneously high values were obtained using cold vapor atomic absorption. Gaseous vapors, such as sulfur dioxide and ammonia, which absorb at the 253.7-nm wavelength, showed positive interference. The chemicals listed in Table III are some typical examples of the troublesome types of samples that cause interference in the direct determination of mercury. The attractive feature of the gold film system is that each of these samples can be analyzed directly and accurately without interference from possible gaseous emissions that may be misinterpreted as mercury.

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Quantitative Analysis of Mercury Vapor by Gold Film Sensors

by Richard T. McNerney

JEROME INSTRUMENT CORPORATION

PRESENTED AT THE 1983 MEETING OF THE
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PHILADELPHIA, PA

The detection of elemental mercury vapor by a thin Gold Film sensor was developed and patented (U.S. Patent #3,714,562) by J. McNerney, founder of the Jerome Instrument Corporation. (Figure 1)

The sensor, produced by high vacuum deposition onto a ceramic substrate, undergoes an increase in electrical resistance proportional to the mass of mercury in a sample. Two films, a reference and a sensor, are placed in opposite arms of a Wheatstone Bridge, a sensitive electrical circuit capable of detecting small changes in resistance. (Figure 2) Since mercury vapor is unique in its ability to alter the resistance of the Gold Films, interferences common to atomic absorption (AA) instruments, i.e. water vapor, SO_2, organic vapors, and particulates, are eliminated.

The Model #411 Gold Film Mercury Vapor Analyzer, designed for the analysis of mercury vapor in the workplace environment, incorporates a pump and digital display with microprocessor control. (Figure 3) Activating either the 10 second sample or 1 second survey mode starts an internal pump which draws a precise volume of air over the Gold Film sensor. The microprocessor computes the concentration of mercury, displaying the results on an LCD meter. This reading remains displayed until the next sample cycle is activated at which point the microprocessor automatically resetes the meter.

The microprocessor will ensure a linear response until the Gold Film has absorbed approximately 500 nanograms of mercury. (Figure 4) As mercury accumulates on the sensor, the percentage of saturation is indicated by pressing the Sensor Status button. Approximately forty 10 second or 400 1 second samples can be taken in atmospheres containing 0.1 mg of Hg/m³ (current OSHA TLV) before saturation reaches 100% (500 ng). At that point, a 10 minute film heat cycle is activated to desorb the accumulated mercury from the sensor and return it to its original baseline resistance. (Figure 1)

CALIBRATION

The Gold Film technique determines the mass of mercury per unit volume of sample. Thus, calibration of the Model #411 can be performed simply and directly by using the most basic standard possible: the vapor pressure of mercury.

A small drop of liquid mercury in a closed container, e.g. a 300 ml polyethylene or thermos bottle, will saturate the enclosed air at a value which depends only on temperature. (Figure 5)

The concentration of mercury is calculated by utilizing relationships of pressure, temperature and volume as expressed in the Ideal Gas Law. It should be noted that the concentration is not dependent on atmospheric pressure (P_A) but the vapor pressure of mercury (P_{Hg}) and the measured temperature of air saturated with mercury (T_m). (Figures 6 & 7)

With the calibration vessel maintained at a constant temperature, a known mass of mercury saturated vapor is injected directly into the flow path of the Gold Film sensor of the Model #411 using a gas-tight syringe.

Referring to Figure 8, 1.12 ng of mercury is introduced into the Model #411 using this procedure and activating the 10 second sample cycle. With the pump rate set at 0.75 L/min (12.5 cc/sec), the 1.12 ng of injected mercury will be diluted with 125 cc (12.5 cc/sec X 10 sec) of "Mercury free" air. This is equivalent to a mercury vapor concentration of 0.106 ng/cc (1.12 ng/125 cc)*. The digital meter response of the Model #411 is adjusted electronically to reflect this concentration. The linear response of the Model #411 (Figure 10) through its full operational range allows a single point calibration.

* 1 ng/cc = 1 mg/m³

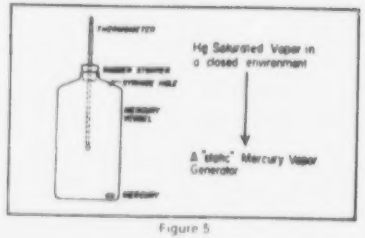


Figure 5

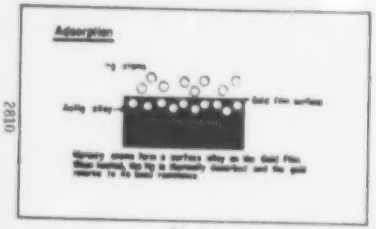


Figure 1

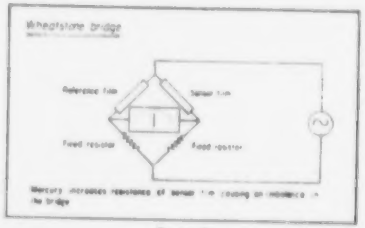


Figure 2

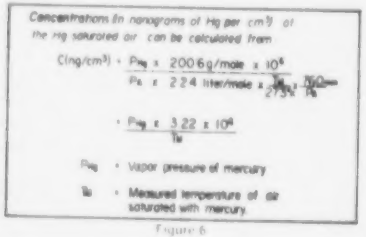
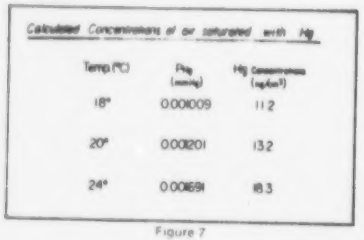


Figure 6


Calculated Concentrations of air saturated with Hg

Temp (°C)	P_{Hg} (mmHg)	Hg Concentrations (ng/cm³)
18°	0.001009	11.2
20°	0.001201	13.2
24°	0.001691	18.3

Figure 7

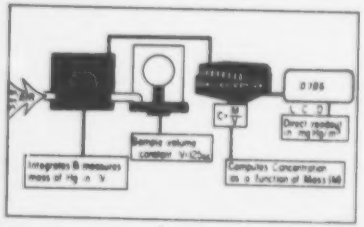


Figure 3

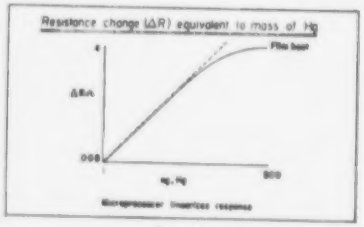


Figure 4

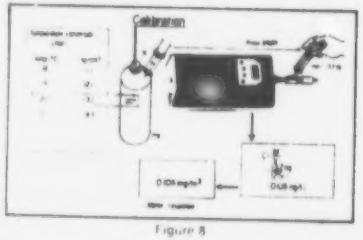


Figure 8

PRECISION & LINEARITY OF THE MODEL #411

The integrating characteristics of the Gold Film sensor, together with microprocessor-control, ensure excellent reproducibility and linear response.

Figure 9 represents a series of repetitive 10-second samples taken by the Model #411 in an atmosphere with a mercury concentration of 0.129 mg/m^3. Sampling was initiated with "Mercury-free" Gold Film sensors and concluded when sensor status indicated 60% saturation. The standard deviation and precision for this set of data is 2.44 and 2%, respectively.

Similarly, the Model #411 sampled atmospheres containing mercury concentrations ranging from 0.010 to 0.375 mg/m^3. Sampling was initiated with a "Mercury-free" Gold Film sensor and concluded when the sensor status indicated 30% saturation. The graph in Figure 10 illustrates the direct correlation between the meter response of the #411 and the known mercury concentration.

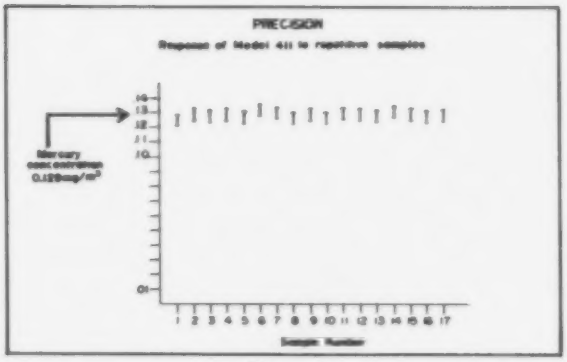


Figure 9

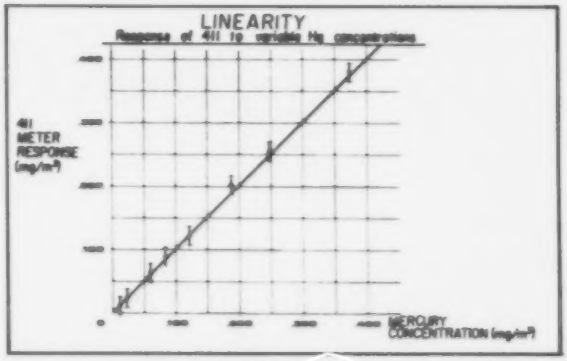


Figure 10

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SUMMARY OF TREATMENT TECHNOLOGY - MERCURY

Technology	Lower Limit of Treatment Capability (ppb Hg)
Sulfide Precipitation	10-20
Ion Exchange	1-5
Alum Coagulation	1-10

SUMMARY OF TREATMENT TECHNOLOGY - MERCURY (Continued)

Technology	Lower Limit of Treatment Capability (ppb Hg)
Iron Coagulation	0.5-5.0
Activated Carbon	
- High Initial Hg	20
- Moderate Initial Hg	2.0
- Low Initial Hg	0.25

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CHAPTER 45

MOLYBDENUM Mo

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INTRODUCTION

Molybdenum does not commonly occur in mine-mill effluents. It is also an element of little or no environmental concern. Despite years of investigation AMAX, INC., the largest producer of molybdenum in the world, and the U.S. EPA as well as the state of Colorado, have yet to find a case where molybdenum has been responsible for environmental damage. Excessive molybdenum in livestock water supplies can, however, give the trots to cattle. Why then should molybdenum be removed from water?

First, if there is enough of it, molybdenum removed from effluents may one day represent a profitable resource although that is not the case at current prices. Second, regulatory limits have been promulgated in some states, apparently motivated by the attitude of some regulators that everything should be regulated on principle, and molybdenum should have to be removed to meet some arbitrary standard "In case there are environmental effects

that are not yet known." One can always hope that a new trend toward more pragmatic regulatory attitudes may one day dawn.

OCCURRENCE OF MOLYBDENUM IN THE MINE-MILL ENVIRONMENT

Molybdenum is mined as a primary product as molybdenite MoS_2 in several porphyry deposits in the western U.S.A. and Canada. It also occurs as a by-product of copper mines in the U.S.A., Canada, and several South American countries, notably Chile and Peru.

Molybdenum also occurs in volcanic formations associated with and/or overlying primary uranium deposits in the southwestern U.S.A. and is sometimes associated with other minerals (e.g., uranium, tungsten and gold) in breccia pipe deposits scattered throughout the western U.S.A.

In the mining and milling of primary molybdenum deposits, e.g., at Climax, Henderson, Colorado, etc., residual particles of MoS_2 in the tailings may oxidize with time to release small concentrations of molybdenum to the seepage water and tailings decant solutions. Drainage from wasterock dumps may also contain some molybdenum. Molybdenum in minewater and tailings seepage and decant water from the Climax Mine was described by GOTT and LAFFERTY (1978) and by RAMADORAI (1978).

In uranium ore milling, molybdenum can build up in process solutions or occur in mine drainage.

At in situ leach test projects for uranium recovery from deep deposits in New Mexico, molybdenum was identified in the leach liquor that was pumped from the wellfield and represented a potential metallurgical interference in the ion exchange uranium recovery process.

Molybdenum also occurs associated with the gold ores recently discovered in the major Hemlo gold district and is expected to range between 0.5-3.0 mg/l in wastewater from this operation before being treated and below 1.0 mg/l in the discharged effluent.

The PEDCO (1983) report provides an interesting insight into approximate ranges of molybdenum levels in mine-mill effluents. In the case of some mine categories, e.g., taconite, phosphate, etc., molybdenum was not considered important enough to be included in the investigation. On the other hand, elevated molybdenum levels in effluents, process water, and leachates were observed for molybdenum, copper, and gold-silver recovery operations. A question arises as to whether molybdenum may possibly be a pathfinder element for gold mineralization in volcanic environments.

Molybdenum was generally found in the PEDCO (1983) investigation to occur in mill tailings decant solutions, minewater, and leachates of tailings solids, wasterock, and ore in a range of 0.002-2 ppm but averaging less than 0.5 ppm. Examples of industry classes where molybdenum exceeded 1 ppm are considered unusual except in some uranium, molybdenum, copper, and gold districts:

SUMMARY OF PEDCO (1983) DATA

	Average (ppm)	Number of Samples	Maximum (ppm)
NEW MEXICO URANIUM DISTRICT			
Surface Mine Waste and Leachate	LT 0.01	4	LT 0.01
Surface Mine Waste Water Leachate	0.02	4	0.034
Minewater Pond Liquid	0.436	5	0.76
Minewater Pond Settled Solids			
- Solids Total	139	6	230
- Acid Leachate	0.369	6	2.10
- Water Leachate	0.376	5	1.24
OTHER URANIUM DISTRICT			
Untreated Mine Water	0.395	3	1.1
Minewater Pond Liquid	0.57	2	1.1
Minewater Pond Settled Solids Water Leachate	0.381	3	1.0
SOUTHWESTERN COPPER DISTRICT			
Surface Mine Waste Water Leachate	0.215	8	1.3
Tailings Pond Liquid	1.53	6	2.5
Leach Liquors (H_2SO_4)	1.41	3	2.1
OTHER COPPER DISTRICT			
Tailings Pond Liquid	0.41	3	0.9
MOLYBDENUM DISTRICT			
Fresh Tailings	0.693	3	1.1
Tailings Pond Liquid	5.87	3	11
Untreated Mine Water	3.20	3	2.05
Lowgrade Ore Water Leachate	1.09	2	1.25
NEVADA GOLD-SILVER DISTRIC			
Tailings Pond Liquid	0.32	2	0.51

A granular activated alumina is used for fluoride adsorption. The material is a by-product of aluminum production. It is primarily an aluminum oxide which has been activated by exposure to high temperature and caustic soda. The material is highly porous, and the surface area per unit of weight is quite high.

RUBEL (1984) recommends the use of 28-48 mesh Alcoa F-1 grade alumina in defluoridation processes.

CAPACITY OF ACTIVATED ALUMINA FOR F^- REMOVAL

Capacity of activated alumina for F^- removal is very pH dependent as demonstrated by WU (1978) who first suggested that activated alumina capacity for fluoride uptake from water is much greater at pH 5.5 than at 7.0. He reported maximum removals of 4,200 grains/ft^3 at pH 5 with pure NaF solutions. Other investigatiors who have made bench, pilot, or commercial installation studies have reported much lower capacities because they have not understood or chosen to operate at optimum pH conditions.

RUBEL (1984) cites three plants which have operated routinely for years at a low cost meeting the municipal fluoride levels. These are listed below. By paying close attention to pH control, the three plants are able to routinely remove in excess of 2,000 grains/ft^3 (4,600 g/m^3). For higher fluoride concentrations, the activated alumina adsorption capacity increases. For a water with 22 mg/l F^-, the alumina capacity reaches 4,500 grains/ft^3 (10,400 g/m^3).

In this optimum pH range (5.0-6.0), other ions that compete with fluoride for the same adsorption sites are not adsorbed. Included are silica, which is adsorbed in the pH range 6-10, and some hardness ions which are removed in the pH range 7 through 10. Hardness removal occurs at the start of a treatment run. However, activated alumina preferentially adsorbs fluoride; therefore, as the run progresses, hardness removal ceases. At the optimum fluoride removal pH, some organic molecules and some trace heavy metal ions are also adsorbed. However, except for arsenic, these are completely regenerated along with the fluoride. Arsenic presents a problem as it is preferentially adsorbed over fluoride by the alumina at the same optimum pH. Arsenic is more difficult to regenerate than fluoride. Therefore, when excess fluoride and arsenic are present in a water supply, a special treatment technique is required as described by RUBEL and WOOSLEY (1978).

EXAMPLES OF PLANTS USING Al_2O_3 ADSORPTION OF F^-

	Startup Year	U.S. gpm	m^3/d
Lake Tamarisk, Desert Center, California	1970	1,100	6,000
Rincon Water Co., Vail, Arizona	1972	500	2,700
Town of Gila Bend, Arizona	1978	900	4,900
Roolberg Tin Mine, Transvaal	1985	95	518

CONCEPTUAL DESIGN

Of the many configurations to choose from, i.e, gravity or pressure flow, single or multiple treatment beds, upflow or downflow treatment flow direction, and series or parallel treatment vessel arrangement, RUBEL (1984) reports that the most efficient, cost effective configuration is a parallel downflow multiple bed pressure system. Best cost effectiveness is achieved (for both capital and operating costs) with two treatment beds.

The two-bed series combination yields the highest fluoride loading on the media, and the lowest fluoride level in the treated water, but this is often too low to be desirable. The parallel system allows an opportunity to blend two streams.

REGENERATION OF ALUMINA

Alumina is regenerated using a 1% sodium hydroxide solution. Optimally, 50 percent NaOH solution is used which may require heating as it freezes at 55°F and is very viscous below 70°F. Fluoride ions are repelled from the alumina granules when the pH rises above 10.5.

0.4 gallons (5 lbs.) of 50% NaOH solution is required per ft^3 per regeneration. The caustic requirement for regeneration is a function of the raw water fluoride level which dictates the frequency of regeneration and the volume of water over which the cost must be distributed.

Use of too highly concentrated NaOH solution enhances comsumption of alumina granules.

MEDIA CONSUMPTION

Consumption of alumina should be close to zero in a well-operated activated alumina fluoride water treatment plant. Excessively long backwash periods cause excessive

alumina losses through attrition and elutriation. Monitoring of backwash fluids can help detect this.

During regeneration, excessively high and/or low pH exposure attacks the media. If the regeneration solution exceeds 1.5% NaOH, the solution is aggressive to activated alumina.

Also, if the pH of the post regeneration neutralizing solution (acid addition) is below pH 2.0, the alumina dissolves very rapidly with resulting losses.

Finally, alumina can be lost through the effluent underdrain collection system within the bed. If alumina grains ever appear in the treated effluent, this indicates that the collection system is in need of repair.

A conservative bed replacement estimate according to RUBEL (1984) is ten percent per year.

OPERATING SEQUENCE

1. Feed pH adjustment to Ph 5.0-6.0.
2. Adsorption mode - downflow.
3. Backwash mode.
4. Regeneration.
5. Neutralization after regeneration.

Raw water is used in each of these steps.

Details of the operation of an activated alumina plant for defluoridation are provided by RUBEL (1984) including several knowhow items which would prove helpful in optimizing results for a given plant.

Fines that accumulate on top of the alumina bed should be removed to avoid an unnecessarily high pressure drop across the bed when commencing a run.

BACKWASHING

Backwashing of the bed with raw water after each run prior to regeneration is important to remove suspended solids filtered from the feedwater. Upflow backwash expands the bed. Backwash at 8-9 gpm/ft^3 expands the bed about 50%, which is recommended. Normally, backwashing lasts ten minutes. RUBEL (1984) provides a valve operation chart for the backflush mode.

REGENERATION

Regeneration of the bed on completion of an adsorption run generally includes two discrete regeneration steps. First is upflow regeneration following draining of the bed after backflushing. Regeneration is followed by an upflow rinse. The unit is then drained to the top of the bed prior to the second regeneration step which is downflow. Both steps use 1% (by weight) NaOH solution.

A skilled operator can reduce the concentration of NaOH to 0.75% and achieve the same high regeneration efficiency; however, below 0.75%, the efficiency drops rapidly. At this lower caustic concentration, the saving in NaOH consumption amounts to 20%.

As a rule of thumb, fifteen gallons of 1% NaOH solution is needed per cubic foot of treatment media. The minimum time for the regenerant solution to flow through the bed is thirty minutes. Thirty-five minutes is recommended for a 5' bed. A flow of 2.5 gpm/ft^2 for thirty-five minutes per regeneration is usually sufficient, which equates to 0.2 gallons of 50% NaOH per cubic foot of treatment media for each regeneration step (upflow and downflow).

After backflush, prior to upflow regeneration, the bed must be drained to remove water which dilutes the caustic concentration. Upon completion of draining, the upflow regeneration starts. On completion of the upflow regeneration, the caustic feed pump is turned off and the day tank refilled. Raw water continues to flow for sixty minutes at 2.5 gpm/ft^2 upward through the bed to flush out the fluoride. After this rinse step is completed, the vessel is drained to the top of the treatment bed, again to remove dilution water. Then, downflow regeneration is followed by a draining period prior to the start of the neutralization mode.

NEUTRALIZATION

Neutralization is critical to the success of the following adsorption (treatment) run. The objective of this mode is to return the bed to the treatment mode as rapidly as possible without dissolving the activated alumina. The pH of the alumina upon completion of regeneration is 12 plus. It must be adjusted down to 5.5. Therefore, it must pass through pH ranges where ions that compete for adsorption sites on the alumina will be loaded into the bed. The minimum pH that can safely be reached is pH 2.5. A lower pH is too aggressive and is not recommended.

After 15 minutes of downflow regeneration, the flow is adjusted to the normal treatment mode rate. The acid pump is started, and the pH of the raw water adjusted to 2.5. Acid feed rate again varies with the alkalinity of the raw water. The raw water flow rate may have to be reduced to achieve pH 2.5 at the maximum acid pump feed rate.

As the neutralization mode proceeds, pH of the treated water gradually drops below 12. The rate of pH reduction increases at an increasing rate. As the treated water drops below ten, the treated water fluoride level begins to drop below that of the raw water. At that time, treatment begins. At the point where the fluoride level drops below the MCL, the water becomes usable and can be directed to storage even if the pH is still high (say pH 9.5).

When the treated water pH drops to 8.5, the raw water pH is adjusted up to 4.0 as the bed rapidly neutralizes. When the treated water drops to pH 6.5, the raw water is adjusted up to pH 5.5 where it remains through the duration of the run.

Volume of wastewater produced during the regeneration of the alumina bed varies with the physical and chemical characteristics of the raw water. A useful rule of thumb is 300 U.S. gallons per ft^3 of media, i.e., 40 m^3 wastewater per m^3 media per regeneration.

Typical volumes of wastewater generated during each regeneration cycle for a hypothetical plant as described by RUBEL (1984) are:

Backwash	60 U.S. Gal.
Upflow Regeneration	15 U.S. Gal.
Upflow Rinse	30 U.S. Gal.
Downflow Regeneration	15 U.S. Gal.
Neutralization	180 U.S. Gal.
TOTAL	300 U.S. Gal.

Operating experience for each given plant will soon come up with deviations from these quantities.

DISPOSING OF WASTEWATER

All the known fluoride treatment plants using activated alumina are located in areas with net evaporation climates and, as such, are suitable for disposal of the regeneration wastewater containing flouride into lined evaporation ponds.

LABORATORY REQUIREMENTS

RUBEL (1984) recommends that the operator of an activated alumina fluoride removal plant be equipped with the operations and maintenance (O&M) manual for the plant and also the latest edition of Standard Methods for the Examination of Water and Wastewater by AWWA-APHA and basic laboratory equipment. Primary analytical needs are to determine pH and fluoride. Fluoride measurement can be by ion-specific electrodes provided the

:t buffer (TISAB) is employed for the water to be treated. There are also two te wet chemistry methods using SPADNS and Alizarin. Distillation and/or correction terferring ions (e.g., alkalinity, aluminum, iron, sulfate, etc.) are required for te results.

,TING COSTS FOR DEFLUORIDATION BY ACTIVATED ALUMINA

include the following:

- Treatment chemicals.
- Operator labor costs.
- Utility costs.
- Replacement alumina.
- Replacement parts and miscellaneous materials.

L (1984) discusses each cost item in some detail.

ding to RUBEL (1984), the U.S. price for ALCOA F-1 28-48 mesh activated alumina s from $0.697/lb to $0.516/lb depending on quantity.

ıting costs (1984) vary as follows:

Operating Cost Items		U.S. Dollars per 1,000 U.S. Gallons Min. $	Max. $	U.S. Treated Ave.
Treatment Chemical -	Acid	0.02	0.08	0.05
	Caustic	0.02	0.12	0.05
Operating Labor		0.03	0.10	0.06
Utilities		0.005	0.05	0.01
Replacement Media		0.005	0.03	0.02
Replacement Parts, Etc.		0.05	0.10	0.01
TOTAL		0.085	0.39	0.20

FLUORIDE

	$/m³ Min. $	Treated Water Max. $	Ave. $
Treatment Chemicals - Acid	0.005	0.020	0.013
Caustic	0.005	0.030	0.013
Operating Labor	0.008	0.030	0.016
Utilities	0.001	0.013	0.003
Replacement Media	0.001	0.008	0.005
Replacements Parts, Etc.	0.013	0.026	0.003
TOTAL	0.033	0.127	0.053

CAPITAL COST FOR ACTIVATED ALUMINA DEFLUORIDATION PLANT

RUBEL (1984) estimated costs for a 600 U.S. gpm (3300 m³/d) defluoridation plant in a warm Arizona climate at $347,000 of which $138,000 was for the lined wastewater evaporation pond. The cost breakdown was as follows:

Flowrate: 600 U.S. gpm, 3300 m³/d.

Process Equipment	
Treatment Vessels	$ 33,000
Treatment Media - Alumina	20,500
Process Piping, Valves, and Accessories	16,400
Instruments and Controls	8,300
Chemical Storage Tanks	21,000
Chemical Pumps, Piping and Accessories	6,300
Subtotal	$105,000
Process Equipment Installation	
Mechanical	$ 36,000
Electrical	7,000
Painting and Miscellaneous	4,500
Subtotal	$ 47,500
Miscellaneous Installed Items	
Wastewater Evaporation Pond - Lined	$138,000
Building and Concrete	28,000
Sitework, Fence, and Miscellaneous	11,000
Subtotal	$177,000
Contingency 4%	17,000
TOTAL	$347,000

The Removal of Excess Fluoride From Drinking Water by Activated Alumina

Frederick Rubel Jr. and R. Dale Woosley

Described here are cost-effective operating practices developed at three water treatment plants for removing excess fluoride from drinking water by activated alumina. By use of these methods the fluoride removal capacity of alumina was increased by a factor of five.

Under the national Interim Primary Drinking Water Regulations maximum contaminant levels (MCL) in potable water supplies have been established for ten inorganic chemicals, including fluoride. The MCL for fluoride varies from 1.4 to 2.4 mg/L, depending upon the annual average of the maximum daily air temperatures (Table 1). If the prescribed maximum level is to be enforced, its achievement must be technically and economically feasible.

Since it became known that excess fluoride in drinking water caused mottled teeth in children,[1] many methods of removing fluoride have been developed. One of them employs activated alumina to defluoridate water supplies. Although many investigators have found that activated alumina is quite effective in reducing fluoride to very low levels in treated water, there is an abundance of confusion as to the useful capacity of activated alumina.

Churchill,[2] in his 1936 patent on the use of activated alumina for fluoride removal, states that a pH of 5 to 6.5 should be used during treatment for best results. There is no stated capacity in his patent. E.A. Savinelli and A.R. Black,[3] in their 1958 bench experiments, showed that a capacity of 7800 g/m³ (3400 grains/cu ft) was achieved when treated water pH was 5.6. Their studies were made with tap water to which sodium fluoride had been added. Yeun C. Wu,[4] in a recent article, again shows that treatment pH is quite important for high removal capacities. He reports maximum removals of 9600 g/m³ (4200 grains/cu ft) with treatment at pH 5.0 in pure sodium fluoride solutions. Other investigators[5,6] who have made bench, pilot, or commercial installation studies report much lower capacities because they have not understood or chosen to operate at optimum pH conditions.

Two plants that have had several years of low-cost experience in producing waters with fluoride concentrations reduced to acceptable levels are the Lake Tamarisk plant at Desert Center, Calif., with nine years of operation, and the Rincon Water Co. plant at Vail, Ariz., with six years of operation. A third plant began operation in Gila Bend, Ariz., in May 1978. By paying close attention to pH control, the three plants are able to operate routinely with removal capacities exceeding 4600 g/m³ (2000 grains/cu ft). Removal capacities exceeding 7000 g/m³ (3300 grains/cu ft) were observed during the pilot work done at Gila Bend, Ariz., to confirm that the developed operating practices would work on that water supply.

Development work with pilot-plant equipment on a continuing basis has perfected the water treatment and alumina regeneration processes at each of these locations. This article outlines the operating practices developed for removing fluoride to acceptable levels.

Fluoride Removal Technology

This article is based on pilot-plant experiments and plant data for which granular activated alumina* (mesh size 28 to 48) was used.

The basic principles of fluoride removal technology are

1. Optimizing the environment for sorbing of fluoride ions to activated alumina surfaces
2. Preventing competing ions from occupying alumina surfaces that should be reserved for fluoride ions
3. Upon regeneration of an expended treatment bed, taking all steps necessary to remove all fluoride ions from the bed before returning it to treatment.

There are also many "common sense" principles that apply to the process which, though important, are not as critical as the three listed.

There are four modes of operation: treatment, backwash, regeneration, and neutralization. Operating details for each mode are discussed here.

Treatment mode for virgin or regenerated treatment bed. The optimum environment for fluoride removal exists when raw water pH is adjusted to 5.0–6.0 by sulfuric acid injection. Because acid feed rates are a function of the raw water alkalinity, they vary from one water to another. The best results obtained to date have occurred when the raw water pH has been held carefully at 5.5. In this environment the attraction of the fluoride ion to the activated alumina surface is most favorable and interference by competing ions is minimal. Adsorption is the most probable mechanism for fluoride ion removal from water, but because work in this area is still in progress, discussion of mechanism is premature. In applications

*F-1 Alcoa, Pittsburgh, Pa.

TABLE 1
Maximum Contaminant Levels For Fluoride

Average Maximum Daily Temperature °C	°F	Fluoride Level mg/L
≤12.0	≤53.7	2.4
12.1-14.6	53.8-58.3	2.2
14.7-17.6	58.4-63.8	2.0
17.7-21.4	63.9-70.6	1.8
21.5-26.2	70.7-79.2	1.6
26.3-32.5	79.3-90.5	1.4

TABLE 2
Water Analyses At Existing Operations

Parameter	Facility: Lake Tamarisk	Rincon Water Co.	Town of Gila Bend
Ca—mg/L	11	51	31
Mg—mg/L	0.5	5.0	<1
Na—mg/L	56	151	306
SO_4—mg/L	40	293	160
Cl—mg/L	67	22	540
Hardness (as $CaCO_3$)—mg/L	30	152	78
Total alkalinity (as $CaCO_3$)—mg/L	77	171	30
Phenolphthalein alkalinity (as $CaCO_3$)—mg/L	0	0	2
Fe—mg/L	0.2	<0.05	0.2
SiO_2—mg/L	22	55	21
F—mg/L	7.5	4.5	6.0
Total dissolved solids—mg/L	407	650	1121
pH	7.9	7.5	8.1
Year	1970	1973	1974

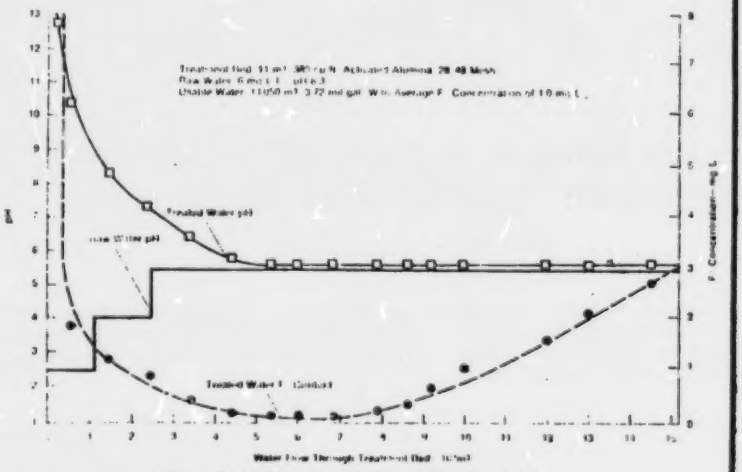


Fig. 1. Typical Operational Run at Gila Bend, Ariz.

to date, treatment bed capacities consistently have exceeded 4600 g/m³ (2000 grains/cu ft), and some runs have exceeded 9200 g/m³ (4000 grains/cu ft).

As raw water pH moves above 6.0 or below 5.0, fluoride removal capacity deteriorates at an increasing rate. For example, from previous experiments it has been shown that at pH 7.0 bed capacity is about 1100 g/m³ (500 grains/cu ft). Though efficiency might appear to be the same, breakthrough occurs earlier and treatment runs are shorter. Fluoride removal efficiency at optimal pH approaches 100 percent, as indicated by treated water fluoride concentration well below 0.1 mg/L during portions of the treatment run at each installation. This efficiency is achieved in waters with different chemistries including varying fluoride levels (Table 2). Superficial residence time (flow time through the bed neglecting the volume of bed material) is also a limiting factor: a 5-min minimum is a practical limit for maximum removal efficiency. Best results occur with flow directed down through the bed. Care must be taken to prevent a wall effect or channeling.

The initial effluent pH is high, with no fluoride removal, as explained in the discussion on neutralization mode. After a short period both pH level and residual fluoride drop to acceptable levels. At that point usable water can be directed to storage or distribution. Fluoride level drops rapidly to a very low level and remains there until breakthrough begins, at which point it increases gradually until the treatment run is terminated.

Treated water pH drops below 6. Because water of this pH is corrosive, the treated water pH must be adjusted to a desirable level (about 7.5) by injection of sodium hydroxide or by blending.

Backwash mode. For two reasons it is important that the bed be backwashed with raw water before each regeneration: first, any suspended solids that have been filtered from the raw water by the treatment bed tend to blind the bed and must be removed; second, even though filtration may not have taken place, the downward flow tends to pack the bed. Therefore, an upflow backwash expands the bed, breaking up any tendency toward wall effects or channeling. A backwash rate of 5–6 mm/s will expand the bed about 50 percent, which is adequate. Care must be taken to avoid backwashing granular bed material out of the treatment unit. Normally, backwash is completed within 10 min.

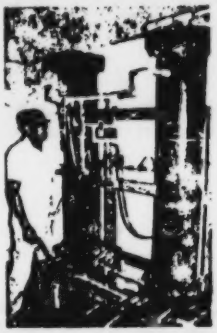
Regeneration mode. The object of regeneration is the removal of all fluoride ions from the bed before any part of the bed is returned to the treatment mode. The most successful regeneration is accomplished in two steps: the first is upflow immediately after backwash while the bed is still expanded, followed by an upflow rinse. The unit is then drained to the top of the treatment bed. The second regeneration step is downflow immediately followed by the neutralization mode. Regeneration steps employ 1 percent (by weight) sodium hydroxide solution flowing at a rate of 1.7 mm/s. With a standard treatment bed depth of 1.5 m, each regeneration step takes 35 min. Chemical consumption in each regeneration step is 27 L of 50 percent NaOH per cubic metre of treatment media (0.2 gal/cu ft). The intermediate upflow rinse flows at a rate of 3.4 mm/s for a period of 30 min. If the treatment bed depth varies from standard, flow rates and times must be adjusted. The regenerant solution is usually an in-line dilution of 50 percent sodium hydroxide with raw water, with the sodium hydroxide maintained at or above 21° C to prevent freezing. *

Neutralization mode. The object of this step is to return the bed to the treatment mode as rapidly as possible without dissolving the treatment media. As soon as the second (downflow) regeneration step has been completed, all of the fluoride should have been removed from the bed. At this point the bed is drained again to the top of the treatment media. Raw water with pH adjusted to 2.5 is then fed downflow at the normal treatment flow rate (Fig. 1). Sulfuric acid concentrations again vary with the alkalinity of the specific raw water. The entire bed has a pH range from 12.5 to 13.0, and as the top of the bed begins to

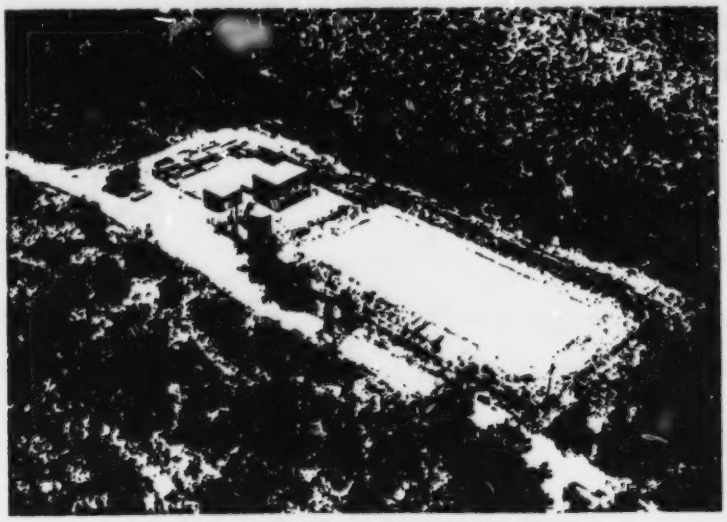
* this is ambiguous: 27 or (2x27 = 54L) ?

TABLE 5
Operating Costs At Existing Treatment Plants

Item	Location					
	Lake Tamarisk		Rincon Water Co.		Gila Bend	
	¢/1000 L	¢/1000 gal	¢/1000 L	¢/1000 gal	¢/1000 L	¢/1000 gal
Treatment chemicals	2.2	8.3	1.3	5.1	1.0	3.7
Operating labor	1.3	5.0	1.1	4.1	1.6	6.0
Electric utility	0.1	0.5	0.1	0.4	0.1	0.6
Media replacement	0.2	0.7	–	–	–	–
Spare parts & misc	0.1	0.3	0.2	0.8	0.2	0.8
Total	3.9	14.8	2.7	10.4	2.9	11.1



Pilot-Plant Equipment in Use at Gila Bend, Ariz.



Aerial View of Rincon Water Co. Treatment Plant, Vail, Ariz.

neutralize and enter a treatment mode, the fluoride level in the treated water starts to drop below that of the raw water. Treated water pH also begins to drop. As the fluoride level drops below the mandatory limit, the water becomes usable and can be directed to storage or distribution. pH may still be high (9.0–9.5) in the treated water; however, this water can be blended with treated water of lower pH from other treatment units. When the pH is 9.0 to 9.5, the raw water pH is adjusted to 4.0 as the bed rapidly neutralizes. When the treated water pH drops to 7.5, the raw water pH is adjusted to 5.5, where it is maintained throughout the remainder of the run.

Initial Start-Up Procedures

When the bed material is first placed into the treatment unit, the vessel should be half filled with water. As the activated alumina is poured into the bed from above, the water dissipates the heat generated by the heat of wetting of the activated alumina, thereby preventing cementing of the bed. The water also aids in separating fines from the granular material; protects the underdrain assembly from impact; and initiates stratification of bed material. Once the bed is in place, it must be backwasned for an extended period until all of the alumina fines are flushed from the virgin bed. The flow is then reversed and downflow treatment begins for the virgin run.

Blending of Treated Water

Blending can take place in either large reservoirs or the treated water main. During a treatment run there is a long period when the fluoride level of the treated water is well below desired levels. As breakthrough occurs there is a long period of slowly increasing fluoride concentration in the treated water. It has been found that treated water can continue to flow to storage or distribution until the fluoride concentration reaches one and one half to two times the maximum allowable level; the resulting total average fluoride level continues to meet the prescribed fluoride level (one half the maximum allowable level).

When there is a large reservoir in which the major portion of a treatment run can be stored, blending takes place there. At locations where the reservoir is not large and there are two or more treatment units, staggered regenerations accomplish the same result; that is, a regenerated treatment unit will produce water of very low fluoride content while a second unit in the later stages of its treatment run may be producing water of a higher fluoride level. By mixing the effluent from the two units in the treated water main, an average fluoride concentration near the prescribed level can be maintained. Similarly, the treated water of high pH occurring early in the run for one unit can be blended with the low pH effluent of another unit in a later stage. The benefit of this blending is short-lived; soon the pH of the blended streams requires adjustment.

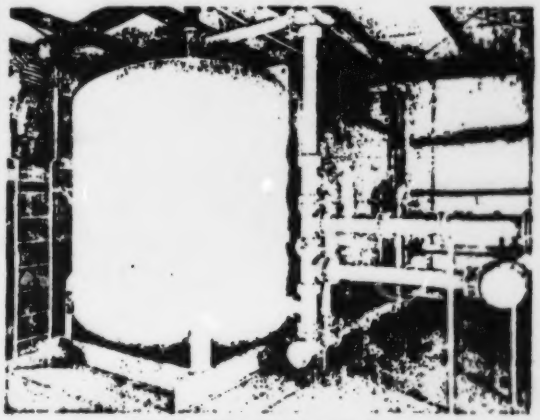
Disposal of Wastewater

The wastewaters resulting from backwash, regeneration, and the early part of neutralization are not suitable for consumption and must be discarded. The backwash water, which is only raw water, can be discharged to existing storm water disposal systems. The only objectionable feature of the regeneration waste is the high concentration of fluoride ions that cannot be returned to the groundwater aquifer. Its high pH can be neutralized. Disposal of waste of high fluoride concentration must comply with local wastewater discharge standards, which vary. Existing plants concentrate the waste in lined evaporation ponds; eventually the concentrated waste must be transferred to an acceptable disposal site or the fluoride must be reclaimed.

The volume of wastewater is approximately 4 percent of the total throughput.

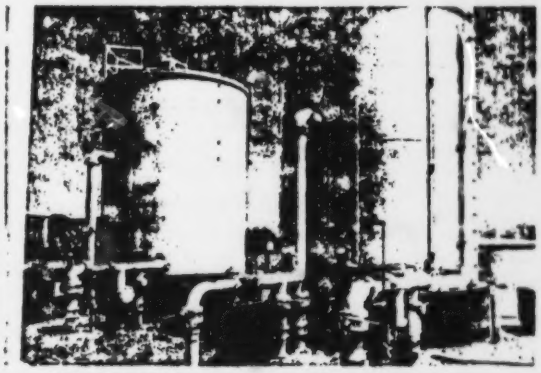
Materials of Construction

The cost of a treatment plant is a function of the quality of the construction materials in its design. Trouble-free, low-cost plant operation can be achieved only by proper selection of materials to meet the service requirements of the process. Without considering the materials for concentrated acid and caustic

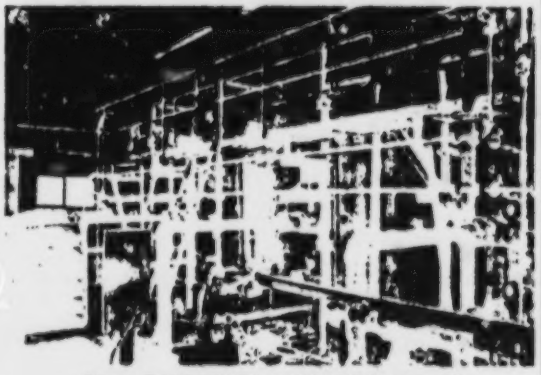


Treatment Units at Gila Bend, Ariz.

Treatment Plant at Gila Bend, Ariz.



Lake Tamarisk Treatment Plant at Desert Center, Calif.



Rincon Treatment Unit. Acid Line in Foreground

systems, treatment system materials must be suitable for service under the following conditions: (1) potable water system; (2) ambient temperatures (provision for thermal expansion); (3) exposure to sunlight (or protected); (4) pH 2-13; and (5) ease of maintenance (remove and replace with minimum logistics). Materials for the chemical storage and handling systems should comply with chemical manufacturers' guidelines.

Operator Requirements

A qualified operator for a fluoride removal water treatment plant requires thorough fluoride removal process training, preferably at an existing treatment plant. The operator must be able to service pumps, piping systems, instrumentation, and electrical accessories. The operator must be totally informed about the characteristics of sulfuric acid in all concentrations and sodium hydroxide in all concentrations. Safety requirements as to clothing, equipment, and antidotes must be thoroughly understood and executed. The operator must be trained to run routine water analyses including at least two methods for determining fluoride levels. He needs simple mathematics for record keeping during a treatment run and for operation cost accounting. Above all, the operator must be dependable and conscientious.

Cost of Operation

The cost of operating an alumina fluoride removal system including chemicals, electricity, bed replacement, replacement parts, and labor, currently falls in the range of 2-5¢/kL (8-20¢/1000 gal) of treated water. Individual plant operating costs vary as functions of raw water fluoride level, plant capacity, treated water consumption, electric utili-

ty rate, labor costs, delivered chemical costs, and so forth. The low operating costs at the three operational plants discussed in this article are shown in Table 3. The 1977-78 materials and construction costs for the plant at Gila Bend were less than $200 000. The plant was designed for 2.8×10^3 m³/day (0.75-mgd) average production with peak capacity of 4.8×10^3 m³/day (1.3 mgd).

Conclusion

Low operating costs for removing fluoride from potable water can be achieved with an activated alumina system. Reliability of plant equipment, materials, and operational costs have been documented through nine years of commercial field experience. Installation and operating costs are compatible with limited public budgets and funding programs. All materials and equipment are available, and there is existing technology to assist in designing a plant to meet fluoride MCLs.

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75383 4260

Not included in the capital costs are engineering, finance charges, real estate cost, and taxes.

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His excellent design manual "Removal of Fluoride from Drinking Water Supplies by Activated Alumina," EPA Report No. EPA-600/2-84-134 of August, 1984, is available from:

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In 1984, two water defluoridation plants, each of 518 m^3/d, were installed to treat minewater containing 6-10 mg/l F as described in Appendix I.

In this case, the original testwork was carried out by the National Institute for Water Research. Final design and construction was by:

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Edenvale 1610

609-5216
John A. Buchanan

Capital investment for the two plants including the reticulation system was R0.75 million. Operating costs are estimated at U.S. \$0.20/m^3 U.S. \$0.76/1000 U.S. gallons which is relatively high even taking into account that these are smaller plants with higher relative overhead, and the cost includes engineering and taxes.

In this case, the regeneration wastewater is used to pump tailings to the tailings dams.

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CHAPTER 42

IRON Fe

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INTRODUCTION

Iron occurs in solution as ferrous and/or ferric ions depending on pH and dissolved oxygen concentration. At neutral pH and in the presence of oxygen, soluble ferrous iron (Fe^{2+}) is rapidly oxidized to ferric iron (Fe^{3+}) which readily hydrolyzes to form the insoluble precipitate ferric hydroxide $Fe(OH)_3$.

Below pH 6, the rate of ferrous iron oxidation to ferric is extremely slow. Therefore, acid and/or anaerobic conditions are necessary for iron to exist in solution.

In addition, at pH values above 12, ferric hydroxide will redissolve due to the formation of the $[Fe(OH)_4]^-$ complex anion. Also, even in acidic, anaerobic conditions, if a source of sulfide ions is present, iron will be removed from solution as FeS or Fe_2S_3. Ferric and ferrous ions are also solubilized in the presence of cyanide due to the formation of ferri- and ferrocyanide complexes. Such complexes present considerable difficulties for both iron and cyanide removal. Since the sulfide precipitates are more stable than the cyanide complexes, however, addition of sulfide to polish solutions may offer one possible way to remove iron and to render any cyanide ions amenable to oxidation if necessary.

Ferrous ions and ferrous hydroxide are greenish in color. Ferric ions in solution are yellow, but when ferric hydroxide precipitates, the precipitate is red-brown and gelatinous. Acid mine drainage in contact with air turns red brown in color because of the suspension of colloidal ferric hydroxide particles.

Acid mine drainage, which includes water draining or pumped from both underground and open pit mines, seepage and runoff from mine wasterock, tailings ponds, and surface runoff from any area affected by mining (e.g., concentrate stockpile areas, mine-mill-smelter yards, roadbeds, and rail beds constructed with wasterock, etc.), usually contains iron often with minor amounts of other metals, e.g., Cu, Zn, Ni, and Mn.

Iron in acid mine drainage often helps in the removal of other metals because it acts as excellent co-precipitant. However, ferric hydroxide is a gelatinous, difficult to settle precipitate usually with a very low terminal solids density which requires large lagoons for disposal unless special measures are adopted.

OCCURRENCE OF IRON

Surprisingly, iron contamination of water occurs prolifically around mines other than iron mines. Acid mine drainage is one of the most formidable challenges facing the mining industry. It affects base metal mines, especially massive sulfide deposits, uranium mines particularly of the Elliot Lake and Witwatersrand type, gold and silver mines associated with sulfides and, of course, the enormous coal mining industry. It is the ubiquitous occurrence of iron sulfide minerals, e.g., pyrite, pyrrhotite, and marcasite, that generates acid mine drainage on oxidation.

Acid mine drainage inhibition and treatment has been discussed in separate chapters, and most of that discussion would be applicable to this discussion on iron removal.

Iron sulfide minerals may comprise only 1-3% of a mine tailing, or they may be as much as 95% of a tailing material. Both generate acid mine drainage.

In waters of low dissolved oxygen, iron may be reduced to the ferrous form, and some iron may be in solution as the ion. Ferrous iron may be released from lake sediments if the water above the sediments becomes totally anaerobic; the release of iron is the result of a shift in the redox potential below a critical level at the sediment surface according to ONTARIO MOE (1974).

ENVIRONMENTAL IMPACT OF IRON

Iron is an essential mineral constituent for just about all life forms.

In the public water supply, soluble iron at levels in excess of 0.3 mg/l Fe can cause staining of tile surfaces.

Excessive levels of iron in drinking water (around 0.5 ppm and more) start to impart a flavor to water, and 1.0 mg/l Fe is cause for rejection as drinking water.

Iron in receiving waters (lakes and streams) interferes with aquatic biota. It is the fouling properties of iron hydroxide that apparently does more damage than soluble iron in water. There are several types of impact:

1. impairment of fish larvae respiration.
2. Impairment of gill action through fouling.
3. Impairment of streambed habitats by formation of ferricrete.
4. Fouling of streambed plants and algae.

It is concluded that iron released into the aquatic environment will almost always be precipitated. Fine flocs formed at low iron concentrations may sometimes do more damage than large flocs formed at higher iron concentrations.

The criteria for total iron levels in freshwater at which the environment is protected is 300 ug/l total iron in Canada, and 1,000 ug/l total iron in the U.S.A. U.S. EPA (1972), CANADA (1979).

In the marine environment, a criteria level of 300 ug/l has been set by U.S. EPA (1972). ONTARIO MOE (1979) provides a lengthy discussion on the effects of iron on several aquatic algae and organisms which was found to be highly variable. Below 300 ug/l Fe, it was concluded, all aquatic species would be protected since below this level iron flocs would be unlikely to form.

Another environmental effect of iron in solution is the pH reduction that occurs during the hydrolysis of ferrous to ferric iron.

REGULATORY LIMITS FOR IRON

In reviewing the permits for discharge of effluents encountered during the course of this investigation, it was found that iron is not very often included. The only cases found which limit iron levels in their discharge are as follows:

	Iron Total Limit (mg/l)
Mount Emmons, Colorado NPDES	1.0
NORANDA Grey Eagle Zero Discharge Except Excess Water Can Be "Irrigated" After Treatment	0.20
Climax Molybdenum, Climax, Colorado	0.60
Typical Arizona Copper Concentration	
25-Hour Max.	1.00
30-Day Ave., Max.	0.50
Public Water Supply, U.S. EPA (1976)	0.30
Public Water Supply, Canada (1979)	0.05
South African Drinking Water SABS (1971)	
Recommended Maximum	0.10
Rejection Limit	1.00

TREATMENT FOR IRON

The most usual treatment process for iron is oxidation to ferric and precipitation of ferric hydroxide near pH 7 where the solubility of iron is at a minimum. Often, when other metal ion contaminants must be removed as well, a somewhat higher pH is employed.

Fe (ug/L) IRON

Summary of North American Water Quality Criteria for Iron

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	1,000	--	<300 *	--	--	300	300-1,000	300	--
MAX. PERMISSIBLE LIMIT		--	--	--	--	300	10-300	--	--	--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<50	--	--	< 50 *	--	--	--	300-1,000	--	--
MAX. PERMISSIBLE LIMIT		300	--	--	<300 *	--	--	--	--	--	--
PUBLIC WATER SUPPLY		300	300	--	50	300	50-100 (obj) 300 (limit)	--	--	300	300
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	No upper Limit	(300)	--	--	--	--	--	--	--	--
	IRRIGATION	5,000	(300)	--	5,000	5,000	--	--	--	--	--

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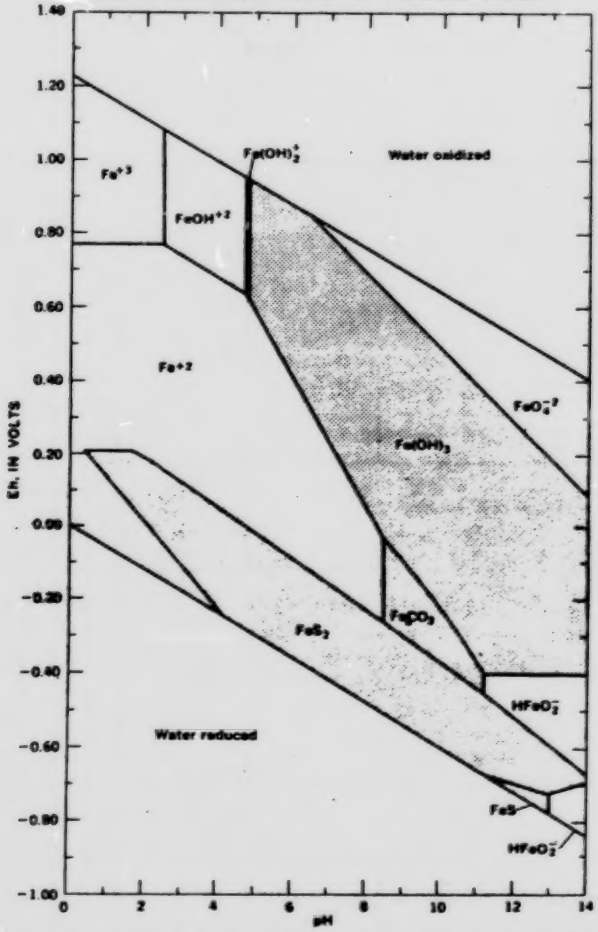

FIGURE 14.—Fields of stability for solid and dissolved forms of iron as function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of sulfur species 96 mg/l as SO_4^{-2}, carbon dioxide species 1,000 mg/l as HCO_3^-, and dissolved iron 0.0056 mg/l.

At pH 7.0-7.5 and above, conversion of ferrous to ferric iron occurs very rapidly as described in the section on acid mine drainage treatment. Spontaneous formation of ferric hydroxide then results in iron removal by precipitation.

JOBIN and SHOSH (1972) found that the rate of ferrous oxidation is dependent on pH, buffer intensity in bicarbonate systems, and upon the concentration of organic matter. Organic compounds containing hydroxyl and carboxyl functional groups seem to greatly reduce oxidation rates and can result in high soluble iron levels if the organic substances do not readily break down.

If iron is present in acid waters as the ferric ion, simply neutralizing the acid will precipitate the iron.

In some cases where there is a significant quantity of dissolved CO_2 in the water, this will be present as bicarbonate HCO_3^- in the acidic water. The bicarbonate/carbonate system buffers the water and consumes more lime than would otherwise be required to increase the pH over 7. By vigorous aeration of the water to remove CO_2 from solution, it is possible to reduce the amount of lime needed to modify the pH and precipitate iron. This process is applied at BETHLEHEM STEEL CORP.'s Panther Valley Division anthracite coal mine water treatment plant.

Iron removal from municipal water supplies has been practiced for many years. Iron levels in ground water supplies are characteristically 1-10 mg/l as ferrous iron. Ground waters are typically anoxic and weakly acid, usually high in CO_2. Aeration to remove CO_2 (and consequently increase pH) and to oxidize ferrous to ferric comprises the standard municipal water treatment. Lime is frequently employed for additional pH adjustment. The following table summarizes the treatment performance for some municipal iron treatment plants as reported by PATTERSON (1975).

SUMMARY OF MUNICIPAL PLANT PERFORMANCE FOR IRON

Process	Iron Concentration mg/l		
	Influent	Effluent	Reference
1. Chlorination, Alum-Lime-Sodium Silicate Precipitation and Sand Filtration	1.5	0.05	HANEY (1964)
2. Aeration, Lime, Sand Filtration	2.4	0.0	HANEY (1964)
3. Aeration, Sand Filtration	2.5	0.13	GARDNER and STIKA (1964)
4. Aeration, Coke Bed Filtration, Sedimentation, Sand Filtration	5.7	0.13	McCRACKEN (1961)
5. Lime, Aeration, Diatomite Filtration	10	1.10	KOLLIN (1962)

In the treatment of acid mine drainage, it is usually necessary to neutralize relatively high concentrations of acid and to precipitate considerably higher concentrations of iron;

this consumes much more lime and generates much larger volumes of precipitate sludges which must be disposed of.

TREATMENT OF IRON IN ACID MINE DRAINAGE

Treatment Chemical	pH	Initial Iron (mg/l)	Effluent Iron (mg/l)	Reference
Limestone Slurry		145	5	PATTERSON (1975)
Lime		157	1.6	PATTERSON (1975)
Soda Ash		126	2.3	PATTERSON (1975)

During the course of this investigation, the following iron removal results were idendified:

Operation	Reagent	Treatment pH	Iron in Influent (mg/l)	Iron in Effluent (mg/l)	Plant Capacity
AMAX, Mount Emmons	Lime, F_L, F	10.6	27-800	0.05-0.30	11,000 m^3/d
Brunswick Mining	Lime, D	9.03	951	2.35	
ERPM - Rand Mines	HDS	7.3	650	Nil	50,000 m^3/d
ERPM - Rand Mines	R.O. Pilot	4.5	6.0	0.06	5 m^3/d
Falconbridge, Onaping	Limestone, D	7.0	2-4	0.04-0.60	-
Gilman, Colorado	Lime, D	9.60	50-180	0.10-1.20	500-700 m^3/d
INCO, Copper Cliff	Lime, S	10.0	13.4	0.35	272,000 m^3/d
JABILUKA Uranium	Lime, S	8.0	2,000	1.0	-
Noranda, Waite-Amulet	Lime, HDS	9.80	254	1.40*	4300 m^3/d
Ontario Cu, Pb, Zn Mill G	Lime, HDS	8.9	676	0.77	4300 m^3/d
Ontario Cu, Pb, Zn Mill M	Lime, S	10.2	4.70	0.48	4000 m^3/d

* Drops to 0.30 mg Fe/l in polishing pond decant.

LIME: Lime Neutralization
FL: Precipitate Flotation
F: Multi-Media Filtration
D: Decantation

HDS: High Density Sludge Process
S: Settle in Thickener-Clarifer
R.O.: Reverse Osmosis

TREATMENT COSTS

Operation	Plant Size	Cost/m³	Capital
INCO Copper Cliff	272,000 m³/d	US $0.06/m³	C $4.1 Million (1975)
Eastern Canada Mine #6	2,900 m³/d	US $0.60/m³	
Falconbridge, Sudbury	16,000 m³/d	US $0.01/m³ (1979)	C $257,000 (1978)
R. Osmosis	Conceptual	US $0.50/m³	

DISCUSSION

1. The HDS process described in Appendix I in trip reports for:

   RAND MINES, ERPM
   KROMDRAAI COAL MINE
   NORANDA, GECO
   NORANDA, WAITE-AMULET

   The HDS process offers a significant advantage in the treatment of acid mine drainage containing high levels of iron in that a dense, stable sludge can be produced which is compact and safe to dispose of and non-amphoteric.

2. In the section on acid mine drainage, HDS application at several additional operations is discussed in which sludges with up to 50% solids are generated.

3. BETHLEHEM INTERNATIONAL ENGINEERING CORP., Bethlehem, Pennsylvania, has shown that HDS sludge from acid mine drainage yields a stable waste material when mixed with a pozzolan that is suitable for landfill disposal.

4. The Wannamaker Continuous Concentrator has been demonstrated for acid mine drainage treatment from the Argo tunnel. This is a form of cross-flow micro-filtration technology using sludge recycle which also achieves a relatively low iron value in the treated effluent and a precipitate with a higher percent of solids.

5. The USBM at Pittsburgh has shown the effect of a natural bog in raising the pH of acid mine drainage and precipitating iron as ferric hydroxide.

6. BARRET, HAENTJENS AND CO. of Hazelton, Pennsylvania, has developed a new jet pump which effectively flash-precipitates iron from acid mine drainage at a lower pH. This device is described in the section on AMD treatment.

7. Although various processes will be needed to polish effluents from mining and milling operations, the magnitude of the acid mine drainage problem is so great that attention will have to focus on prevention of the problem rather than treatment technology.

8. It was pointed out above that neutralization of acid mine drainage to a pH in excess of 7.0 at which ferrous ions oxidize rapidly to ferric ions can be quite expensive. An interesting innovation in this respect was proposed and described by MIHOK (1969) who found in laboratory batch flow tests conducted with high iron acid mine drainage treated with activated carbon that the iron was rapidly catalytically oxidized by the activated carbon. The ferrous iron content of an acid mine water flowing through an aspirated activated carbon column was reduced from around 700 to 10 ppm in less than one minute at pH around 2.5.

   The activated carbon was used repeatedly with little loss in efficiency and no discoloration or solids deposition. In the batch tests, about one-third of the iron was adsorbed by the carbon, but with continuous flow, little iron adsorption is expected. (No reasons were given.)

   It was proposed that a catalytic oxidation step in the treatment of acid mine waters containing ferrous iron would facilitate neutralization providing precise control of pH, lower reagent costs, and elimination of aeration equipment. Also, limestone might possibly then be suitable for acid mine drainage neutralization which would result in further cost savings compared with lime, provided ferruginous coatings that passify limestone can ve avoided.

   Although this revelation was made in 1969, no commercial application has been identified. No reasons for this were identified. In the original tests, a commercial type coal-base activated carbon 12 x 40 mesh was used.

9. At Jabiluka Uranium, LEVINS (1979) reported levels of 2,000-5,000 mg/l Fe in acidic uranium ore leach tailings/raffinate waste at the Alligator Rivers region of Northern Territory, Australia. After adjustment to pH 8, the iron level dropped to 1 ppm. Several other contaminants are precipitated when lime is added to pH 8, including Al, Ba, Cr, Cu, Mg, Mn, Pb, U, V, Zn, P, Si, and SO_4, which all would accumulate in the precipitate sludge.

10. <u>Biological Oxidation of Ferrous Iron Aids Precipitation</u>: WICHLACZ (1985) described the kinetics of ferrous iron Fe(II) oxidation by attached bacteria in bench-scale

rotating biological contactors (RBC). Oxidation efficiencies of better than 80% were obtained over the range of Fe(II) mass loadings tested (0.14-2.34 mg Fe(II)/ cm^2/hr.). The amount of oxidation and the rate depended on a combination of influent and bulk fluid Fe(II) concentration as well as flow rate. A model describing attached bacterial growth and oxidation rate as a saturation function of substrate utilization was developed and tested. The maximum oxidation rate constant was proportional to flow rate, and the substrate concentration in the reactor varied with influent substrate concentration. The model allowed prediction of metabolic constants and included terms for both constant and growth rate dependent maintenance energies.

Toward the end of Chapter 25 on "Removal of Contaminants," reference is made to additional testwork in which rotating biological contactors have been used to oxidize ferrous to ferric.

P. L. WICHLACZ
E. G. & G. Idaho, Inc.
Idaho Falls, ID

11. Dissolved Air Flotation: An expensive aspect of neutralization and precipitation plants is the removal of the iron hydroxide precipitate. Clarification plants are sized for the hydraulic flow rate pretty much regardless of the precipitate loading being removed from suspension. BOSMAN (1983) of the ANGLO AMERICAN RESEARCH LABORATORIES pointed out that for low precipitate loadings, dissolved air flotation can offer a much more compact clarification step. Since the volume of precipitate in such cases is small in any case, solids density of the floated concentrate is pretty much irrelevent.

    This aspect is also discussed in chapters 12 and 24 on removal of suspended solids and acid mine drainage treatment.

12. Reverse osmosis using the seeded slurry innovation has been successfully demonstrated at RAND MINES LTD. ERPM mine as described in the Appendix I trip report. At pH 4.5, a 95% plus water recovery was achieved, and the iron content was reduced from 6.0 ppm to 0.06 ppm. WILMOTH and SCOTT (1976) found that Fe^{2+} ions could be removed from 64 ppm to 0.5 ppm in their tests of R.O., also yielding a product water at pH 4.5.

    A summary of the results achieved by WILMOTH and SCOTT (1976) is provided in the following table:

Chemistry Analyses Illustrating Effluents from Various Processes to Treat AMD

Sample	*Cond*	*Acid*	*pH*	*Ca*	*Mg*	*Total iron*	*Fe^{2+}*	*Na*	*Al*	*Mn*	*SO_4*	*Alk*	*TDS*
Example One - Limestone Neutralization: Ferrous(A) versus Ferric(B) Using No Coagulants													
Raw feed A	4,000	610	5.2	360.	110.	270.	260.	480.	5.4	5.9	3,000	12.	4,200
Feed B (H_2O_2)	4,000	590	3.1	340.	95.	270.	0.	440.	8.2	5.9	2,500	0.	3,500
Effluent A	4,000	230	6.5	420.	90.	150.	150.	380.	1.0	5.8	2,400	88.	3,500
Effluent B	4,000	13	6.5	380.	70.	6.2	0.	370.	1.2	5.0	2,000	50.	2,900
Example Two - Limestone Neutralization with Extended Aeration, Sludge Recycle, and Coagulant Addition													
Raw feed	3,650	460	5.5	370.	110.	230.	220.	470.	12.	5.4	2,800	8.	4,000
Effluent	3,650	0	7.4	520.	110.	0.9	0.	440.	0.4	3.9	2,700	47.	3,700
Example Three - Lime Neutralization Comparing *p*H 8(A) versus *p*H 7(B) Using Coagulant Addition													
Raw feed	4,000	520	5.7	400.	130.	280.	260.	510.	9.8	6.4	3,200	23.	4,500
Effluent A	4,100	0	7.9	600.	120.	2.1	0.	500.	0.4	1.6	3,300	88.	4,700
Effluent B	4,100	0	7.0	620.	120.	10.	0.7	490.	0.6	4.9	3,300	50.	4,400
Example Four - Combination Limestone-Lime Treatment(A) versus Lime Treatment(B) Using Coagulants													
Raw feed	3,600	630	5.2	340.	100.	290.	270.	380.	15.	3.4	2,700	4.4	3,800
Effluent A	3,500	0	8.0	560.	83.	2.3	0.	370.	0.5	2.2	2,500	100.	3,500
Effluent B	3,500	0	8.0	560.	95.	1.4	0.	360.	0.2	1.2	2,500	110.	3,500
Example Five - Lime-Soda Treatment Where Effluent Hardness Is Less Than 100 mg/liter													
Raw feed	820	170	3.0	28.	18.	17.	—	1.8	13.	4.5	270	0.	350
Sed. eff.	930	0	11.	140.	1.1	0.8	—	1.8	2.7	0.2	240	100.	500
Softener eff.	1,000	0	10.8	41.	0.4	0.3	—	140.	2.5	0.05	220	110.	510
Recarb. eff.	790	0	9.2	33.	0.4	0.3		140.	2.4	0.06	220	74.	470
Example Six - Alumina-Lime-Soda Treatment													
Raw feed		700	2.8	8.	25.	100.	—	2.	40.	4.0	750	0.	950
Effluent		0	7.5	20.	10.	0.3	—	150.	0.2	0.04	250	—	450
Example Seven—Reverse Osmosis Treatment													
Raw feed	1,000	240	3.4	130.	90.	77.	64.	—	12.	12.	750.	0.	1,300
Waste brine	3,600	810	2.9	490.	310.	330.	250.	—	44.	24.	2,800.	0.	4,500
Effluent	17	32	4.5	0.5	0.6	0.5	0.5	—	0.2	0.08	2.2	0.	5
Example Eight - Ion Exchange Treatment (Design Values)													
Raw feed	—	240	3.4	130.	90.	77.	64.	1.0	12.	12.	750	0.	1,300
Cation eff.	—	800	1.9	13.	5.	6.	5.	3.	0.2	0.6	750	0.	800
Anion eff.		0	8.0	13.	1.5	1.2	1.0	20.	0.2	0.3	40	20.	110
Neu. eff.	—	0	7.5	20.	1.5	0.1	0.1	20.	0.2	0.04	50	30.	120

Note: All units are mg/liter except for conductivity (micromhos/cm) and *p*H. Alkalinity and acidity are expressed as $CaCO_3$.

It is noted in the above table that ferrous iron could be reduced using H_2O_2 as an oxidant and limestone from 270 mg/l to 6.2 mg/l, although the same solution with limestone addition and extended aeration reached pH 7.4 and iron was reduced to 0.9 mg/l.

CATALYTIC OXIDATION OF IRON

In Chapter 39 where removal of copper is discussed, a paper by FAULKNER (undated) describes how iron can be catalytically oxidized from ferrous to ferric with the use of SO_2 and activated carbon, even at an acid pH.

CALGON CORPORATION
Activated Carbon Division
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
William D. Faulkner

KAIDA, et al. (1978) described a bench scale treatment of mine effluent containing iron, copper, Cd, and zinc. The process employs catalytic air oxidation of ferrous to ferric ions using $NaNO_2$, allowing fractional precipitation of ferric hydroxide prior to removal of other metals.

Both of these processes are petentially useful.

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CHAPTER 43

MANGANESE Mn

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OCCURRENCE OF MANGANESE IN THE MINE-MILL ENVIRONMENT

Manganese, although not nearly as abundant as iron in rocks and soils, is nonetheless very abundant. Manganese frequently occurs in mine drainage and is often associated with zinc, copper, and silver ores. In South Africa, MnO_2 is used as an oxidant in uranium leaching with the consequence that Mn^{2+} can occur at high levels in uranium plant tailings and raffinates.

The PEDCO (1983) report which lists the findings of analyses of thousands of mine waste, mill tailings, and mine water samples from mines in the U.S.A., leads to the conclusion that manganese is relatively susceptible to the acetic acid leach tests from mined materials used in the EPA's EP leach test criterion for "hazardous waste."

MAREE and DEWET (1980) showed how manganese in the Vaal River suddenly increased in acidified river water from 140 mg/l to 4400 mg/l at Orkney, Transvaal, where it caused a problem in treatment for use as municipal service water. It was suspected at the time that seepage of gold-uranium mill effluents and runoff from manganiferous soils could have been responsible. Since then, manganese levels have dropped to much less than 1 mg/l as a result of advanced, yet simple, water management and practices by mines from which effluents drain into the Vaal River in that area. (Drainage from several mining companies enters the Vaal River upstream of Orkney.)

HILL (1972) reported manganese in mine waters at 1.2-8.0 mg/l, and KUNIN and DOWNING (1971) reported one acid mine drainage flow with 50 mg/l Mn.

At ENOXY COAL, INC., Buckhannon, West Virginia, coal waste is mixed with a carbonate rock to avoid the generation of acid mine drainage. Although the carbonate rock does inhibit the generation of acid, manganese in the carbonate waste rock goes into solution and reaches 30-150 ppm. This manganese is difficult to remove. To precipitate manganese, at a pH of over ten is needed; then the treated water must be pH adjusted to meet effluent pH limits, all of which require expensive reagents according to:

ENOXY COAL, INC.
Post Office Box 710
Buckhannon, WV 26201
(301) 447-9272
Allan Meek

SUMMARY OF PEDCO (1983) DATA (mg/l or ug/g)

	Surface Mine Waste T	Surface Mine Waste A	Surface Mine Waste W	Underground Mine Waste T	Underground Mine Waste A	Underground Mine Waste W	Untreated Mine Water	Mine Water Pond Settled Solids T	Mine Water Pond Settled Solids A	Mine Water Pond Settled Solids W	Tailings Pond Solids T	Tailings Pond Solids A	Tailings Pond Solids W	Tailings Pond Liquid	Leach Liquors
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
URANIUM-OTHER															
Ave.	570	2.4	0.23	84.6	4	0.01	0.63	180	4.53	L	-			-	
No. of Samples	6	6	5	8	8	6	3	3	3	L	-			-	
Minimum	123	0.03	0.10	93.6	1.34	0.01	0.19	108	3.8	L	-			-	
Max.	1090	8	0.42	3510	7.5	0.01	1.22	250	8.6	L	-			-	
SOUTHWESTERN COPPER															
Ave.	225	1.49	4.36								268	3.2	0.06	0.30	640
No. of Samples	14	1.3	8								6	6	1	6	3
Minimum	35.7	0.09	0.02								57.3	0.05	-	0.01	550
Max.	373	5.10	34								687	10.7	-	1.40	710
COPPER-OTHER															
Ave.	938	2.15	0.80	-	-	-	-	-	-	-	369	5.5	0.68	100	110
No. of Samples	7	7	6								7	6	7	3	1
Minimum	93.4	0.53	0.04								10	1.29	0.03	0.09	
Max.	2640	7.3	1.5								1050	9.8	2.65	300	
WESTERN LEAD-ZINC															
Ave.	10400	4.2	0.76				78				1610	18	3.3	1.5	
No. of Samples	2	2	2				1				1	1	1	1	
Minimum	7950	2.6	0.63												
Max.	12900	5.8	0.88												
MISSOURI LEAD-ZINC															
Ave.				1310	1.6	0.4					1030	2.13	0.07		-
No. of Samples				1	1	1					3	4	4		
Minimum											411	0.84	0.03		
Maximum											2100	4.01	0.12		
MOLYBDENUM															
Ave.	369	1.10	0.32	846	7.35	0.08	23	-	-	-	715	5.25	0.54	4.26	-
No. of Samples	2	2	2	2	2	2	3				3	3	3	3	
Minimum	169	0.24	0.22	615	6.5	0.05	12				212	0.74	0.16	0.29	
Maximum	568	2.00	0.42	1080	8.2	0.12	41				1380	9.6	0.77	9.50	

SUMMARY OF PEDCO (1983) DATA (mg/l or ug/g) (Continued)

	Surface Mine Waste			Underground Mine Waste			Untreated Mine Water	Mine Water Pond Settled Solids			Tailings Pond Solids			Tailings Pond Liquid	Leach Liquors
	T	A	W	T	A	W		T	A	W	T	A	W		
	ppm			ppm			ppm	ppm			ppm			ppm	ppm
NEVADA GOLD-SILVER															
Ave.	239	1.61	0.03	-	-	-	-	-	-	-	337	2.34	0.009	0.55	-
No. of Samples	5	5	3								4	4	3	2	
Minimum	126	1.23	0.01								71.8	0.99	0.001	0.008	
Maximum	325	2.10	0.07								635	4.35	0.02	1.1	
OTHER GOLD-SILVER															
Ave.	18.4	0.04	0.23	3960	10.3	3.63	-	-	-	-	6110	72.2	2.97	0.12	-
No. of Samples	2	2	2	3	3	3					5	5	4	4	
Minimum	13.4	0.02	0.05	3190	0.01	0.19					25.4	0.01	0.01	0.02	
Maximum	23.4	0.07	0.40	4910	16	7.80					19500	201	10.8	0.20	
TACONITE															
Ave.	3830	3.35	0.23	-	-	-	0.47	-	-	-	4340	19.3	0.17	3.89	-
No. of Samples	13	13	6				2				8	8	6	4	
Minimum	261	0.42	0.01				0.43				433	0.016	0.008	0.03	
Maximum	19300	9.9	0.99				0.51				7340	76	0.36	15	

T = Total A = Acetic Acid Leach W = Water Leachate

Mn (ug/L) MANGANESE

Summary of North American Water Quality Criteria for Manganese

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	--	--	--	Undefined Tolerance Limits	10-50	50	100-1,000	50	--
MAX. PERMISSIBLE LIMIT		--	--	--	--		50	--	--	--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<20 .02 (96-hr LC50)	100	--	<100 *	--	--	--	100-1,000	--	--
MAX. PERMISSIBLE LIMIT		100	--	--	100 *	--	--	--	--	--	--
PUBLIC WATER SUPPLY		50	50	--	<10	50	50 (limit)	(50)	--	50	50
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	-- Only few notes	(50)	--	--	--	--	(50)	--	--	--
	IRRIGATION	200	(50)	--	200	200	--	(50)	--	--	--

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ENVIRONMENTAL SENSITIVITY OF MANGANESE

Manganese is undesirable in the public water supply. Even very low levels, manganese causes staining of plumbing fixtures and ceramic tilework.

The U.S. EPA (1972, 1976) shows a public water limit for manganese of 0.05 mg/l manganese. CANADA (1979a, b) has set a limit for manganese in the public water supply of 0.01 mg/l.

At 1.0 ppm Mn and more, the hatchability of trout eggs has been found to be affected.

The ONTARIO MOE (1979) discussion of the rationale for establishment of Ontario's Provincial Water Quality Objectives does not review manganese. The U.S. EPA and Canada do not define criteria for manganese at which the environment is considered protected. In U.S. EPA (1976), an objective of 100 ug/l Mn is established for marine water. The U.S. EPA does not state whether this is total manganese or soluble Mn.

Information on the toxicity of manganese to aquatic life (both freshwater and marine) is very limited. DAVIES (1981) found that the LC_{50} of manganese for trout in soft water ranged between 14.5 and 30.0 ug/l. The hardwater LC_{50} for 20 cm fish was 116 ug/l.

REGULATORY LIMITS FOR MANGANESE

Quebec has set a maximum limit of 0.05 mg/l for manganese in receiving waters. There does not seem to be any factual substantiation for this limit other than the fact that this limit is the same as for drinking water.

The U.S. EPA maximum permissible limit in marine waters is 0.10 mg/l Mn.

The U.S. EPA (1972, 1976) limit for the public water supply is 50 ug/l.

The South African Bureau of Standards (1971) standard for manganese in drinking water is 0.1 mg/l recommended and 0.4 mg/l maximum allowable.

The SOUTH AFRICAN GOVERNMENT GAZETTE (1962) does not list a limit for manganese in the General Limit for Effluents. However, in the SPECIAL LIMIT which was designed for effluents discharging into a list of specific creeks and rivers (supposedly those that are capable of supporting trout), a limit of 0.01 mg/l Mn was imposed.

During the course of this investigation, the only examples of Mn limits in effluents found were as follows:

MANGANESE-SOLUBILITY CONTROLS

The solubility of manganese in natural water and the predominant dissolved forms to be expected can be effectively summarized by means of Eh-pH diagrams.

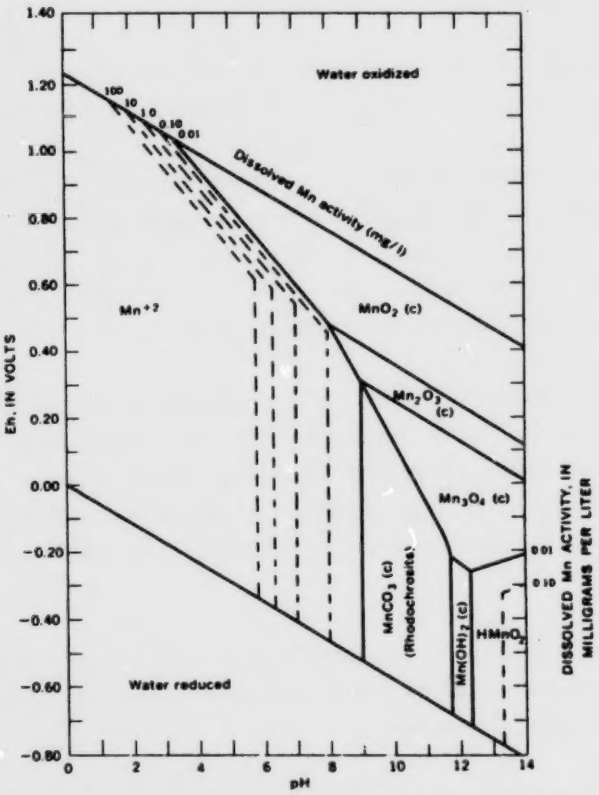


FIGURE 18.—Fields of stability of solids and solubility of manganese as a function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of dissolved carbon dioxide species 100 mg/l as HCO_3^-. Sulfur species absent.

	MANGANESE
	Mn_T (mg/l)
Mount Emmons	1.0
Climax Molybdenum Co.	
25-Hour Max., 30d Ave.	1.0
New Mexico Water Quality Control	
Commission, August 27, 1971	0.10
Gilman, Colorado	1.0

TREATMENT FOR MANGANESE

The solubility diagram for manganese in water inserted above was provided by HEM (1970) and indicates that to precipitate Mn^{+2} as a hydroxide, a pH of close to 12 is needed.

Of the various oxidation states of manganese, only the strongly oxidizing form permanganate and the divalent manganese in manganous ions are soluble in water.

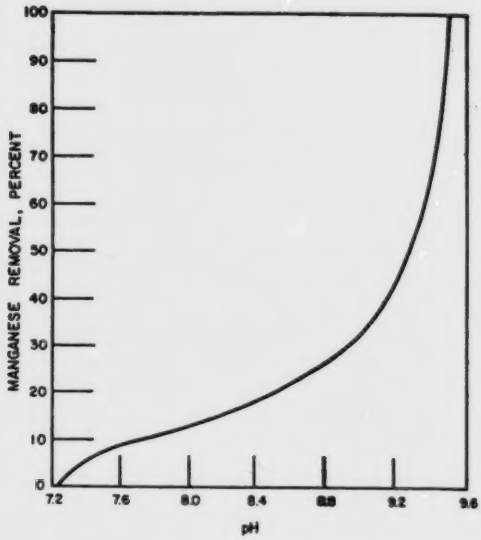
Removal of soluble manganese has been practiced for many years in the treatment of municipal water supplies and industrial process waters.

Treatment technology basically involves the conversion of the soluble manganous ion to an insoluble precipitate. In water treatment, this generally means simultaneous removal of iron since conditions under which high iron levels occur in water supplies are essentially the same as for soluble manganese. Removal of manganese is achieved by oxidation of the manganous ion and by separation of the resulting insoluble oxides and hydroxides of manganese.

Because of the low reactivity of manganous ions with oxygen, simple aeration is not an effective oxidation technique below pH 9, and even above pH 9, the air oxidation reaction is slow according to WELCH (1963).

BORGREN (1962) found that organic matter in solution can combine with manganese and prevent its oxidation by simple aeration, even at a high pH.

OWENS (1963) showed the effect of pH on manganese removal by lime. A reaction above pH 9.4 is required to achieve significant manganese reduction.



Effect of pH on efficiency of manganese removal using lime.
[From Owens (7), courtesy of *Water and Sewage Works.*]

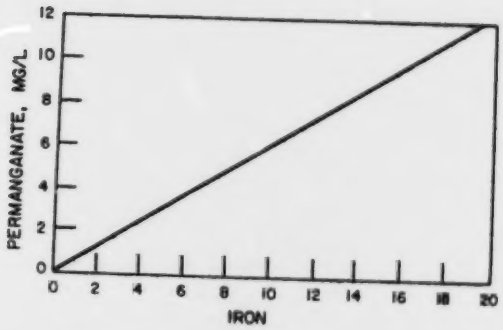
HILL (1972) reported that manganese can be reduced to less than 0.5 mg/l by simple neutralization and precipitation, but no pH values were mentioned. The use of calcium carbonate plus lime for iron and manganese removal from Japanese acid mine waters had proven successful.

The use of chemical oxidants to convey manganous ions to insoluble manganese dioxide in conjunction with coagulation and filtration has been recommended, although BORGREN (1962) reported that this may cause filtration problems. Apparently, the type of manganese flocs produced when strong oxidants are used tends to clog sand filters.

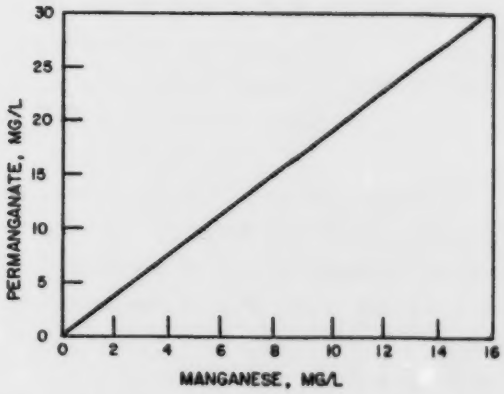
WELCH (1963) reported that manganese oxidation by chlorination may not be effective. OWENS (1963), on the other hand, reported removal of manganese at concentrations as high as 5.7 mg/l with chlorination followed by lime coagulation and rapid sand filtration. Sodium silicate was used as a coagulant aid. This is similar to the process currently in use by the Rand Water Board at their regional water supply treatment plant at Vereeniging, South Africa, which treats Vaal Dam water.

According to HARRIS (1962), effective manganese oxidation by chlorination requires a free chlorine residual of 0.5 mg/l and a dosage of 1.29 mg chlorine per mg manganese oxidized.

The successful use of potassium permanganate as a chemical oxidant has been reported. Addition of 1.5-2.0 mg/l of potassium permanganate reduced 1.0 mg/l of manganese to less than 0.05 mg/l according to HANEY (1964).



Permanganate requirement for oxidation of ferrous iron. [From Willey and Jennings (10), courtesy of American Water Works Association.]



Permanganate requirement for oxidation of manganous manganese. [From Willey and Jennings (10), courtesy of American Water Works Association.]

$KMnO_4$ was added 30 minutes upstream from the prechlorination point which was followed by lime-alum-sodium silicate coagulation (4-10 hours retention) and rapid sand filtration.

Since iron is generally present, the quantity of permanganate used must include that needed for oxidation of the iron content. The stoichiometric relationship between permanganate required and the quantity of iron and manganese present is shown in diagrams reproduced from PATTERSON (1975) above.

HOLLAND (1964) demonstrated the ability to remove manganese at lower pH with simultaneous removal of iron by permanganate oxidation. The addition of 0.04 mg/l sodium alginate reduced 0.35 mg/l manganese to less than 0.02 mg/l in the filtered supernatant. BORGREN (1962) further pointed out an additional advantage of permanganate over chlorination as the absence of residual taste or odor.

CONSTABILE and PERRON (1971) described the use of a vacuum diatomite filter in conjunction with permanganate oxidation for manganese removal from a municipal water supply. Manganese was reduced from 1.23 mg/l to 0.05 mg/l or less. The unit required 250 lbs. diatomite per million gallons filtered (30g diatomite/m^3).

Permanganate may be used indirectly for manganese removal in the manganese greensand filter method. The filter is a combination of New Jersey glauconite (greensand), manganese sulfate, and potassium sulfate which results in a filter bed of sand grains containing high oxides of manganese as described by WILLEY and JENNINGS (1963). Upon contact with manganous ions, an oxidation-reduction reaction occurs resulting in the formation of insoluble manganese dioxide which remains in the filter bed. The bed is periodically reoxidized with permanganate, and solids are backwashed from the bed. With this system, manganese was reduced from 1.7 mg/l to zero at pH 7.2 using a pressure greensand system (ALLING, 1963). This plant, with 500-700 gpm (2,700-3,800 m^3/d), cost only a third in capital compared with a conventional aeration, lime coagulation-clarifer-filter-recarbonation system. A permanganate dosage of 13 mg/l was used. The water had a manganese concentration of 13 mg/l manganese. Treatment costs in absolute terms are meaningless because it was so long ago, but these were comparable with lime costs for conventional treatment. This plant was continuously regenerated with periodic backwashing of the greensand filter. Generalized removal capacities for greensand filters are given as 0.09 pounds manganese per ft^3 of filter volume with regeneration requirements of 0.18 lb/ft^3 of $KMnO_4$.

Flow rates of 3 gpm/ft^2 are considered normal by ALZENTER (?).

NETZER, et al. (1975) investigated the use of ozone in conjunction with lime as a manganese removal technique in laboratory studies. The following results were reported by PATTERSON (1975) for solutions of manganous chloride initially containing 94 mg/l manganese:

See Chloride Removal

United States Patent [19]

Bolton et al.

[11] **4,379,037**

[45] *** Apr. 5, 1983**

[54] **REMOVAL OF MANGANESE AND CHLORIDE IONS FROM AQUEOUS ACIDIC ZINC SULPHATE SOLUTIONS**

[75] Inventors: **Gerald L. Bolton, Fort Saskatchewan; Verner B. Sefton; Nicolaus Zabryckyj, both of Edmonton, all of Canada**

[73] Assignee: **Sherritt Gordon Mines Limited, Toronto, Canada**

[*] Notice: The portion of the term of this patent subsequent to Sep. 22, 1998, has been disclaimed.

[21] Appl. No.: **271,723**

[22] Filed: **Jun. 8, 1981**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 86,877, Oct. 22, 1979, Pat. No. 4,290,866.

[30] **Foreign Application Priority Data**

Dec. 20, 1978 [GB] United Kingdom 49267/78

[51] Int. Cl.[3] C25C 1/16; C25B 1/26

[52] U.S. Cl. 204/119; 204/114, 204/128; 423/50; 423/500

[58] Field of Search 423/50, 500, 502; 204/114, 119, 128

[56] **References Cited**

U.S. PATENT DOCUMENTS

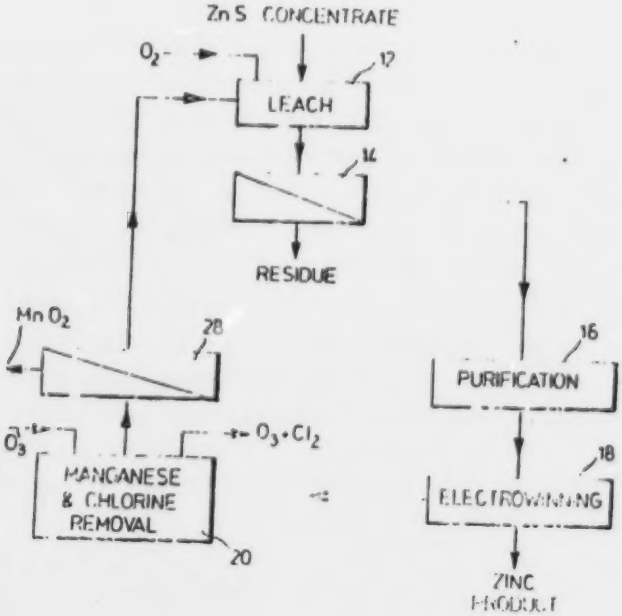
2,577,808	12/1951	Pye et al	423/502
4,120,941	10/1978	Nowak et al.	423/500
4,290,866	9/1981	Bolton et al.	204/119

Primary Examiner R. L. Andrews
Attorney, Agent, or Firm Robert F. Delbridge; Arne I. Fors

[57] **ABSTRACT**

A process for removing manganese and chloride ions from an aqueous acidic sulphate solution containing zinc, manganese and chloride ions without removing a substantial amount of zinc ions from the solution includes adjusting the free acidity of the solution if necessary to at least about 0.1 molar. The solution is then treated with ozone to oxidize manganese ions to manganese dioxide, and the ozone treatment is continued after the manganese concentration has fallen to a low level to oxidize chloride ions to chlorine gas. The precipitated manganese dioxide is removed from the solution.

11 Claims, 2 Drawing Figures



FINAL MANGANESE CONC. (mg/l)

pH	Lime Only	Lime Followed By Ozone
7.0	-	0.8
8.0	90	0.3
9.0	17	LT 0.1
10.0	0.15	LT 0.1
11.0	LT 0.10	-

Ion exchange has been used for manganese removal, and many advantages are claimed by ALZENTER (?). PATTERSON (1975) pointed out one drawback of ion exchange as its non-selective removal of manganese with other ions. ALZENTER mentions performance of the IX plant over three years during which manganese in feedwater was routinely reduced from 1.7 ppm to 0.10 ppm Mn and less on a regular basis with iron removal from about 50 mg/l to 0.3 ppm Fe.

Brine was used for regeneration of the resin, and manganese remained in solution in the brine presenting a disposal problem. An anaerobic waste stream is necessary for the ion exchange system to avoid air oxidation of manganese in the feedwater with resultant precipitation and clogging of the ion exchange bed.

PATTERSON (1975) points out that the cost of the above processes for manganese removal from wastewaters may be increased by the presence of acids, other oxidizable metals, or organics in the waste stream. He points out that the unit operation costs for coagulation-sedimentation-filtration should be similar to those for iron removal systems. Additional costs are attributable for chlorine (or chlorine dioxide) and chlorination equipment plus lime needed to meet the higher pH.

MANGANESE (TOTAL) IN TREATED MINE MILL WATER EFFLUENTS

	Inflow	Outflow	Treatment
Gilman, Colorado AMC	80-453	1.12	Lime pH 9.6
Denison Mines, Mine Water	1.9	0.44	Neutralization pH8 and dilution.

MANGANESE (TOTAL) IN TREATED MINE-MILL EFFLUENTS (Continued)

	Inflow	Outflow	Treatment
Mount Emmons			
Mine Water	6.5-80	0.05	pH 10.6 and
Tailings Seepage	400-500	0.05	Lectroclear flotation and filtration.
Noranda, Waite-Amulet	5.12	0.02	Lime HDS pH 9.80
Vaal Reefs, Raffinate	1670 ppm	LT 1.0 ppm	Lime pH 9.5; settle mix with tailings.
Rand Mines ERPM			
Mine Water	8.0	0.50	Pilot R.O. slurry seeded.
Rössing Uranium			
Tailings Decant	1900-2500		Geochemical adsorption and natural neutralization to pH 6.7.
Collected Tailings Seepage		1100	

During the course of this investigation, it was interesting that manganese was not monitored much of the time in effluents. In other cases, manganese removal required special conditions in water treatment.

MOUNT EMMONS, COLORADO

Manganese occurs in the old zinc mine water at 6.5-80 mg/l and in seepage from the stabilized tailings ponds at 400-500 mg/l. Through pH adjustment to pH 10.6, Lectroclear flotation of the precipitate, and multi-media filtration, Mn is reduced to 0.05 mg/l in the treated effluent.

Manganese removal requires a higher pH in the treatment plant than would otherwise have been needed.

Capital costs of this plant were $10 million, and operating costs for the 2000 U.S. gpm capacity plant run $700,000-1,000,000 per year operating at partial capacity.

An alternative means of removing precipitated metals that has been tested with promising results is dissolved air flotation.

GILMAN, COLORADO

Mine drainage from the underground zinc-silver mine located on the mountainside above the Eagle River runs 80-453 mg/l Mn. Originally, the ore was milled underground, and the tailings deposited to a tailings dam alongside the river in the valley below.

For years mine water has been segregated into a stream which requires treatment and one which does not. Treatment comprised raising the pH to 9.6 and settling in underground chambers to decant the water. However, during the 1970's, the Colorado Dept. of Health imposed an NPDES permit in which the maximum allowable manganese discharge is a level of 1 ppm.

The trip report in Appendix I includes reference to testwork by The New Jersey Zinc Company and the Colorado School of Mines Research Institute in which various oxidants were tested.

Although NaOCl was selected as the best oxidant from among $NaClO_3$, $K_2S_2O_8$, and H_2O_2, the amounts required were considered uneconomical in 1973. At that time, the addition of 1 lb. lime per 1,000 U.S. gallons of tailings effluent was deemed to be the best solution if operation of the mine seepage pumps were carefully synchronized with lime addition.

When 64 lbs. $Ca(OCl)_2$ equivalent were added per 1,000 U.S. gallons, manganese was dropped to 0.5 ppm Mn at pH 8.2. The addition of 22 lbs. of $Ca(COCl)_2$ equivalent and 23 mg lime per liter, reduced Mn to 0.9 ppm. Because $Ca(OCl)_2$ costs around $1.43/lb, it was concluded that this reagent would be uneconomical. Addition of 0.56 lbs. lime per 1,000 gal. resulted in a pH of 9.5 and reduced Mn to 1.1 ppm Mn, resulting in the conclusion that lime addition of 1.0-1.5 lbs. per 1,000 gal. would be the logical answer to reduce Mn to below 1.0 ppm Mn--cheap at 1.9 cents/lb lime at that time.

The Colorado School of Mines Research Institute showed that by passing the mine water through a column of crushed pyrolusite--which occurred in a vein in the mine--manganese levels could be dropped from 5 mg/l Mn to below 1.0 mg/l. The adsorption rate was shown to be a function of the manganese content of the feed solution and the retention time in the column. pH did not influence the adsorption rate in the range tested (pH 7.8-8.8). The pyrolusite adsorption of manganese II was found to be self-regerative to a degree. Mn II is adsorbed and in time oxidizes to $MnO_{1.3}$ and then to $MNO_{1.9}$ which is an adsorbent for incoming Mn II in solution. The granules in the column must be treated to restore permeability.

It was found that 1,000 gallons per minute of mine water containing 5 mg/l Mn II, a total of 5,407 m^2 of surface area would be required, or 32.8 tons of 1/2" x 1/4" pyrolusite. Assuming 120 lbs. per ft^3, this would require two 12 ft Ø tanks with 5' high beds of crushed pyrolusite.

It is believed that the pyrolusite adsorption tanks were never installed at the Gilman Mine. It is nonetheless of interest that the laboratory scale tests demonstrated the effectiveness of pyrolusite for Mn II removal from mine water at lower pH without the need for oxidation.

ENOXY COAL, INC.

At ENOXY COAL, INC., coal waste acid mine drainage is inhibited by adding a calcerous carbonate rock waste to the coal waste. This neutralizes any acid that is generated. However, although the AMD is neutralized and iron precipitated, manganese contained in the high $CaCO_3$ neutralizing waste goes into solution.

It was found that in solutions containing low levels of iron and up to 100-130 mg/l Mn II, it is very difficult and expensive to precipitate manganese. Randol International Ltd. recommended to ENOXY COAL that they test the HDS process.

THE HDS PROCESS

HERMAN (1984) of the BETHLEHEM STEEL CORP. showed at the Randol Workshop on Water Management that manganese can effectively be precipitated from acid mine drainage at a pH around 6.8 through the use of the high density sludge HDS process. In this process, lime is mixed with recycled sludge prior to being added to incoming acid mine drainage.

Manganese can be precipitated in this way even in the absence of iron.

A precipitate sludge is generated which lends itself to stabilization for landfill disposal by addition of a pozzolon. Apparently, if precipitated in the absence of iron, manganese redissolves readily unless stabilized in this manner.

More details on this process are available from:

BETHLEHEM INTERNATIONAL
ENGINEERING CORP.
Bethlehem, PA 18106
(215) 694-2424
Stewart T. Herman

RØSSING URANIUM LTD.

Manganese dioxide is used as an oxidant to dissolve uranium from RØSSING ore using a sulfuric acid leach at elevated temperature. Solution in the uranium tailings contains

2,000-2,500 mg Mn II/l at pH around 2. The tailings impoundment is porous, and seepage is collected by interceptor trenches. The natural rock and sediments contain carbonates which help to neutralize seepage solution. It is of interest that the seepage collected has pH 6.7, and the manganese level has dropped to 1100 ppm Mn.

In inspecting the trench faces, it is interesting to observe manganese oxide precipitating in the strata. Clearly, manganese oxides and hydroxides act as an excellent adsorbent for manganese from solution, even at relatively low pH.

Natural soils form good geochemical adsorbents for manganese: this property could undoubtably be exploited in special cases.

ORKNEY MUNICIPALITY, SOUTH AFRICA

River water from the Vaal River, when treated for use as municipal water by the municipal water treatment plant at Orkney (or Klerksdorp), Transvaal, was found in 1976 to be higher in manganese than the drinking water standard.

The National Institute for Water Research of the CSIR investigated various ways to remove manganese from this water. Their investigation concluded that:

1. The oxidation rate of Mn II is pH dependent.

2. The reaction Mn II and O_2 = MnO_2 is autocatalytic.

3. Measurable oxidation of Mn (II) by O_2 occurs only at pH in excess of 8.5.

4. Manganese is effectively removed from solution by adsorption on MnO_2. This adsorption is also pH dependent, requiring a pH of at least 7.7 to proceed at any pace.

5. Adsorbed metal ions on hydrated oxides are released when the pH is dropped.

6. The higher the amount of Cl_2 added, the faster the removal of manganese at around pH 7.

7. At 15 mg/l Cl_2 addition, the rate of Mn (II) removal is enhanced by increasing pH just one unit from 7 to 8.

8. Addition of 500 mg/l MnO_2 at pH 7.5 has a dramatic increase on removal of Mn (II) ions from solution.

9. In the presence of Cl_2, just 0.66 ppm $Mn^{+/}$ increases the rate of Mn II removal by 100%.

Eventually, it was found that allowing MnO_2 to coat filtersand in the filtration plant makes it possible to effectively precipitate manganese from the raw municipal water when it is filtered. The NIWR report with details has not been published. However, industry can approach the NIWR for help on manganese removal problems.

NATIONAL INSTITUTE FOR WATER
RESEARCH (NIWR)
Post Office Box 395
Pretoria 0001
(012) 86-9211
Telex: 3-630
G. R. Botha
Assistant Director
J. P. Maree

High manganese has been found in several other South African raw municipal water supplies.

VAAL REEFS EXPLORATION AND MINING CO. LTD., ORKNEY, TRANSVAAL

Manganese is used as an oxidant in acid uranium leaching on the Witwatersrand including Vaal Reefs. Typical uranium plant raffinates contain 1670 ppm Mn. Effluents from various Vaal Reefs plants are currently treated by mixing them with tailings pulps and adding lime to raise the pH to 9.5. A considerable amount of iron in the form of raffinate (730 ppm Fe^{2+}, 500 ppm Fe^{3+}) is added. This requires 10-12 Kg lime per ton which, at Vaal Reefs, costs R7.76 million/year in lime costs alone to yield a tailings dam decant solution with less than 1 ppm Mn.

Effluent neutralization in this way costs R0.80-R1.00 per ton ore treated which is a sizable percentage of total metallurgical costs, but allows zero discharge and recycle of all water that can be reclaimed.

Since the implementation of effluent neutralization at Vaal Reefs, the manganese level in the Vaal River water has been reduced to less than 1 ppm in the vicinity of the huge metallurgical complex.

RAND MINES LTD., ERPM SEEDED SLURRY R.O.

At the Hercules shaft of the ERPM Mine on the eastern Witwatersrand, a mine water was desalinated on a test basis in 1984 to demonstrate the seeded slurry reverse osmosis process.

Manganese levels were reduced from 8 mg/l in feedwater at pH 4.5 to 0.5 ppm Mn in the product water. This demonstrated a much higher tolerance to manganese than can normally be tolerated by membrane desalination processes, and a high water recovery in excess of 95%. More information on seeded slurry reverse osmosis is available from:

RESOURCES CONSERVATION COMPANY
3101 N.E. Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Reams Goodloe
Tom Wolfe

Fundamental to the success of seeded slurry reverse osmosis is the availability of a new cost effective tubular R.O. unit referred to in the chapter on reverse osmosis.

BUREAU OF MINES, PITTSBURGH, JET AERATOR

ACKMAN and KLEINMANN (1984) described a new in-line aeration and treatment system for acid mine drainage. The principle is to add NaOH solution via a nozzle to the acid mine drainage via a jet pump followed by a static mixer ahead of discharge to a settling pond.

Although NaOH is more expensive than lime, in this case the equipment simplicity would enable significant capital cost savings.

Manganese was dropped in demonstration runs by 50% from a level of around 70 mg/l. at pH 4-6, and almost quantitatively from the same solution at pH 7-9.

Commercial jet pumps for the purpose are now available as described in Chapter 24 on acid mine drainage treatment. More information is available from:

BUREAU OF MINES
U.S. DEPT. OF THE INTERIOR
Post Office Box 18070
Pittsburgh, PA 15236
(412) 675-6422
Terry Ackman
Robert L.P. Kleinmann

ARGO TUNNEL TEST, WANNAMAKER CONTINUOUS CONCENTRATOR

The Colorado Dept. of Natural Resources, Dept. of Mine Land Reclamation, demonstrated a device known as the Wannamaker Continuous Concentrator in 1981 to treat ARGO TUNNEL acid mine drainage containing 108 ppm Mn.

The precipitate was recirculated through the Wannamaker Continuous Concentrator as described by HOLM and SIMPSON (1981).

In this test, manganese was reduced to 0.65 ppm at pH 9.2 and to 0.005 ppm at pH 9.8. The proposed water standard was 1.1 ppm Mn.

More information is available from:

COLORADO DEPT. OF NATURAL RESOURCES
Mined Land Reclamation Division
1313 Sherman Street
Denver, CO 80203-2273
(303) 866-3567
J. David Holm

Randol International Ltd. believes that the effectiveness of manganese removal would be enhanced if the cross-flow filter were to be used in an HDS mode--ie., mixing the filtercake slurry with lime before it contacts the influent water to be treated.

DRY MGO PRECIPITATION OF METALS

SCHILLER and KHALAFALLA (1983) describe a patented process for removal of heavy metals and manganese from wastewater employing a substantial excess of essentially dry powdered reactive MgO as the precipitant. The resulting precipitant settles rapidly to a small volume of solids which is not readily redispersed or redissolved. A water product with low suspended solids can readily be recovered by decantation. More information can be requested from:

S. E. KHALAFALLA
U.S. Bureau of Mines
Twin Cities Research Center
5629 Minnehaha Avenue South
Minneapolis, MN 55417

SULFIDE PRECIPITATION

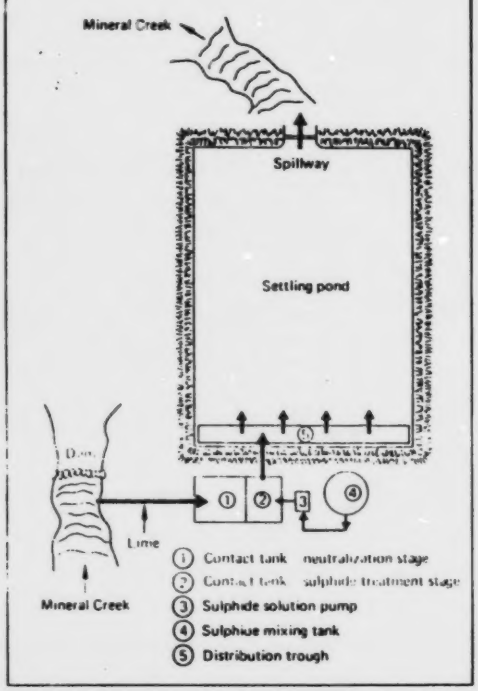
LARSEN and ROSS (1976) showed the effect of addition of lime and then Na_2S to acid mine drainage containing various metals including manganese.

It is of interest that manganese is one of the last metals to be precipitated in this way, and, even after 700 ml solution containing 0.1M Na_2S was added to an AMD sample containing 126.3 mg Mn/l, all manganese had still not been precipitated.

Two-stage process chemically treats mine drainage to remove dissolved metals

H. Peter Larsen and Laurence W. Ross, University of Denver

Fig. 1—Field treatment system for mine drainage



TREATMENT OF MINE DRAINAGE WATERS has fast become a necessity for all mining operations, and regulations governing discharge into local waterways can be expected to become even more stringent. One aspect of mine water treatment—removal of dissolved metals—can be accomplished by a two-stage process developed at the Denver Research Institute (DRI). The first stage of the process treats the waters by lime neutralization to eliminate Fe and Al. A second stage then removes Cu, Zn, Mn, and heavy toxic metals (Hg, Cd, As) by adding sulphide to the waters.

The quantitative effect of both stages of treatment can be predicted by a mathematical description based on the equilibrium relations involved:

$$mM^{+d} + dD^{-m} \rightarrow M_mD_d \downarrow \qquad (1)$$

where M is the metallic cation of charge $(+d)$ and D is the anion of charge $(-m)$.

The removal of dissolved metals by neutralization (stage 1) is predicted quantitatively. Total sulphide addition to achieve removal of specific metals is predicted for stage 2.

Table 1 provides the set of numerical constants used to describe the system mathematically. These values were selected from the literature as yielding the best approximation to measured results. Butler[1] has pointed out that K_{sp} values are often so small that they are outside the realm of realistic measurement. Therefore, a set of values that gives consistent results is all that is needed.

DRI process successful in field studies

Field investigation for the DRI process included erection of a treatment pond beside Mineral Creek in the

Fig. 2—Results of sulphide addition to Idaho drainage sample

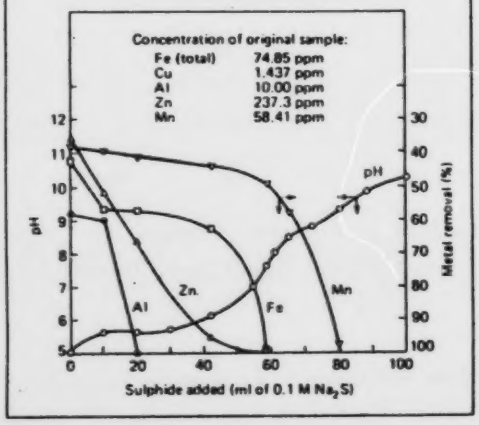
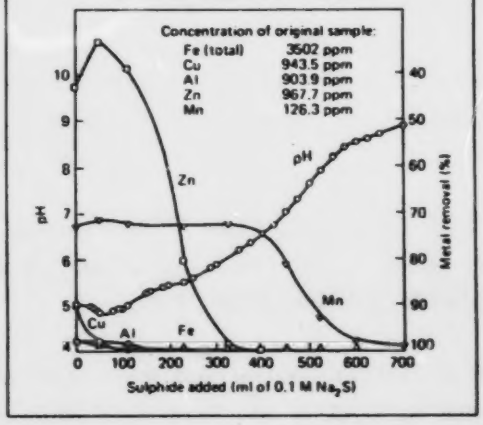


Fig. 3—Results of sulphide addition to Montana drainage sample



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CHAPTER 44

MERCURY Hg

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Regulatory authorities in most industry centers are "paranoid" about mercury and not without some justification. Mercury poisoning has resulted in an extremely unpleasant and even fatal illness in some of the people who worked with mercury in the past and also to people who ingested mercury via the food chain. Memories of contaminated tuna and the tragic Minamata Bay accident in Japan which resulted from an industrial discharge of an effluent containing mercury are still fresh in our minds.

Mercury can be a problem in the workplace when allowed to build up in recirculating metallurgical process solutions; for example, in zero discharge gold and silver recovery operations. Restrictions on mercury in mine-mill effluents are very strict indeed to protect aquatic life.

Mercury occurrences in nature are common especially in and around mineralized zones, particularly of volcanic origin (epithermal), gold and silver deposits and base metal deposits. Mercury also occurs as a primary resource and is often enriched in soils around mineralized zones even where base metals may be only weakly enriched.

During the late 1960's and early 1970's, mercury was considered to be a likely pathfinder element in mineral exploration. Numerous techniques were developed to analyze mercury in soils and soil gas, but the ultimate result was that mercury anomalies occur so much more frequently than mineral deposits that this technique has not become widely applicable.

Mercury probably occurs more often than it has been recognized in the effluents of mine-mill complexes. There are reliable quantitative ways to monitor the air in the work environment, but the EPA limits for mercury in water are so low that they are well below the best analytical techniques.

OCCURRENCE OF MERCURY IN THE MINE-MILL ENVIRONMENT

Based on data contained in the PEDCO (1983) report to the EPA, mercury levels in mine and mill effluents and leachates seldom exceed one ppm and are usually in the ppb range or less. A summary of their data for mercury has included below.

Historically, mercury was extensively employed for amalgamation recovery of gold from both placer and lode deposits but its use has now been almost entirely replaced by other processing methods. Mercury poisoning was apparently not all that uncommon among workers who operated amalgamation plants or amalgam treatment facilities. Even in recent times, amalgamation was used at the DUVAL CORP.'s Battle Mountain operation and at HOMESTAKE's Lead operation. At Lead, amalgamation of slimes has been entirely replaced by cyanidation leaching and carbon in pulp. At Battle Mountain, amalgamation has been replaced by the installation of jigs ahead of cyanidation to catch coarse gold. There are

still numerous plants in South America and South Africa which employ amalgamation to treat gravity concentrates as do small placer operations in Alaska, although in South Africa the trend is increasingly toward intensive cyanidation and electrowinning.

Mercury dissolves in alkaline cyanide solution with the result that if solutions are to be recycled, mercury levels can build up despite the fact that it generally follows gold through zinc dust precipitation into the precipitate or also through carbon adsorption and electrowinning.

Mercury is consequently recovered as a minor by-product at several gold mining operations including the CARLIN GOLD MINING CO., Nevada; PUEBLO VIEJO, Dominican Republic; PINSON GOLD MINING CO., Winnemucca, Nevada; and at FREEPORT GOLD, Elko, Nevada, to name a few.

When mercury is present in a milled ore, it may build up in solution as process water is recycled. If zinc precipitation is used, then mercury must be retorted from the precipitate and recovered prior to smelting. If carbon adsorption processes (either carbon columns for solution or CIP for slurries) are to be used, then mercury can report in the plant around the carbon regeneration kiln, the electrowinning cells, and over the elution vessels, as well as around the steel wool cathode smelting operation. In metallurgical solutions, mercury levels are likely to increase until an equilibrium level is reached and maintained. Interestingly enough, it is not only epithermal deposits that contain mercury. The Witwatersrand fossilized placer deposits also contain low levels of mercury along with other metals, but studies by the Chamber of Mines of South Africa have concluded that these present no cause for alarm from a safety or environmental standpoint.

In California, where PLACER SERVICES, INC. employs a dredge to rework an old placer deposit by digging deeper, amalgamation is used for gold recovery. However, more mercury is recovered than lost in the process. In this case, previous operations left mercury in their tailings which is now being recovered in PLACER SERVICES' more efficient gravity process.

Based on the PEDCO (1983) report data, mercury in copper, lead, zinc and other operations is generally present at very low levels. This data is relatively "spotty," but it is the best currently available. In some gold cyanidation operatons, the mercury levels undoubtably reach levels in the tens and likely in the hundreds of ppm.

PEDCO (1983) DATA SUMMARY - MERCURY

URANIUM - NEW MEXICO

All minewater and both acetic acid and water leach of solids are reported as less than 0.0005 mg/l Hg.

URANIUM - WYOMING

Surface mine waste acid leachate reached a maximum of 0.046 mg/l and a minimum of less than 0.0001 mg/l Hg. Acid leaching of low grade ore containing 0.046 mg Hg/Kg ranged between a maximum of 0.014 mg/l and a minimum of 0.0001 mg/l. All other leachates ranged between 0.0008 mg/l and less than 0.0001 mg/l Hg.

URANIUM - OTHER

Mercury levels are somewhat higher in this district as illustrated by the following summary although still well below the criterion of 0.2 mg/l.

Levels of up to 0.027 mg/l Hg were encountered in the aqueous leachate from surface mine waste and 0.046 mg/l Hg in the acid leachate from underground mine waste, and minewater pond liquid and untreated mine water are shown at less than 0.0076 mg/l or 8 ppb Hg.

WESTERN LEAD/ZINC DISTRICT

The average mercury in underground mine waste is shown as 0.34 mg/Kg with less than 0.00005 mg/l Hg in the acid leachate and an average of less than 0.0051 mg/l in the aqueous leachate. The maximum level in mine backfilled tailings aqueous leachate was 0.048 mg/l.

EASTERN LEAD/ZINC DISTRICT

Tailings pond liquid varied from less than 0.0002 mg/l to 0.0018 mg/l Hg. Tailings pond settled solids ranged from 0.01 g/t Hg but maximum acid leachate and water leachate reached 0.032 and 0.102 mg/l respectively. Averages were 0.0077 mg/l and 0.0303 mg/l.

MISSOURI LEAD/ZINC

Only one leachate, the aqueous leachate from tailings pond settled solids, exceeded 1.0 ppb at 0.0011 mg/l Hg. All the rest were very low, in the range 0.0002-0.0008 mg/l.

MOLYBDENUM

Tailings pond liquid and untreated mine water are listed at less than 0.0076 mg/l Hg, but the report does not specify how low.

NEVADA GOLD/SILVER DISTRICT

Not surprisingly, mercury reaches somewhat higher levels in leachates from gold and silver milling operations, but considering the known association between mercury and gold-silver orebodies, it was surprising that the leachable levels were not even higher.

Aqueous leachate from surface mine waste ran 0.022 mg/l Hg. Tailings pond liquid interestingly enough varied between 0.358 and 0.526 mg Hg/l, probably reflecting mercury leached in the cyanidation process. Even tailings pond solids run between 0.0025 mg/l and 0.0415 mg/l Hg.

Even though the EP toxicity test criteria were not exceeded by the leach test, decanted tailings pond liquid exceeded the EP leach test criteria for mercury in some cases.

OTHER GOLD/SILVER DISTRICTS

In this area, leach test results for three samples yielded less than 0.0011 mg/l Hg, but tailings pond liquid ran 0.0423 mg/l, and the acid EP leach test with acid from settled solids in the tailings pond exceed 5.7 mg/l. It is clear that from one gold mining district to another, there are major changes in mercury levels and also in the amount of mercury that is acid and water soluble.

TACONITE DISTRICT

Even in the taconite district, mercury levels in ore are higher than one might expect at 0.0013 mg/l in acid leachate. Although not a high level in itself, the acid leachate exceeds 1 ppb.

In the course of this investigation, it was surprising how seldom mercury is monitored on a regular basis; it having been determined in the past (it is assumed) that mercury levels are of no consequence in the effluents. The only references to mercury monitoring in mine and mill effluents encountered are as follows:

	Effluent Hg (ppb)	Permitted Hg (ppb)
Kidd Creek Mines, Timmins		
- Underground Mine Drainage	LT 1	
- Treated Mine Drainage in Holding Pond	LT 1	
- Recycled Minewater	LT 1	
- Kidd Creek Water After Mixing with Treated Water	LT 1	
Mount Emmons Operation, Climax Molybdenum Division		
- Maximum Permissible Limit (Daily)	0.05	0.05
- Measured in Treated Water Discharge	LT 0.20*	

	MERCURY	
	Effluent Hg (ppb)	Permitted Hg (ppb)
Kidd Creek Concentrator, Timmins		
- Tailings Decant After Lime Treatment	LT 1.0 ppm	

* Detection Limit

Most gold and silver recovery operations located in the western U.S.A. are "zero discharge" operations and consequently, effluent limitations do not apply as there is no effluent. These operations would be expected to have somewhat higher mercury levels in their recycled process solutions.

BYCROFT, et al. (1982) reported on mercury contamination of the Lerderberg River, Victoria, Australia, from an abandoned gold field. This paper was not obtained but could be requested from the authors at Monash University, Clayton.

PATTERSON (1975) refers to observations that caustic soda manufactured by chloralkali processes that use mercury may contain "very high" levels of mercury. Literature references report mercury levels of 0.2-150 mg/l in caustic solutions. Caustic from Swedish chloralkali plants contained an average of 3.26 mg/l Hg. Considering the very low levels of mercury allowed in effluents, even the possibility of levels of this magnitude in caustic soda reagents must be taken into account where caustic soda is used for pH adjustment. The addition of 0.3 lb. caustic per ton of solution, for example (150g/t), would add 1 ppb Hg to the effluent which is of the order of the maximum level permitted in mill effluents.

It is possible, but not confirmed, that environmental concerns about mercury losses in chloralkali plants may well have resulted in steps to reduce levels in caustic soda product since PATTERSON (1975) reported the results.

REGULATORY LIMITS FOR MERCURY IN EFFLUENTS

Objectives and maximum permissible limits for mercury in receiving waters are listed below. It is interesting that the MINISTRY OF THE ENVIRONMENT OF ONTARIO (1979) has set two objectives. First is a concentration of 0.2 ug/l Hg of total mercury in filtered water and second, a maximum level of 0.5 ug/g Hg in whole fish (wet basis) for the protection of aquatic life and fish-consuming birds as well as the human consumer.

Compiled by NORANDA

Hg (ug/L) MERCURY

Summary of North American Water Quality Criteria for Mercury

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9,**] 1979 For Final Effluent	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE				24-hr mean	0.1						
OBJECTIVE		0.05	0.05	0.57 x 10⁻⁶	0.2	..2	N.D.	--	NIL-5.0	--	--
MAX. PERMISSIBLE LIMIT		0.2	--	0.0017	--	0.2	0.2	0.1	--	0.1	--
PROTECTION OF MARINE LIFE				24-hr mean							
OBJECTIVE		--	0.1	0.075	..10*	--	--	--	NIL-5.0	--	--
MAX. PERMISSIBLE LIMIT		0.10 ug/L	--	3.7	.10*	--	--	--	--	--	--
PUBLIC WATER SUPPLY		2.0	2.0	0.144	1.0	--	N.D. (obj) 1,2,5 (limit)	(0.1)	--	--	2.0
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	10	(2.0)	--	3.0	10	--	(0.1)	--	--	10
	IRRIGATION	--	(2.0)	--	No limit Recommended	--	--	(0.1)	--	--	<.02

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Mercury, EPA 440/5-80-058.
4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada. 1979. Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances, Mercury.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Gouin, D. et Malo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9. ** British Columbia Ministry of the Environment. 1979. Pollution Control Objectives for Mining, Smelting and Related Industries. (Receiving water objectives not available)
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

TABLE

MERCURY

The U.S. EPA criteria objective for mercury in receiving waters for the protection of the environment has been set by the U.S. EPA (1980) at 0.00057 ug/l with a maximum permissible concentration of 0.0017 ug/l.

Since the detection limit of most commonly used analytical measuring instruments is much higher than this, the U.S. freshwater criteria are considered unrealistic. The U.S. objective and maximum permissible concentration are also well below background levels in many streams and lakes. The most sensitive detection equipment in common use is the U.V. detection system employed in the flameless atomic absorption cold vapor technique. This method has an accepted detection limit of 0.01 ug/l as Hg. Although the detection limit can be decreased to 0.001 ug/l, accuracy at this level is poor, and at such extremely low levels, there is no way of knowing whether the mercury measured is in fact in the water or introduced from other sources, e.g., adsorption on the walls of the laboratory glassware. Possibly the objective is meant to be regarded as a target with no serious intention of ever meeting it; the basis for the U.S. mercury objective and maximum permissible concentration is not known.

WATER QUALITY CRITERIA FOR MERCURY

Freshwater	Hg (ppb)
U.S. EPA (1980) Max. 24-Hour Average Hg Objective	0.00057
U.S. EPA (1980) 24-Hour Mean Max. Permissible	0.0017
NEW MEXICO (1971)	1.0
CANADA (1979) 24-Hour Mean Objective	0.10
CANADA (1979) Max. Permissible Objective	0.20
ONTARIO (1979) 24-Hour Mean Objective	0.20
ONTARIO (1979) Max. Permissible Limit	0.20
ALBERTA (1977) Max. Permissible Limit	0.10
SASKATCHEWAN (1975) Max. Permissible Limit	0.10
BRITISH COLUMBIA (1979) Objective	Nil-5.0
SOUTH AFRICA (1983) Proposed Limit for Effluents	20
Marine	
EPA (1980) Objective 24-Hour Mean	0.025
EPA (1980) Max. Permissible Limit	3.70
CANADA (1979a) Objective	LT 0.10
CANADA (1979a) Max. Permissible Limit	0.10
BRITISH COLUMBIA (1979) Final Effluent	Nil-5.0

Public Water Supply

U.S. EPA (1980)	0.144
CANADA (1979)	1.0
MANITOBA (1979)	2.0
SOUTH AFRICA (1971) Drinking Water Recommended Limit	5
SOUTH AFRICA (1971) Drinking Water Max. Allowable	10

MERCURY LIMITS IN MINE-MILL OPERATING PERMITS

Most of the operations visited did not have a stipulated mercury limit in their effluents because, in most cases, mercury was not deemed to be a problem. The few cases where mercury limits were included in the permit are as follows:

	Hg (ppb)
HOMESTAKE MINING COMPANY, Lead	
- Final Effluent (NPDES)	1.0
HOMESTAKE - McLaughlin Project	
- Treated Runoff Water, 30-Day Ave.	1.0
- Treated Runoff Water, Daily Max.	2.0
AMAX, INC., Mount Emmons	
- Final Effluent After Treatment (NPDES)	0.5

EFFECTS OF MERCURY ON METALLURGICAL EFFICIENCY

RENCO MINES LTD. in Zimbabwe recovers gold by cyanidation and CIP from an ore containing undersirable contaminants which interfere with the process. One of these (MENNE, 1984, personal communication) is bismuth which is believed to interfere with gold adsorption on carbon.

RENCO MINES LTD. adds 200g $HgCl_2$ to the pulp just before it reaches the first agitator. The $HgCl_2$ is added with the cyanide solution at the pump sump between the pulp pre-aeration tanks and the first leach agitator.

The 200g $HgCl_2$ dose was found to be critical. Any less than that, and gold recovery drops off. Any more does not help recovery but adds to expenses.

RENCO MINES LTD. made the fascinating observation that within minutes of being added, the mercury which was added in soluble form cannot be detected in the pulp solution. Of 200g $HgCl_2$ added in the circuit, only 50-70% can be found in the final tails.

Although the precise role of the mercury in gold leach and CIP enhancement is not yet understood, more information may be available from:

MR. H.G. BURKS
Consultant
19 Sable Way
Mshumavale - Gatooma
Zimbabwe
Telephone: Gatooma 2310

DAVID MENNE
Edward L. Bateman (Pty) Ltd.
Post Office Box 7028
Cloisters Square
Perth, WA 6000
(09) 322-4740
Telex: AA95066

A second effect of mercury on gold leaching was referred to at a verbal presentation on gold recovery on the Witwatersrand by P.J.D. Lloyd (recollection only) who then was Research Director of the Chamber of Mines Research Laboratories in South Africa. He presented data which supported his view that gold dissolution by cyanide from Witwatersrand ores was inhibited by the presence of small amounts of mercury in the ore which necessitated a leach residence time long enough to dissolve the mercury before the last of the gold could be brought into solution. Information may be requested from:

DR. P.J.D. LLOYD
Managing Director
EMS Minerals
Post Office Box 585
Bedfordview - Johannesburg
South Africa

The above indicates that the addition of mercury in soluble form may enhance gold extraction, but mercury in mineral form may retard leach kinetics. It must be stated that the latter observation was presented more as a tentative hypothesis than a fact.

ENVIRONMENTAL SENSITIVITY - MERCURY

The biologically significant form of mercury is methyl mercury which is very much more toxic to aquatic organisms than inorganic mercury. According to JOHNELS, et al. (1967) and KAMPS, et al. (1972), the bulk of mercury found in fresh water fish occurs in the form of methyl mercury. Methyl mercury may also be demethylated by bacteria in sediments according to SPANGLER, et al (1973).

Methylation of mercury in the environment occurs by at least two mechanisms as described by WOOD, et al. (1968) and LADNER (1971).

Administrative guidelines for fish for human consumption promulgated by the U.S. Food and Drug Administration and the Canadian Food and Drug Directorate are set a 0.5 ug/g mercury in edible portions. There is no evidence according to ONTARIO (1979) that concentrations of 0.5 ug/g mercury in fish have any effect on the fish themselves. Concentrations of mercury in fish that have been killed by chronic exposure to methyl mercury ranged from 9.5 to 23.5 ug/g Hg according to ONTARIO (1979).

ONTARIO (1979) provides a table showing the results of a series of toxicity studies which demonstrate that most organic mercury compounds are more toxic than inorganic mercury salts.

ONTARIO (1979) concluded that fish-eating birds should be protected if the concentration of total mercury in whole fish does not exceed 0.5 ug/g.

Bioaccumulation of mercury occurs in many fish, bird, and other aquatic species, and some examples are cited in ONTARIO (1979).

With the exception of some of the most severe cases of mercury pollution, aqueous mercury concentrations, U.S. EPA (1980) and NRCC (1979), are generally well below levels which would affect the wellbeing of aquatic and marine life.

According to HEIT and FINGERMAN (1977), the method used by the EPA to extrapolate to the objective figure and the MPC provided an erroneous result. The figures must be erroneous considering the bountiful fish populations that thrive in water with significantly higher mercury background levels.

Crayfish are apparently particularly sensitive to mercury with LC-50 of 50 ug/l and LC-50 of 250-1,000 ug/l reported by two papers which is about 2,500 times higher than that reported by another worker.

The second most sensitive species listed by the U.S. EPA is Daphnia magna which was observed to have a 48-h LC-50 of 5 ug/l as Hg_2Cl_2 (data from BEISINGER and CHRISTENSEN (1972)). The LC-50 value found in their study is 2,940 times greater than the MPC.

Rainbow trout LC-50 value of 250 ug/l Hg is tested as Hg_2Cl_2 compared with 20 ug/l for methylmercuric chloride according to the U.S. EPA (1980). Rainbow trout are generally considered to be one of the most sensitive fish species, and their LC-50 values are 147,000 and 17,000 greater than the MPC which suggests that the MPC derived by the EPA (0.0017 ug/l) is unrealistic.

Several studies showed that no toxic effects were observed at the Environment Canada 0.1-0.2 ug/l total mercury objective level, but if 10-20% of the total mercury is in a methylated form, then bioaccumulation could potentially occur. However, methylmercuric chloride concentrations of less than 0.01 ug/l Hg do not appear to cause great increases in fish mercury concentrations over background levels.

It is concluded that in arid regions where metallurgical operations can be operated on a zero discharge basis, mercury is of less concern environmentally than worker exposure to mercury vapor derived from processing solutions containing levels of mercury that have become elevated due to water recycling.

In areas where effluents must be discharged, the Canadian MPC and objective for 24-hour average levels of mercury are reasonable, whereas the U.S. EPA objective is both unenforceable for lack of suitable analytical equipment and unrealistic, being not supported by environmental evidence.

Even if methods could be devised to detect mercury at the EPA objective levels, there are no known processes that can reliably remove mercury from water to the levels cited.

The U.S. EPA marine criteria for MPC and 24-hour average concentration (3.7 and 0.025 ug/l) are based on the results of toxicity tests rather than bioaccumulation potential. Industry observers find these limits scientifically defensible as opposed to the freshwater criteria.

Generally, the 24-hour average objective of 0.025 ug/l is close to typical background levels which suggests that little if any addition to the environment over a long period of time would be permitted although, of course, the oceans have such a large volume that they can tolerate significant additions before the average background level would be impacted.

The U.S. Marine MPC of 3.7 ug/l is in line with toxicity test results and should not be exceeded.

Ultimately, objectives may have to distinguish between methylated and inorganic mercury levels in effluents.

TREATMENT FOR MERCURY REMOVAL

1) Selective Leaching: Gold and Silver Cyanidation

The Bureau of Mines of the U.S. Dept. of the Interior has conducted research into the question of mercury in gold and silver cyanidation solutions and pulps. STAKER, et al. (1983) investigated selective extraction of Au and Ag from a

low-grade Au ore containing Hg. Gold and silver were extracted from the ore in cyanide slurries, and mercury extraction was suppressed with sodium or calcium sulfide. Maximum Au extraction and minimum Hg extraction were obtained using solutions containing 0.34 lb. NaCN/ton solution. Increasing the cyanide concentration increased the mercury extraction without increasing gold extraction. Mercury extraction from the ore was suppressed with 0.5-2.9 lb. CaS/lb. Hg in the ore. Gold to mercury ratios of 100:1 to 400:1 were obtained in the leach solution and on the activated carbon in a CIP circuit.

The above is potentially very significant, especially in low-grade ores in the western U.S.A. which may contain, for example, 2-3 g Au/t with 5-15 g Hg/t. During cyanidation, 10-30 percent of the mercury is extracted along with Au and Ag, and once in solution, mercury follows gold or silver through the process requiring extra precautions in the plant.

Mercury vapor may cause health hazards in the electrowinning, retorting, and carbon reactivation as well as carbon elution steps.

The USBM process to inhibit mercury dissolution is potentially useful in that mercury then stays in the tailing solids. However, careful scrutiny of the effect of CaS addition on cyanide consumption, gold and silver leach rates and efficiency, and adsorption characteristics on activated carbon would be necessary before employing this process.

Further information on progress in this direction and reference to commercial plants that employ this process would be available from:

W. L. STAKER
Salt Lake City Research Center
Bureau of Mines
U.S. Dept. of the Interior
Salt Lake City, UT 84108
(801) 524-6100

For applications where effluents must be discharged for water balance considerations, the question remains whether inhibition of mercury leaching would be adequate to keep mercury in effluents down to levels that would meet the regulatory requirements.

MERCURY REMOVAL FROM GOLD MILL SOLUTION/EFFLUENTS

In the course of this investigation, not one case was encountered where mercury is deliberately removed from a process solution stream or an effluent prior to discharge.

However, mercury is involuntarily recovered as a byproduct by the same extraction process as is used for gold and silver recovery. Examples of such operations are:

Zinc Precipitation - Retorting
Rosario Dominicana, Pueblo Viejo, Dominican Republic
Carlin Gold Mines, Carlin Nevada

Carbon-in-Pulp - Elution - Zinc Precipitation Retorting
Freeport Gold Company, Elko, Nevada

Carbon in Pulp - Elution - Electrowinning - Retorting of Steel Wool
Pinson Gold Mining Co., Winnemucca, Nevada
Getty Mercur Gold Co., Toelle, Utah

It is believed that Harrison B. Salisbury of the Dawson Metallurgical Laboratories has conducted research into ways to remove metals such as mercury and thallium from gold leach solutions.

DAWSON METALLURGICAL LABORATORIES
5217 Major Street
Murray, UT 84107
(801) 262-0922
Harrison B. Salisbury

Several other methods have been employed or are under development to remove mercury from industrial effluents, mostly on a smaller scale:

Precipitation
Ion Exchange
Chelating Compounds
The Devoe-Holbein Process
Coagulation
Reduction to Metallic Mercury and Filtration

PRECIPITATION

In industrial applications, sulfide addition to precipitate mercury sulfide is commonly used. This may be combined with flocculation and separation by gravity settling, filtration, or dissolved air flotation and is also the basis for keeping mercury out of cyanide solution in the leaching of gold and silver from mercury-rich ores. Sulfide precipitation was discussed by BOUVENG (Undated).

PATTERSON (1975) points out that for high initial mercury levels, sulfide precipitation will achieve 99.9% removal at alkaline pH but even with filtration or activated carbon polishing, minimum effluent mercury achievable by sulfide precipitation appears to be 10-20 ug/l. Most effective precipitation appears to be in the near neutral pH range as far as minimizing sulfide dosages according to PERRY (1974).

In addition to the lack of capability to reduce mercury below 10 ug/l, other drawbacks of this method include: 1) formation of soluble mercury sulfide complexes at high levels of excess sulfide; 2) the difficulty of monitoring excess sulfide levels; and 3) the problem of toxic sulfide residual in the treated effluent according to PERRY (1974).

Although the last two of these obstacles have now largely been overcome, the inability to reduce mercury levels to below 10-20 ug/l does not meet the EPA or Canadian ambient water criteria for protection of the environment.

SULFEX PROCESS

Mercury sulfide solubility in pure water is reported to be 1×10^{-21} by YELIGAR, et al. (1981) making it one of the least soluble sulfides. The Sulfex process, described by YELIGAR, et al. (1981) and SCOTT (Undated), employs an iron sulfide sludge bed in a sludge blanket-type clarifier to precipitate mercury and other metals. In this way, sulfide levels are maintained at a constant concentration regardless of the rate of sulfide demand.

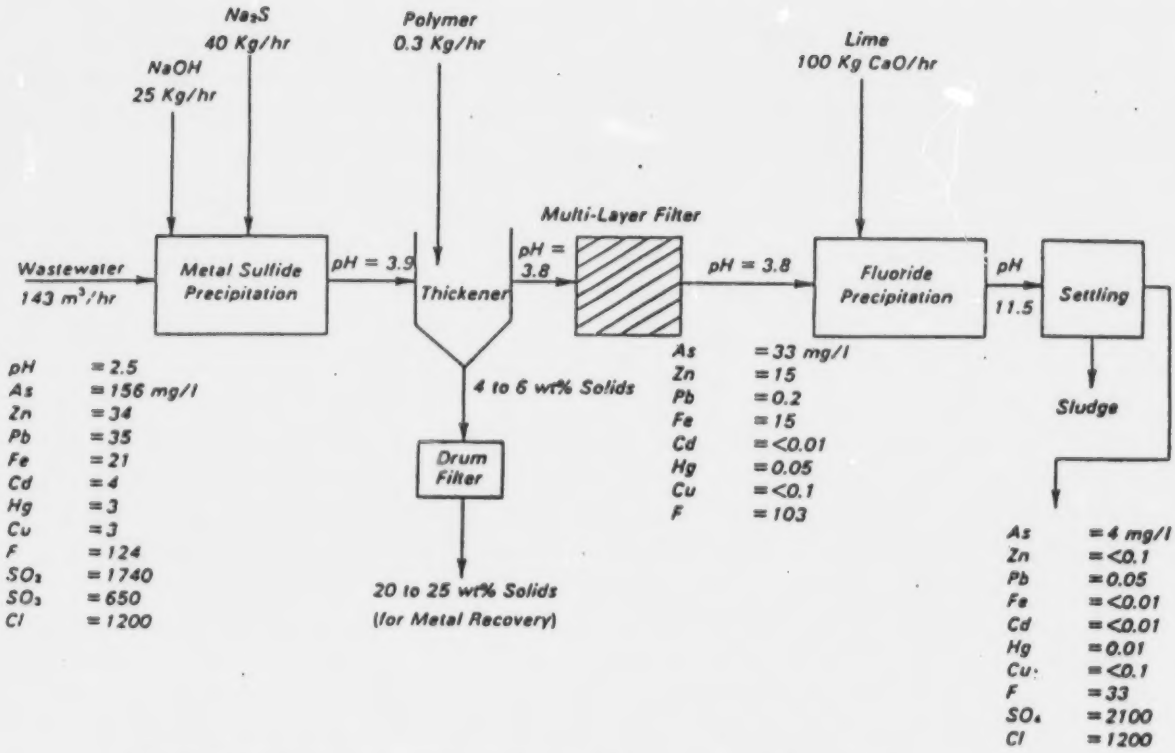
The Sulfex process is patented and, together with the sludge blanket reactor clarifier, is offered by:

THE PERMUTIT CO., INC.
Post Office Box 355
E49 Midland Avenue
Paramus, NJ 07652
(201) 967-6000

To date, the Sulfex process has been employed primarily to treat metal finishing and plating effluents, and no operations are known where it is used to treat metallurgical plant effluents although in principle there are no reasons for it not to work.

BOLIDEN METALL, SKELLEFTHAM PLANT, SWEDEN

Sulfide precipitation is employed by BOLIDEN METALL at their Skellefteham plant in Sweden to remove arsenic at low pH 3.9 followed by filtration to remove the precipitate and lime addition to the filtrate to precipitate fluoride as CaF_2 followed by settling and decantation. This process is described by BLYTHE, et al. (1981) from which the following schematic diagram is taken showing that mercury in feed solution is dropped by sulfide precipitation from 3 ppm to 50 ppb and further to 10 ppb by lime addition and settling.



Typical residual metal concentrations obtained by full-scale test run (Boliden Metall).

SOURCE: BLYTHE, et al. (1981)

More information on this process, as well as the pitfalls to be guarded against when a complex solution is to be treated, is contained in the project summary by BLYTHE, et al. (1981). Additional insight may be possible from:

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According to BHATTACHARYYA (1985, personal communication), one of the problems is excessive cost at low pH when $SO_3^{=}$ is present because it consumes expensive sulfide reagent. A second problem is the efficient removal of finely divided sulfide precipitates. It is noted that at the low pH, mercury is removed only to 50 ppb and with subsequent

lime addition, to 10 ppb which more or less confirms the performance noted above for sulfide precipitation.

ION EXCHANGE

Most ion exchange treatments of inorganic mercury involve formation of a negatively charged mercuric chloride complex by adding chlorine to oxidize metallic mercury or chloride salts and removal of the mercuric chloride complex on an anion exchange resin. Most experience, according to PATTERSON (1975), has been with chloralkali plant wastes which contain high background chloride levels. There is some evidence, (PERRY, 1974, and GARDINER and MUNOZ, 1971), to indicate that the best ion exchange results are achieved in two stages with a roughing and a polishing step. Table 56 below from PATTERSON (1975) shows that anion exchange reduced mercury to 1 ppb in some cases.

Ion Exchange Treatment for Mercury.

Resin Type	Mercury Form	Treatment pH	Mercury (μg/l) Initial	Mercury (μg/l) Final	Additional Treatment	Reference
Mtylon-T	Inorganic	5–6	5,000–25,000	1	—	22
Lewatit	Inorganic	na	na	15	—	23
Anion[a]	Inorganic	7	850	2.5	—	24
Macroreticular	Inorganic	na	10,000	<10	—	25
Anion[a]	Inorganic	na	470	30	—	26
Osaka IE[a]	Inorganic	"acidic"	3,000–10,000	100–150	Prefilter	21
Osaka MR[a]	Inorganic	na	100–150	2–5	Osaka IE Resin	21
Imac-TMR	Inorganic	3	na	5	Carbon Prefilter	27
Anion[a]	Inorganic	5–7	na	100	—	18
Activex	Inorganic	na	10	<5	—	28
Ajinomoto	Inorganic	1.5	60	5	—	20
		6.0	87	3	—	
		11.0	1,800	990	—	
Billingsfors-	Inorganic	6.5	35	1	—	20
Langed Q13		na	na	10–20	absorption filter	19

[a] Mercury removed as mercuric chloride complex, $HgCl_4^{(x-2)}$

22 FEDONINA (1972)
23 OEHME (1971)
24 YOKOTA (1972)
25 EGAWA (1971)
26 OEHME, et al. (1972)
21 GARDINER and MUNOZ (1971)
27 ROSENZWEIG (1975)
18 CHEREMISINOFF and HABIB (1972)
28 LOGSDON, et al. (1974)
20 PERRY (1974)
19 U.S. EPA (1971)

Where chloride levels are low, cation exchange resins are effective. Although information on the cation exchange behavoir of mercury is scarce, Amberlite IRA-120 and Dowex-50W-X8 are both reported by ROESMER (1970) to be effective. Since then, of course, resin manufacturers have undoubtably developed improved resins for mercury removal, and it is recommended that sponsors get in touch with their local ion exchange salesmen for more information.

Resins that contain mercapto groups R-S-H such as polythiostyrene are highly specific for mercuric ions according to ROESMER (1970).

PATTERSON points out that regardless of whether anionic resins are used for mercuric chloride complex removal or cationic resins for mercuric ion removal, the best ion exchange treatment for inorganic mercury appears to yield an effluent with 1-5 ug/l. Most effective treatment results from two-stage treatment at neutral to slightly acidic pH.

Most available data relates to the treatment of inorganic mercury, and there is relatively little information on organic mercurials. However, efficient treatment of methyl mercury acetate has been reported with Dowex A-1 Chelate by MUZZARELLI and ISOLATI (1971) and Ionac SRXL resins by LAW (1971) whose paper is inserted below along with one by FREELAND, et al. (1974) who showed how polyethylamine-modified wool fibers can adsorb mercury as Hg^{2+} from solution. The process is said to be effective on 1 ppm Hg solutions, and effluents with only 0.02 ppm were achieved. Additional information on further progress in this field may be available from:

CSIRO
Division of Textile Industry
Post Office Box 21
Belmont, Victoria 3216
Australia

PATTERSON (1975) refers to the Osaka ion exchange process for mercury removal from acid solution which is available under license using an Osaka resin which achieves, according to GARDINER and MUNOZ (1971), levels as low as 5 ppb Hg. This reference may also include the address of the Osaka Company that markets this process and the resin.

A Swedish company (AKTIEBOLAG BILLINGSFORS-LANGED) has developed an ion exchange system which is similar in concept to the Osaka process. A strong base first stage exchanger is regenerable while the second stage polisher is not. Removal is as the mercuric chloride complex anion, thus requiring pretreatment of mercurous and organic mercury. More information is reported by CHEREMISINOFF and HABIB (1972) and ROSENZWEIG (1971).

WILMOTH, et al. (1979) tested lime neutralization, reverse osmosis, and ion exchange for their effectiveness in removing mg/l levels of ten trace elements from acid mine drainage under typical operating conditions. The contaminants were As, B, Cd, Cr, Cu, Hg, Ni, P, Se, and Zn. Treatment by lime neutralization was very effective in removing As, Cd, Ni, and Zn and ineffective for B removal. Dual-bed (strong acid-weak base) ion exchange was very effective in removing all the trace elements except P and B but including mercury.

Methyl Mercury and Inorganic Mercury Collection by a Selective Chelating Resin

Abstract. *A commercially available chelating resin selectively and quantitatively collects methyl mercuric and inorganic mercuric forms of mercury to the exclusion of all other metals studied, except the noble metals. Both forms of mercury can be collected from pH 1 to 9. Collected mercury is readily eluted with a slightly acid, 5 percent solution of thiourea, and the resin can be reused for many cycles. Selectivity, pH effects, capacity, and elution characteristics of the resin are described. A resin-loaded paper composed of 50 percent resin and 50 percent cellulose shows properties similar to those of the loose resin.*

The purpose of this report is to summarize available tests on a chelating resin, Ionac SRXL (*1*), which should provide new opportunities for analysis and for recovery of mercury from industrial and natural aqueous solutions. Previous studies have shown that the resin is highly selective for gold and platinum metals, but its usefulness for mercury had not been considered (*2–4*). My results indicate that the resin has a high affinity for dissolved mercury in both the methyl mercury and the inorganic forms.

Kuster and Schmuckler, original developers of the resin (*2*), explain the selectivity for noble metals by stating that it will ". . . bind only ions with the d^8 electronic configuration forming square planar complexes. . . ." They further explain that the resin has redox properties because of double bonds, enabling it to collect a species such as Pt^{4+} which is reduced to the Pt^{2+} and then bound as a square planar complex. The mechanism for Hg^{2+} and CH_3Hg^+ collection has yet to be determined.

The properties of SRXL resin were studied in two ways. Data were obtained with resin as received from the manufacturer and with resin-loaded paper, consisting of 50 percent SRXL resin (−325 mesh) and 50 percent cellulose (*4*). Comparisons were made between the resin behavior in a column and its behavior in the resin paper. All solutions were prepared with reagent-grade chemicals, and tracer studies were performed with the ^{203}Hg radioactive isotope and a NaI(Tl) detector.

Selective collection of noble metals, especially gold, from solutions containing high concentrations of more common metals has been reported (*2–4*). I have found also that the resin quantitatively collects dissolved mercury as methyl mercury or as inorganic mercury from solutions of high common metal concentration. A column of resin, 30 by 15 mm, quantitatively collected 100 μg of Hg^{2+} from 250 ml of chloride solutions of iron, nickel, copper, and zinc in amounts up to 10 g/liter. Radioactive ^{203}Hg was used to determine the completeness of collection (Table 1).

Selectivity tests for mercury in the CH_3HgCl, $HgCl_2$, and $Hg(NO_3)_2$ forms were conducted by filtering solutions containing a mercury salt mixed with various metals through paper disks (3.5 cm in diameter) containing SRXL resin; the solution was passed six times through each disk. The disks were rinsed with dilute HCl solution, dried, and analyzed by fluorescent x-ray spectrography. From solutions containing Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} or CH_3Hg^+, only the mercury was detected on the disks; the instrument conditions were sensitive to less than 5 μg for any one of the metals. Neutron activation analysis of SRXL paper disks which were used to collect gold from solutions containing nitrate or chloride salts of metals failed to show any common metal collection (*4*).

Comparisons with another resin, Chelex 100, reported to have a high affinity for Hg^{2+}, show that the Chelex 100 resin fails to collect the methyl mercury form although it does quantitatively collect Hg^{2+}. A paper specially prepared (H. Reeve Angel & Co.) with the Chelex 100 resin, was compared chromatographically with the SRXL

Table 1. Mercury ion (Hg^{2+}) collection from solutions of high metal concentration.

Conc. of Fe, Ni, Cu, and Zn mixture (g/liter)	^{203}Hg (count/min)*			Hg collected (%)
	Before	After	Background	
0.5	5202	217	224	~ 100
1.0	5318	214	213	~ 100
5.0	5498	225	209	~ 100
10.0	5510	225	209	~ 100

* Average of four or more 1-minute counts.

References and Notes

1. The SRXL resin, used to obtain the data for this report, is no longer commercially available from the Ionac Chemical Co., Birmingham, N.J. A resin reportedly identical is available from the Ayalon Water Conditioning Co., Ltd., P.O. Box 506, Haifa, Israel, under the trade designation of Srafion NMRR. Trade names and company names are used in this report for identification only and do not imply endorsement by the Bureau of Mines.
2. G. Kuster and G. Schmuckler, *Anal. Chim. Acta* 38, 179 (1967).
3. T. E. Green and S. L. Law, *U.S. Bur. Mines Rep. Invest. No. 7258* (1970).
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6. I thank T. E. Green and W. J. Campbell, College Park Metallurgy Research Center, College Park, Md., for suggestions and advice.

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paper. Metal mixtures including Hg^{2+} and CH_3Hg^+ were placed on both papers and developed under identical conditions. The SRXL paper showed complete separation of all metals examined (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}) from the Hg^{2+} and CH_3Hg^+ spot, which always had an R_f value of 0. The common metals showed no tendency to be retained by the paper. The Chelex 100 paper showed some affinity for most of the metals. Some spreading of the Hg^{2+} was also noticed. This comparison emphasizes the fact that the SRXL resin has the ability to discriminate between mercury and base metals instead of merely exhibiting varying degrees of affinity for the different ions as is more commonly observed in ion exchange.

The effect of *p*H on the collection of mercuric chloride, mercuric nitrate, and dissolved methyl mercury by the resin and the resin paper was examined over the *p*H range of 0.1 to 9. The results (Fig. 1) suggest the possibility of separating the forms of mercury in solution by *p*H adjustment. The trends and not the magnitudes are significant because different experimental procedures were necessary depending on whether the resin or the paper was used. Collection times were restricted to avoid quantitative collection as the purpose of this study was to observe differences in diffusion and absorption kinetics.

For the loose resin (Fig. 1A), a 200-ml solution, adjusted to the desired *p*H with dilute HCl and NaOH and containing ^{203}Hg radioactive tracer and 1000 μg of Hg^{2+}, or $CH_3{}^{203}Hg^+$ tracer and 990 μg of Hg as CH_3Hg^+, was shaken with 0.33 g of resin on a mechanical shaker for 2 hours. Portions (3 ml) were taken for the determination of radioactivity before resin addition and after shaking, in each case, to determine the amount of mercury collected by the resin. Although mercury is collected at *p*H > 7, use of the resin is probably best confined to *p*H < 7 as recommended by Koster and Schmuckler (*2*). The lowest collection of inorganic mercury is at *p*H 6. One liter of a *p*H 6 solution containing ^{203}Hg tracer and 100 ppm of Hg^{2+} as the chloride was prepared and passed through a small column (1 by 1.5 cm; 0.75 g) of the resin. The effluent from the column was periodically checked for ^{203}Hg activity. After about 600 ml of the solution had passed through the resin at an initial flow rate of 3 ml/min, a small amount (about 2 percent) of

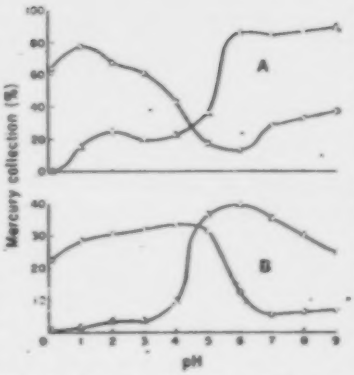

Fig. 1. Effect of *p*H on the collection of inorganic mercury (○) and dissolved methyl mercury (△), by SRXL resin (A) and SRXL resin-loaded paper (B).

mercury tracer began to come through the column. When the flow rate was reduced to approximately 1.5 ml/min, the mercury collection was again quantitative, and no further escape of mercury from the column was observed for the remainder of the 1000 ml of solution. These observations indicate that the total capacity of the resin is probably the same at *p*H 6 as at the lower *p*H values, but the rate of collection of Hg^{2+} is slower at *p*H 6. Therefore, a slower flow rate will be all that is required for quantitative recovery of inorganic mercury at this *p*H.

For the SRXL paper (Fig. 1B), small disks (1.3 cm in diameter) of the paper were suspended by thread for 24 hours in solutions of various *p*H, each solution containing 1000 μg of Hg as $HgCl_2$ or 930 μg of Hg as the methyl mercuric chloride. The disks were dried, and the mercury content was determined by fluorescent x-ray spectrography.

The sudden decrease in collection of the inorganic mercury at *p*H 6 is apparently the result of a reduction-precipitation reaction occurring on the surface of the suspended disks. The surface of the paper disk turns dark, and a white precipitate forms in the solution around the disk, suggesting the reduction of the Hg^{2+} to Hg^0 and Hg_2^{2+} followed by precipitation. An essentially identical curve of the effect of *p*H on behavior, with darkening of the disks and formation of a white precipitate, is also observed in the collection of $Hg(NO_3)_2$ from nitrate solutions containing no chlorides. Filtering solutions of *p*H 6 or greater through SRXL resin-loaded paper results in quantitative recovery of the inorganic mercury. No precipitate formation or darkening of the disks was noticed in the solutions containing the methyl mercury.

The capacity of the SRXL resin for Hg^{2+} was determined by shaking 1-g portions of the resin with chloride solutions at *p*H 1.5 containing 2 g of $HgCl_2$ and 10 μc of ^{203}Hg. Portions were taken at intervals for the determination of radioactivity until no further loss of tracer from solution was observed. The capacity of the resin under these conditions was 540 to 550 mg of Hg^{2+} per gram of dry resin. This compares well with the 488 mg per gram of dry resin found by Koster and Schmuckler for Pt^{4+} (*2*).

A 5 percent aqueous solution of thiourea containing 5 ml of hydrochloric acid per liter will elute gold and platinum metals from the resin, permitting its reuse for many cycles (*3*), therefore this eluent was investigated for the removal of mercury from the SRXL resin. A series of eight cycles of mercury collection and elution were performed with the same 2-g portion of resin. For each cycle, mercury was collected from 100 ml of solution containing ^{203}Hg tracer, and each cycle contained the same amount or more mercury than the one preceding. The 100-ml volumes contained from 100 μg to 1 g of Hg. Tracer activity of 3-ml portions of each effluent showed that the collection was 100 percent at all concentrations. Mercury was then eluted from the resin with 10-ml portions of the 5 percent thiourea solution. More than 90 percent of the mercury was removed with the first 10 ml of eluent in each case, and elution was essentially complete after passing 30 ml through the resin. A rate of approximately 3 ml/min was used for the elution and the collection. After elution of the mercury, the excess thiourea was washed from the resin with distilled water, and the next 100 ml of solution were passed through the resin, starting the next cycle.

Thus the ability to selectively and quantitatively collect the highly toxic methyl mercury as well as inorganic mercuric salts, and the ability to be reused for many cycles, make this resin a very promising tool for attacking both the analytical and the industrial problems of mercury pollution.

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Adsorption of Mercury from Aqueous Solutions by Polyethylenimine-Modified Wool Fibers

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■ When used in a packed column or a standing bath, polyethylenimine-modified wool (PEI-wool) had a substantially greater ability to adsorb mercury (Hg^2) from aqueous solution than unmodified keratin. A capacity of 3.3 meq/g was achieved within 30 min using solutions of 1000 ppm (Hg^2). Sorption from liquours passing through a column was rapid and effective at the 1-ppm level. The sorbed mercury was readily desorbed and the PEI-wool used repeatedly.

There have been several recent reports of the ability of protein fibers to adsorb mercury from aqueous solution (*1–4*), and the possibility of using them in effluent purification processes or for clinical purposes (*5*) has been discussed. Likewise, amine-modified cotton could adsorb mercury from solutions (*6, 7*). Here we report that the adsorptive capacity of wool for mercury (Hg^2) is substantially increased by polymerization of ethylenimine onto the fibers.

Experimental

PEI-Wool. Commercially scoured 64's quality Australian merino wool fibers (40 grams) were immersed (2 hr) in a 0.2% solution of ferrous ammonium sulfate (800 ml) and then squeezed before allowing to dry (48 hr) at 20°C. To the wool was added 0.25% hydrogen peroxide solution (600 ml) and ethylenimine (30 ml) (*8*). [Because of potential hazards from exposure to ethylenimine, it has been recommended (*9*) that protective gloves and goggles be used and that all operations be performed in a fume hood.] The fibers were heated (19 hr) at 50°C under nitrogen, rinsed under running tap water (2 hr), dried as before, and chopped to 1–3 mm lengths in a rotary mill. The uptake of ethylenimine (as bound PEI) was 10% w/w.

PEI-Reduced Wool. Unmodified wool (10 grams) was chemically reduced with 0.5M thioglycollic acid (300 ml) at 50°C for 3 hr, washed with distilled water, dried (100°C, 5 min), and converted to PEI-reduced wool as above. The uptake of ethylenimine (as bound PEI) was 20.2% (w/w).

Adsorption onto Columns of Chopped Wool Fibers. The wool (5 grams) was wet out in water containing 0.01% Antarox C0630 (a polyoxyethylated nonylphenol, GAF Corp.) and the resulting slurry poured into a glass column fitted with a porous plug and stopcock. When the fibers had settled they were equilibrated with solutions at the pH of the test solutions. The test solutions contained 1000 ppm Hg^2 (as $HgCl_2$ or a combination of $HgCl_2$–NaCl, Table I) and adjusted to various pH values with NaOH or HCl. Test solutions were admitted at the rate of one bed volume/min. The column effluent was collected in fractions and their mercury concentration measured.

Adsorption onto Wool in Standing Bath. The wool (5 grams) was stirred in a glass beaker with a solution (1 liter) adjusted to the required pH, containing 1000 ppm Hg^2 (as $HgCl_2$ or $HgCl_2$–NaCl, Table I) for prescribed periods.

Capacity of Wool Fiber Beds. Here the capacity of the beds has been expressed as milliequivalents of mercury per gram of wool (meq/g). For adsorption onto columns it was the amount of mercury adsorbed by the bed when its concentration in the column effluent reached 1% of the influent concentration. For adsorption onto wool in standing baths it was the amount adsorbed from the liquors after the prescribed period, and the value was calculated from the decrease in mercury concentration of the bath liquor. All adsorption measurements were made at 20°C.

Mercury Analysis. This was by atomic absorption spectrophotometry. Separate procedures used for solutions containing 1–1000 ppm (*10*) and up to 1 ppm Hg^2 (*11*) were essentially as described.

Results and Discussion

PEI-Wool. Protein fibers will bind approximately 1% of polyethylenimine irreversibly (*12*). This quantity will increase slightly if the fibers are pretreated with chlorine. By polymerization of ethylenimine monomer onto wool fibers, as reported here, irreversible binding of 10–20% PEI can be achieved. It is not known whether the PEI-wool composite so formed contains the PEI as a physically occluded or chemically grafted component. In the present work, wool treated by the last method has been used as packed beds in columns and in stirred standing baths to examine its potential in both continuous and batchwise mercury recovery processes.

Table I shows that maximum adsorption occurred in standing baths where, within 30 min, equilibrium was established. The capacity of 3.3 meq/g is of the same order as that of many granular ion exchangers. Even in solutions containing 10% NaCl, the adsorption of 1 meq Hg^2/g was still significant and may indicate that PEI-wool could

Table I. Mercury Adsorption by Polyethylenimine-Modified Wool

Liquor pH	Experimental method[a]	NaCl concn., %	Capacity, meq Hg^2/g wool
	PEI-Wool		
6	S_{30}		3.3
6	S_{60}		3.3
6	S_{15}	10	1.0
6	S_{30}	10	1.1
6	S_{15}	25	0.6
6	S_{30}	25	0.6
2	C		1.4
7	C		2.4
6	C	25	0.2
	PEI-Reduced Wool		
6	S_{10}		3.6
6	S_{30}		3.6
6	S_{10}	3	2.0
6	S_{10}	10	1.1
6	S_{10}	25	0.9
7	C		2.8
6	C	3	1.6
	Unmodified Wool[b]		
6	S_{30}	25	0
2	C		0.58
7	C		0.29

[a] S with a numerical subscript refers to adsorption in a standing bath for the indicated period (min); C refers to a column adsorption. [b] From (*1*).

have practical advantages in adsorbing mercury from electrolyte solutions (*13*).

In column adsorption tests, where the contact time was 1 min, the capacity was lowered slightly to 2.4 meq Hg^2/g at pH 7, indicating that adsorption was a rapid process. Sorbed mercury was quantitatively recovered by extracting the PEI-wool with *N* HCl (50°C, 15 min) or with citric acid solution (1%, pH2, 40°C, 15 min). The wool that was stripped in this way could be reused, an adsorption capacity of 2 meq/g persisting after 15 cycles.

Adsorption onto columns was effective when low concentrations of mercury were used. When 500-bed volumes of liquor containing 1 ppm Hg^2 (pH 6) were passed through the column (1 bed vol/min), the concentration in the effluent did not exceed 0.02 ppm. Greater efficiency could be expected from longer contact times in the column.

When we consider the pH range 2–7, we note that modification of wool with PEI changes the pH of maximum adsorption from 2 to 7; corresponding differences in the adsorption mechanisms might be inferred. Probably, at pH 2, the association of protonated amino groups with anionic mercuric complexes such as $HgCl_3^-$ or $HgCl_4^{2-}$ occurs (*1*). At pH 7, the adsorption probably involves chelation of Hg^2 with ligands located in both the PEI (*14*) and the wool.

PEI-wool appears to have a mercury adsorbing capacity exceeding cross-linked PEI-cotton (*6*) by a factor of 100. Although strict comparisons have not been made its rate of adsorbing mercury seems substantially greater than that reported for the modified cotton (*7*).

PEI-Reduced Wool. Ethylenimine was polymerized onto thioglycollate-reduced wool in the expectation that the chemically modified fibers, released from the restraint of protein disulfide bonds, would swell more readily in aqueous media. An increased PEI add-on and correspondingly improved mercury adsorption might then have resulted.

Practically, the amount of PEI formed in reduced wool was double that formed in native wool. Only minor increases were observed in the mercury-adsorbing capacity of PEI-reduced wool, consequently no advantage can be seen in using wool in the reduced form.

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Removal of Mercury from Aqueous Solutions by *N*-(2-Aminoethyl)aminodeoxycellulose Cotton

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■ *N*-(2-Aminoethyl)aminodeoxycellulose cotton (AEAC) was prepared in yarn form by reaction of ethylenediamine with chlorodeoxycellulose. The adsorption of mercuric ion by AEAC (degree of substitution 0.4) was studied over a wide range of concentrations. In the concentration range 0.5–43 g/l., the adsorption of mercuric chloride follows the Freundlich relationship, $\log_{10} x = 0.21 \log_{10} C + 2.7$, where x is the mg of mercuric chloride bound per gram of AEAC and C is the residual concentration in g/l. At concentrations in the range of 3.1–0.6 ppm, 100 mg of AEAC removed about 90% of the mercury present in 200 ml of solution, in a single equilibration. The results of this study suggest the possible use of AEAC as an agent for the collection of mercury in industrial processes.

The possibility of employing ion exchange or chelating resins as a means of removing heavy metal ions from solution has been explored by a number of workers (*1–5*). However, cost considerations have prohibited the widespread application of this technique on an industrial scale. A possible solution to the cost problem might be to use naturally occurring polymers or agricultural by-products as the basis for the exchange resin. In this regard, Friedman and coworkers (*6, 7*) have shown that mercuric ion is bound in large amounts by certain agricultural byproducts and polyamine derivatives.

This investigation concerns the use of cotton cellulose as the insoluble support matrix; however, the same techniques could be readily applied to other celluloses or synthetic polyalcohols. In the study reported here, we have attached an ethylenediamine group to the anhydroglucose unit of the cellulose backbone via chlorodeoxycellulose (CDC) cotton yarn to give *N*-(2-aminoethyl)aminocellulose cotton (AEAC). AEAC very efficiently adsorbs mercury over a broad range of concentrations. Suprisingly, we observed that at very low concentrations (approximately 100 ppb), untreated cotton yarn also removes significant amounts of mercury. This adsorption may be due to carboxyl end groups and trace materials present in native cotton.

Experimental

Materials. Cotton was loose twist 12/3 (tex-151) Pima kier-boiled yarn unless otherwise specified. The phosphorus oxychloride ($POCl_3$), dimethylformamide (DMF), and

CHELATING COMPOUNDS - INSOLUBLE STARCH XANTHATE

Recently a company in Texas, POLLUTION TECHNOLOGY SYSTEMS, INC., has offered a process and a chelating organic product which removes metals including mercury from solution.

The product, DX-2000, is a buffered forty percent active organic material that effectively precipitates complexed or chelated cationic heavy metals from difficult to treat process waters. The vendors claim that the product is effective over a pH range of 3 to 11. Residual heavy metals are claimed to usually be well below local, state, and EPA-NPDES discharge limit permit requirements.

DX-2000 is claimed to be effective in removing metals also in the presence of complexing agents which would normally interfere with most other removal processes. The metal-DX-2000 sludge cake containing 40% solids is claimed to be more stable than metal hydroxide sludges.

Dosages of DX-2000 for metal removal vary from metal to metal as the loading ability of a liter of DX-2000 varies from metal to metal. For example, Mn^{+2} loads 77 g per liter of DX-2000 whereas gold loads to 550 g Au^{+1}, and silver loads to 300 g Ag^{+1} per liter of DX-2000. Mercury loads to 280 g Hg^{+2} per liter of DX-2000.

The manufacturer-vendor does not make claims regarding the level of mercury that can be achieved using DX-2000. In a pamphlet by the same vendor describing the use of insoluble starch xanthate, it is claimed that mercury levels were reduced to 0.7 and 1.0 ppb in two test solutions.

It is not known what the nature of the DX-2000 product is although the same vendor is known also to manufacture insoluble starch xanthate based on technology developed by the U.S. Dept. of Agriculture.

NORTHERN REGIONAL RESEARCH LABORATORY
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U.S. Dept. of Agriculture
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(309) 685-4011
Robert E. Wing

The insoluble starch xanthate is claimed to have removed mercury from 100 ppm to 1 ppb in one case and from a second solution containing 10 ppm to 0.7 ppb Hg.

The development of insoluble starch xanthate for heavy metal removal (including mercury) has been described by SWANSON, et al. (1973), WING, et al. (1974), GREENBERG and WING (1983), and WING (1983).

The vendor does not release much detail about how its process works as they wish to sell consulting and engineering services as well as product. More information can be obtained from:

POLLUTION TECHNOLOGY SYSTEMS, INC.
3015 Benton Street
Garland, TX 75042
(214) 272-4010
Mike Coward
Manager, Systems Engineering

IKEBE (1974) of SUMITOMO CHEMICAL CO. LTD., Japan, described a process whereby heavy metal ions, especially Cu^{2+} and Hg^{2+}, are sequestered with a dialkyldithiocarbamic acid and are treated with NaOH and Na_2S to produce a scum of CuS and PbS separating the sulfide scum by either precipitation or flotation and regenerating the dialkyldithiocarbamate ion which is then recycled "quantitatively." The use of NaOH in this process improves the efficiency of separation by preventing the formation of colloidal CuS. Thus, $Cu[S(S)CNEt_2]_2$ was suspended in one litre water, and two equivalents of NaOH was added and stirred. One mole Na_2S/l was added, and the CuS formed was removed by precipitation.

When one equiv. of Na_2S was added, approximately 100% of the $NaS(S)CNEt_2$ was recovered. The light yellow liquor recovered had a pH of 12.8 and contained only 1-2 ppm Cu. When NaOH was not used, the recovered $NaS(S)CNEt_2$ contained about 35% of the colloidal CuS in suspension.

DEVOE-HOLBEIN

Devoe-Holbein has also developed a metal removing process which relies on a "composition" or solid adsorbent to precipitate and remove metals. Examples are cited in their literature in which mercury was removed from 12.0 ppm to 4.8 ppb in one case and from 120 ppm Hg to 1.2 ppb in another. A schematic flowsheet for a process employing Devoe-Holvein compositions has been developed and an association formed with an engineering company to develop a practical process.

More information can be requested from:

DEVOE-HOLBEIN (CANADA), INC.
175 Bouchard Avenue
Dorval, Quebec H9S 1A9
(514) 636-6042
Telex: 05-821538
Bruce Holbein

Devoe-Holbein has not released data on the costs of the process or their "compositions." It was stated that in experimental quantities, the composition would be expensive. Prices

would be much, much lower if the product were in such demand as to justify mass production.

COAGULATION TREATMENT

Removal of mercury by coagulation has been reported for a variety of mercury-containing wastewaters. Coagulants employed include aluminum sulfate (alum), iron salts, and lime. The process has been applied successfully to both organic and inorganic mercury. In pilot plant tests of alum and iron treatment of inorganic and methyl mercury, inorganic mercury was removed effectively only by iron while neither coagulant provided effective methyl mercury removal according to O'CONNOR (1974).

Treatment data for alum and iron coagulation are summarized in the following table . Effluent levels of mercury achieved by alum treatment range from 1.5-102 mg/l and by iron treatment from 0.5-12.8 mg/l. Iron appears to be better than alum for the purpose achieving a lower effluent limit.

Alum and Iron Coagulation Treatment for Mercury.

Coagulant Salt	Dosage (mg/l)	Treatment pH	Mercury (μg/l) Initial	Mercury (μg/l) Final	Additional Treatment	Ref.
Alum	1000	3	11,300	102	Filtration	37
Alum	100	na	90	11	—	38
Alum	100	na	na[a]	10	—	38
Alum	21–41	6.7–7.2	5.9–8.0	5.3–7.4	Filtration	28
Alum	na	7.0	50	26.5	Filtration	35
Alum	20–30	na	3–8	1.5–6.4	—	36
Alum	20–30	na	3–16[a]	2.3–21.3	—	36
Iron	34–72	6.9–7.4	4.0–5.0	1.5–2.5	Filtration	28
Iron	na	8.0	50	3.5	Filtration	35
Iron	20–30	na	1–17	0.5–6.8	—	36
Iron	20–30	na	2–17[a]	1.2–12.8	—	36

[a] Organic mercury.

37 HONDA, et al. (1973)
38 HELLESTAN, et al. (1972)
28 LOGSDON, et al. (1974)
35 O'CONNOR (1974)
36 LOGSDON and SYMONS (1973)

ACTIVATED CARBON

The effectiveness of carbon treatment is dependent on several factors according to PATTERSON (1975). These include the chemical form of mercury in solution, concentration of mercury, dosage and type of activated carbon, as well as contact period. Increasing carbon dosage and contact times improves removal of both inorganic and organic mercury as would be expected and as described by LOGSDON and SYMONS (1973). Organic mercury is more effectively removed than inorganic mercury, and a

review of available treatment data by PATTERSON (1975) and shown below in tabular form indicates that the highest percentage removals (85-90%) result from carbon treatment of more concentrated mercury solutions. However, the lowest effluent mercury results from the treatment of lower initial mercury concentrations although the relative efficiency is less. Thus, carbon treatment of initial mercury levels of below 1 mg/l yields an efficiency of removal of less than 70%, but an effluent mercury of less than 0.25 mg/l. Carbon treatment of initial mercury of 10-100 mg/l yields 90 or more percent efficiency but effluent levels of 1-10 mg/l.

Activated Carbon Treatment for Mercury.

Mercury (μg/l)		Additional	
Initial	Final	Treatment	Reference
na	<100	Presettling	39
12–46	<0.5	—	
5.8	0.9	Iron Coagulation	35
9.3	1.6	Alum Coagulation	28
na	0.8	—	36
na	0.2	—	36
100	10–20	Precipitation	19
60–57	4.5–6.0	—	20
0.40–0.81	0.13–0.19	Polymer Added	40
0.5	0.21	Polymer Added	40

Source: PATTERSON (1975)

39 SUZUKI, et al. (1973)
35 O'CONNOR (1974)
28 LOGSDON, et al. (1974)
36 LOGSDON and SYMONS (1973)
19 U.S. EPA Report 805-25 (1971)
20 PERRY (1974)
40 SAN SCI DIV. (1974)

REDUCTION PROCESSES

Inorganic ionic mercury can be converted to the metallic form by reduction and separation by filtration or other solids separation methods. Several reducing agents are available including aluminum, zinc, hydrazine, stannous chloride, and sodium borohydride. PATTERSON (1975) references the use of reductive processes to treat solutions with initial mercury concentrations of 1.8-26 ppm Hg which resulted in final mercury levels in the effluents of 5-830 ug Hg/l.

In gold and silver recovery processes using the Merrill-Crowe process (zinc precipitation), mercury will be reduced as well as gold and silver and ends up in the zinc precipitate. If there is enough mercury present, this necessitates an additional step to retort the zinc precipitated metals to remove the mercury before the gold and silver can be smelted to a dore.

The data provided by PATTERSON indicates that in order to achieve mercury levels below 100 g/l, the use of reductants would have to be supplemented by a second polishing step by one of the other treatment steps discussed in this chapter. For example, where gold plant effluents are treated by ferrous sulfide addition and settling to remove cyanide, chances are excellent that mercury will also be precipitated as a sulfide. If carbon columns are used to recover incremental gold from effluents or recirculating solutions, the likelihood of further mercury removal is also excellent by carbon adsorption. If, in future, anionic ion exchange resins are used to recover gold as a cyanide complex, then possibly a pretreatment with chlorine to destroy cyanide will render the mercury in the chloride complex form suitable for loading onto the resin as well, or mercury may load as the anionic mercury cyanide complex.

Performance of Reduction Processes for Mercury Treatment.

Reductant Used	Mercury (μg/l) Initial	Mercury (μg/l) Final	Additional Treatment	Reference
Zinc	5,000–10,000	5–10	—	41
Zinc	1,800	140	(pH 11.5)	20
	12,500	830	(pH 10.0)	
	12,500	750	(pH 6.0)	
	[illegible]	470	(pH 2.5)	
Zinc	na	600	—	19
Stannous Chloride	2,800	500	—	20
Sodium Borohydride	10,000	220	—	20
	4,000	420		
	26,000	820		
Sodium Borohydride	4,700	200		42
Sodium Borohydride	na	<10	(pH 9-11)	18

Source: PATTERSON (1975)

41 WALTRICH (1973)
20 PERRY (1974)
19 U.S. EPA (1971)
42 COULTER (1973)
18 CHEREMISINOFF and HABIB (1972)

A full-scale commercial process based on the reduction of mercury by sodium borohydride is marketed as the Ventron process and is described by CHEREMISINOFF and HABIB (1972) and ROSENZWEIG (1971).

ADSORPTION PROCESSES

RANDALL (1974) tested the adsorptive properties of a wide range of agricultural wastes for the removal of toxic metal cations from synthetic solutions as well as mining and industrial effluent streams with a view to recovering metal values. Several of these wastes were reported to remove metals effectively to "below the levels prescribed by local or federal standards." Rate, selectivity, and capacity of the agricultural substrates for heavy metal cations were measured in the laboratory, and the authors claim very effective

removal of Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}. As with several of the processes mentioned above, this approach was not observed in commercial application although it may be worth further evaluation.

OTHER TECHNOLOGY

PATTERSON (1975) refers to a variety of other processes that are mentioned in the literature. These include solvent extraction with high molecular weight amines, the use of silicon alloys for reduction to elemental mercury (McKAVENEY, 1972), removal by insoluble starch xanthate-cationic polymer complexation (SWANSON, 1973; WINZ, et al. 1974), adsorption onto ground rubber and onto wool at sulfhydryl sites (FREELAND, et al., 1974).

Several of these processes appear promising yet in the course of this investigation, none were found in commercial application ten years after they were announced. It is emphasized that such experimental processes require considerable further development and pilot-scale testing before they could be considered suitable for commercial-scale application.

CONCLUSIONS

There are many treatment technologies available for mercury control. The more effective are summarized in the following table which was assembled by PATTERSON (1975). Among the processes listed, ion exchange, iron or alum coagulation, and activated carbon adsorption have the capability to reduce mercury below 10 ug/l, but the effects of cyanide on performance needs to be determined. The trip report on COTTER CORP.'s Schwarzwalder Mine in Appendix I describes an innovative new ion exchange process that reduces uranium and base metals to extremely low levels. Possibly this system would make further improvement possible in the performance of IX for mercury removal.

Conventional precipitation systems employing sulfide and flocculating aids seem capable of achieving mercury levels of 10-20 ug/l. However, RANDOL INTERNATIONAL suggests that combining the HDS process with ferrous sulfide or Na_2S addition may make it possbile to improve this when treating acid solutions.

Other methods, particularly the reduction process for small-scale use, are capable of producing very low-effluent concentrations of mercury. Many of these methods have not been tested in full-scale operation.

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By Richard T. McNerney

Analysis of mercury using a gold film detector

ATOMIC ABSORPTION (AA) flameless spectrophotometry is currently the most commonly used method for the determination of mercury in liquid matrices. However, serious limitations of the technique, including inconsistencies in the liquid calibration standard, interferences, and poor reproducibility, have raised questions regarding the accuracy of the AA method. The thin gold film (gf) technique described in this paper overcomes these limitations and at the same time reduces the complexity of mercury analysis.

The detection of elemental mercury vapor by thin gf sensors is a technique developed and patented by the Jerome Instrument Corporation.[1] The adsorption of elemental mercury vapor on a gold film approximately 200 Å in thickness produces a pronounced resistance change in the film; this resistance change is linear in the range of 1–100 ng of mercury.[2]

Dedicated, portable instruments utilizing the thin gf sensor for the analysis of mercury in dry soils by direct combustion and in air by direct sampling have been in use for several years. Recently a thin gf mercury analyzer and sample delivery system, the Jerome Instrument model 511, has been designed for the analysis of mercury in liquid matrices.

Mercury vapor, released in an air stream from aqueous solutions using wet-chemical procedures described later, is drawn into the instrument by an internal pump. The elemental mercury passes over, and is adsorbed and integrated by, the thin gf sensor. This integrated electronic signal is converted by a microprocessor to the mass of mercury per unit volume of sample. Data presentation by direct digital readout is in nanograms of mercury. Saturation of the sensor occurs after 500 ng of mercury has been accumulated; full sensitivity is reestablished in 10 min by thermal desorption of the mercury from the sensor.

Mercury concentrations normally found in liquid matrices such as water, urine, and blood are in the low nanograms per milliliter range. But quantitative analysis depends on a system that is not only sensitive to mercury, but is also selective for the element. A serious limitation to the AA technique for mercury analysis is the presence of interfering substances such as H_2O, SO_2, O_3, and a variety of organic and inorganic compounds.[3–6] The complexity of the techniques developed for the preparation and analysis of liquid samples for mercury are a result of the efforts to overcome these interferences.

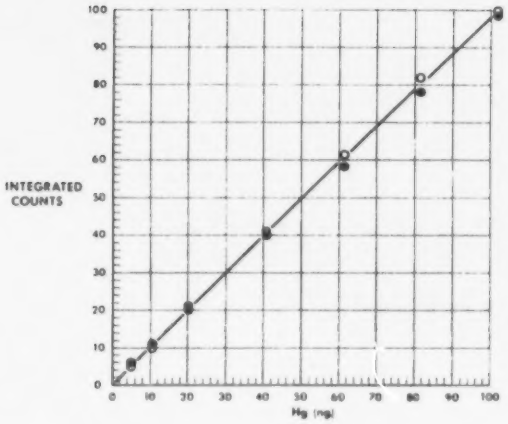
The thin gf sensor's specificity for mercury eliminates most interferences common to the AA technique,[7,8] and its design has resulted in significant improvements in signal reproducibility, calibration technique, and full-range linear response. The glassware system for sample preparation and delivery eliminates potential mercury loss from the sample. Microprocessor control reduces the complexity of the instrument's operation to a single manual control. With a minimum detection limit of 1.0 ng of mercury, the volume of sample necessary for analysis is usually less than 5 mL. Thus, the amount of reagent used in sample preparation is significantly reduced, minimizing the reagent blank. The system is field portable for on-site analysis where degradation of the sample due to transportation and long storage is a concern.[8]

Calibration

The thin gf technique determines the mass of mercury per unit volume of sample; thus, calibration can be performed using the most basic standard possible—the vapor pressure of mercury.[9] A small drop of liquid mercury in a closed container, e.g., a 300-mL polyethylene bottle, will saturate the enclosed air at a value which depends only on temperature. The effect of total pressure on the vapor pressure of mercury is negligible. The relationship of mercury concentration in ng/cm³ to temperature is shown in *Table 1*.

With the saturated mercury vapor maintained at a constant temperature, a known mass of elemental mercury is injected directly into the flow path of the thin gf sensor using a gas-tight syringe. The ana-

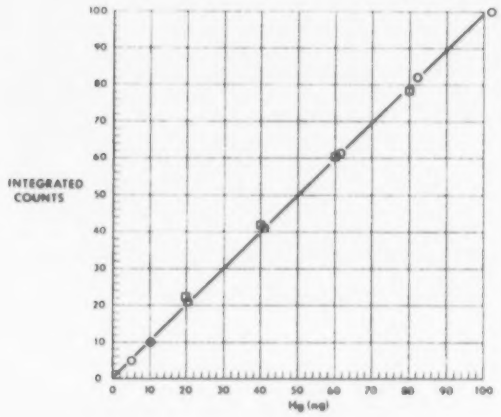
Mr. McNerney is Sales Manager, Jerome Instrument Corporation.



CALIBRATION RESPONSE

Hg	○ BEFORE	● AFTER
0	0	0
5.2	5	6
10.3	10	11
20.6	21	20
41.2	41	40
61.8	62	57
82.4	83	77
103.0	100	98

Figure 1 *Vapor standardization.*



□ AQUEOUS Hg	RESPONSE	○ VAPOR Hg	RESPONSE
0	0	0	0
20	23	5.3	5
40	41	10.3	10
60	61	20.6	21
80	78	41.2	41
		61.8	62
		82.4	83
		103.0	100

Figure 2 *Aqueous vs vapor standardization.*

lyzer responds linearly to a series of mercury vapor standards. After a 10-min film heat which thermally desorbs the accumulated mercury, sensitivity and full range linearity are restored. This is illustrated in *Figure 1*.

Figure 2 shows the excellent correlation that exists between the vapor phase and aqueous mercury standards. However, the correlation will suffer due to the instability of liquid standards and the errors that occur in the preparation of the stock and working liquid solutions.

An accurate vapor standard depends on maintenance of the calibration vessel at a constant temperature and withdrawal of a precise volume of the standard. Dilution is not necessary since the vapor standard is within the working range of the instrument. Oxidation of the mercury droplet, which could reduce the vapor pressure of mercury, is prevented by periodic light shaking of the calibration vessel.

However, liquid standards for mercury, both stock and working solutions, have shown varying degrees of instability. For example, a 1000-ppm ± 1% mercury reference solution (certified AA standard), with an expiration date sixteen months from the date of initial use, over a period of four months decreased in mercury concentration by more than 20%. Working solutions of 20 ppb prepared from a liquid standard according to well-documented procedures will, when shaken slightly, evolve elemental mercury in significant quantities in the head space

Table 1

Temperature conversion table

Temp., °C	Ng/cm³
16	9.4
16.5	9.8
17	10.2
17.5	10.6
18	11.1
18.5	11.6
19	12.1
19.5	12.6
20	13.2
20.5	13.7
21	14.3
21.5	14.9
22	15.5
22.5	16.2
23	16.9

above the solution. As a result, the linear correlation that is observed for the vapor versus aqueous standards immediately after preparation of the working solution can deteriorate significantly over several hours.

Mercury reference standards for mercury in solution are prepared by weighing out and dissolving crystals of $HgCl_2$ in distilled water that has been slightly acidified. The significant sources of error in this technique are the weighing of the $HgCl_2$, the purity of the $HgCl_2$, and the possible mercury contamination of the labware used. The solution is then subject to decomposition as noted previously.

Whether the reference standard is purchased in liquid form or prepared by dissolving $HgCl_2$ in distilled water, concentrated stock solution must be diluted from one million ng/mL to a working solution containing 20 to 100 ng/mL. Possible sources of error include the dilution process itself, and the possibility exists for mercury contamination or the loss of mercury to the glassware used in the dilution process.

Inteferences

Independent studies regarding the lack of response of the thin gf sensors to interferences common to AA have been published,[6,7] and some of the results are shown in *Table 2*. Murphy[6] considers the chemicals listed in Table 2 to be some typical examples of the troublesome types of samples that cause interference in the direct determination of mercury. The gold film system permits each of these samples to be analyzed directly and accurately without interferences from possible gaseous emissions that may be interpreted as mercury.

SO_2, ozone, organic and inorganic compounds, and fine particulates do not cause a response of the thin gf sensor; the gf sensor also does not respond to water vapor. As a result, drying agents such as magnesium perchlorate, which have been shown to be a negative interference with AA instruments, are not necessary with the gold film detector.[4]

Also noteworthy is that several wet chemical preparations include two or three additional reagents to eliminate potential AA interferences such as sulfides and chlorine. The lack of response by the gf method to these interferences can thus simplify the chemical preparation of a sample.

Reproducibility, precision, and accuracy

In AA analysis, reproducibility is dependent on the rate at which mercury is liberated from solution. Factors which affect this rate of release are pump rate, bubbler characteristics, sample matrix, sample volume, and relative strength of the reducing agent.[10,11]

In contrast, the integration of the mercury signal by the thin gf sensor makes the analyzer relatively independent of the factors which affect the rate of release.

The precision of the analyzer was demonstrated in an independent evaluation comparing the model 511 to a flameless AA spectrophotometer.[12] Forty-five urine samples were analyzed in triplicate with each instrument. The sample size analyzed by the gold film detector was 0.2 mL, as compared to a 2.0-mL sample required by the AA spectrophotometer. The results listed in *Table 3* gave a coefficient of correlation of 0.985 between the two instruments. The relative standard deviation of the results

Table 2

Interference study, cold vapor AA (CVAA) vs gf mercury detector (GFMD)*

	CVAA		GFMD	
Sample (in water)	Hg added, ng	Hg measured, ng	Hg added, ng	Hg, measured, ng
Acetone (20%)	100	>1000	100	95
Sodium sulfite (10%)	100	220	100	100
Sodium thiosulfate (10%)	100	750	100	102
Pyridine (5%)	100	>1000	100	91
Ammonium hydroxide (20%)	100	>1000	100	96

*Source: Murphy, P.J., "Determination of nanogram quantities of mercury in liquid matrices by a gold film mercury detector," *Anal. Chem. 51*, 1599 (Aug. 1979).

Table 3

Comparison of gf detector with AA method for Hg in urine*

Sample no.	Thin gf method 8-20	8-24	9-1	AA 8-20	8-24	9-1
2	272	275	273	296	275	267
41	35	28	30	12	19	24
30	99	100	101	128	97	101
13	22	17	17	14	15	20

*All results are reported in micrograms mercury per liter.

obtained with the gold film detector was 2.4%, as compared to 6.8% for the AA instrument.

As mentioned previously, the linear range of the gold film detector is 1 to 100 ng with gf saturation occurring at 500 ng. At levels above 100 ng, the microprocessor automatically corrects for nonlinear response. A series of 2-mL injections of mercury-saturated vapor gave responses of between 21 and 26 ng, totaling 470 ng, 94% of film saturation. The vapor reference was maintained at 18.5°C. The RSD for this set of data was 5.7%.

Suggested analytical procedure for mercury in solution

Gold film technology coupled with microprocessor control and an improved glassware delivery system have enhanced the quantitative analysis of mercury in liquid matrices, while at the same time reducing its complexity.

An illustration of this is the recommended procedure for the preparation and subsequent analysis of mercury in urine. The sample preparation is a modification of the American Congress of Government Industrial Hygienists (ACGIH) method No. 165, published in the ACGIH *Analytical Methods Manual*.

It is extremely important to immerse new glassware in concentrated HNO_3 for at least 8 hr. After this initial mercury decontamination, normal rinsing in acid is required to ensure mercury-free glassware. To prevent contamination of the stored glassware, continuous immersion in distilled water is recommended.

It is important that the sample preparation glassware *never* come into contact with reducing agents such as stannous chloride or sodium borohydride, because mercury in the sample can be lost due to carry-over of these reagents.

The detailed procedure is as follows: Under a fume-hood, add 1 mL of concentrated HNO_3 to a 30-mL Pyrex test tube. Pipet 0.25 mL of a urine sample into the test tube; allow 5 min for the digestion of the sample at room temperature. Add enough distilled water to bring the final volume to approximately 30 mL; the final volume is not critical.

Transfer the diluted sample to the reaction vessel. Attach the vessel to the bubbler. Inject 0.5 mL of 10% stannous chloride solution into the reaction vessel. This closed system eliminates the possibility of mercury loss from the sample to the atmosphere.

Immediately press SAMPLE START—the system automatically rezeroes and aeration commences. The 60-sec cycle will automatically go to completion, and the mercury value will be displayed in nanograms with the reading held until the next sample cycle. Data can also be displayed on a chart recorder or entered into a computer.

Forty urine specimens with an average mercury concentration of 50 μg/L can be analyzed before film saturation occurs.

Summary

The incorporation of thin gf sensors into an analytical system designed for the determination of total mercury in an aqueous matrix represents a distinct improvement over the AA method. The integrating characteristics and the selectivity of the gf sensor to a mercury signal are the major reasons for this improvement.

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Determination of Nanogram Quantities of Mercury in Liquid Matrices by a Gold Film Mercury Detector

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Many papers have been published in recent years dealing with mercury analysis. One of the most significant mercury methods was developed by Hatch and Ott (*1*), who reported that mercury could be directly reduced to the elemental state in an aqueous medium and the mercury vapor measured by atomic absorption spectrometry. Another important technique was developed by Anderson (*2*), who demonstrated that mercury could be collected on gold for subsequent determination by atomic absorption. McNerney (*3*) and Ohkawa (*4*) have taken advantage of the amalgamation properties of mercury and gold and utilized a sophisticated instrument based on a change in the resistivity of a gold film detector. However, while this instrument has improved sensitivity (*4*) and analytical versatility, the technology developed using this important nonatomic absorption technique was limited to air samples or those samples decomposed by combustion.

It is the purpose of this paper to describe the use of a gold-film mercury detector coupled with a direct reduction technique to determine mercury in aqueous media. The system allows analysis of a wide variety of samples while eliminating most of the interferences usually associated with cold vapor atomic absorption techniques.

EXPERIMENTAL

The instruments used in this study were a Gold Film Mercury Detector, Jerome Instrument Corporation, and a Coleman MAS-50, Coleman Instruments. Additional equipment included Coleman MAS-50 aerators and Standard 500-mL BOD bottles.

Two reducing agents were employed: tin(II) chloride solution (10% in 10% HCl) and sodium borohydride solution (0.2% in 40% NaOH). The standard solution used was prepared using reagent-grade mercury sulfate.

All other chemicals used were reagent-grade and "mercury-free" and included acetone, sodium sulfite, sodium thiosulfate, pyridine, ammonium hydroxide, hydrochloric, nitric, and sulfuric acids.

RESULTS AND DISCUSSION

Figure 1 shows the adaptation of a gold film mercury detector set up to monitor mercury in aqueous solutions. In this system, mercury vapor is volatilized from solution onto the gold collector coil by means of a suitable reducing agent. The collected mercury is then thermally volatilized and collected on the gold films located internally in the instrument. Mercury adsorption onto these films causes an increase in resistance (displayed on the digital galvanometer) and that increase is proportional to mercury content. The instrument is calibrated after each determination using standard addition techniques.

Since the proposed system involves quantitative collection of the volatilized mercury, a time study was needed to determine the optimum collection conditions. Table I shows that 2 min are necessary to complete the collection cycle. The remainder of the data were obtained using the 2-min collection cycle, which begins after introduction of the reducing agent.

Table II shows comparative data of the proposed system and a conventional cold vapor atomic absorption analyzer. The different sample preparations included: Group 1, direct dissolution in water; Group 2, wet digestion with nitric and sulfuric acids; Group 3, direct dissolution in water plus addition of hydroxide (since acidification of sodium thiocyanate with nitric acid is potentially hazardous, hydroxide is added before the addition of the reducing agent. Hydroxide effectively competes with thiocyanate and allows for direct reduction of the mercury); Group 4, use of 0.2% sodium borohydride solution as the reducing agent (mercury forms a strong complex with iodide (HgI_4^{2-}) which keeps the mercury from becoming completely reduced on the acid side with tin(II)

Table I. Aeration (Collection) Time Study (50 ng Hg added in each case)

aeration (collection), s	mercury measured,[a] ng
5	6
15	13
30	22
60	35
120	50
300	52
600	51

[a] Average of triplicate determinations.

Table II. Comparison Study—Conventional Cold Vapor Atomic Absorption vs. Gold Film Mercury Detector

sample	CVAA[a]	GFMD[a]
Group 1		
KCl	1000	900
HNO_3	<1	<0.1
KOH (40%)	21	19
CH_2OHCH_2OH	<1	<0.1
Group 2		
ground bone-1	3900	4300
ground bone-2	285	264
EK11623, gelatin Hg ref. (*6*)	2200	2300
organic dye	410	390
Group 3		
NaCNS-1	1	1
NaCNS-2	<1	<0.1
Group 4		
NaI	6	7
NaBr	37	40
Group 5		
waste water-1	5.2	5.5
waste water-2	0.3	0.3
Group 6		
$AgNO_3$-1	<10	<1
$AgNO_3$-2	95	94

[a] Average of duplicate determinations expressed as ng/g or ng/mL.

Table III. Interference Study—Cold Vapor Atomic Absorption vs. Gold Film Mercury Detector

	CVAA		GFMD	
sample (in water)	mercury added, ng	mercury measured, ng	mercury added, ng	mercury measured, ng
acetone (20%)	100	>1000	100	95
sodium sulfite (10%)	100	220	100	100
sodium thiosulfate (10%)	100	750	100	102
pyridine (5%)	100	>1000	100	91
ammonium hydroxide (20%)	100	>1000	100	96

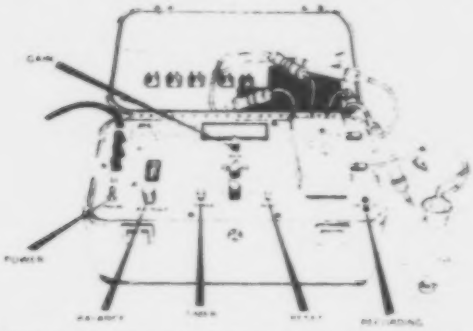

Figure 1. Adaptation of a gold film mercury detector using a direct reduction technique

chloride. Therefore, it is desirable to use a stronger reducing agent such as sodium borohydride in alkaline medium to quantitatively produce atomic mercury. All other data in this paper were obtained utilizing tin(II) chloride as the reducing agent); Group 5, addition of nitric acid followed by boiling (nitric acid addition and boiling allows for degradation of any organic mercury to the ionic state. It also might be noted that the proposed system allows for mercury analysis in water samples at the nanogram per liter level); and Group 6, precipitation of silver with a potassium bromide solution (5). There were no significant differences between the results obtained by the analyzers (correlation coefficient, r_{xy} = 0.9995), except that the gold film system offers lower detection levels (see Groups 1, 3, and 6, Table II).

The chemicals in Table III represent an interference study to show the advantages of the proposed system over cold vapor atomic absorption. Each chemical was dissolved in distilled water and diluted to 100 mL to give the indicated percentage by weight. Mercury and tin(II) chloride were added to the diverse matrices and the element was monitored by both techniques. In each case, erroneously high values were obtained using cold vapor atomic absorption. Gaseous vapors, such as sulfur dioxide and ammonia, which absorb at the 253.7-nm wavelength, showed positive interference. The chemicals listed in Table III are some typical examples of the troublesome types of samples that cause interference in the direct determination of mercury. The attractive feature of the gold film system is that each of these samples can be analyzed directly and accurately without interference from possible gaseous emissions that may be misinterpreted as mercury.

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Quantitative Analysis of Mercury Vapor by Gold Film Sensors

by Richard T. McNerney

JEROME INSTRUMENT CORPORATION

PRESENTED AT THE 1983 MEETING OF THE
AMERICAN INDUSTRIAL HYGIENE ASSOCIATION
PHILADELPHIA, PA

The detection of elemental mercury vapor by a thin Gold Film sensor was developed and patented (U.S. Patent #3,714,562) by J. McSherney, founder of the Jerome Instrument Corporation. (Figure 1)

The sensor, produced by high vacuum deposition onto a ceramic substrate, undergoes an increase in electrical resistance proportional to the mass of mercury in a sample. Two films, a reference and a sensor, are placed in opposite arms of a Wheatstone Bridge, a sensitive electrical circuit capable of detecting small changes in resistance. (Figure 2) Since mercury vapor is unique in its ability to alter the resistance of the Gold Films, interferences common to atomic absorption (AA) instruments, i.e. water vapor, SO_2, organic vapors, and particulates, are eliminated.

The Model #411 Gold Film Mercury Vapor Analyzer, designed for the analysis of mercury vapor in the workplace environment, incorporates a pump and digital display with microprocessor control. (Figure 3) Activating either the 10 second sample or 1 second survey mode starts an internal pump which draws a precise volume of air over the Gold Film sensor. The microprocessor computes the concentration of mercury, displaying the results on an LCD meter. This reading remains displayed until the next sample cycle is activated at which point the microprocessor automatically rezeroes the meter.

The microprocessor will ensure a linear response until the Gold Film has absorbed approximately 500 nanograms of mercury. (Figure 4) As mercury accumulates on the sensor, the percentage of saturation is indicated by pressing the Sensor Status button. Approximately forty 10 second or 400 1 second samples can be taken in atmospheres containing 0.1 mg of Hg/m³ (current OSHA TLV) before saturation reaches 100% (500 ng). At that point, a 10 minute film heat cycle is activated to desorb the accumulated mercury from the sensor and return it to its original baseline resistance. (Figure 1)

CALIBRATION

The Gold Film technique determines the mass of mercury per unit volume of sample. Thus calibration of the Model #411 can be performed simply and directly by using the most basic standard possible: the vapor pressure of mercury.

A small drop of liquid mercury in a closed container, e.g. a 300 ml polyethylene or thermos bottle, will saturate the enclosed air at a value which depends only on temperature. (Figure 5)

The concentration of mercury is calculated by utilizing relationships of pressure, temperature, and volume as expressed in the Ideal Gas Law. It should be noted that the concentration is not dependent on atmospheric pressure (P_a), but the vapor pressure of mercury (P_{Hg}) and the measured temperature of air saturated with mercury (T_m). (Figures 6 & 7)

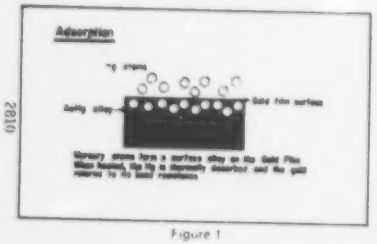

Figure 1

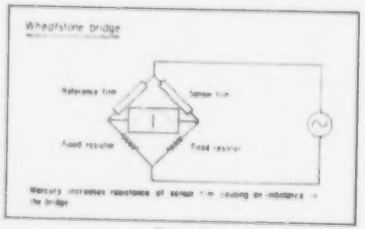

Figure 2

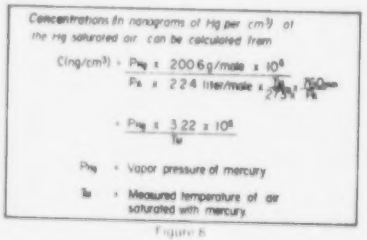

Figure 6

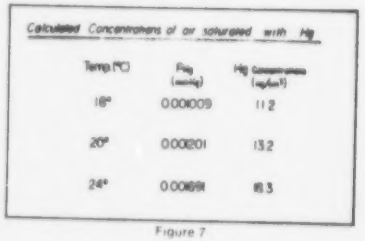

Figure 7

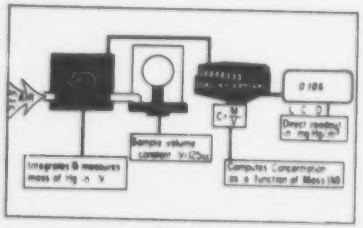

Figure 3

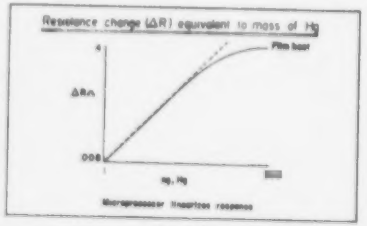

Figure 4

With the calibration vessel maintained at a constant temperature, a known mass of mercury saturated vapor is injected directly into the flow path of the Gold Film sensor of the Model #411 using a gas tight syringe.

Referring to Figure 8, 13.2 ng of mercury is introduced into the Model #411 using this procedure and activating the 10 second sample cycle. With the pump rate set at 0.75 l/min (12.5 cc/sec), the 13.2 ng of injected mercury will be diluted with 125 cc (12.5 cc/sec X 10 sec) of "Mercury free" air. This is equivalent to a mercury vapor concentration of 0.106 ng/cc (13.2 ng/125 cc)*. The digital meter response of the Model #411 is adjusted electronically to reflect this concentration. The linear response of the Model #411 (Figure 10) through its full operational range allows a single point calibration.

* 1 ng/cc = 1 mg/m³

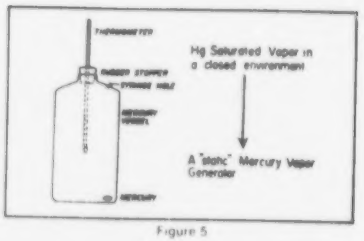

Figure 5

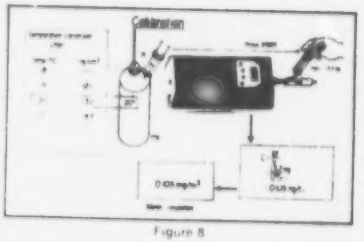

Figure 8

PRECISION & LINEARITY OF THE MODEL #411

The integrating characteristics of the Gold Film sensor, together with microprocessor-control, ensure excellent reproducibility and linear response.

Figure 9 represents a series of repetitive 10-second samples taken by the Model #411 in an atmosphere with a mercury concentration of 0.129 mg/m^3. Sampling was initiated with "Mercury-free" Gold Film sensors and concluded when sensor status indicated 60% saturation. The standard deviation and precision for this set of data is 2.44 and 2%, respectively.

Similarly, the Model #411 sampled atmospheres containing mercury concentrations ranging from 0.010 to 0.375 mg/m^3. Sampling was initiated with a "Mercury-free" Gold Film sensor and concluded when the sensor status indicated 30% saturation. The graph in Figure 10 illustrates the direct correlation between the meter response of the #411 and the known mercury concentration.

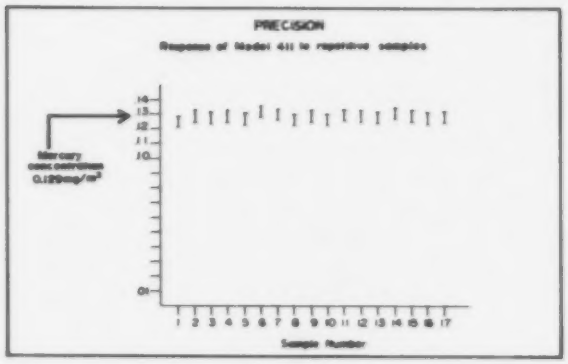

Figure 9

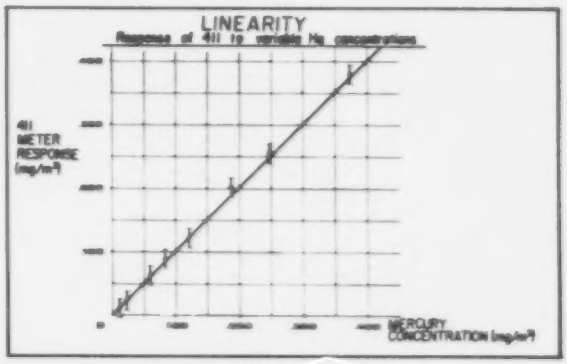

Figure 10

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SUMMARY OF TREATMENT TECHNOLOGY - MERCURY

Technology	Lower Limit of Treatment Capability (ppb Hg)
Sulfide Precipitation	10-20
Ion Exchange	1-5
Alum Coagulation	1-10

SUMMARY OF TREATMENT TECHNOLOGY - MERCURY (Continued)

Technology	Lower Limit of Treatment Capability (ppb Hg)
Iron Coagulation	0.5-5.0
Activated Carbon	
- High Initial Hg	20
- Moderate Initial Hg	2.0
- Low Initial Hg	0.25

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CHAPTER 45

MOLYBDENUM Mo

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INTRODUCTION

Molybdenum does not commonly occur in mine-mill effluents. It is also an element of little or no environmental concern. Despite years of investigation AMAX, INC., the largest producer of molybdenum in the world, and the U.S. EPA as well as the state of Colorado, have yet to find a case where molybdenum has been responsible for environmental damage. Excessive molybdenum in livestock water supplies can, however, give the trots to cattle. Why then should molybdenum be removed from water?

First, if there is enough of it, molybdenum removed from effluents may one day represent a profitable resource although that is not the case at current prices. Second, regulatory limits have been promulgated in some states, apparently motivated by the attitude of some regulators that everything should be regulated on principle, and molybdenum should have to be removed to meet some arbitrary standard "In case there are environmental effects

that are not yet known." One can always hope that a new trend toward more pragmatic regulatory attitudes may one day dawn.

OCCURRENCE OF MOLYBDENUM IN THE MINE-MILL ENVIRONMENT

Molybdenum is mined as a primary product as molybdenite MoS_2 in several porphyry deposits in the western U.S.A. and Canada. It also occurs as a by-product of copper mines in the U.S.A., Canada, and several South American countries, notably Chile and Peru.

Molybdenum also occurs in volcanic formations associated with and/or overlying primary uranium deposits in the southwestern U.S.A. and is sometimes associated with other minerals (e.g., uranium, tungsten and gold) in breccia pipe deposits scattered throughout the western U.S.A.

In the mining and milling of primary molybdenum deposits, e.g., at Climax, Henderson, Colorado, etc., residual particles of MoS_2 in the tailings may oxidize with time to release small concentrations of molybdenum to the seepage water and tailings decant solutions. Drainage from wasterock dumps may also contain some molybdenum. Molybdenum in minewater and tailings seepage and decant water from the Climax Mine was described by GOTT and LAFFERTY (1978) and by RAMADORAI (1978).

In uranium ore milling, molybdenum can build up in process solutions or occur in mine drainage.

At in situ leach test projects for uranium recovery from deep deposits in New Mexico, molybdenum was identified in the leach liquor that was pumped from the wellfield and represented a potential metallurgical interference in the ion exchange uranium recovery process.

Molybdenum also occurs associated with the gold ores recently discovered in the major Hemlo gold district and is expected to range between 0.5-3.0 mg/l in wastewater from this operation before being treated and below 1.0 mg/l in the discharged effluent.

The PEDCO (1983) report provides an interesting insight into approximate ranges of molybdenum levels in mine-mill effluents. In the case of some mine categories, e.g., taconite, phosphate, etc., molybdenum was not considered important enough to be included in the investigation. On the other hand, elevated molybdenum levels in effluents, process water, and leachates were observed for molybdenum, copper, and gold-silver recovery operations. A question arises as to whether molybdenum may possibly be a pathfinder element for gold mineralization in volcanic environments.

Molybdenum was generally found in the PEDCO (1983) investigation to occur in mill tailings decant solutions, minewater, and leachates of tailings solids, wasterock, and ore in a range of 0.002-2 ppm but averaging less than 0.5 ppm. Examples of industry classes where molybdenum exceeded 1 ppm are considered unusual except in some uranium, molybdenum, copper, and gold districts:

SUMMARY OF PEDCO (1983) DATA

	Average (ppm)	Number of Samples	Maximum (ppm)
NEW MEXICO URANIUM DISTRICT			
Surface Mine Waste and Leachate	LT 0.01	4	LT 0.01
Surface Mine Waste Water Leachate	0.02	4	0.034
Minewater Pond Liquid	0.436	5	0.76
Minewater Pond Settled Solids			
- Solids Total	139	6	230
- Acid Leachate	0.369	6	2.10
- Water Leachate	0.376	5	1.24
OTHER URANIUM DISTRICT			
Untreated Mine Water	0.395	3	1.1
Minewater Pond Liquid	0.57	2	1.1
Minewater Pond Settled Solids Water Leachate	0.381	3	1.0
SOUTHWESTERN COPPER DISTRICT			
Surface Mine Waste Water Leachate	0.215	8	1.3
Tailings Pond Liquid	1.53	6	2.5
Leach Liquors (H_2SO_4)	1.41	3	2.1
OTHER COPPER DISTRICT			
Tailings Pond Liquid	0.41	3	0.9
MOLYBDENUM DISTRICT			
Fresh Tailings	0.693	3	1.1
Tailings Pond Liquid	5.87	3	11
Untreated Mine Water	3.20	3	2.05
Lowgrade Ore Water Leachate	1.09	2	1.25
NEVADA GOLD-SILVER DISTRIC			
Tailings Pond Liquid	0.32	2	0.51

	Average (ppm)	Number of Samples	Maximum (ppm)
OTHER GOLD-SILVER DISTRICT			
Tailings Pond Liquid	0.827	4	1.80

The fact that molybdenum occurs in minewater and/or tailings pond decant solution and tailings leachate by no means implies that it presents an environmental or groundwater contamination problem. Most of the operations where molybdenum occurs in this way are in the western U.S.A. where there is net evaporation and can be operated for zero discharge. Due to heavy winter snowfall, this may not always be possible as, for example, at the Climax Mine. The Henderson Mine and Mill is, however, a zero discharge operaton as are most Nevada gold-silver operations.

Elsewhere in the west as, for example, at NORANDA's Brenda Mine and other molybdenum/copper operations located in areas with net precipitation, zero discharge is not possible, and water must be discharged eventually. In one copper-molybdenum operation in British Columbia, 1,500 acre feet per year of water are added to the tailings impoundment. Thus far, the tailings pond has been expanded to contain the excess water, but this will not be possible indefinitely. It is believed that during the last few years, a significant amount of water was discharged from the impoundment and that this met with regulatory disapproval to the extent that an alternative long-term solution is required. It is not exactly clear why excess solutions cannot be discharged after a straight forward lime addition and settling (or HDS) to remove other heavy metals if molybdenum is not environmentally damaging. In British Columbia, most drainage eventually leads to salmon rivers, and possibly regulators are not prepared to risk any possibility of damage to fisheries.

ENVIRONMENTAL SENSITIVITY - MOLYBDENUM

Molybdenum up to several ppm in water has not been identified as the cause of any environmental damage so far.

HELLUMS and BAILEY (1979) referred to studies on molybdenosis in 1965 and 1972 in which it was found that areas that had been used for stockpiling uranium ores "during the old AEC days" showed a high rate of molybdenosis in cattle. This condition was caused by the effect of windblown ore dusts and surface water transport of copper and molybdenum to the dietary intake of cattle locally. This study reinforced the state of Texas' determination to isolate tailings permanently. Information on the molybdenosis studies could be requested from:

WILLIAM E. HELLUMS
Supervisor of Industrial Licensing
Radiation Control Branch
Division of Occupational Health
and Radiation Control
Texas Dept. of Health
Austin, TX

EDGAR D. BAILEY
Administrator
Radiation Control Branch
Division of Occupational Health
and Radiation Control
Texas Dept. of Health
Austin, TX

High levels of molybdenum can upset ruminants such as cattle and impart to them the trots. Apparently, grazing irrigated by water containing high concentrations of molybdenum may affect cattle in this way. Information on evaluation of environmental sensitivity to molybdenum might be available from:

AMAX, INC.
1707 Cole Blvd.
Golden, CO 80401
(303) 234-9020
James Gilliland

AMAX would, of course, be interested in knowing about any reputed effects of molybdenum on the environment anywhere in the world.

REGULATORY LIMITS FOR MOLYBDENUM

Molybdenum is of such little environmental concern that it is not included in state and federal reviews of their water quality objectives. However, some mine-mill operating and NPDES permits do include a regulatory limit for molybdenum in their effluents.

Limits for molybdenum in effluents were identified in the following small number of operating permits:

Operation	Limit (ppm)	Permit Type
AMAX, Mount Emmons	2.0	Daily Limit NPDES
Climax Molybdenum Mine	2.0	24 Hour Maximum NPDES
New Mexico Water Quality Control Commission 8/27/1971	0.01	General Discharge Limit

TREATMENT FOR MOLYBDENUM REMOVAL

Straightforward lime precipitation and settling does not effectively remove molybdenum from acid solutions, especially in very cold climates or else AMAX would have employed it.

Discussion of molybdenum removal from effluents in operating plants is very limited, and two papers on the development and evaluation of processes for molybdenum removal along with other metals by GOTT and LAFERTY (1978) and by RAMADORAI (1978) are inserted below. These papers were written by employees of AMAX, INC.

Also included below is a copy of U.S. Patent 4,219,416 issued to RAMIREZ and RAMADORAI (1980) describing a process for recovering molybdenum from effluents employing co-precipitation with iron and dissolved air flotation (using electrolytically generated gas bubbles).

Subsequently it is believed that dissolved air flotation using mechanically generated bubbles was tested with encouraging results. Suppliers of reputedly suitable DAF units are:

POLLUTION CONTROL ENGINEERING, INC.
10751 South Lakewood Blvd.
Downey, CA 90241
(213) 861-1297

ENVIREX-WATER QUALITY CO.
Division of Rexnord
1901 South Prairie Avenue
Waukesha, WI 53186

To date, no commercial-scale examples of DAF for metals precipitate removal from effluents have been identified.

BIOLOGICAL REMOVAL OF MOLYBDENUM

As far as frontier technologies are concerned, an interesting example of biological metals removal is described by BRIERLEY, et al. (1980) for which the abstract is inserted below.

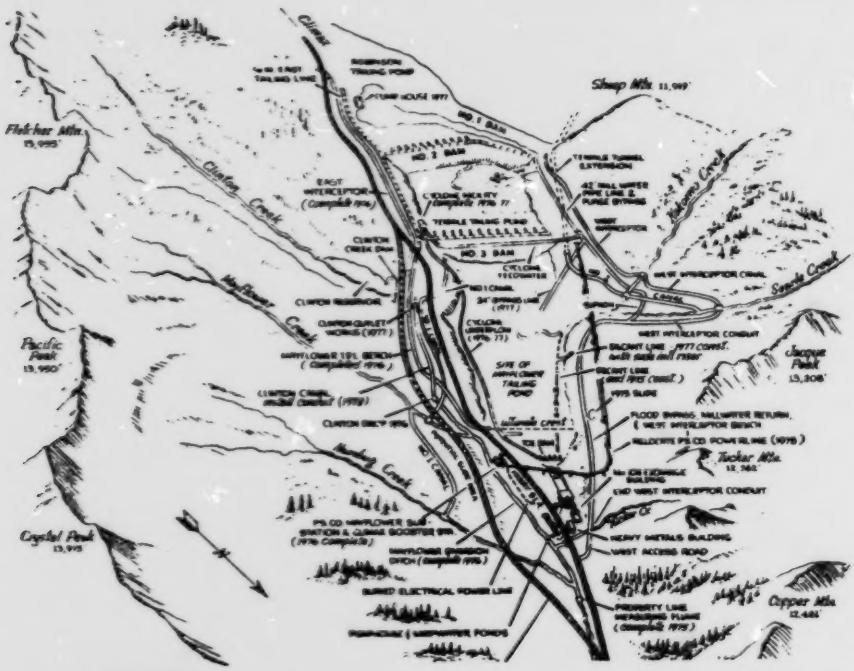
ACTIVATED CHARCOAL ADSORPTION OF MOLYBDENUM

FAULKNER (Undated) refers to the use of activated carbon in the mid-'50's to remove molybdenum from acid uranium circuits which became an established practice although at this time few if any uranium operations are believed to use activated carbon for this purpose.

Development of Waste Water Treatment at the Climax Mine

by Richard D. Gott and John M. Laferty, Jr.

Prepared for the
1977 American Mining Congress
San Francisco, California



Introduction

Since the 1930's Climax Molybdenum Company has operated a water recycle system utilizing active tailing dams and water storage facilities to collect mill water and return that water for reuse in the plant. This system allowed total containment of waste water, except during the annual spring snow melt period. The rapidly increasing runoff into the tailing system made it necessary to discharge some industrial water to keep the total system in balance. Annual discharge, occuring historically between April and June, averaged 2,400 acre feet per year and was bled into Ten Mile Stream at a controlled and monitored rate to maintain stream quality.

In addition to the recycle system, seep water pump facilities have long term been incorporated below each tailing dam at individual drainage areas to pick up all seep water for return into the tailing system.

Climax, desiring to go to a continuous discharge mode of operation, has been involved for the last four years in the development of technology to effectively treat plant waste water prior to any discharge from the Climax property. To implement this program, it was essential to define the drainage system surrounding the tailing impoundment area and effectively reduce this area with a series of interceptor canals to bypass as much runoff waters around the tailing system and into the natural streams. This series of interceptors then allowed for projections of the amount of runoff waters which could not be excluded from the tailing system and would amount to an inflow quantity of water which would have to be handled on an average annual basis to maintain total system integrity. Figure 1 graphically details the Climax tailing system with interceptors.

Climax outfall water contains small concentrations of heavy metals such as molybdenum, copper, and zinc in levels of a few parts per million. These metal constituents are the result of minor metal solubilization during the molybdenite flotation process. The mill water also contains combined cyanide in concentrations of less than one part per million. This is introduced into the mill circuit in the Regrind Plant as sodium cyanide where it is used as a copper depressant.

Laboratory work on removing impurities from Climax mill outfall water was started in 1973 with the removal of molybdenum from the mill water. This work led to the operation in 1975 of the Chem-Seps continuous Counter current ion exchange (CCIX) Pilot Unit. Through 1976, an intensive effort including pilot plant tests with the Swift Lectra Clear process has been underway to develop a system to remove the remaining heavy metals and cyanide. This paper discusses the process route selected to remove molybdenum, heavy metals, and cyanide.

Table I	Effluent and Feed Analysis						
	Fe	*Mn*	*Cu*	*Zn*	*Mo*	*Cd*	*CN*
Effluent Target-mg/l	2.0	1.0	0.05	0.2	2.0	0.015	0.025
Feed Ranges-mg/l	3.0-7.0	5.0-7.0	0.025-0.16	0.20-0.40	2.0-20.0	0.015	0.2-0.5

Laboratory and Pilot Plant Development

Laboratory and pilot plant programs directed at developing Climax waste water treatment technology were divided into two major efforts. Our first objective was to remove molybdenum to levels of 2.0 parts per million Our second effort focused on removal of heavy metals and cyanide. Target effluent concentrations for the heavy metals of interest and cyanide are listed in Table I along with typical influent concentration ranges of these same contaminants.

Development of a Molybdenum Ion Exchange Recovery System

The development of ion exchange technology for the removal of molybdenum to the low concentrations of 1-2 parts per million was started in mid-1973. The test work was restricted exclusively to the weak-base amine type anion exchange resin for two reasons: 1) the molybdenum absorption capacities were greater, and 2) the resin's high affinity for the hydroxyl ion allows for effective molybdenum elution with smaller alkaline requirements. Earlier column loading tests indicated that the amine type resins had a low capacity to absorb molybdenum when the resin was in the hydroxyl form but had a much greater capacity in the bisulfate or chloride form. Sulfuric acid was selected as the regenerant not only because of its lower cost, but also to avoid contamination of the effluent water with chloride ions.

Column Upflow Loading-Acidified Feed

Because of previous work done by AMAX[1] and others,[2] it was recognized that Mo sorption is most efficient at a pH between 3.0 and 4.0. Accordingly, the feed was acidified to pH 3.5 to 4.0 before entering the column. Amberlite XE-299 was selected after comparing loading capacity of the weak-base type resins available. With Amberlite XE-299, laboratory loadings of up to 12 pounds of Mo per cubic foot of resin at a cumulative percent recovery of 90.8 were obtained.

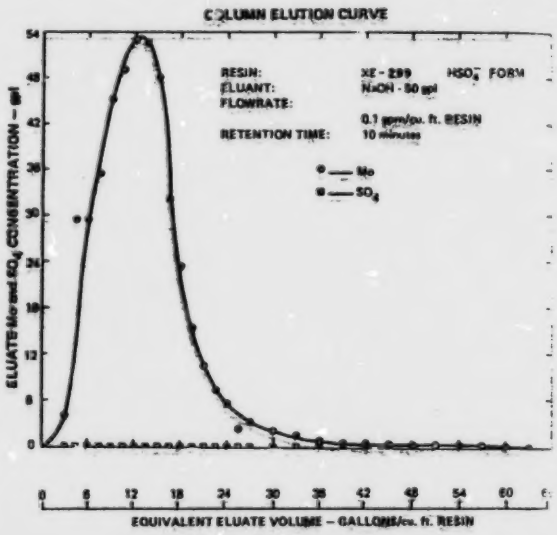
Resin Elution

Resin molybdenum elution efficiencies in excess of 98% were obtained. A typical elution curve is shown in Figure 2.

[1] Zundel, W.P., August 1965, Metal Extraction by Ion Exchange: French Patent 1,458,378.

[2] MacInnis, M.B., Kim, T.K., and Laferty, J.M., 1973, The use of Solvent Extraction for the Production and Recovery of High-purity Ammonium Paramolybdate from Normal Alkali Molybdate Solution. Paper presented at a Symposium jointly sponsored by the University of Reading and the Climax Molybdenum Company.

Figure 2



Ion Exchange Pilot Plant Operation

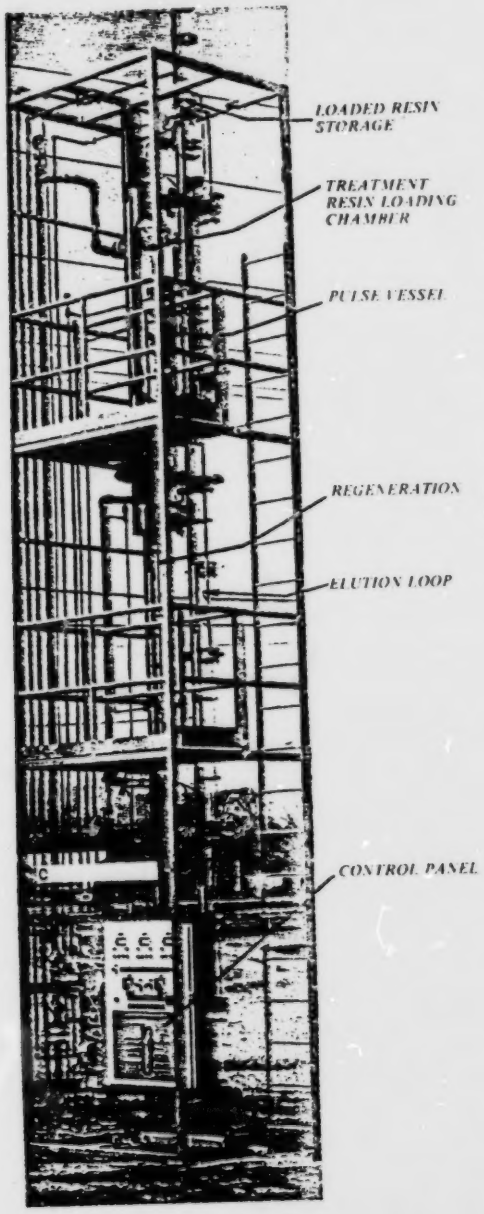
Chem-Seps Counter Current Ion Exchange Unit (CCIX)

The final phase in the molybdenum recovery program was to decide on an operating system to translate the laboratory procedure developed to a commercial plant. The CCIX unit was selected for piloting because, when compared to a fixed bed system, it requires considerably less resin inventory, it offers operating advantages at the high flow rates to be treated, and it occupies much less space.

The water processed in the CCIX unit was primarily Robinson Pond Tailing water. The Mo level in this water at the beginning of the test period was 11 parts per million. By the end of the period due to the dilution during the spring runoff the Mo concentration had dropped to 1 part per million. It was therefore decided to "spike" the feed with sodium molybdate to the level of 20 to 25 parts per million to facilitate the collection of the data required to design a full scale plant (resin loading, cycle time, elution efficiency, and resin degradation in operation).

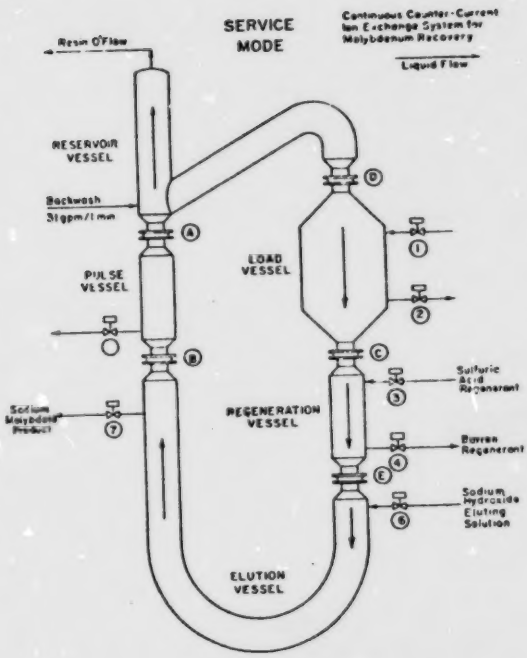
The resin used was Rohm and Haas XE-299, a macroreticular weakly basic anion exchange resin, with tertiary amine functional groups. Sodium hydroxide and sulfuric acid were used exclusively for resin elution and regeneration at a concentration level of approximately 50 grams per liter. A photograph of the pilot CCIX unit is shown in Figure 3. Figures 4 and 5 describe the operation of the column in the service and pulse modes respectively.

Figure 3
CCIX PILOT PLANT UNIT
Tested at Climax, Colorado



The CCIX Unit is installed within a frame of structural steel tubing 5' x 5'6" x 27' high. The column is 31'6" total height. The pulse and load chambers are made of 304 stainless while the regenerate and elution sections are of tempered glass (later many were changed to PVC). The load chamber is 12" diameter. All others are 3" *diameter.*

Figure 4



Service Mode

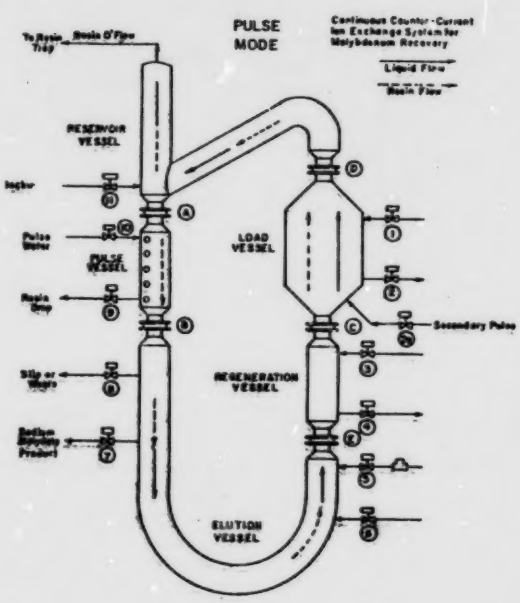
The fully automated system operates by continuously cycling between a "service mode" and a "pulse mode." During a service mode, the loop valves A, B, C, D, and E are closed, effectively dividing the loop into five sections: loading, regeneration, elution, pulse, and resin storage. In the resin loading chamber feed water is pumped (Valve 1) downflow through the resin bed and treated effluent is delivered (Valve 2) from the bottom of the resin loading chamber.

Sulfuric acid regenerate at 50 grams per liter is pumped (Valve 3) through eluted resin in the regenerate section between loop Valves C and E and exits (Valve 4) as a barren regenerate after sorption by the resin of the bisulfate ion. Simultaneously, sodium hydroxide eluting solution at 50 grams per liter is pumped (Valve 6) through loaded resin in the elution section between loop Valves E and B and exts (Valve 7) as a sodium molybdate solution after desorption of the molybdenum on the resin by the hydroxyl ion.

Backwash water, which enters at the base of the reservoir vessel, fluidizes the loaded resin bed and carries foreign materials and resin fines out the resin overflow line.

Following backwashing, loaded resin from the resin storage area is gravity fed through loop Valve A into the pulse section. Sonic pulse control sensors close Valve A when the pulsing section is properly filled.

Figure 5



Pulse Mode

During the pulse mode, loop Valve A is closed and loop Valve B, C, D, and E are open. Valves 1, 2, 3, 4, 5, 6, 7, 8, 9, and 11 are closed. A hydraulic pulse of water (Valve 10) and a hydraulic secondary pulse of water (Valve 2a) transfer the resin around the loop for a preselected distance. This movement puts loaded resin from the pulse vessel into the elution section, moving stripped and rinsed resin from the elution section into the regenerate section into the loading chamber, and finally moving the loaded resin from the loading chamber around to the storage area. The pulse mode takes about 30 to 45 seconds. The unit then returns to the "service mode."

Evaluation of Pilot Plant Test Run

The test series demonstrated that an average Mo concentration of 2.0 parts per million could be obtained from feed concentration ranging from 2 to 24 parts per million. Average resin loadings were 3.66 pounds Mo per cubic foot of resin.

Molybdenum resin elution efficiencies in excess of 98% were obtained. Average eluate Mo concentrations ranged between 16 and 19 grams per liter.

At a downflow rate of 41 gallons per minute per square foot the pressure drop through the resin bed was 40 pounds per square inch. This was within the allowable maximum of 50 pounds per square inch as recommended by the resin manufacturer to avoid excessive physical resin degradation. No evidence of physical resin degradation was found during the pilot plant test period. A 20% resin loss per year has been established in laboratory test work.

Tabulated pilot plant test results are presented in Tables II, III, and IV.

Table II

RESIN MO ADSORPTION EFFICIENCIES
DURING 24 HOUR OPERATING PERIOD

Feed: ph 3.5
Pulse Loading: 41 minutes

Test Date 1975	Feed (gpm)/Sq ft *	Assay Mo - ppm Feed	Assay Mo - ppm Effluent	Avg. lbs Mo. Loaded Per cu ft Resin
7/24-7/25	40.8	20.5	1.18	3.8
7/28-7/29	42.0	23.0	0.91	4.4
7/29-7/30	42.0	22.4	1.30	4.1
7/31-8/01	42.0	24.4	1.75	4.6
8/01-8/02	42.0	19.5	1.14	3.3
8/05-8/06	40.8	22.0	1.30	4.0
8/06-8/07	40.8	23.6	1.35	3.8
8/07-8/09	40.8	22.2	1.32	3.6
Average	41.4	22.2	1.30	3.9

* Square Foot Chamber Cross Sectional Area

Mo DISTRIBUTION

	Feed	Effluent	Slip	Calc. Eluate	Meas. Eluate
lbs Mo/Service	0.2448	0.0145	0.0001	0.2323	0.2382
% Mo Dist.	100.0	5.9	—	94.1	—

Table III

EFFLUENT Mo CONCENTRATION: DURING PERIOD WHEN FEED Mo CONCENTRATION DECREASED FROM 10.6 to 1.3 parts per million

Test Date 1975	Feed (gpm)/ sq ft Chamber Cross Sectional Area	Mo Conc. ppm Feed	Mo Conc. ppm Effluent
Pulse Cycle - 120 Minutes			
4/27-4/28	28.7	10.6	1.0
4/06-4/07	29.3	10.5	1.1
5/13-5/14	29.3	10.0	0.90
5/20-5/21	28.0	4.9	0.82
5/21-5/22	28.0	5.6	0.76
5/22-5/23	28.0	5.5	0.48
6/03-Swing	28.0	3.2	0.90
6/04-Day	28.0	3.1	0.60
6/05-Day	28.0	3.8	0.67
6/09-Day	28.0	1.6	0.67
6/09-Swing	28.0	1.3	0.40

Table IV

SUMMARY OF KEY ECONOMIC FACTORS

(Basis: 1000 gallons treated water)

Reagent	Use	Amount Used, lbs.	Cost
Lime	Effluent pH control	0.36	1.20¢
Sulfuric Acid	Influent pH control and resin regeneration	0.84	.75¢
Caustic	Resin Elution	0.49	2.41¢
Resin	Molybdenum removal	2.5×10^{-4} cu ft	2.50¢
		Total	7.86¢

Heavy Metals Removal

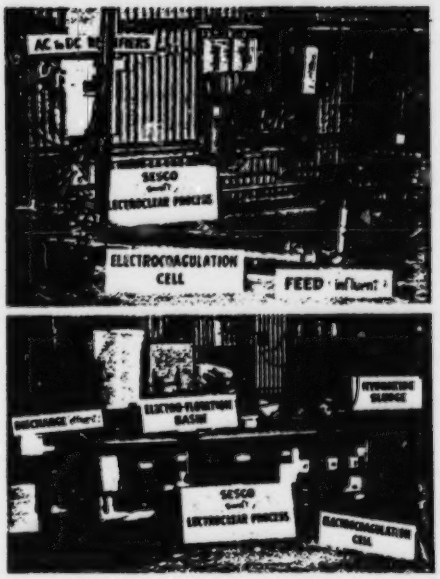
As shown in Table 1, the total amount of contaminant is quite small, however the difficulty of developing a viable process to remove that small quantity of contaminant is significant. After reviewing potentially applicable technologies, it was decided that five possible routes might yield workable processes for heavy metal removal. After running bench tests on all five options, it was clear that the only viable process was Swift's Lectro Clear system. The five technologies evaluated are reviewed below.

1. *Lime Precipitation:* Lime precipitation by itself was not successful as a potential solution due to the poor settling rates of the precipitated heavy metal hydroxides. Low water temperatures (0-4°C) and very low solids concentrations were responsible for the observed precipitate settling characteristics.
2. *Cation Exchange* — Column Loading Tests: Column loading tests showed that manganese, cadmium, and cyanide were not sorbed in any appreciable quantities.
3. *Sorption of Heavy Metals — MnO_2:* Column loading tests using a commercial grade pyrolusite (-6 +20M) as the absorbent was not effective because of early breakthrough of the heavy metals (250 gallons per cubic foot of sorbent).
4. *Ferric Hydroxide Sorption:* Increasing the amount of ferric-hydroxide via the addition of ferric sulfate prior to the lime precipitation step at a 8.6 pH showed no contribution to heavy metals or cyanide removal through physical sorption by the hydroxides, nor did it aid in solids settling.
5. *Swift Lectro Clear Process:* Positive bench scale tests and tests with a mobile trailer-mounted demonstration pilot unit at Climax during July, 1976 showed that the *Swift Lectro Clear* process held the most potential for meeting effluent requirements and thus should be tested further.

The Swift Lectro Clear process is a primary waste water treatment technique, designed to remove suspended material and/or hydroxide precipitates. After lime precipitate is conditioned in an electrocoagulation cell via contact with hydrogen and oxygen gases that are generated by electrolysis. The slurry is then mixed with a polymer flocculant and is floated in the electroflotation basin by "micro bubbles" of electrolytically generated oxygen and hydrogen and is subsequently skimmed off for disposal. The pilot unit was designed for an average flow of 10 gallons per minute and at this flow rate, residence times in the mobile unit were ten minutes in the neutralization tank, one minute in the electrocoagulation cell and 25 minutes in the electroflotation basin. Because of time limitations, the mobile pilot plant run used reagents in amounts necessary to produce a stable skim produce without attempting any optimization. Encouraging results of the preliminary trailer run led to a follow-up laboratory program to optimize reagent type and usage. During the laboratory testing program, a 10 gallon per minute pilot plant, Figure 6, was purchased from Swift and assembled in the No. 3 Mill Building at Climax. Laboratory findings were incorporated into a three month pilot plant program that culminated in an around-the-clock verification run. Table V presents performance results on the Lectro Clear system operation.

Table VI gives operating costs based on results from the continuous verification run.

Figure 6



Removal of Cyanide

There are currently many processes available for the detoxification of water cyanides. From a fundamental basis most of the commercially available methods utilize an oxidative approach to accomplish removal of both free cyanide and transition metal coordination cyanide complexes. A number of these processes have been evaluated in the context of Climax's needs and the results are summarized below.

Table V

PERFORMANCE OF LECTRO CLEAR PILOT PLANT PROCESS

Sample	Heavy Metals - mg/l						pH	CN	Turbidity
Analysis	Fe	Mn	Zn	Cu	Cd	Mo		mg/l	Ntu
EPA Permit Max. July 1977	2.0	1.0	0.2	0.05	0.013	2.0	6.0-8.5	0.025	N/A
Feed	3.0	5.4	0.28	0.16	0.02	3.1	7.4	0.25	15
Effluent	1.0	1.8	0.08	0.06	0.01	2.7	10.3	0.13	9.5
Filtered*	<.1	0.35	0.05	0.035	0.01	2.7	10.3	0.05	0.2

*Filtered Effluent is effluent filtered through No. 5 Whatman Paper

Table VI

[illegible]

Reagent	Projected Dosage(mg)	Amount Used(lbs)	New Net Cost
Lime	190	0.92	2.4¢
Polyelectrolyte (NC-700)	2.0	0.017	2.7¢
Surfactant (85-43)	2.0	0.017	0.48¢
NaClO	20.0	0.17	1.48¢
Total			9.6¢

POWER REQUIREMENTS:

Type	Usage	Cost
Electrocoagulation Cell	4.5 amps/gal	1.44¢
Electroflotation Basin	2.6 amps/gal	0.79¢
Total		1.70¢

ELECTRODE CONSUMPTION:

	Cost
Cell	2.14¢
Basin	1.00¢
Total	3.14¢

Total Estimated Cost

13.44¢/1000 gallons

Table VIII

Laboratory Testing
Effect of Resident Time, pH, and NaOCl Concentration on CN^- Degradations

pH	8.8		10.6		11.6	
NaOCl Conc	10 ppm	20 ppm	10 ppm	20 ppm	10 ppm	20 ppm
30 minutes	—	0.08	0.04	0.03	0.03	0.01
60 minutes	—	0.05	0.03	0.02	0.03	0.02
90 minutes	—	0.07	0.04	0.02	0.03	0.02

Feed cyanide concentration was 0.19 parts per million.

Table IX

Lectro Clear Pilot Plant Test
Effect of Residence Time, pH, and NaOCl Concentration on Cyanide Degradation

Date	pH	NaOCl (ppm)	Residence Time (33 Min)	(48 Min)	(78 Min)	
5 and 11 Nov.	8.8	10	.06	.04	.05	
11 Nov.		20	.07	.08	.07	
5 and 11 Nov.	10.6	5	.03	—	—	CN^-
11 Nov.		20	.04	.03	.03	(ppm)
5 and 11 Nov.		10	.02	.03	.01	
11 Nov.	11.0	20	.04	.04	.04	
17 Nov.		40	.05	.03	.04	

Table VII

Laboratory Test
Alkaline Chlorination of No. 3 Mill Water

CN CONCENTRATION

pH	9.5		10.5	
Residence Time	15 min	30 min	15 min	30 min
20 ppm Cl_2	0.07	0.05	0.06	—
30 ppm Cl_2	0.13	0.05	0.05	—
50 ppm Cl_2	0.04	—	0.02	—
Feed	0.18	0.18	0.18	0.18

Table X

Lectro Clear Pilot Plant Test
Concinuous Verification Run

Date	Effluent pH	NaOCl	Residence Time	Feed CN^-	Shift Number	(ppm)
4-17	10.6	20.9 ppm	33 minutes	0.2	1	.09
Nov.				Average	3	.05
					4	.04
					5	.06

Alkaline Chlorination

The alkaline chlorination process oxidizes cyanide by the addition of chlorine gas. The cyanide solution is first rendered alkaline (pH 10.5-11) and chlorine gas is injected into the process water stream. Laboratory test results, studying the effect of residence time, pH, and chlorine concentration are summarized in Table VII. Temperature was maintained at less than 10°C throughout all testing.

A confirmation test was carried out in our 10 gallons per minute Lectro Clear pilot plant at Climax. Chlorine gas was introduced directly after the lime precipitation step. Cyanide concentration was reduced from 0.14 parts per million to 0.07 parts per million with chlorine additions ranging from 5 to 50 parts per million. The low levels of 0.02 to 0.04 parts per million obtained in the lab were not reproducible in the pilot operation.

Hypochlorite Treatment

Essentially the same reactions as in alkaline chlorination result from the addition of aqueous solutions of sodium or calcium hypochlorite. The use of sodium hypochlorite has been extensively studied in the lab as well as in the pilot plant at Climax. The use of calcium hypochlorite was evaluated in the lab and performed as well as sodium hypochlorite, however, economics dictate the use of the sodium form as it can be electrolytically generated from sodium chloride solutions.

Table VIII summarizes the laboratory tests utilizing NaOCl. Feed solution was fresh No. 3 Mill water and all tests were carried out at less than 10°C.

Based on the results of these tests, a continuous verification run, utilizing the most appropriate operating conditions and reagent addition levels, was executed. In

Table XI

PILOT PLANT RUN TO VERIFY FINAL PROCESS PERFORMANCE

Analysis	Heavy Metals milligrams per liter							CN	Turbidity
Sample	Fe	Mn	Zn	Cu	Cd	Mo	pH	mg/l	N/A
EPA permit Max. July 1977	2.0	1.0	0.2	0.05	0.015	2.0	6.0-8.5	0.025	N/A
Feed	4.3	6.4	0.29	0.19	0.01	5.9	6.5	0.28	19-30
IX Effluent	---	6.2	0.28	0.17	0.01	1.1	3.5	0.08	---
Effluent[1]	0.65	1.0	0.05	0.05	0.01	0.6	10.5	0.035	7-9
Filtered Effluent[2]	0.10	0.10	0.022	0.013	0.01	0.6	10.5	0.01	---
Lectro Clear Skim	8.9	11.7%	0.5%	0.22%	10 ppm	0.35%	10.5	10 ppm	---

Specific flow through filter: 5.0 gallons per minute per foot squared

[1]Effluent after Lectro Clear treatment for heavy metals removal

[2]Lectro Clear effluent after filtration

the pilot plant effort, the effect of pH, residence time, and NaOCl concentrations were studied. As is shown in Tables IX and X, the laboratory results were not reproduced in the Lectro Clear unit. The initial pilot plant cyanide test results were erratic with CN^- levels in the effluent varying between 0.04 and 0.08 parts per million. The average cyanide concentration in the effluent during the 66 hour run was 0.052 milligrams per liter. Also noted was that increasing the amount of hypochlorite addition did not materially affect cyanide degradation. Concentrations as high as 40 parts per million NaOCl resulted in no significant decrease in effluent cyanide levels as compared with 5 parts per million.

Although the laboratory results for cyanide degradation were not fully realized in the pilot plant circuit, the combined effects of cyanide removal in the ion exchange process and in the hypochlorite addition allowed the effluent to meet the cyanide limits.

Concurrent with the cyanide removal pilot plant testing it became evident that the heavy metal removal goals were not fully met with the Lectro Clear process. The problem centered on the requirement for a more complete elimination of precipitate. A decision was made to incorporate a high rate sand filter into the process scheme to "polish" or insure the quality of the effluent.

Tables XI and XII present a total circuit analysis including ion exchange, Lectro Clear process, oxidation, and sand filtering.

Table XII

PILOT PLANT RUN - OVERALL MATERIAL BALANCE*

Description	Fe	Mn	Zn	Cu	Mo	CN
Mass into System-grams	641	959	43	28	884	42
Removal by IX Column	---	3.1%	3.7%	11.6%	81%	71%
Removal in Lectro Clear	85%	61%	60%	63%	9.5%	16.1%
Removal by Filtration	15.1%	15.6%	10.2%	18.4%	-0-	8.9%
Leaving Filter to Pond	-0-	-0-	7.4%	6.8%	9.7%	3.4%
Removal by Total System	100%	100%	93.4%	93.2%	90.3%	96.4%

*Basis: 66 hours, 2.66% solids in skim, effluent pH = 10.5, feed pH to IX column 3.5.

Conclusion

Process definition for waste water treatment at Climax incorporates counter current ion exchange for molybdenum removal, followed by Swift electrocoagulation-electroflotation for heavy metals removal with a polishing filter for final effluent clarification. Sodium hypochlorite is added prior to the electroflotation basin as an oxidant for cyanide destruction. Pilot scale operations indicate essentially all the iron and manganese and in excess of 90% of the zinc, copper, molybdenum and cyanide are removed. The molybdenum removed by the ion exchange unit will be processed by solvent extraction-crystallization producing a marketable sodium molybdate. Skim electroflotation products will be chem fixed and returned to the tailing area for impoundment. The above processes are now being incorporated into a dual 2,000 gallon per minute plant with all pilot processes included in the production facilities. Full scale operation is planned in early 1978, to treat process water prior to that year's annual snowmelt.

The success of this process development is attributable to the cooperative effort between the Climax Mill, AMAX Extractive Research Group in Golden, and the AMAX Environmental Services Group, all providing specific expertise in outlining specific goals and objectives to this complex problem. The inclusion and adaptation of the Swift Lectro Clear process to treatment of process water at Climax is, we think, a first for the mineral industry and provides a novel and exciting approach to waste water treatment in the minerals industry for the future.

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In the development of this process, special thanks are due to Paul Zundel and Gary Van Riper of the Golden Lab and, also, to John Richards, Climax, Chief Metallurgist.

Treating Tailings Waters From Moly Operations—A Review

Gopalan Ramadorai

Removing pollutants from tailings water is a prime concern at Climax's Henderson mine.

Tailings water from primary flotation concentrators usually contains minor amounts of pollutants such as heavy metals, cyanide and solubilized molybdenum, which are solubilized in the flotation process. A review of various techniques to reduce pollutants to acceptable levels is presented.

Generally, molybdenite ores are processed by conventional size-reduction techniques, followed by flotation to produce a metallurgical-grade concentrate of 88% to 92% MoS_2. Reagents commonly used in the milling process include: vapor oil (collector); pine oil, MIBC (frother); Dowfroth 250 (water-soluble frother); lime (rougher pH control); and sodium cyanide (Fe and Cu depressor). For lead depression, Nokes reagent is stage-added to the regrind mills and cleaners. Floeculant is added to obtain clear overflows in the intermediate thickeners.

What's Needed to Treat Moly Talls Waters

About 2120 L (560 gal) of water or 2.33 st are required to process one short ton of ore; if 80% recycle is practiced, the fresh water usage will be 420 L (112 gal) or 0.47 st per ton of ore processed. In areas where there are significant quantities of rainfall, bleeding a part of the tailings pond decant water prior to discharge is essential to maintain water balance.

The flotation process tends to solubilize small amounts of heavy metals such as molybdenum, copper, manganese, and zinc. Low levels of cyanide are also present in the water; this can usually be attributed to the use of sodium cyanide in the milling circuit. If clarification is inadequate, total suspended solids content in the tailings pond decant water may increase.

Most of the flotation collector normally reports into the final concentrate. The balance of the collector is adsorbed in the tailings with very little reporting in the decant water. The same comments are valid for water-insoluble frothers like MIBC and pine oil; but the amounts of frother used are significantly smaller compared to the collector level. If the tailings pond decant water is visually frothy, it is an indication that excessive levels of frother are being used. The obvious solution would be to lower frother use in the mill.

Close control of the usage of water-soluble frothers like DF 250 in the mill will alleviate visual frothing of tailings

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ponds decant water. This is also applicable to surfactants like Syntex L.

In general, pollutants that may require treatment are the heavy metals, including molybdenum and cyanide.

Treatment of tailings water is done for two reasons; minimize heavy metal pollutants so as to meet pollution control requirements, and minimize the effect of MoS_2 recovery loss upon water recycle. However, the constituents of the recycle water that contribute to MoS_2 losses in the flotation circuit are not clearly defined.

Molybdenum Reduction

The Mo level of tailings water is in the range of 2 to 4 ppm and 7 to 10 ppm Mo with water recycle. The levels after treatment will depend upon the water flow since the discharge limit is usually in pound per day. With no recycle, these concentrations are expected to be below 1.0 ppm and 2.0 ppm with the recycle. A review of the important techniques follows.

Coprecipitation with hydroxides of Al and Fe—Molybdenum can be removed from aqueous solution by sorption or coprecipitation with flocculant hydroxides of iron (III) and aluminum (III). However, the quantity of dissolved aluminum required is greater than iron. For this reason, testwork with aluminum has been limited.

The chemistry of the Mo removal process with ferric iron is fairly straightforward. The optimum pH is between 3 and 4 and the Fe/Mo ratio controls the degree of Mo removal with the residual Mo concentration dependent upon the initial[5] concentration. The Fe/Mo ratio required for optimum removal is in the range of 6 to 10.

The technology for removal of the Fe-Mo complex is more complicated. Conventional solid-liquid separation of the complex by thickening may not be practical in view of the slow settling characteristics of the Fe-Mo precipitate. The use of flotation techniques for its removal has been investigated by the USBM and the Moly Project at the University of Colorado for solid-liquid removal.[6,7]

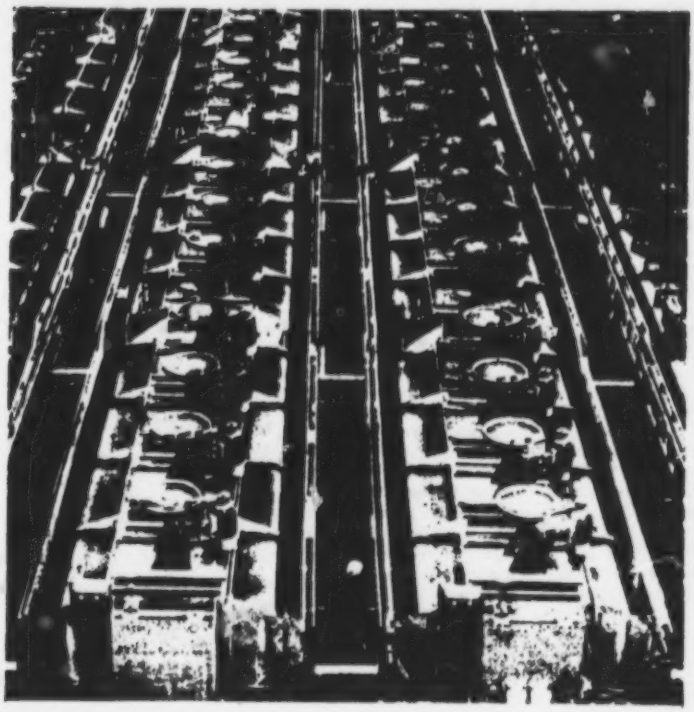
The Bureau of Mines has investigated the technique of dissolved air flotation (DAF) for removal of the Fe-Mo complex. An Fe/Mo ratio of 6 was found to reduce the Mo level from 4.0 to 0.5 ppm on synthetic solutions. Further testwork simulating recycle liquors with higher levels of Mo is continuing.[6]

Small-scale pilot testing using a specially designed DAF unit has been conducted by Jordan and coworkers at the University of Colorado under the sponsorship of the "Molybdenum Project."[7] The overflow rates were in the range of 122 to 367 L/min per m^2 (3 to 9 gpm per sq ft). Available commercial units usually operate at lower rates of 41 to 82 L/min per m^2 (1 to 2 gpm per sq ft).

Both the USBM and Jordon et al used a surfactant like sodium lauryl or capric sulfate to promote the flotation of the Fe-Mo complex.

While the technique appears to be feasible, several problems remain, including: (1) Will the treated water meet regulations for total iron and total suspended solids levels; (2) Will there be a further need for polishing of the treated effluent by filtration techniques; and (3) What about the handling and disposal of the Fe-Mo sludge? Finally, the overall question of the process economics remains, as the technical problems are solved.

Ion exchange—The literature has many references on the chemistry of Mo removal by ion exchange techniques. The removal of Mo is most efficient in the pH range of 3.0 to 4.0; amine-type anion exchange resins are used. Weak



In moly mills, the flotation process tends to solubilize small amounts of heavy metals such as molybdenum, copper, manganese, and zinc. Low levels of cyanide are also present in the water, owing to the use of sodium cyanide in the milling circuit.

base amine types were selected by Climax due to their higher Mo absorption capacities and smaller alkaline requirements for elution. Plus, the resin in the bisulfate or chloride form had a greater capacity to load Mo compared with the free form.

Amberlite XE 299 was chosen for development work. Laboratory loadings of up to 192 kg of Mo per m^3 (12 lb per cu ft) of resin at a cumulative percent recovery of 90.8 were obtained. Resin moly elution efficiencies in excess of 98% have also been obtained.

Ion exchange on a commercial scale is performed in several ways. A brief reference to these follows:

■ Fixed Bed Downflow Ion Exchange—It is essential to present a clarified liquor as free of solids as possible to the fixed bed column. Feed liquor is clarified by filtration; if the slimes are ultra-fine, coagulation and flocculation precede filtration. When this is done, care must be exercised in the use of flocculant; an excess may be deleterious to the resin.

If algae is a problem, addition of an algicide would be recommended. If this is not done, fouling of resin will probably occur. Chlorination could also be used to destroy the algae.

■ Resin in Pulp (RIP) Process—The process was developed to handle turbid liquors by ion exchange from U_3O_8 leach liquors. High maintenance costs and excessive resin losses have made the process obsolete.

■ Chemseps Countercurrent Ion Exchange (CCIX)—Pioneered by Climax for Mo removal in tailings water, the fully automated system operates by continuous cycling between a "service" mode and a "pulse" mode. During the service mode, loading regeneration, elution, pulsing and resin storage are performed in five separate sections in a continuous loop. The resin is moved from one section to another by sonic pulsing. Backwashing removes suspended solids and fine resin.

This system attempts to minimize the problem of TSS while maintaining high flow rates; it requires less resin inventory. An average Mo concentration of 2.0 ppm could be obtained from feed concentration ranging from 2 to 24 ppm. Average resin loadings were 59 kg/m^3 (3.66 lb per ft^3) of resin.

■ Fluid Bed Ion Exchange—Several designs have been described in the literature, including the Cloete and Streat, the USBM design by Rosenberg and Ross, Ritchey et al, Haines et al,[18] and the Himsley Contactor.[9] All of these have potential application in moly removal from wastewater streams.

Removal of Heavy Metals

The effluent guidelines are noted in Table 1. Data on Climax are found in Reference 2; information on other operations is not generally available. The levels of heavy metals in the feed will vary depending on the degree of recycle and the solubilities of the different metals in the tailings waters. The heavy metals to be found in molybdenum milling water are usually inorganic in nature.

The chemistry of the removal of heavy metals from process wastewater has been reviewed.[20] Technology available for heavy-metal removal is varied; e.g., the chemical precipitation of heavy metals by pH adjustment followed by flocculation and clarification, activated carbon adsorption, reverse osmosis, ion exchange, and cementation.[2] Conventional lime precipitation is not generally useful due to the poor settling nature of the metal hydroxides. The solids content is also low due to the relatively low levels of pollutants in the recycled water. Cation exchange does not appear to be feasible, as noted by Climax.[2] Cementation is not generally applicable since it is done in acid solutions.

Table 1—Effluent Guidelines for the Ferroalloy Ore Mining and Dressing Industry

	Effluent 24 hr. (max.*)	Effluent 30 day (average*)
F-	3.0	—
T. Fe	0.6	—
Mn	1.0	1.0
As	1.0	0.5
Cu	0.1	0.05
Mo	2.0	1.0
Zn	0.2	0.10
Cd	0.10	0.05
CN	0.04	0.02
TSS	30.00	30.00
pH	6-9	6-9
COD	50.0	25.0

* All values in mg/L except pH.

In addition, the more active metal used as the cementing agent will dissolve in the process and may need to be removed. Reverse osmosis as noted by Lenouette[21] is still in the development stages.

The use of ferric chloride or sulfate as a coagulant followed by lime to pH 8.6 was attempted by Climax with little success;[2] solids settling was not improved.

Several flotation techniques are available. These include Dissolved Air Flotation (DAF), Induced Air Flotation (IAF) and the Swift Lectroclear process.

Dissolved air flotation (DAF)—Primarily used in the removal of oils and grease from industrial wastewaters, the process saturates wastewater under air pressure. When the pressure is reduced, excess air is released, forming bubbles of 30 to 120 microns in diameter. These bubbles attach themselves to the suspended matter or oil and are floated to the top of the flotation basis since the average density of the aggregates is less than that of water. Chemical coagulants and flocculants are usually added to ensure good separation. The DAF process as a means of heavy metals removal (except molybdenum) does not appear to have been evaluated.

Induced Air Flotation—The IAF system operates on the same principle as the pressurized DAF units with one difference; the gas is self-induced by a rotor-dispersed mechanism, and is dispersed in the water.

Swift Lectroclear Process—The process is applicable for solid-liquid separation when the total suspended solids (TSS) is below 8000 mg/L. It is especially valuable in separating solids which are easily destabilized by electrodes.[22] In the Swift process, the heavy metals are precipitated as hydroxides into lime. The hydroxide precipitate is electrolyzed in an electrocoagulation cell. Hydrogen and oxygen are produced in the process. These attach themselves to the slurry and render them lighter than water. Subsequently, a polymer flocculant is added to agglomerate the precipitate, which is then floated off in the electroflotation basin by electrolytically generated oxygen and hydrogen. The skim containing the hydroxides of the heavy metals and excess lime is disposed of, while the effluent from the cation removal process has to be filtered in a high-rate sand filter to remove the residual TSS.

Gott[2] has reported optimum results in the removal of heavy metals with the Lectroclear process at a pH of 10.5 on mine tailings wastewater at Climax, Colo.

Treating Cyanide

Several treatment techniques are available to lower cyanide to the target level of 0.02 mg/L.[24] The feed cyanide level can range from a low of 0.02 to a high of 0.50 mg/L. Chemical oxidation by alkaline chlorination is appropriate for these levels. The oxidant can be chlorine gas, sodium

hypochlorite or calcium hypochlorite; cyanide is rapidly oxidized to cyanate. Retention times for oxidation are in the range of 0.5 to 2.0 hr; a pH of 10 or higher is necessary. Additional chlorine can be used to oxidize the cyanate further to nitrogen and carbon dioxide or to carbon dioxide and ammonia by acid hydrolysis at a pH of 2 to 3. This requires readjustment of treated water to a pH range of 6 to 9 prior to discharge.

Alternatively, excess chlorine can be added at pH 8 to 8.5 to oxidize the cyanate to nitrogen and carbon dioxide; retention time of 1 hr is essential. Excess chlorine is needed to prevent the formation of highly toxic cyanogen chloride.

Hydrogen peroxide plus formaldehyde has been used by DuPont in their Kastone process to oxidize cyanide to cyanate.[25] The major disadvantage of the process is its inability to oxidize cyanide below the level of cyanate. However, if the cyanide is present as "free" cyanide and not complexed, the process could be attractive since no problems of cyanogen chloride are encountered.

Hydrogen peroxide alone will probably by equally effective in lowering cyanide levels. The same comments on "free cyanide" will apply to this as those stated above for the Kastone process.

Climax has used hypochlorite in lowering cyanide to acceptable levels on the effluent from the Chemseps Ion Exchange unit used for lowering Mo levels in tailings water.[3]

Fluoride

Several approaches are possible; choice of a specific process depends on the effluent.[26,27]

The most widely used treatment consists of the addition of a soluble calcium salt to form insoluble calcium fluoride which is removed by liquid-solids separation. The optimum pH for precipitation is between 8 and 9. The fluoride levels after treatment vary from the theoretical solubility limit of 7.8 mg/L to about 30 mg/L. For lowering the fluoride levels even further, the most promising treatments are alum precipitation and adsorption on activated alumina.

Alum (aluminum sulfate) has been used to lower fluoride levels in potable waters in the pH range of 6.5 to 7.5. The quantity of alum needed depends on the initial fluoride level and the desired final level; this increases as the residual fluoride level decreases. Extensive amounts of sludge are produced in the process; settled sludge will amount to 18% to 40% of the volume treated.[28]

Activated alumina can reduce fluoride ion levels to less than 2 mg/L. Problems of handling regenerant and the effect of regenerant on overall effluent quality are yet to be resolved.[28]

In general it can be said that technology for fluoride reduction to low concentrations is not well established. An extensive development program will be essential to determine the applicability of the defluoridation techniques discussed earlier to the effluent in question. □

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Ramirez et al.

[11] **4,219,416**

[45] **Aug. 26, 1980**

[54] **PROCESS FOR RECOVERING MOLYBDENUM AND TUNGSTEN FROM MINING WASTEWATER**

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[73] Assignee: Dravo Corporation, Pittsburgh, Pa.

[21] Appl. No.: 920,259

[22] Filed: Jun. 29, 1978

[51] Int. Cl.[2] C02B 1/20; C02C 5/12

[52] U.S. Cl. 210/44; 75/109; 210/51; 210/53; 210/DIG. 30; 423/58; 423/87

[58] Field of Search ..... 75/108, 109; 204/149; 210/42 R, 44, 49, 51-54, DIG. 30; 423/55, 58, 87

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Assistant Examiner—Peter A. Hruskoci
Attorney, Agent, or Firm—Parmelee, Miller, Welsh & Kratz

[57] **ABSTRACT**

A process for removal of heavy metals in their anionic state, particularly tungsten and molybdenum, from industrial mining wastewater by chemical precipitation of the heavy metal values, followed by gas flotation.

10 Claims, No Drawings

PROCESS FOR RECOVERING MOLYBDENUM AND TUNGSTEN FROM MINING WASTEWATER

This invention relates to the recovery of heavy metal values from mining wastewater, and more particularly, to the recovery of heavy metals such as tungsten and molybdenum which are present in their anionic state, by forming insoluble precipitates of these values and thereafter removing same by gas flotation.

Formerly, heavy metal values were removed from mining wastewater only if they were present in sufficient amounts that their recovery would enable sale for profit. However, more recently, in view of Environmental Protection Agency standards directed to the composition of industrial discharge waters, it has become necessary to treat various industrial wastewaters to obtain a discharge water composition having low levels of heavy metals. Accordingly, it has become necessary to devise an efficient, inexpensive method of treating mining wastewaters to minimize their content of heavy metals.

One such process which has been used in the past consists of an ion exchange process wherein heavy metal values, such as molybdenum and tungsten, are replaced with other anions in an ion exchange bed. A second prior art process entails treating mining wastewaters by reverse osmosis wherein wastewater is subjected to high pressures (about 100 psi) and the wastewater is selectively passed through a semi-permeable membrane to separate the heavy metal values from the remaining wastewater. Both the ion exchange process and the reverse osmosis process require very expensive capital installations and high operating costs. Accordingly, such processes are not feasible when applied to removing relatively small quantities of heavy metal values from wastewater, e.g. 20 ppm.

Another general concept for removal of heavy metal values from wastewater comprises forming heavy metal precipitates, and thereafter removing such precipitates from the wastewater. Removal is generally effected by allowing the precipitates to settle out. This means of separation is very inefficient. The present invention, on the other hand, involves a unique and surprising process for efficiently and inexpensively removing heavy metal values.

It is an important object of the present invention to provide an improved process for treating wastewaters to remove heavy metal values.

It is an additional object of the present invention to provide an improved process for treating mining wastewaters to remove molybdenum and tungsten values.

It is also an object of the present invention to provide an improved process for forming insoluble complexes of molybdenum and tungsten within the wastewaters, and thereafter removing such complexes by gas flotation.

It is a further object of the present invention to form insoluble tungsten and molybdenum complexes in mining wastewater, and thereafter removing such complexes by flotation with electrolytically generated microbubbles.

Generally, the objects of the present invention are carried out by a selective precipitation of anionic metal complexes within a narrow pH range of between about 2.0 and 6.0, followed by gas flotation. The process is amenable to any aqueous medium containing heavy metal values in their anionic form, but is primarily directed to the treatment of mining wastewater, such as

mine water tailings, that contain trace amounts of heavy metals. Heavy metals that may be removed include tungsten (as tungstates), molybdenum (as molybdates), chromium (as chromates) and arsenic (as arsenates).

Initially, the pH of the mining wastewater is adjusted to a value of between 2.0 to 6.0, and preferably between 3.0 and 5.0. This is accomplished by the addition of a mineral acid to the wastewater in sufficient amounts to provide the desired pH. Although any mineral acid may be utilized to adjust pH, it is preferred to use sulfuric acid in view of its availability and low cost.

Also, a trivalent metal cation is added to the wastewater, either before or after pH adjustment. The trivalent metal ion may be ferric, cobalt, aluminum, chromium or rhodium. Preferably, however, ferric sulfate is used to provide trivalent ferric ions in view of its availability, low cost, and ease of use. The trivalent metal cation is added to the wastewater in amounts so as to provide from about 6 to 20 parts per million (ppm) of the trivalent metal cation to each ppm of the heavy metal ion, and preferably, from 8 to 12 ppm of the trivalent metal cation to each ppm of the heavy metal ion. One part per million (1 ppm) is equivalent to one milligram per liter. The treated wastewater is then preferably retained for at least 3 minutes prior to any further processing, so as to enable the formation of insoluble ferric molybdate, tungstate, chromate and arsenate salts.

After retention, a basic chemical is added to the wastewater in order to provide hydroxyl ions to form insoluble ferric hydroxide with the excess ferric ions. Any source of hydroxyl ions is suitable, but preferably, calcium hydroxide (lime) is used. The base should be added in an amount to raise the pH slightly, but not in excess of pH 6. Preferably, the base will be added in an amount to increase pH about 0.5 units above the pH obtained subsequent to acid addition. The hydroxyl ions will form, at acidic pH, a gelatinous precipitate with aluminum as well as ferric ions. Apparently, the gelatinous ferric hydroxide co-precipitates with the insoluble heavy metal salts.

After treatment of the mining wastewater in accordance with the above-described procedures, the wastewater stream is subjected to a dense flow of gas bubbles to create embryo flocs of heteropoly molybdate and tungstate salts as well as metal hydroxides. The dense zone of bubbles may be supplied by a source of dispersed gas or dissolved gas (such as pressurized air). Preferably, however, the dense zone of very fine microbubbles is generated electrolytically, usually by decomposition of the wastewater. Generally, the wastewater flow is horizontal while the gas bubbles initially contact the wastewater flow in a substantially vertical orientation. It has been found that the microbubbles for flotation are most effective when exhibiting diameters of 10–500 microns, preferably 20–300 microns, and most preferably 30–150 microns. Moreover, the bubbles should be generated in sufficient quantity to provide from 10^4–10^9 bubbles per liter of wastewater treated, and preferably from about 10^6–10^8 bubbles per liter of wastewater treated. Also, the microbubbles should comprise from 0.1 to 10.0 volume % of the wastewater being treated.

As previously mentioned, the dense zone of bubbles is preferably generated electrolytically. This may be carried out by passing the wastewater stream through an electrocoagulation cell which contains an electrode grid positioned horizontally just above the bottom of

the cell. This electrode grid will consist of appropriately spaced pairs of anodes and cathodes to provide a suitable current density across the bottom of the cell to generate the desired volume of microbubbles. Depending on the density and volume of microbubbles to be generated, the electrode grid is generally designed to provide an energy input of between about 0.5 to 20 ampere-minutes per gallon of wastewater treated, and preferably from about 5 to 10 ampere-minutes per gallon. Design of the electrode grid arrangement should be in accordance with U.S. Pat. No. 3,959,131 of Ramirez et al., the description of which is incorporated herein by reference.

Treatment of the wastewater stream with a dense zone of gas microbubbles causes insoluble molybdate and tungstate complexes to agglomerate together in embryo flocs, buoyed upwardly by the rising microbubbles. These embryo flocs could be allowed to collect at the surface, and could then be removed as by skimming. However, it is greatly preferred to add a polyelectrolyte polymer flocculent to the embryo floc-containing wastewater at this point, and then flowing the wastewater into a basin where it is subjected to a second flotation with gas microbubbles. The flocculant can be any high molecular weight polyelectrolyte polymer normally used to floc particulates, but preferably it will be an anionic polyacrylic acrylamide, usually in amounts of from about 0.5 to 6 ppm (mg/L).

Microbubbles in the basin can be generated by means of dispersed gas, dissolved gas, or preferably, may be generated electrolytically. When electrolytic microbubble generation is contemplated, the wastewater may be flowed into a large, open rectangular basin having an electrode grid horizontally positioned across the bottom. Preferably, this electrode grid will extend over only a portion of the length of the basin, and will be designed to provide a decreasing density of microbubbles along the length of the basin from influent end towards effluent end. To effect gradient current density zones, and thus gradient bubble density zones, grids may be designed in accordance with the disclosures in U.S. Pat. Nos. 3,959,131 of Ramirez et al. and 4,012,319 of Ramirez, the descriptions of which are hereby incorporated by reference.

The microbubbles generated in the flotation basin act to promote further floccing of the embryo flocs, resulting in full-grow flocs that are buoyed to the surface of the basin. These full flocs may then be skimmed from the surface, as with countercurrent directed skimmer blades positioned above the basin, and treated to remove molybdenum and tungsten values. Generally, the present invention is operable to reduce total Mo and W values down to levels of less than 1 ppm, and often as low as 0.3 ppm. Also, total iron content is reduced due to the formation of insoluble ferric hydroxide. Moreover, the present invention is operable to treat relatively large volumes of wastewater in the range of up to several thousand gallons per minute.

Another advantage of the present invention is that it may be carried out utilizing relatively low capital equipment costs. In addition, chemicals normally used to form the insoluble heteropoly heavy metal precipitates are sulfuric acid and ferric sulfate, both of which are inexpensive and readily available. Finally, in addition to providing a wastewater suitable for discharge in accordance with EPA regulations, heavy metals, such as tungsten and molybdenum, in the skimmings are readily recoverable for their market value.

While we are not positive as to how the insoluble heteropoly heavy metal complexes are formed in accordance with the present invention, it is believed that with respect to molybdenum, the following reactions take place. It is hypothesized that in an acidic solution with a pH of between 2.0 and 6, the addition of ferric sulfate salt to the wastewater stream results in the formation of the ferric salt $(Fe_2Mo_4O_{24})^{-6}$. It is further believed that this ferric salt, when in the presence of excess ferric ion, is subsequently converted to the ferric heteropoly molybdate salt $Fe_2(Fe_2Mo_4O_{24})$. We also believe that pH control is especially critical in carrying out the present invention because at pH values in excess of about 5 or 6, ferric hydroxide becomes less soluble than the ferric heteropoly molybdate, and therefore, the ferric ion is depleted by forming ferric hydroxides, and so becomes unavailable to form the insoluble heteropoly molybdate salt.

The following examples are intended to set forth illustrative embodiments of the process and are not to be taken in any manner as limiting the scope of the invention as defined by the appended claims.

EXAMPLE I

A molybdenum processing wastewater exhibited the following metal components: 1.6 ppm molybdenum, 2.0 ppm iron. The pH of the wastewater was 6.8. The wastewater was treated with 400 ppm of sulfuric acid to adjust pH to a value of 2.0. Thereafter, ferric sulfate in an amount sufficient to provide 19 ppm of ferric ion per ppm molybdenum ion was added to the wastewater. Subsequently, 100 ppm calcium hydroxide was added. The wastewater was then treated with four (4) ampere minutes of electrical energy per gallon within an electrolytic cell so as to form embryo flocs of ferric heteropoly molybdate salts and ferric hydroxide. Thereafter, 2 ppm of anionic polymer flocculant was added to the wastewater, which was then subjected to an additional four (4) ampere minutes of electrical energy per gallon such that the entire floc of ferric molybdate salt and ferric hydroxide was floated to the surface by gas buoying. Analysis of the resulting treated water showed molybdenum values at 0.33 ppm and total iron values of 0.5 ppm.

EXAMPLE II

A molybdenum processing wastewater was doped to contain 18 ppm Mo and 1.5 ppm iron. 216 ppm of ferric ion was added as ferric sulfate, and pH was adjusted to 2.0 by addition of 100 ppm sulfuric acid. 200 ppm lime was then added to raise pH to 4.5. The solution was then treated in an electrocoagulation cell with 5 ampere-minutes current per gallon. 4 ppm of an anionic polymer flocculant was added and thoroughly mixed. The solution was then treated with an additional 3 ampere-minutes of electrical energy per gallon, causing flotation of the ferric molybdate salt and ferric hydroxide. Analysis of the treated solution showed the presence of Mo at 0.35 ppm and total iron at 0.6 ppm.

EXAMPLE III

Mine tailing effluent containing 1.86 ppm molybdenum was treated by this process. Ratio of ferric sulfate added was either 6 ppm ferric to 1 ppm molybdenum or 12 ppm ferric to 1 ppm molybdenum. Initial pH adjustment was made by addition of from 120–760 ppm sulfuric acid, giving a solution pH of from 2.0 to 3.09. A second pH adjustment was made by addition of from 0

to 120 ppm lime, giving a final pH of from 2.0 to 10.8. The precipitates formed were coagulated with electrolytically generated microbubbles, after which 3 ppm of anionic polymer was added. Additional electrolytically generated microbubbles were utilized in effecting flotation of the coagulated precipitate. Flotation skimmings were removed, and the remaining solutions were analyzed for molybdenum. Results were as follows:

Initial Conc. of Mo	Ratio Fe/Mo (ppm)	ppm H_2SO_4/pH	ppm Lime/pH	Final Conc. of Mo	% Removal
1.86 ppm	6:1	700 (2.0)	0 (2.0)	1.9 Mo ppm	0
"	6:1	140 (3.0)	0 (3.0)	1.9 Mo	0
"	6:1	140 (3.0)	25 (3.65)	0.94 Mo	54.8
"	6:1	140 (3.0)	40 (4.34)	1.0 Mo	46.2
"	6:1	140 (3.0)	80 (6.30)	1.6 Mo	14.0
"	6:1	140 (3.0)	120 (9.83)	1.7 Mo	8.6
"	12:1	100 (3.14)	0 (3.14)	1.3 Mo	30.1
"	12:1	110 (3.03)	25 (3.58)	0.58 Mo	68.8
"	12:1	120 (3.02)	40 (4.00)	0.24 Mo	87.1
"	12:1	120 (3.05)	80 (5.80)	0.54 Mo	71.0
"	12:1	120 (3.03)	90 (6.26)	0.72 Mo	61.3
"	12:1	120 (3.09)	120 (10.8)	1.56 Mo	16.1

EXAMPLE IV

Synthetic "doped" solutions were prepared containing either 20 ppm molybdenum, 20 ppm chromium or 20 ppm tungsten. The ratio of ferric ion to Mo, Cr or W was either 6:1 or 12:1. Initial pH was adjusted by addition of sulfuric acid, with pH being subsequently adjusted by addition of lime. As in Example III, the solutions were treated with electrolytically generated microbubbles, anionic polymer added, and again treated with microbubbles. Flotation skimmings were removed and final solutions analyzed for Mo, Cr or W. The results were as follows:

Initial Conc. of Mo, Cr or W	Ratio of Fe to Mo, Cr or W	ppm H_2SO_4 and pH	ppm Lime and pH	Final Conc. (ppm)	% Removal
20 Mo ppm	6:1	200 (3.08)	40 (3.58)	1.27 Mo	93.6
"	6:1	200 (3.02)	80 (4.30)	1.32 Mo	93.4
"	6:1	200 (2.99)	100 (5.35)	1.46 Mo	92.7
"	6:1	200 (3.09)	250 (8.25)	12.0 Mo	40.0
"	12:1	60 (2.97)	60 (3.30)	0.57 Mo	97.2
"	12:1	60 (3.00)	100 (4.42)	0.56 Mo	97.1
"	12:1	60 (3.30)	250 (8.41)	9.4 Mo	53.0
"	12:1	40 (4.30)	280 (9.05)	10.7 Mo	46.5
20 Cr ppm	12:1	60 (3.02)	100 (4.55)	10.0 Cr	50.0
20 W ppm	12:1	100 (2.70)	100 (4.30)	5.0 W	75

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method for removing heavy metals selected from the group consisting essentially of molybdenum, tungsten, chromium and arsenic from wastewater in their anionic forms as molybdates, tungstates, chromates and arsenates comprising the steps of adding to a wastewater having a pH of between about 2.0 to 6.0, a trivalent metal ion selected from the group consisting of ferric, cobalt, aluminum, chromium or rhenium to the wastewater in an amount sufficient to provide from 6 to 20 ppm trivalent metal cations per ppm of total molybdate, tungstate, chromate and arsenate ions to form insoluble heteropoly molybdate, tungstate, chromate and arsenate salts within the wastewater; adding a hydroxyl providing base to raise the pH yet maintain it within the acidic range to form a gelatinous precipitate; subjecting the wastewater to a dense zone of microbubbles to form embryo flocs from the insoluble salts; adding an anionic polyelectrolyte polymer flocculant to the wastewater; and thereafter subjecting the wastewater to an additional dense zone of microbubbles to form from the embryo flocs full flocs that are buoyed to the surface.

2. The method of claim 1 wherein the microbubbles are electrolytically generated in an amount of from 10^4–10^9 microbubbles per liter of wastewater and comprise from 0.1 to 10 volume % of the wastewater being treated.

3. The method of claim 2 wherein the microbubbles exhibit a diameter of from 20–300 microns and wherein the bubbles are provided in amounts of from 10^4–10^8 per liter of wastewater.

4. The method of claim 2 wherein the pH of the wastewater is initially adjusted to from about 3.0 to 5.0 and wherein from about 8 to 12 ppm of trivalent metal ion per heavy metal ion is added.

5. The method of claim 2 wherein the trivalent metal ion is ferric ion supplied by ferric sulfate.

6. The method of claim 2 wherein the flocculant is an anionic polyacrylic acrylamide and is added in the amount of 0.5 to 6 ppm.

7. The method of claim 2 wherein the second dense zone of microbubbles to which the wastewater is subjected exhibits a decreasing density of microbubbles from the influent end toward the effluent end of the zone.

8. The method of claim 2 wherein the wastewater is mining wastewater.

9. The method of claim 2 wherein the hydroxyl providing base is calcium hydroxide.

10. The method of claim 2 wherein the initial pH is adjusted by addition of sulfuric acid.

* * * * *

McDOUGALL (1984, personal communication) has tested and possibly patented a process whereby molybdenum is removed from acidic solutions by adsorption on activated carbon. By simply modifying the pH, molybdenum oxide-hydroxide can be either in an uncharged polymeric form, or the polymer can be depolymerised releasing molybdenum back into anionic form. Since the uncharged polymer adsorbs readily onto activated charcoal while charged ionic species do not adsorb well, carbon's affinity for molybdenum can be controlled.

A similar observation concerning fouling of ion exchange resins by molybdenum polymers was made at a New Mexico in situ leach test at Nose Rock by BATEMAN URANIUM CORP. Anton R. Hendricksz, now of BECHTEL CORP., and Wayne C. Henderson of KENNECOTT MINERALS CORP., Salt Lake City, would be familiar with this phenomenon.

No commercial scale application of carbon adsorption for molybdenum removal from effluents is known to be in current operation.

ION EXCHANGE

As mentioned above by GOTT and LAFERTY (1977) and RAMADORAI (1978), ion exchange is an effective way to remove molybdenum from acidic solutions. The process works best around pH 3.8, and there are several ion exchange systems to choose from, notably NIMCIX from MINTEK, South Africa, the PORTER System, HIMSLEY System, and CHENSEPS, INC. plugflow system.

When considering installation of such a system, some conservatism is in order in the sizing of commercial-scale CHEMSEPS units as in the past these seem perhaps to have been somewhat ambitious.

At CLIMAX MOLYBDENUM's water treatment plant, molybdenum was first recovered by a counter-current CHEMSEPS anion exchange system. This was followed by heavy metal precipitation and removal of the precipitate by dissolved air flotation followed by cyanide destruction using chlorine at pH 10.5-11.0.

COAGULATION WITH IRON

RAMIREZ (1981) described a process whereby molybdenum and arsenic were removed from a uranium tailings wastewater by electrocoagulation in which $Fe_3(FeMo_6O_{24})$ was precipitated by the addition of $Fe_2(SO_4)_3$ at pH 3.5-4.5 maintaining a Fe/Mo ratio of 10. The precipitate was skimmed from a flotation cell for Mo recovery and iron recycling. In the laboratory, W and Cr were also removed by the process. This process formed the

basis for the RAMIREZ and RAMADORAI (1980) patent for molybdenum and tungsten removal from mining wastewater.

In 1981, Ernest Ramirez was emloyed at AMERICAN STANDARD, INC. Wayne, New Jersey, and in 1985 Gopalan Ramadorai was completing his contract at AMAX R&D, Inc., Golden, Colorado, and could be reached at:

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It is believed that dissolved air flotation would work as effectively as the DRAVO Lectroclear Process for the removal of the precipitate after coagulation. In the case of some western U.S.A. operations which are at high altitude and hence in a cold climate, coagulation kinetics are of importance.

GEOCHEMICAL ADSORPTION

KATZ and RUNNELLS (1974) of the University of Colorado showed that soils with higher pH values with correspondingly lower amounts of organic matter and lower extractable Al levels are much less effective in removing Mo from mill solutions than acidic soils containing higher amounts of organic matter or soils containing oxyhydroxides. They pointed out that mill effluents containing Mo enter and percolate through the soil environment to contaminate groundwater reservoirs. KATZ and RUNNELS examined the ability of soils to remove Mo from infiltrating solutions. The maximum adsorption capacity of soil for Mo was 9.5 mg/g soil by desert soils and 50 mg/g Mo by agricultural soil. Alpine soils, however, showed an average sorption value of 160 mg Mo/g soil. The mountain soils had significantly higher extractable Al levels. Low soil pH values (5-6) with a higher percentage (10-14%) organic matter were also a characteristic of alpine soils. Desert and agricultural soils had almost no organic matter and had a high pH (7.8-8.2). KATZ and RUNNELLS concluded that acidic mountain soils offer far more protection to groundwater than do alkaline desert and agricultural soils.

Once again, the characteristic polymerization of molybdenum at lower pH may play a role in its mobility.

Experts experienced in ion migration phenomena through soils who can offer interesting and useful insights include:

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REMOVAL OF SELECTED INORGANIC POLLUTANTS FROM URANIUM MINE WASTE WATER BY BIOLOGICAL METHODS

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ABSTRACT

Water from underground uranium mines located in the Ambrosia Lake district near Grants, New Mexico, U.S.A., is treated to reduce levels of uranium, selenium, radium and molybdenum. The treatment system consists of a series of ponds and an ion exchange plant. Bacterial and algal populations present in the pond system are considered agents which actively assist in removal of the pollutants present in the water. Pond-bottom sediments maintain a reducing zone and a large population of sulfate-reducing bacteria of the genera Desulfovibrio and Desulfotomaculum. Uranium, molybdenum, and selenium accumulate in the pond sediment. Stimulation of the microbial sulfate-reducing activity resulted in a decrease of soluble concentrations of these elements in laboratory systems. Predominant components of the treatment ponds' algal flora are the filamentous Spirogyra and benthic Chara. Laboratory study indicates that Spirogyra is more active than Chara in removal of uranium and molybdenum from solution. However field-collected algal samples of both of the genera contain uranium and molybdenum. Laboratory studies indicate that death and decay of the algae in association with pond sediment does not result in return of cell-bound uranium and molybdenum to the water. The algae appear to act as bio-filters for accumulation of particulate pollutants and agents for adsorption and/or absorption of soluble pollutants.

INTRODUCTION

The mining of uranium ore may produce water from de-watering operations containing dilute concentrations of uranium, molybdenum, selenium, radium and other associated ions. This water presents a waste disposal problem, as the contaminants must be removed before the water can be discharged from a mining property. In addition, it is a potentially valuable source of economically important elements. Reclamation of mine wastewater can serve two purposes: removal of potential pollutants and concentration of resources. Several processes are available for soluble ion concentration including precipitation, ion exchange, solvent extraction and electrowinning. However, these systems are quite often ion specific and expensive when treating large volumes of water. An alternative system for resources concentration is based upon biological processes. Such a system has the potential for low cost, ion non-speci-

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Lubricants, cutting oils, hydraulic fluids, fuel, reagents and surfactants, sewage and treated sewage, fats from mine hostel kitchens, and runoff from new asphalt surfaces and even decaying vegetation all introduce organics into the operational environment. Industrial activity located near a mine-mill water supply can add organics which can interfere with recovery as has been observed recently on the Witwatersrand. In this case, an abattoir effluent is discharged into a stream from which a flotation/CIP plant draws its water or, more correctly, formerly drew its water. It is doubtful if there is a single mill operator who does not believe that organics can have a significant impact on metallurgical processes. Yet, when it comes to asking ourselves how much organics and which organic species are present and what their individual effects are on metallurgical results, then one usually draws a bank. In many cases, operators are oblivious to the presence of organic species in their effluent and process water. Yet, even in very remote locations far from the nearest industry, organics can be introduced as natural hydrocarbons in the ore or as humic and fumic acids generated from decaying vegetation or perhaps as end products from decrepitating bacterial biomass, etc. Recent Landsat applications have identified hydrocarbons leaking to the surface of the earth. Such leakages would represent serious organics contamination of ore which would not be obvious to an operator working at a plant that treats it.

Once aware of the possibility that organic contaminants may have an effect on plant performance, it remains to find a way of measuring the level of contamination, determine the cost of its effect, either find and curtail the source, find a way of treating the water, or find another means of overcoming the problem.

A basic conclusion of this investigation is that when it comes to organics in mine-mill water, knowledge and insight is lacking. Further investigation and R&D are needed:

- Detection and identification of organic species in water and/or ore pulps.
- Determination (quantitative, if possible) of the effect of organic species on mining, metallurgical, and mineral processing operations.
- Development of ways to keep organics out of mine-mill waters.
- Development of cost-effective treatment technologies to remove organics from mine-mill water.

POSSIBLE SOURCES OF ORGANIC SPECIES IN MINE-MILL SOLUTIONS

Organics in mine-mill water can be derived from a surprising number of sources; these include:

- Lubricating Oils Used Underground
  - Vehicle Leaks, Mechanical Equipment
  - Poor Housekeeping in u/g Maintenance Shops
  - Use of Mine Tailings as Dumps by Industry
- Diesel Fuel Leaks
- Hydraulic Fluid
  - Line Breakages
  - Maintenance/Repair Shops
- Compressor Oil
- Cutting and Grinding Oils
- Soaps, Fats, and Waxes from Industry and Mine Hostels
- Natural Hydrocarbon Seeps
- Industrial Contaminants, e.g., Abattoirs and Oil Refiners
- SX Reagents
- Phenol from Explosives and Mineral Flotation Reagent Degradation
- SulfoLignate Dust Control Reagents and Lignins from Rotting Underground Timbers
- Sewage (Raw or Treated)

It is of interest, ONTARIO (1979), that industrial and sewage effluent discharge of oil to the Great Lakes has been estimated at 64,000 tons per year which is the equivalent to several tanker wrecks per year. Depending on location relative to industry centers, lake and river water may itself contain enough organic contaminants to be a possible factor in metallurgical efficiency. Fortunately, mines and mills are more often than not located at remote sites where this is not a problem.

A potential source of groundwater contamination by organics is through the development of leaks in underground fuel and solvent storage tanks. These can result in costly losses of fuel or solvent in addition to groundwater contamination.

ENVIRONMENTAL SENSITIVITY TO HYDROCARBONS AND PHENOLS

ONTARIO (1979) has set an objective of 1 microgram phenol/l in waters (i.e., 1 ppb) phenol to protect against the tainting of edible fish.

ONTARIO (1979) estimated "safe" levels of various hydrocarbon oils for fish as follows:

Bunker Oil	180 ul/l (ppm)
Used Crankcase Oil	120 ul/l
Crude Oil Slicks	45 ul/l
Jet Aviation Fuel	45 ul/l
Diesel Oil	15 ul/l
Automobile Gasoline	9 ul/l

CHAPTER 46

ORGANICS

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INTRODUCTION

The presence and effect of organic species on metallurgical performance must surely be one of the least understood aspects of metallurgical and mineral processing operations. In this report, metal contaminants have been discussed one by one. The number of different organic species in modern industry is a large multiple of the number of inorganic species, and yet we know so little about them that all organics are lumped together in one brief section for a cursory discussion.

The above levels are higher than those that would be expected to cause problems of odor and aesthetics. ONTARIO (1979) has set the following objective for oil and petrochemicals which should not be present in concentrations that:

-- can be detected as a visible film, sheen, or discoloration on the surface;
-- can be detected by odor;
-- can form deposits on shorelines and bottom sediments detectable by sight or odor or are deleterous to resident aquatic organisms.

McKEE and WOLF (1963), following a review of world literature, concluded that phenol in a concentration of 1 ug/l phenol would not interfere with domestic water supplies, 200 ug/l would not interfere with fish and aquatic life; 50 mg/l would not interfere with irrigation; and 1,000 mg/l would not interfere with stock watering although this author for one would not be eager to eat beef watered with 0.1% phenol.

HAWLEY (1977) reviewed the use and toxicity of a wide range of mine-mill reagents in the province of Ontario which provides some insight into the environmental sensitivity of a wide range of organic reagents. This document, which is too extensive to be summarized here, is available from:

JOHN R. HAWLEY
Head, Mining, Metallurgy, and Inorganic
Chemistry Unit
Quality Protection Section
Water Resources Branch
Ontario Ministry of the Environment
1-4 St. Clair Avenue West
Toronto, Ontario

DAVIS, et al. (1976) reviewed the environmental problems of flotation reagents in mineral processing plant tailings water.

REGULATORY LIMITS ON OIL, GREASE, AND ORGANICS IN MINE-MILL EFFLUENTS

Organic substances currently are generally not listed on mine-mill operating permits. The Colorado Dept. of Health - Water Quality Control Division, which polices mine-mill effluents, currently does not test effluents for organic constituents, oils, or greases, although the U.S. EPA recently fined one Colorado operator for spilling PCB from a transformer.

During the course of this investigation, the only cases where organics were found to be included in mine-mill permits or regional/national effluent permits were:

	Maximum Average 30d	Maximum 24-Hour Average	ORGANICS Maximum Grab Sample
Con Mine, N.W.T., Oil/Grease	-	-	5.0 ppm
South Africa Proposed New Regulation for Witwatersrand Phenolic Compounds	-	-	0.1 ppm
South Africa SABS Public Water Supply, Odor/Taste	-	-	Not Objectionable

The California Regional Water Quality Control Board - Central Valley Region NPDES No. CA0081477 waste discharge requirements for the McLaughlin Mine, HOMESTAKE MINING COMPANY, permit merely states:

> "...the discharge shall not cause visible oil, grease, scum, foam, floating, or suspended material in the receiving waters or watercourses."

EFFECTS OF ORGANICS ON MINE-MILL PERFORMANCE

VIVIERS (1980) reviewed several cases where organic contaminants in recycled water interfered with mineral flotation processes and included a short literature survey. Even small amounts of some organic contaminants can have a significant impact on metallurgical efficiency or could result in environmental impacts that have to be taken into account. For example:

1) Ion exchange was selected over solvent extraction for uranium at the Agnew Lake Mine in Canada because of environmental objections to small amounts of SX reagent reaching a local trout stream in tailings decant solution. Metallurgically, SX would have been the logical choice.

2) At the HOMESTAKE MINING COMPANY, Lead, South Dakota, in late 1984, an oil slick was observed floating on the surface of CIP adsorption tanks. Diesel-driven equipment is employed underground to mine the ore. Carbon adsorption process performance would be severely impacted by the presence of oil in the pulp as carbon selectively adsorbs gold and is thereby rendered hydrophobic. This occurrence at a leading U.S. gold mining/milling operation is not at all unique and must be guarded against wherever mechanical equipment is used in mines.

Even where an underground conveyor system is installed, overzealous greasers can introduce excess grease to an ore.

3) At PRESIDENT BRAND G.M. CO. LTD. in Welkom, South Africa, part of the initially poor performance when the calcine CIP circuit was started up was ascribed to organic species in the recycled water used at the plant.

4) Flotation of gold and pyrite from Witwatersrand ores is believed by operators to be adversely affected when treated sewage water is blended into the water supply. Extensive tests have been performed at the ANGLO AMERICAN RESEARCH LABORATORIES, but results show sporadic reproducibility.

5) Testwork at ANGLOVAAL RESEARCH LABORATORIES has indicated that if sewage is treated by the conventional biofilter process the effluent, when used for flotation, results in impaired recovery of gold and pyrite. However, if treated by the activated sludge process, the water can be used in flotation without these problems. However, the tests were preliminary and require confirmation on more samples. The quality of treated sewage effluents from the two plants has subsequently been shown to be highly variable. A trip report on the STILFONTEIN Sewage Treatment Works in Appendix I provides data on the variability of water quality from municipal water treatment works in small towns.

6) At the PRESIDENT BRAND GOLD MINING CO. it has been found that if recycled water containing a blend of treated sewage effluent is used in the flotation plant, recovery of gold and pyrite may drop sporadically. If, however, the water is first used as cooling water in the Peabody scrubber which is installed in the roaster-acid plant gas entrainment system, then this negative effect on flotation is avoided. In the Peabody scrubber, the water is exposed to heat and SO_2 gas.

7) Chris Flemming of the Council for Mineral Technology, MINTEK, in Johannesburg, undertook a test in which carbon adsorption efficiency for gold recovery was tested after addition of each of a long list of commonly used organic reagents such as flotation reagents, flocculants, etc. Although in most cases the effects were negative, there were some cases in which gold adsorption and recovery was actually enhanced.

8) At GIANT YELLOWKNIFE MINES, a gold mine at Yellowknife, Northwest Territories of Canada, carbon in leach is used to recover gold from precipitator dust collected from the roaster gas entrainment system. This dust contains arsenic and iron oxide as well as other constituents. GIANT YELLOWKNIFE adds 0.8 lbs. of an amine acetate flotation reagent which is found to improve leach recoveries. Falconbridge believes that the amine acetate helps release gold from arsenic compounds in the dust.

9) At NORANDA's Mattabi operations, recycled water accounts for about 70-75% of total mill water needs. Collector is used as sparingly as possible as otherwise it follows the recycle water back to the front of the process where it causes problems in that selectivity of the primary flotation step is interferred with.

10) Several gold mill tailings dumps have been used over the years as convenient unofficial dump sites for waste oils by industry. Now that this tailings material is being processed again, this oil can cause problems in the carbon adsorption of gold. Wherever tailings are to be reprocessed, operators must always be on the lookout for oils as in some cases the contaminated sand may be segregated to minimize the problem.

11) When TENNECO's Borealis heap leach operation started up in Nevada, the clarification filter and zinc precipitate filter press was soon clogged up by an oily substance. It was found to be related to an aqueous emulsion washed off the asphalt pad surface by the pregnant solution. The type of asphalt sealant used turned out to be critical. In this case, zinc precipitation was used, but carbon adsorption would experience equal problems if the carbon was exposed to the same organics. Larry Hartzog of BECHTEL, San Francisco, investigated the problem and may have further insights.

12) When surface ore in a desert environment is heap leached using alkaline cyanide, occasionally organics can be introduced to the ore and hence solutions by creosote bush roots that are crushed with the ore and saponified by the alkali solution.

13) In one of the base metal mines where backfill is used, concern was expressed that organics in the water resulted in poor cement strength of the backfilled stopes.

14) At AMAX's Mount Emmons project, Crested Butte, Colorado, control of the plant treating minewater was interfered with by a coating of saponified oil that coated the pH probes whenever underground exploration/development activity was in progress. This was found to be the result of hydraulic fluids from underground equipment reacting with lime used for pH adjustment to yield a suspension which coated on the probe.

15) Organic flotation reagent degradation products were detected in mill effluents at the New Lead Belt, Missouri, by JENNETT and WIXSON (1973), JENNETT and WIXSON (1977), JENNETT and CALLIER (1977), and discussed in general by JENNETT (1976).

According to JENNETT and CALLIER (1977), organics extracted from samples of effluent were taken from a control stream and two different mill treatment systems were generally $CHCl_3$ soluble and were extracted more efficiently when the

extractions were performed between pH 3 and 7. Data strongly implied that rainfall and runoff dilutes trace organics from the two mills. There was also no evidence of a correlation between pH, turbidity, alkalinity, COD, etc., and the level of trace organics extracted from a sample.

In spite of having identified organic species in mill effluents which are partly recycled, at least in the case of one of the mills, no evidence of a negative effect on mineral recovery has been identified at the New Lead Belt mines of AMAX or ST. JOE MINERALS.

16) Various types of dust control chemicals are used around open pit mines and haulways. One product that is believed to be very effective is a range of ligno-sulfonates which is a by-product of the pulp and paper industry. One industry observer has indicated that this type of product plays havoc with flotation performance if the roadway is ultimately mined and milled. The effect of ligno sulfonates on flotation is discussed in more detail in Chapter 54.

BARBARA A. KREBS
Technical Consultant - Metallurgy
ARCO Corp.
2397 515 South Flower Street
Los Angeles, CA 90071
(213) 486-3511

CONKLIN PRODUCTS offers a reasonably cost-effective liquid dust control product. This liquid contains a variety of glycols and alcohols and, as such, would likely interfere with carbon adsorption of gold from pulps or solutions if it were to get into the ore or process water at such operations, but this cannot be said with any certainty unless tested.

17) Several years ago when the mining camp serving the Climax Molybdenum Mine at Climax, Colorado, was located at Climax, mining camp sewage was discharged with tailings. Tailings solution was decanted for reuse in the mill. However, because of interference in flotation by organic species added with the sewage, activated carbon was added to remove them. Since the mining camp has been relocated to Leadville, sewage is no longer discharged with tailings, and carbon addition is no longer necessary. Climax Molybdenum staff demonstrated the effect on flotation recovery when sewage was discharged with tailings in the laboratory; however, quantitative data is not available as these tests were performed many years ago.

18) FISHER and RUDY (1976) carried out tests to determine which constituents of waste water, such as secondary treated sewage effluent, were detrimental to the flotation of molybdenite and copper sulfides. These tests included treating the waste water in Barnstead cartridges to remove specific groups of ions and assessment of the effect on the flotation metallurgy of the treated water.

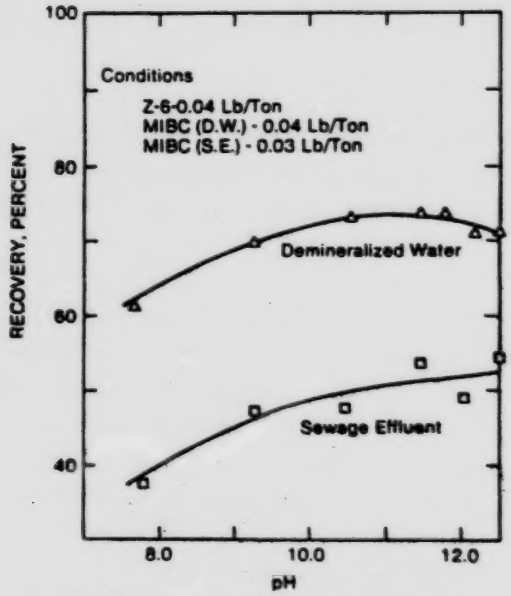


Fig 1 Molybdenite recovery versus pH for demineralized water (D W.) and sewage effluent (S.E.). After Fisher and Rudy[1]

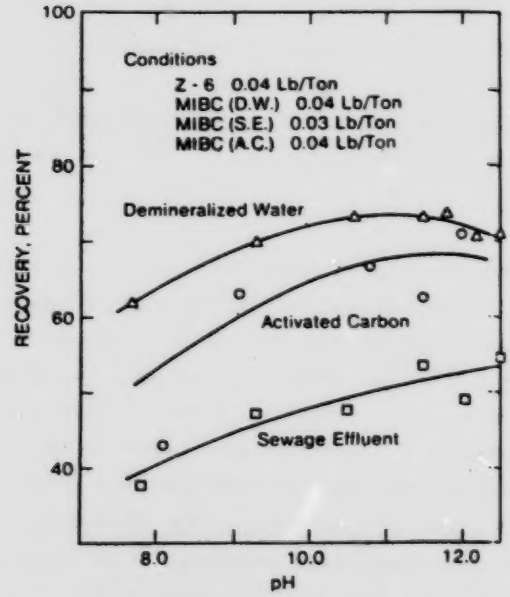


Fig. 2 Molybdenite recovery versus pH for demineralized water (D.W.), sewage effluent (S.E.) and activated carbon (A.C.). After Fisher and Rudy[1]

Some of the experimental results obtained from the flotation tests are illustrated in their Figures 1 and 2. These results were summarized as follows:

a) The use of sewage effluent caused a decrease in recovery of 16.2% for MoS_2 and 2.4% for copper sulfides.

b) Dilution of the sewage effluent with distilled water resulted in a proportionate decrease in the detrimental effects associated with the use of waste water effluent.

c) Removal of cations from the sewage effluent resulted in a slight improvement of the recoveries.

d) Removal of the anions from the sewage effluent resulted in the most significant improvement in copper and molybdenum recovery.

e) Foam fractionation to remove surface-active material did not improve the quality of sewage effluent and, hence, the recoveries were at the same level as with untreated sewage effluent.

f) Tertiary treatment of sewage effluent by activated carbon resulted in a significant improvement in water quality in terms of recovery of metals but not to the level achieved by removal of anionic species.

Similar results have been reported by many concentrators that have attempted to recycle process water, but published data on the effects of recycle water are scarce. All known data demonstrate a strong influence of soluble water constituents on the recovery of molybdenite and provided the basis for a more detailed review by HOOVER (Post 1979), which is inserted in Chapter 54 on water quality effects in flotation processes.

Apart from the important effects mentioned above, it is known that hydrophilic polymers and ligninsulfonates are excellent depressants for molybdenite, e.g., dextrin, starch, glue, dyes, and condensation products of aldehydic substances with aromatic sulfonic acids. In addition, tannic and humic acids known to exist in recycle mill waters are known to depress molybdenite.

One of the strongest depressants of molybdenite are ferric ions which are commonly found in recycle mill solutions, especially in the presence of calcium. Colloidal slimes also have very great impact on molybdenite supression.

19) HISCOX and BUZA (1975) described a new system using lignin sulfonate to depress molybdenum sulfide. The ANACONDA CO.'s Metallurgical Research Dept. discovered

that large quantities of lignin sulfonate in combination with a high pH milk-of-lime depressed the molybdenite while allowing talcs and clays to float.

Elsewhere, where small quantities of lignins got into process water due to decay of underground timbers, the froth in flotation plants is reported to have become uncontrollable, and the concentrate at at least one copper moly mill is said to have spilled to the floor sump when lignin from natural sources got into the water.

20) Many gold leaching plants employ air agitation in pachucas. Similarly, air agitation may be used for carbon-in-pulp adsorption vessel agitation. Many air compressors employ oil lubricated pistons and unless the compressed air is cleaned of oil through use of an oil trap and filter, it will introduce oils to the pulp in the leach and CIP stages. This oil will blind the activated carbon and interfere with gold adsorption and recoveries.

21) At FALCONBRIDGE's Onaping Mine, Onaping, Ontario, small volumes of raw sewage are discharged to a settling pond together with underground minewater to which NaOH is added to precipitate nickel. The sewage settles to the bottom of the pond together with $Ni(OH)_2$ which is precipitated and accumulates as a bottom layer. As the sewage undergoes bacterial degeneration, gases (methane) are generated which attach to particles of bottom sediment. As a result, pieces of sediment rich in nickel float to the surface and leave the settling pond with decant solution, ultimately to find their way to the main tailings decant system and the effluent discharge to the receiving waters where a maximum limit for Ni has been set at 1 ppm. Not much of the floated sediment running 5-10% Ni need get into a water sample to wreak havoc with monitored results.

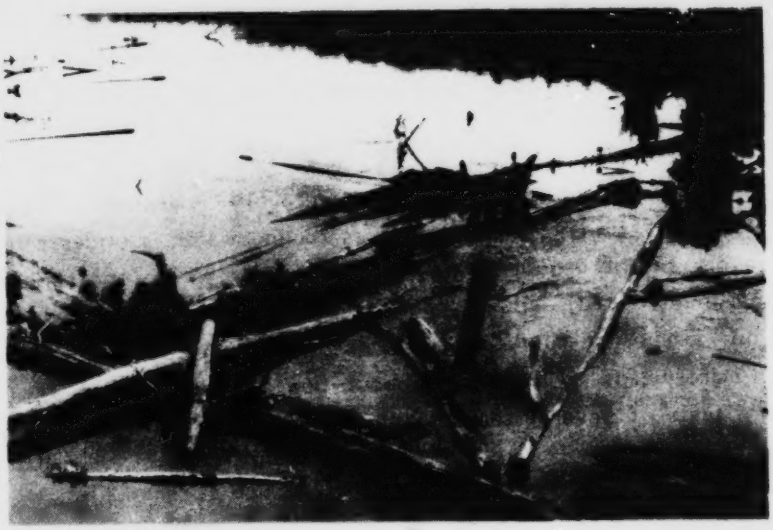
PREVENTION OF ORGANICS CONTAMINATION OF PROCESS WATER/EFFLUENTS

Very often the contamination of metallurgical process water and effluents can be prevented by eliminating the source of the contamination. This may require making the mining or maintenance department aware of the impact of malpractices on overall metallurgical efficiency and profitability.

1. At INCO LTD.'s Copper Cliff operations, a survey of supplies consumed underground led to the observation that the consumption of hydraulic fluids was excessive. Further investigation led to the discovery that hydraulic lines on underground equipment were rupturing far too frequently despite the fact that operating pressures were within limits. It was established that the pressure ratings of the lines at elevated underground temperatures had to be reduced. Replacement of hydraulic lines by a more expensive version solved the problem, reduced

consumption of hydraulic lines and fluid, and resulted in an improvement in metallurgical performance.

2. Very often, mine tailings and decanted tailings water are impounded in densely wooded terrain. One recommendation is to avoid contact between water that is to be recycled to the mill or discharged as an effluent with rotting vegetation and timbers. Rotting vegetation can introduce humic acids into water which chelate metals and may interfere with metal or mineral recovery processes.



3. It is essential that underground mine supervisors and maintenance/lubrication crews be made aware of the costly consequences of lubrication oil, fuel, hydraulic and cleaning fluids, greases, etc. being discarded or applied excessively in the mine. Through good housekeeping, education, and discipline, excess organics can be kept out of the ore and minewater in the first place. In observing lubrication crews going underground carrying grease canisters, it is interesting to note how many bring a used or half-used canister back out of the mine. The question remains as to the fate of the unused grease and the empty canisters that remain in the mine.

4. Mine tailings areas should always be fenced off and/or patrolled. Today's tailings can well become tomorrow's ore and should be inaccessible to the dumping of toxic or oily wastes by local service stations, etc.

5. Mine management can do a lot to avoid organic contamination of ore and water through surveying the quantities and fate of all supplies consumed in the mine as well as the disposal practices of waste from workshops and maintenance areas.

6. If surfactants are used for dust control, the possible effect of these on metallurgical processes should be examined in the laboratoy and in the field through appropriate testing. This could allow potential problems to be avoided through appropriate product screening.

7. On the Witwatersrand, a new type of hydraulic power is under development in which the hydraulic head of water from the surface to the underground workings is used to hydraulically power mine drills and other tools as well as to generate hydropower underground. Replacement of organic hydraulic fluid with water will in fact avoid a considerable potential for contamination of ore and mine water with hydrocarbons from leaking hydraulic equipment and lines. However, the water used will be mixed with an additive, and it remains to be seen what the effect of this additive is on metallurgical processes.

8. At all Witwatersrand gold and uranium recovery operations, the use of treated municipal sewage effluents in the mines as cooling water is under consideration. Due to the severe recent drought, uses for this water within the mine/mill complex are also being investigated. In gold and uranium circuits, there have been no adverse effects on some mine-mill complexes (see Vaal Reefs). However, for flotation circuits, more needs to be known about how the sewage was treated and careful laboratory tests of several samples undertaken to be sure that it is suitable on a site-by-site basis.

TREATMENT FOR REMOVAL OF ORGANICS

Although prevention is better than cure, organics can be removed from water in the following ways:

1) Physical Skimmers
2) Adsorption Devices
3) Activated Carbon Treatment
4) Dissolved Air Flotation
5) Biological Processes

PHYSICAL SKIMMERS

Physical skimming devices generally are applicable for the recovery of petrochemicals from small water impoundments containing relatively high concentrations of imiscible organics which float on the surface.

Skimmers of different sizes and capacities are offered by:

1) SLICKBAR, INC.
250 Pequot Avenue
Southport, CT 06490
(203) 255-2601
Telex: 043458

2) MEGATOR CORP.
562 Alpha Drive
Pittsburgh, PA 15238
(412) 963-9200
(800) 245-6211

3) OIL RECOVERY SYSTEMS, INC.
1420 Providence Highway
Suite 128
Norwood, MA 02062

4) PRICE-DANNELL, INC. OF AL
1135-F Hutson Drive
Mobile, AL 36609

5) HUDSON INDUSTRIES
Department P
Box 2212
Hudson, OH 44236

6) FRAMCO
9 Tipping Drive
Branford, CT 06405

ADSORPTION DEVICES

For example, small amounts of oil can be removed from the surface of a water impoundment by installing a floating adsorbant boom across the overflow weir of a settling pond.

At AMAX's Mount Emmons water treatment plant, an adsorbant boom is installed on the settling pond. It was supplied by:

1) ENTROL ENVIRONMENTAL SERVICES, INC.
1390 East Burnett Street
Signal Hill, CA 90806
(213) 424-6016

2) ENTROL ENVIRONMENTAL SERVICES, INC.
1303 Canal Avenue
Richmond, CA 94804
(415) 234-3887

This adsorbant boom is effective in removing a small quantity of floating hydraulic oil from minewater which otherwise ultimately saponifies at pH adjustment by lime and coats the pH probe resulting in malfunction of the automatic pH adjustment system.

ORGANICS CONTAINMENT BOOMS

Floating organics spills can be contained using floating booms. Suppliers include:

1) SLICKBAR, INC.
250 Pequot Avenue
Southport, CT 06490
(203) 255-2601
Telex: 643458

2) GLOBE INTERNATIONAL, INC.
Box 1062
Buffalo, NY 14240
(They also supply flameproof spill barriers.)

OIL RECOVERY SYSTEMS

By recovering usable oil from waste crankcase oil, for example, less waste oil requiring disposal is generated. The use of such systems may result in less chance for waste oil dumping on site with possible future metallurgical interferences. Oil skimmers are used in many underground mines including ST. JOE MINERALS' Fletcher Mine at Boss, Missouri.

Various oil reclamation equipment suppliers include:

1) AQUANETICS, INC.
111 Milbar Blvd.
Farmingdale, NY 11735

2) MEGATOR CORP.
562 Alpha Drive
Pittsburgh, PA 15238

ORGANIC SOLVENT REMOVAL AND RECOVERY

Air stripping removal of volatile organics from water:

1) NEPCCO EQUIPMENT DIVISION
29 Wall Street
Foxboro, MA 02035

Activated charcoal adsorption:

1) DEDERT CORPORATION
20000 Governor's Drive
Olympia Fields, IL 60461
(312) 747-7000
Telex: 25-3889

CARBON ADSORPTION SYSTEMS

1) DEDERT CORPORATION
20000 Governor's Drive
Olympia Fields, IL 60461
(312) 747-7000

2) CALGON MOBILE TREATMENT SERVICE
Calgon Corporation
Activated Carbon Division
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
William D. Faulkner

BIOLOGICAL PROCESSES

Biodegradable organic constituents are routinely removed from wastewater in more sophisticated sewage treatment plants, and books have been written on the subject. Two commonly used approaches are biofilters, usually trickle filters, and activated sludge plants. Both of these seem to depend on relatively high nutrient concentrations in feedwater. An important report on this subject has been prepared by VIVIERS (1980), and water impoundments allow bacterial action to remove some of the undesirable organics in reclaimed tailings decant water prior to recycle to the plant although not one case was found where this had been quantitatively evaluated. Some industry observers have simply observed that the aging of recycled water in a tailings dam results in improved metallurgy. VIVIERS (1980) refers to a R500,000 aging pond installed for this purpose at the Black Mountain Cu-Pb-Zn recovery operation in South Africa.

A most interesting application of an engineered marsh for sewage treatment at a small installation such as a mine-mill complex was demonstrated in Canada where a cattail bog was engineered and tested as a demonstration unit. More information on this innovative biological system is described by BLACK (?) and WILE, PALMATEER, and MILLER (?), or from:

ONTARIO MINISTRY OF THE ENVIRONMENT
135 St. Clair Avenue West
Toronto, Ontario M4V 1P5
S. A. Black
I. Wile

The use of meander systems with plants and algae have been indicated to remove organic species from water with efficiency as described in the New Lead Belt Study by WIXSON (1977).

TREATMENT FOR REMOVAL OF ORGANICS

1. A Cu-Pb-Zn mill in Ontario recovers copper, lead, and zinc concentrates from a mixed sulfide ore. Activated carbon is or was in the past added to the Cu-Pb concentrate to remove any extraneous collectors before the Cu-Pb separation. Concentrate feed is heated to 120°F to disperse Minflo 5007 and conditioned for 30 minutes before further conditioning with SO_2. Then, a collector 2030 (a dithiocarbamate) is added to float the copper from lead. The addition of activated carbon helps achieve a better Pb-Cu separation. Precise details have not been confirmed by the parent company.

2. This mill operates/operated its primary bulk float at starvation collector levels. Too much collector at the front end ruins selectivity of Cu-Pb versus zinc. Some Cu-Pb recovery is sacrificed to keep zinc out of the copper concentrate. Presumably, the addition of carbon helps remove any excess collector that might otherwise return to the front of the process with recycle water although presumably excess collector would be lost with the zinc concentrate solids, and very little would follow the solution.

3. AMAX at their Climax Molybdenum Mine in Colorado formerly discharged raw sewage from their Climax mining camp with tailings. To avoid metallurgical interference at the float plant, activated charcoal was added to tailings to remove organic species from the decanted tailings water which is recycled to the mill. After the mining camp was moved to Leadville, however, sewage discharge to tailings stopped, and it was no longer necessary to add carbon. The carbon addition was last practised many years ago, and the old data on the effect on mill recoveries is no longer available.

4. Many mine-mill complexes employ very large mill tailings dams and water impoundments. Aging of water that is to be recycled and contact with mill tailings solids appears to render the water more suitable for use in mineral processing and metallurgical operations. This is certainly also the opinion of BOLIDEN METALL AB.

5. Where treated sewage water is to be used in a mill, particularly one using flotation processes, possibly installation of a well-run activated sludge process in the sewage plant would render the water quality suitable for use in the mill without losing metallurgical efficiency. Recently, AFROX LIMITED in South Africa introduced their VITOX process which enhances biological oxidation of organics in sewage plants by injecting oxygen into the system ahead of biofilters. One such system was installed in the STILFONTEIN GOLD MINING COMPANY hostel sewage treatment plant. More information is available from:

AFROX LIMITED
Post Office Box 4100
Germiston South 1411
(011) 825-1355
Telex: 4-27090
Jeanette Lewis

To date, no information has been developed on the effect of VITOX on water quality at Stilfontein as far as its possible impact on flotation recovery of gold and pyrite, as far as the use of reclaimed sewage effluent in the mill is concerned.

Since VITOX would be rendered unpractical at many mine-mill complexes due to the distance from an oxygen supply, new oxygen generation technology may prove of interest. ALBANY INTERNATIONAL CORP. has recently developed a reverse-osmosis type membrane for oxygen enrichment from air at a relatively low pressure (100-200 psi). More information is available from:

ALBANY INTERNATIONAL CORP.
Membrane Development Venture
921 Providence Highway
Norwood, MA 02062
(617) 796-6310
Alla Kan
Myron J. Coplan
General Manager

6. At the AMAX-Homestake lead zinc mill at Buick, Missouri, effluents are discharged to the river system after flowing through an artificial meander system. WIXSON (1977), in a report on the environmental impact of mining and milling on the New Lead Belt, showed data developed by W. C. Jennett and coworkers that organics in the effluent are effectively removed by algae in the meander system. A lead to additional sources of information can be obtained from:

DR. BOBBY G. WIXSON
Director of Environmental Health
Center for International Programs
and Studies
University of Missouri - Rolla
Rolla, MO 65401
(314) 341-4208/341-4483

7. Underground hydraulic fluid leaks are not identified as a cause of metallurgical efficiency loss in the mills on the Witwatersrand although undoubtably any hydraulic fluids finding their way into ore underground would have an impact on pyrite-gold flotation and on CIP adsorption efficiency.

Nevertheless, motivated by economic incentives, the Chamber of Mines of South Africa has successfully developed hydraulically powered underground equipment which use water instead of organic liquids such as hydraulic fluid. Chilled water is pumped underground to cool the work environment, and the hydrostatic head of this

water is adequate to drive rockdrills and other equipment. Replacement of organic hydraulic fluids with water-driven tools may also reduce the opportunities for contamination underground due to line breaks, leaks, and from maintenance areas. As mentioned above, this hydraulic water is mixed with an additive.

8. At the Simmer and Jack secton of SIMMERGO LTD., a CIP plant was installed in 1982 to recover gold from reclaimed tailings on the Witwatersrand just east of Johannesburg. The tailings pulp was brought into contact with carbon on two dummy CIP contactors before cyanidation with the intention of removing organics from the pulp that otherwise would interfere with gold adsorption in the CIP section after cyanidation. It is not yet known how effective this step was. More information could be requested from:

EAST RAND GOLD AND URANIUM
COMPANY LTD.
Post Office Box 890
Brakpan 1540
(011) 559050
Harry Brown,
Project Manager

9. GENCOR, at the Chemwes tailings treatment plant at Stilfontein, Transvaal, has reputedly tested organics removal by carbon adsorption ahead of cyanidation and CIP. It is understood that the pilot plant operated in 1983-1984 to test this process performed very well. The GENCOR contacts with knowledge of these tests are:

GENCOR LTD.
Box 1820
Marshalltown 2107
(011) 836-1121
P. Van Aswegen

CHEMWES LTD.
Post Office Stilfontein,
Transvaal
(011) 41131
Piet Haasbroek

10. GENCOR at Buffelsfontein Gold Mining Co. Ltd. adds powdered activated carbon to repulped gold plant filter tailings to recovery incremental gold. The gold on carbons is recovered in the subsequent flotation step. If there were any organic contaminants in the pulp, these would also conveniently be removed ahead of the flotation plant. This process will be described by VAN ASWEGEN (1985).

11. When carbon adsorption is employed for gold-silver recovery, it is essential to keep oils and greases from the feed pulp and solutions to avoid fouling carbon as mentioned above. If compressed air is used for pre-aeration of the pulp to oxidize phmhotite, or for cyanidation leach agitation or for CIP adsorption agitation, or even for carbon transfer within the plant, then it is important that the air used for the

purpose be passed through an oil trap and filter to remove compressor oil that is usually entrained.

12. Dissolved air flotation is effective in removing organic emulsions from aqueous streams. For example, DAF can be used effectively to recover entrained solvent extraction organics from raffinates. More information on this application which has been demonstrated at copper recovery plants would be available from:

POLLUTION CONTROL ENGINEERING, INC.
10751 South Lakewood Blvd.
Downey, CA 90241
(213) 861-1297

13. Humic acids derived from decaying organic matter of plant origin and fumic acids derived from decaying animal matter may, if present in process or effluent waters, result in the chelation of metals rendering them less easily removed from effluents by conventional lime-settle-filter processes. They may also interfere in some metallurgical recovery processes although no hard evidence was encountered during this investigation.

The Rohm & Haas Company has developed an experimental polymeric coagulant XE-392 which is said to be effective for humic acid removal in addition to its primary design function of removing trihalomethanes from potable water. In 1983 this product was not yet on the market, but further inquiry could be direct to:

ROHM & HAAS COMPANY
Independence Mall West
Philadelphia, PA 19105
(215) 592-2817
Fred Flor

14. Solvent extraction organics are often lost in crud which is generated in SX plants in both copper and uranium recovery operations. Often this CRUD is dumped, and it can introduce organic contaminants to surface and groundwater.

A company in South Africa has developed a process employing pressure filtration followed by phase separation in a settler to recover solvent extraction reagents from CRUD:

EFFLUENT CONTROL (PTY) LTD.
Post Office Box 586
Isando 1600
South Africa
(011) 974-1131
Telex: 8-9062 SA

15. VIVIERS (1980) describes laboratory experiments to determine whether biologically activated sludge can be used for the removal of organic contaminants from flotation plant recycle waters. A synthetic sewage spiked with isopropyl thionocarbamate (Z-200) and sodium ethyl xanthate (SEX) was passed through a small test plant that had a capacity of 2.5 litres. When the concentration of SEX in the sewage was 20 ppm, the test plant removed it completely. No more than 23 percent of the Z-200 could be removed under the typical conditions described.

VIVERS (1980) also provides an interesting literature review of the effects of reagents in recycled process water described for other cases and measures adopted for their removal. Workers interested in this aspect could get in touch with him at:

J.M.P. VIVIERS
Council for Mineral Technology MINTEK
Post Office Box X3015
Randburg 2125
South Africa
(011) 793-3511

16. Water quality problems necessitated a change in metallurgical process for the separation of copper-molybdenum at San Manuel, New Mexico. The San Manuel-developed process, which employed $FeCl_3$ or H_2O_2 for the Cu-Mo separation from a bulk sulfide concentrate, had to be abandoned in favor of the addition of NaHS which is now the more commonly employed process for Cu-Mo separation by flotation in the southwestern U.S.A.

The reason for this change and the reason their process did not work as well as expected in the field was that when recycled mine and mill tailings water was used, oil contamination severely impacted the $FeCl_3$ and H_2O_2 addition process efficiency but had a much less pronounced effect on the NaHS depressant process.

More information may be available from Richard Johnson who is now at:

FREEPORT GOLD COMPANY
Mountain City Star Route
Elko, NV 89801
(702) 738-9221

17. FISHER and RUDY (1978) reported results of an investigation of municipal waste water constituents detrimental to froth flotation recovery of copper and molybdenum sulfides. They found that the substitution of secondary treated sewage effluent for normal water in laboratory tests simulating froth flotation recovery of copper and molybdenum sulfides caused a significant deterioration. First, a voluminous froth that is difficult to control and has little mineral carrying ability was generated, even in the absence of a frothing agent. Second, sewage effluent caused a small but significant loss in copper recovery and a large loss in molybdenum recovery.

Removal of surfactants from sewage effluent by foam fractionation eliminated the unmanagable froth but had no effect on the loss in metal recovery. The component of sewage effluent responsible for the loss in metal recovery was found to be an anionic organic substance that has an effect similar to humic acid. One method of water conservation can be realized by the use of municipal waste water for purposes that do not require high quality water. In areas where sizable mining activity is present adjacent to a city, it may be possible to substitute municipal waste water for the surface and ground water normally used in the processing circuits. This investigation was prompted by such a possibility in Tucson, Arizona. These authors were unaware of the successful use of activated carbon to overcome observed problems as practiced years ago at the Climax Molybdenum Mine.

17. South African uranium plant operators avoid the use of cationic flocculants for solid/liquid separation ahead of SX recovery plants. The reason for this is not clear to SOUTH AFRICAN CYANIMID staff. Gold plants in South Africa use cationic flocculants for clarification. Cationic flocculants are also used in uranium plants by NUCLEBAS BRAZIL and some Canadian and French operations. Nevertheless, tradition has it in South Africa that cationic organic flocculants interfere with solvent extraction recovery of uranium. More information may be available from:

S. A. CYANAMID PTY LTD.
Post Office Box 7552
Johannesburg 2000
(011) 538830

AMERICAN CYANAMID
International Chemical Division
Wayne, NJ
(203) 831-2000
Arnold Day
Chief Metallurgist

19. SUPERCHARGED OXYGENATED ACTIVATED SLUDGE PROCESS

MEGOX Process - A small activated sludge sewage plant operated on pure O_2 employing a single tank to process the sludge. The process destroys NH_3 and 70-90% of incoming organics depending on residence time. The idea is to install small rougher sewage plants at the site of effluent generators which otherwise could overload municipal plants.

Municipal plants charge their industry clients a fee based on load and flowrate of sewage discharge. By knocking out the worst of the load, the cost of municipal service will be reduced.

MEGOX is ideal for phenol removal as municipal plants do not want phenols.

The MEGOX process is offered by:

AFROX LTD.
Post Office Box 4100
Germiston South 1411
(011) 825-1355
Jeanette Lewis
Preston White

The vendors claim that the MEGOX process destroys cyanide generated in coal coking process effluents.

WIMPY UNOX PROCESS - In the U.S.A. a similar process known as the Wimpy unox process is offered by the UNION CARBIDE CORPORATION. It is apparently very similar to the MEGOX process except that it employs an enclosed acitvated sludge reactor with a pure oxygen atmosphere above the sludge. Oxygen levels in water saturated with air can reach 8 mg/l O_2 but with an oxygen atmosphere, the dissolved oxygen levels are boosted to 40 mg O_2/l. Oxygen dissolution in water obeys Henry's Law:

$$[O_2] \text{ dissolved} \propto p[O_2] \text{ atmosphere over water.}$$

AFROX VITOX PROCESS - AFROX has also developed a patented design to draw sludge from the bottom of the reactor and to oxygenate it using a Bell oxygenator. They have also patented a Venturi Vitox O_2 injector. Oxygen is sucked into the venturi for flash mixing with sludge pumped through the venturi. The oxygenated sludge is then sparged back into the tank via a special nozzle.

The VITOX nozzle air dissolution technique can be employed also for CO_2 dissolution. CO_2 used for pH adjustment does not raise the TDS.

VITOX is installed at several effluent dams for odor control of anaerobic effluents.

MEASUREMENT OF ORGANICS IN WATER

The measurement of organics in process solutions and effluent is relatively difficult largely because there are so many different kinds of organic compounds. This task is partly described in STANDARD METHODS (1960).

This aspect was not examined in any depth. It was established that the Bureau of Mines in Salt Lake City, Utah, had been involved in a project to develop methods to measure

Sorbent Rolls
E 150

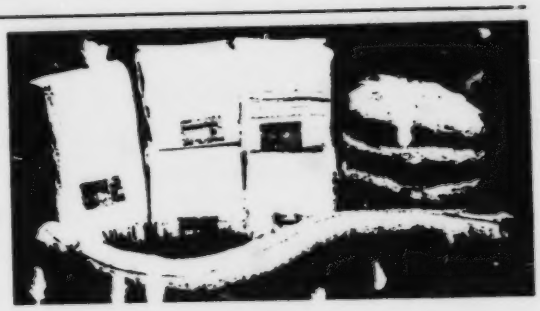
Ergon Sorbent Rolls are designed for use in sumps, along shorelines and ground areas, and for open-water control and recovery of rainbow sheens and thin slicks. They may be used to protect floors and walkways where chemical or oil leakage is apt to occur. Sorbent rolls ar quickly deployed and measure 36"x150'x⅜".

Recyclability

Ergon Oil Sorbent can be reused 30 to 50 times, depending upon the method of oil removal used. Oil can be removed by wringer, centrifuge, or solvents. Over 90% of absorbed oil may be removed without damaging the sorbent material. This capability reduces the amount of sorbent material needed to effectively respond to spills.

Availability

With storage warehouses throughout the Southern United States and dealers in strategic locations throughout the country, you have 24 hour access to Ergon Oil Sorbents.



For availability nearest your operations write or call:

Ergon Environmental

P.O. Drawer 1639
Jackson, MS
39205

(601)948-3472

organics. On investigation it was found that, in fact, this project had been cancelled shortly after it was started.

SALT LAKE CITY RESEARCH CENTER
Bureau of Mines
U.S. Dept. of the Interior
Salt Lake City, UT 84108
(801) 524-6100
J. L. Hulatt

Possibly the best sources of technology and knowhow on the measurement of organics in water might be the companies that manufacture flotation reagents and other chemicals used in mineral processing, for example:

AMERICAN CYANAMID COMPANY
Stamford Research Laboratories
Post Office Box 60
Stamford, CT 06904-0060
(203) 348-7331
Terence Foster
International Technical Sales Service

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CHAPTER 47

PHOSPHATE REMOVAL PO_4^{3-}

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INTRODUCTION

Phosphate contamination of surface waters has become of major concern in most population centers. Phosphates, along with nitrogenous compounds, are key nutrient building blocks not only for plants, but also for algae and bacteria. Excessive phosphate levels in water promote algae and bacterial growth to the extent that it can be so prolific that resulting biomass degradation demand for oxygen can exceed the rate at which oxygen can be replenished. The result is asphyxiation of aquatic life, aesthetic damage, and ugly odors. On the other hand, addition of lesser amounts of phosphate to water actually enhances aquatic life.

OCCURRENCE OF PHOSPHATES IN WATER

Phosphates enter the environment via treated and untreated sewage effluents. Phosphates enter sewage largely as a result of the use of phosphate-containing household detergents although the use of this type of detergent is increasingly being discouraged. Phosphates also enter surface waters in runoff from agricultural land fertilized with phosphate-containing plant foods. Lawn fertilizers containing phosphate applied in a built up area can enter the sewage system via runoff and stormwater drains. In some parts of the

world such as the Pretoria-Witwatersrand-Vereeniging-Sasolburg area of South Africa where sewage treatment plant effluents are discharged back to the drainage of the Vaal Dam and Vaal Dam water is effectively reused many times, the TDS, phosphate, and chloride levels are likely to increase. There is real concern in the Witwatersrand region about the need to reduce phosphate levels in effluents which drain into the Vaal Dam and other recreational bodies of water in the area such as the Hartebeespoort Dam. The Witwatersrand is but one of several such areas in the world.

As a result of this serious general concern for the need to limit phosphate levels in effluents, strict limits on phosphate have been legislated in many major metropolitan areas around the world.

Although mining districts (except the Witwatersrand) are in general relatively remote from heavily populated metropolitan areas, the rules governing phosphate levels in effluents may be generally applicable there as well.

PHOSPHATES IN MINE-MILL ENVIRONMENTS

In phosphate mining areas, one would expect relatively high levels of phosphate in surface and groundwaters. ROUSE and BROMWELL (1983) studied the phosphate levels in groundwater resources of the central Florida area and concluded that:

1) The mining and milling of phosphate rock and the subsequent acidification for production of phosphoric acid has the potential for severe impacts on groundwater resources of the central Florida area.

2) The area is, however, characterized by extremely high geochemical removal capacity which has resulted in the minimizaton of contamination. Contaminant plumes, characterized by reduced pH, elevated metal concentrations, saturated calcium sulfate solutions, and active geochemical mechanisms are only a few feet in lateral and vertical extent. The geochemical removal mechanisms are extremely efficient in removing radionuclides with the result that no significant radionuclide concentration is expected to advance more than a few meters from the source. Sulfate forms the best tracer to evaluate for contaminant mobility from phosphorus processing operatons.

More information could be requested from:

JIM V. ROUSE
President
Envirologic Systems International
2425 South Colorado Blvd.
Denver, CO 80222
(303) 759-2611

In non-phosphate mineral processing facilities, phosphate can enter the process water system through the addition of anti-scaling reagents which often consist of phosphonates which degrade to orthophosphate if dosed in excess of real needs to inhibit scale.

However, in the mine-mill environment, phosphates generally also enter the system primarily in sewage or sewage treatment plant effluents. This would be particularly noticable in those parts of the world where mining and mineral processing is more labor intensive, for example in Africa and South America. Witwatersrand mineworker hostels house several thousand miners each, and mine clothing is laundered using detergents. Detergents are used to scrub down the facilities and kitchens and may sometimes be used in indiscriminate quantities which introduce phosphate to the overall sewage system which ultimately may find its way to mine tailings or be discharged to the local drainage from where it ultimately finds its way to the Vaal River and/or Vaal Dam.

Professor M. J. Hamlin, Professor of Water Engineering at Birmingham University, who has extensive experience in water-related problems on the Witwatersrand, was quoted by STEWART, SVIRIDOV, and OLIVER (1981) as follows on the practicability of including nitrates and phosphates as pollution parameters in a mathematical model for salt and water balances for the region:

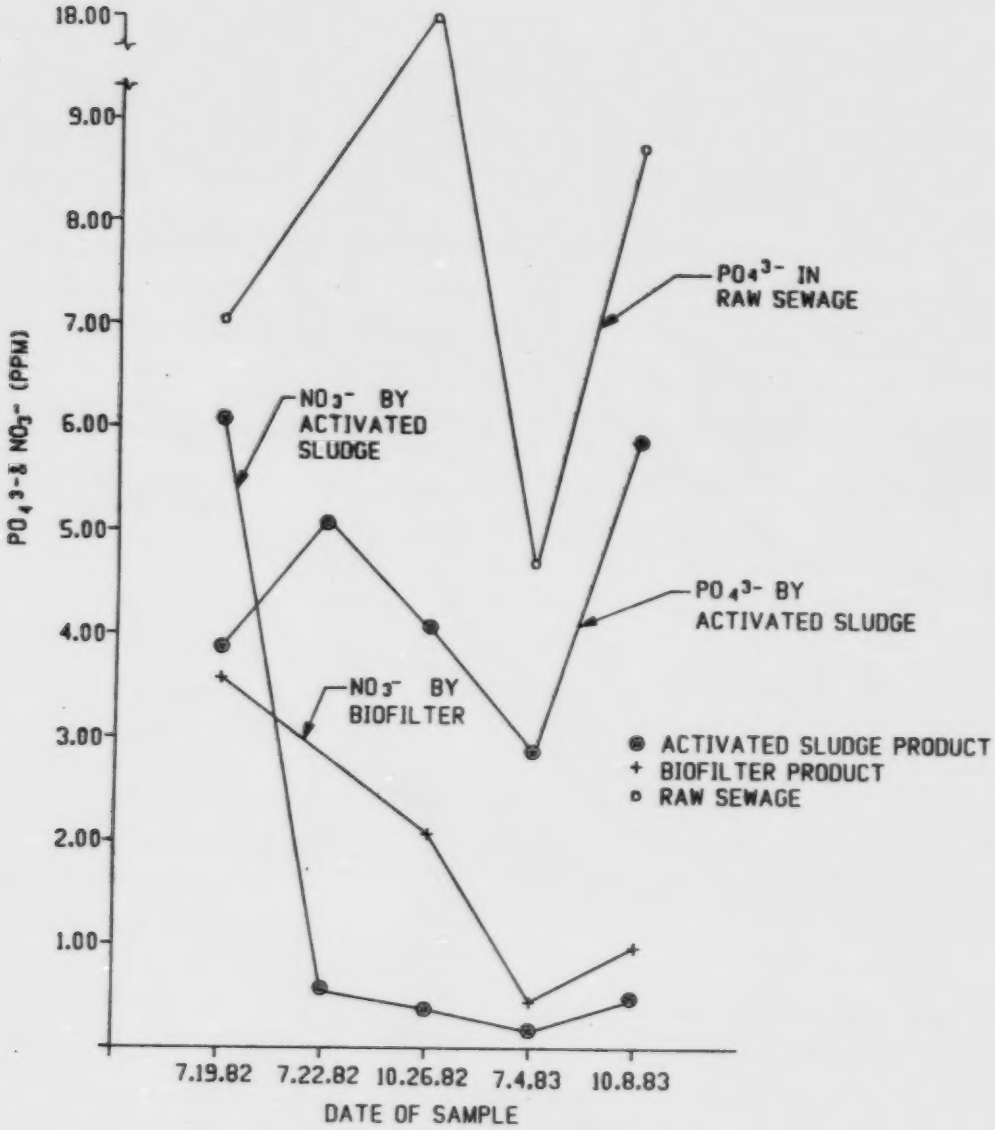
"The modelling of phosphates and nitrates is extremely complex and I have not been able to give more than superficial consideration to this problem. It is not clear what additional physical information may be necessary to construct adequate models, but if the Welkom Dam is to be built, I consider it to be essential to know how nutrients might build up in that reservoir and in the Bloemhof Dam. This suggests that in the current monitoring scheme administered by the Rand Water Board, it would be appropriate to include in the daily analyses at the major points of interest, nitrates, phosphates, and chlorides in addition to TDS."

INFLUENCE OF PHOSPHATE ON METALLURGICAL PROCESSES

In the course of this investigation, no direct correlation was found between PO_4^{3-} in water and metallurgical recovery efficiencies, possibly because no one has looked for such a correlation.

In South Africa, at any rate, it is generally believed by operators that when treated sewage water is blended back into the process water, metallurgical inefficiencies are bound to result. Mill operator understanding of the species in sewage water which cause the problems in flotation recoveries is non-existant. Also, mill operators have little or no understanding of sewage treatment processes and do not distinguish between raw sewage, treated effluent by biofiltration, oxygen enhanced (VITOX) biofiltration, and the activated

NO_3^- & PO_4^{3-} IN TREATED SEWAGE WATER



sludge processes (including Phoredox), nor between various levels of sophistication of operation of these processes--to them all sewage is detrimental.

Since phosphate is added to process water through degradation of commonly used scale inhibitors, apparently without introducing metallurgical problems, it is likely that phosphates themselves in treated sewage waters are not the species responsible for metallurgical interferences. The presence or absence of phosphate may be indicative, however, of the extent to which the unidentified deleterious species have been removed in the sewage treatment process.

There have been preliminary indications that sewage water treated by the activated sludge processes may not have detrimental effects on the flotation of pyrite and gold at high pH as opposed to product water from an adjacent biofiltration plant at Stilfontein, Transvaal. These preliminary but interesting laboratory tests were carried out, and more details could be requested from:

ANGLO-TRANSVAAL RESEARCH
LABORATORIES
Post Office Box 1
Florida 1710
South Africa
(011) 672-0460
Dr. Gerhard Overbeek

LOVELL, et al. (1971) investigated the flotation of phoscorite ores to examine possible correlations between chemical variables in solution and metallurgical performance with a view to improving performance of phoscorite recovery at Phosphate Development Corp. Ltd. (Foskor) at Phalaborwa. Strangely enough, they examined the levels of several contaminants in solution but did not monitor dissolved phosphate levels.

An interesting observation has been made that if phosphorus-containing scale inhibitors are used in excessive doses, the excess converts to ortho-phosphate and scaling effects can actually be enhanced.

ENVIRONMENTAL SENSITIVITY TO PHOSPHORUS

According to ONTARIO (1979), scientific evidence is insufficient to develop a firm objective for phosphate levels in water below which the aquatic environment will be protected. To avoid nuisance concentrations of algae in lakes, total phosphorus concentrations for the ice-free period should not exceed 20 ppb (ug/l). A high level of protection against aesthetic deterioration would be provided by total phosphorus levels for the ice-free period of 10 ug/l or less. In rivers, excessive plant growth would be eliminated at a total phosphorus level below 30 ppb.

PHOSPHATE

Natural algal and macrophyte growths in any lake or river are mainly influenced by the morphology of the water body and the supply of nutrients. The amounts and species of aquatic plants play a major role in establishing the physical appearance and total biological community of a waterway. Lakes with little algal growth will generally have clear water, low primary productivity, and low fish productivity. However, lakes with greater algal growth will be more turbid and have higher primary productivity and higher fish productivity.

It has been shown (ONTARIO, 1979) that phosphorus limits the algal and plant growth in many lakes and rivers and thus, to a large extent, controls the species present, the productivity, and the appearance of surface waters.

According to ZITKO, et al. (1970), phosphorus in the elemental state is very toxic to aquatic life, but this form does not occur naturally. Its occurrence in industrial discharge is a very rare occurrence.

Phosphorus in combined form is not toxic to aquatic life and does not need to be controlled to protect aquatic life from direct effects. Phosphorus levels must be controlled, however, to prevent undesirable changes in the aquatic ecosystem due to increased algal growth which will inevitably result from phosphorus addition to surface wastes.

Increased algal growth resulting from phosphorus inputs to surface waters can be a benefit in some cases by providing more food for fish. On the negative side, increased algal growth increases turbidity, thus reducing the aesthetic appearance of the water. The increased production of water requires more oxygen during decomposition and may adversely affect aguatic life in the bottom layers of lakes by reducing oxygen to unacceptable levels. Fish habitat and spawning grounds may be destroyed and, while total fish production may stay the same or even increase, there can be changes to less desirable species.

Macrophytes are the main form of plant growth of concern in rivers. Algal growth is not generally a problem, and ONTARIO (1979) considers 30 ppb total P to be a reasonable objective.

Regardless of all these wishes and desires, the fact remains that most sewage effluents (treated and untreated) are in the 1-10 ppm range rather than the ppb range that regulators would prefer.

In the trip report on the Stilfontein Sewage Works in Appendix I, the phosphate levels in raw sewage ranged from 5-10 ppm and in activated sludge treated effluents, from 3-6 ppm. The consulting engineer did not have data for the biofilter treated effluent. It is

interesting that the data in Appendix I shows that nitrogen and nitrate levels were reduced further by biofiltration than by this particular activated sludge plant.

REGULATORY LIMITS FOR PHOSPHORUS

Mine operating permits seldom include phosphorus or phosphates. Regulatory limits are, however, frequently imposed on effluents from sewage treatment plants in major metropolitan areas. In South Africa, for example, a new standard has been proposed in 1983 for the Witwatersrand area which would limit total phosphorus to 3.0 ppm P in effluents. Phosphorus in orthophosphate will be limited to 1.0 ppm P.

During the course of this investigation which included only one phosphate mine, no limits were found for phosphate in the mine effluent limits examined.

According to P. J. Pybus of Stewart, Svirirdov, and Oliver, a leading consulting engineer in the field of sewage treatment in Johannesburg, the 1 ppm PO_4^{3-} as P limit in the Witwatersrand is less stringent than in the U.S.A. where at Reno-Sparks, the limit on total phosphorus has now been reduced from 0.7 ppm P to 0.5 ppm P.

STEWART, SVIRIDOV, and OLIVER
Post Office Box 784148
Sandton 2146
(011) 783-5393
P. J. Pybus
Consulting Engineer

The South African Government Gazette, Volume 223, 13 January 1983, presented new regulations limiting phosphate contribution to surface waters by overfertilization of maize fields from which runoff drains into the Vaal River.

REMOVAL OF PHOSPHORUS

WILMOTH, et al. (1978, 1979) tested various technologies for the removal of trace elements from acid mine drainage. Lime neutralization, reverse osmosis, and ion exchange removed As, Cd, Cu, Hg, Ni, Cu, and Zn from acid mine drainage but did not remove B or P. The two-bed ion exchange system was ineffective for removal of P and B, and none of the methods tested removed P.

In practice, there are two main ways to remove phosphates from water--biological and coagulation. Biological processes generally refer to activated sludge processes and the more sophisticated variations thereof such as Badenpho and Phoredox developed by the National Institute for Water Research (NIWR) of the CSIR, Pretoria, South Africa. Biological phosphate removal could also include uptake by plants such as water hyacinths,

cattails, etc. Coagulation processes for phosphate removal generally involve the addition of other metal ions.

By far the greatest experience in phosphate removal belongs to municipal water supply and municipal wastewater treatment industries. With this in mind, an authoritative text on wastewater treatment by CULP, et al. (1978) is probably as useful a source of information as any.

CHEMICAL COAGULATION

Chemical coagulation of phosphate has proven consistently reliable and efficient on a plant scale according to CULP, et al. (1978). In an integrated biological-chemical process approach, the coagulant may be added either ahead of the primary clarifier or directly to the aeration tank in an activated sludge tank. When added ahead of the primary clarifier, alum, iron, or lime may be used. When added directly to the aeraton tank, iron or alum salts are used. If the physical chemical coagulation step is separated from the biological treatment, any of the above coagulants may be added to the secondary effluent with subsequent settling downstream. CULP, et al. (1978) compared the alternative approaches as follows.

PERFORMANCE - COAGULATION

Systems in which coagulation is integrated with the biological process achieve an overall phosphorus removal of 75-85 percent to levels of 1-2 ppm P. Subsequent filtration of effluents from such an integrated process may reduce phosphorus levels to 0.5 ppm P if the coagulant dose is proper.

If chemical coagulation of secondary effluent is applied as a separate process, lower phosphorus concentrations may be achieved. At the South Tahoe project, an average phosphorus concentration of 0.05 ppm P was achieved for an entire year.

By separating the chemical from the biological treatment steps, it is possible to employ efficient rapid mixing and flocculation devices and to optimize the coagulant dose solely for phosphorus removal without being concerned for the effects of such doses on the biological treatment system. The same features which achieve phosphate level reduction also achieve lower suspended solids in the final effluent when the physical-chemical processes are downstream of the biological process.

FLEXIBILITY

Separation of the chemical coagulation process from the biological process keeps the chemical and biological sludges separate. This provides the designer with more options in terms of coagulant choice and sludge handling. For example, the use of lime as a coagulant in a tertiary step has an advantage in that coagulant recovery may be achieved which reduces the quantity of sludge that must ultimately be disposed of and may provide a more economical coagulation process than the use of alum or purchased iron salts.

Separation of the chemical step also provides more operational flexibility to insure maximum removal of phosphorus where this is necessary. Recycle of concentrated chemical sludges to the rapid mix or flocculation basins can be accomplished to maximize phosphorus removal when the chemical coagulation is carried out in a separate step. The coagulant dose can be selected solely on the basis of phosphate removal rather than on the maximum dose compatible with the operation of the biological system.

At the Rondebult Sewage Purification Works at Germiston, Transvaal, South Africa, underground mine water with a high Fe- content was used for PO_4^{3-} removal from sewage effluents to comply with the recently enacted limit of 1 mg/l for the greater Witwatersrand area. VAN DER MERWE, et al. (1983) reviewed the theory of Fe phosphate precipitation and refer to other phosphate removal plants in Wisconsin. The addition of Al and Fe salts does not seem to harm biological life on the filter. The dosing of iron in acid mine drainage appeared to inhibit nitrification and reduce the pH increase through the filters and increase the total dissolved solids in the effluent by about 500 mg/l. An equivalent dosage of 20 mg Fe/l maintained the final phosphorus level at 0.1 cents/m^3 which is only 10% of the cost if $FeCl_3$ had been added as a chemical.

Additional information could be requested from:

P. H. VAN DER MERWE
Rondebult Sewage Treatment Plant
Germiston Municipality
Germiston, Transvaal
South Africa

The National Institute for Water Research, CSIR in Pretoria has also experimented with the addition of ferric chloride for phosphate removal. Their Dr. Lucas R. J. van Vuuren has experimented with lime coagulation.

The NIWR experience indicated that dosages of two to three times the stiochiometric requirement are needed to efficiently reduce phosphates below the 1 ppm limit.

Experiments at Boksburg and the Pretoria Dasspoort Experimental Sewage Plant indicated that the flocs are very light and difficult to settle. Polyelectrolytes were needed to

improve flocculation and settling. The use of polyelectrolyte flocculant alone without the metal containing coagulant results in an extremely fine precipitate which will not settle.

NIWR also experimented with the addition of $FeCl_3$ to the septic end of the sewage plant without success. $FeCl_3$ applied ahead of the primary sludge settling step flocculates out many other species including some organic compounds which helped to reduce the load on the biofilter. They found $FeCl_3$ almost ineffective in removing polyphosphates unless they are bonded to carbon on the suspended solids.

Based on their experiments, the NIWR concluded that it would be best to add $FeCl_3$ at two points--first ahead of primary settling, and then again after the polyphosphates have been hydrolized. The settled sludge goes to digestors in which $FePO_4$ is stable. Ultimately, after the trickle filter step, a humas tank settler is installed where residual phosphate is settled out more efficiently if dosed with $FeCl_3$.

The NIWR pointed out that if $FeCl_3$ is added, the extra chloride added will present a problem on the Witwatersrand where chloride and TDS levels are already building up in the Vaal Dam. Typical does of $FeCl_3$ to sewage would be 100-150 mg/l to be effective.

In South Africa, the major supply of $FeCl_3$ is from KOP who produce $FeCl_3$ from steel pickle liquors. However, $FeSO_4$ in ISCOR pickle liquor can be used as readily, or Al salts can be used instead of iron salts. In this respect, the VAN DER MERWE (1983) idea of using acid minewater containing iron may be a good one near mine-mill installations where such water is available.

NIWR point out that most metal-PO_4^{3-} compounds agglomerate best at relatively narrow pH ranges. $FeCl_3$ works best at pH 4-6 so for sewage at pH 7.5, an increased dose of $FeCl_3$ is necessary.

It is believed that the Boksburg Municipal Sewage Works on the eastern Witwatersrand uses $Fe_2(SO_4)_3$ to precipitate and coagulate phosphate which is more desirable because it adds $SO_4^{=}$ rather than Cl^- to the product water.

It was mentioned that the Rand Water Board uses activated silica for phosphate removal by coagulation, and reference was made to Mr. S. W. Van der Merwe at the Vereeniging Water Treatment Plant, also located near Johannesburg.

RAND WATER BOARD
Post Office Box 1127
Johannesburg 2000
S. W. Van der Merwe

Research into phosphate removal processes is being conducted by the Johannesburg City Engineer's Department: Mrs. Lorraine Lotter, Johannesburg, telephone (011) 728-7373.

A Witwatersrand company, Prentec (Pty) Ltd., offers small package phosphate removal plants which employ coagulation with $FeCl_3$. These plants are suitable for communities such as mines of up to 3,000 people. They are prepared to guarantee a 1 ppm maximum limit for phosphorus in the phosphate form.

PRENTEC (PTY) LTD.
Post Office Box 1433
Edenvale 1610
(011) 609-5216
John A. Buchanan

At Vaal Reefs Exploration and Development Co. operations on the western Witwatersrand, an iron-rich uranium plant raffinate was effectivly used to remove phosphate from sewage effluents. Raffinates are low in pH and contain high concentrations of $Fe_2(SO_4)_3$. This worked well as long as the uranium plant was using ferric ions as an oxidant. When the U-plant switched back to using manganese dioxide as an oxidant, the manganese levels increased in the raffinate to an extent that the raffinate could no longer be added to sewage without causing a manganese problem when the effluent was discharged.

BIOLOGICAL PHOSPHATE REMOVAL

Bacterial processes for phosphate removal include the conventional activated sludge process, biofiltration (trickle filters), and the more sophisticated patented Bardenpho and Phoredox processes. Some of these have been discussed in MATLOCK (1978) but since then, there have been the major new developments in the Badenpho and Phoredox processes.

Typical average feed concentrations for settled sewage and raw sewage from a mainly residential community such as a mining camp would be as follows:

	Settled Sewage				Raw Sewage			
	COD	Total P	TKN	NH_4-N	COD	Total P	TKN	NH_4-N
Maximum (ppm)	359	6.6	36.6	24.5	394	5.4	35.6	22.2
Minimum (ppm)	148	3.3	16.8	12.4	338	4.9	31.5	22.6
Mean (ppm)	271	5.4	28.5	19.9	369	5.4	33.4	21.4

The most definitive description of the various phosphate removal processes is by SIMPKINS and GERBER (1981). This report is inserted below as it contains very useful information about the biological removal of phosphate.

The Phoredox and Bardenpho processes are patented under South African patent 72/5371. Detailed design information is available from:

THE SOUTH AFRICAN INVENTIONS
DEVELOPMENT CORPORATION
Post Office Box 395
Pretoria 0001
South Africa

The most appropriate sources of expertise on these processes would be:

THE NATIONAL INSTITUTE FOR WATER
RESEARCH
CSIR
Post Office Box 395
Pretoria 0001
South Africa
(012) 869-211
Dr. L. R. J. Van Vuuren
Andre Gerber

The following paper lists several activated sludge plants including the "new" Stilfontein plant which is a five-stage Bardenpho Mark III plant designed in 1977 and described in a trip report in Appendix I.

According to Mr. P. J. Pybus of Stewart, Sviridov and Oliver, the Bardenpho plant installed at Windhoek does a good job of removing ammonia to less than 0.5 ppm but is not effective in removing PO_4^{3-}.

BIOLOGICAL PHOSPHATE REMOVAL - PLANTS

The University of the Orange Free State in Bloemfontein, South Africa, has investigated the use of marsh vegetation as a means of purifying acid mine drainage. At least one Ph.D. thesis has resulted, showing that bullrushes in the volunteer marshes that are found in acid mine drainage affected areas do exhibit seasonal phosphate uptakes. More information on his research can be obtained from:

PROFESSOR DAAN TOERIEN
University of Orange Free State
Bloemfontein OFS
South Africa
(051) 70711

Water hyacinths are believed also to remove some phosphate from effluents as well as to remove heavy metals, but these grow only in very warm subtropical water.

SCHWARZ (1983) discussed water reclamation by aquaculture, and his paper may include a discussion on phosphate removal.

TECHNICAL GUIDE ON BIOLOGICAL NUTRIENT REMOVAL: THE PHOREDOX PROCESS

MJNP Simpkins and A Gerber

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The PHOREDOX process falls within the ambit of the Bardenpho patent No. 72/5371 and hence it has been necessary to protect the marketability of the latter by deleting detailed and explicit design information from the main text. The latter information may be obtained by arrangement with the patent holders, Messrs SAIDCOR, at PO Box 395, Pretoria. Further detailed advice regarding application of the design principles under specific circumstances as well as guidance on problems which may arise may be obtained from the NIWR.

CHAPTER 1

INTRODUCTION

In urban and industrial areas throughout the world, the demand and usage of water, and consequently the production of wastewaters, are rapidly increasing due to the population increase and the fact that in the civilized world the use of water has become inseparable from our industrial and domestic way of life. With the introduction of the Water Act in 1956 the previously disallowed practice, of direct discharge of sewage treatment plant effluents into the water courses, was permitted, provided the effluent met the required standard. With the increase of industrial activity in South Africa and the number of people linked to waterborne sanitation, rivers could no longer cope with increasing nutrient loads, particularly nitrogenous and phosphorus compounds, resulting in the enrichment of impoundments. In 1975, approximately 11 % of 98 impoundments studied, including most of the major dams in the country, were heavily eutrophic (i.e. excessively enriched), while approximately 40 % contained nutrient concentrations higher than was considered desirable (Toerien, Hayman and Bruwer, 1975). Effluents from sewage treatment works have been identified as a major contributor to eutrophication and it was realised that nutrient removal from this source, prior to discharge into natural water courses, would be necessary to alleviate this problem.

Ammoniacal nitrogen, apart from its inherent toxicity, is the nutrient which can most immediately cause problems in receiving waters, since the oxidation of ammonia to nitrate can deplete the dissolved oxygen in the water mass, which may lead to the death of both plant and animal life. This problem can be overcome by oxidizing the nitrogenous compounds in the wastewater to nitrate during the treatment process. This, in turn, may lead to undesirable side-effects such as high nitrate concentrations, which are costly to reduce chemically, and injurious to the health of babies, if ingested.

Enrichment of impounded waters can lead to some undesirable results, the primary effect being the accelerated and uncontrolled growth of various strains of algae, water grasses and both rooted broad leaved water plants and floating plants such as water hyacinth and Kariba weed. The prolific growth of these plants may prevent efficient oxygenation of water, causing the hypolimnion to become anaerobic.

Algae which proliferate in eutrophic waters may result in the formation of an unsightly algal scum. Wind-blown deposits on the shoreline are not only unsightly but cause a revolting smell as decomposition occurs. Some strains of algae are toxic to animal life, causing serious problems to farmers who water their stock at impoundments infested with these trains.

Secondary undesirable effects of eutrophication, result from the first and are the upsetting of the social amenity value of the impoundment and the complication of water purification processes. A great deal of money has been invested in developing and utilizing dams and rivers for recreational purposes. By allowing these resources to become eutrophied, their value is seriously limited causing a loss of revenue to resort owners, while individuals who enjoy boating and sailing are unable to utilize their equipment.

Occurrence of algae in water serving as a source for water supply, demands more complex purification treatment and increased plant maintenance, for example, sand filters will require more frequent backwashing.

Control of the nutrient content in effluents is important in areas where eutrophication has occurred or is likely to occur. The Department of Water Affairs (Rudd, 1979), has pinpointed such sensitive areas where control of the nutrient concentration in effluents is likely to be introduced:-

(a) The Vaal River from its catchment area to Bloemhof Dam.

(b) The upper Limpopo – Crocodile catchment including the catchment areas of the following dams: Rietvlei, Hartbeespoort, Roodeplaat, Klipvoor, Bon Accord, Vaalkop.

(c) The Great Olifants River above the Loskop Dam.

(d) The Umgeni catchment except where effluents discharge directly into the estuary or sea.

(e) The Umlaas River.

(f) The Buffalo River from King William's Town to Bridle Drift Dam.

(g) The Great Berg River.

(h) Atlantis.

In natural waters algae require a nitrogen:phosphorus ratio of 15:1, but since this ratio is approximately 4:1 in wastewater treatment plant effluents, it would seem that nitrogen should be the limiting nutrient. However, due to the nitrogen-fixing capability of various algal species it has been shown that in most cases phosphorus is the limiting nutrient (Toerien *et al* 1975). The removal of phosphate-containing compounds is therefore of prime importance when considering treatment methods aimed at limiting eutrophication.

Local authorities in these sensitive areas may be faced with problems of nutrient removal with existing plants or in proposed new works. There are a number of alternatives available for the control of effluent concentrations of phosphate, namely chemical precipitation, biological-chemical techniques and purely biological means. Chemical precipitation is normally used in exist-

ing plants to upgrade the effluent quality, usually by chemical addition to the plant effluent. In biological-chemical applications, the biological ability to remove phosphate is complimented by the addition of chemicals in order to reduce the effluent phosphate concentration to within acceptable limits. Biological processes achieve nutrient removal without the addition of possibly expensive chemicals, consequently the cost of the chemicals and the handling and disposal of an additional chemical sludge are avoided.

This technical guide will be concerned with the removal of phosphate by biological means only. The specific process considered is the Phoredox process, a biological nutrient removal process developed by the National Institute for Water Research, Council for Scientific and Industrial Research, South Africa. This process has been developed to remove both nitrogen compounds and phosphate from the discharged effluent stream. It is an extension of the patented Bardenpho process which was designed to remove the nitrogen compounds only.

The Phoredox process has been tested extensively on pilot plant scale by the National Institute for Water Research, at a Pretoria sewage works. The results are sufficiently promising that design engineers should seriously consider this process for biological nutrient removal. However, the designer must realize that the research into biological nutrient removal is by no means complete and throughout the world researchers are endeavouring to develop general descriptive equations for the kinetics of activated sludge. It is probable that even more efficient and economical processes will be developed for the biological removal of nutrients from wastewaters in the future.

CHAPTER 2

PROCESSES FOR BIOLOGICAL NUTRIENT REMOVAL

The Phoredox process described in this guide achieves nitrogen and phosphate removal without the addition of chemicals. The concept of biological nitrogen removal is not new and many attempts have been made to ensure consistent and reliable performance of nitrification and denitrification in activated sludge plants. A vast amount of literature is available dealing with the basic kinetics of these reactions. A brief summary follows on some of the major developments which have a bearing on this design guide.

Wuhrmann (1957, 1960) and Ludzack and Ettinger (1962) were amongst the earlier researchers who proposed activated sludge process configurations for nitrogen removal. Wuhrmann (1957) proposed a single sludge two-stage process with the sewage fed into an aeration stage together with the recycled sludge from the clarifier (Figure 1). The nitrified mixed liquor passed from the aeration stage to an anoxic stage, (no measurable dissolved oxygen), where denitrification occurred at a very slow rate due to low residual carbonaceous energy. This problem was overcome by introducing a nitrogen-free source of biodegradable organic carbon, such as methanol, thereby allowing a small, more efficient denitrification stage to be designed.

Ludzack and Ettinger (1962) placed the anoxic stage in front of the aeration stage (Figure 2), and created an internal recycle from the aeration stage into the anoxic stage by way of a notch weir in the separating baffle. The mixed liquor found its way back into the aeration stage through a slot provided between the baffle and the tank bottom. The feed sewage was introduced into the anoxic stage and the recycled sludge was returned to the aerated stage. The nitrate entering the anoxic stage was rapidly reduced in the presence of the incoming feed and the nitrate-free underflow was then introduced into the aeration stage where nitrification occurred. By increasing the recycle rate the nitrate concentration in the effluent could be reduced. This configuration resulted in high rates of denitrification without the use of an additional carbon source. For more extensive details on the development of the nitrification and denitrification processes the reader is referred to the publications of Sharma and Ahlert 61977) and Christensen and Harremoës (1977).

The first report of phosphate removal by an activated sludge process dates back to 1943 when Jenkins and Lockett (1943) noted that of the phosphorus entering a treatment works only 54 % was discharged in the effluent. Srinath, Sastry and Pillai (1959) performed the first detailed laboratory analysis of the ability of the activated sludge process to remove phosphate. Further investigations on the metabolic uptake of phosphate in an activated sludge process were reported by Levin and Shapiro (1965). The research indicated that activated sludge was able to remove more phosphate than was required for normal growth, and the term 'luxury uptake' was introduced to describe this mechanism. They were granted patent rights (Levin, 1964) on the 'Phostrip' process in 1964 and the process has proved to be successful both at pilot plant (Levin, Topol, Tarnay and Samworth, 1972), and full-scale application (Levin, Topol and Tarnay, 1975). The 'Phostrip' process (Figure 3) consists of an activated sludge reactor into which recycled sludge is introduced with the influent feed. In the earlier plants no provision was made for the removal of nitrogen, but a subsequent patent (Levin, 1972) was granted covering the removal of nitrogen. The activated sludge reactor is designed to handle the carbonaceous oxidation, nitrification and denitrification following the system proposed by Wuhrmann (1957). The outflowing mixed liquor enters a settler where the activated sludge solids are settled and the supernatant discharged. The solids are passed to a second, anaerobic clarifier where, in the absence of both dissolved oxygen and nitrate, phosphate is released from the organisms into the supernatant of this clarifier. The phosphate-'stripped' sludge is returned to the activated sludge reactor while the phosphate-enriched secondary supernatant is treated with lime, to precipitate the phosphate. This process is capable of producing an effluent with a very low phosphate concentration but achieves relatively poor denitrification, unless an external carbon source is introduced into the anoxic stage. Full-scale biological phosphate removal has been reported by Vacker, Connell and Wells (1967), at the municipal wastewater treatment plant at San Antonio, Texas. The plant consisted of three modules operated in parallel and fed with the same influent feed. By varying the form and degree of treatment they were able to observe what parameters were correlated to effective phosphate removal, while each module was operated within the limits of maximum BOD removal. Based on this study the author concluded that under conditions of limited nitrification, 'luxury' metabolic uptake occurred. In terms of more recent thinking, the successful removal of phosphate may be attributed to the limitation of nitrate which allowed the process to become anaerobic, most likely in the clarifier, and as a consequence of this the biological sequence for phosphate uptake was supported.

With regard to the basic procedure of phosphate removal, two schools of thought soon developed. On the one hand was the theory of chemical precipitation as outlined by Menar and Jenkins in 1970, and later modelled by De Boice and Thomas (1975). On the other there was the biological uptake theory, described as 'luxury' uptake or 'enhanced' removal. The chemical precipitation theory holds that the biological incorporation of phosphate into the organisms, in an activated sludge mass, results in a maximum of approximately 2 % by mass of phosphate (as P). Phosphate

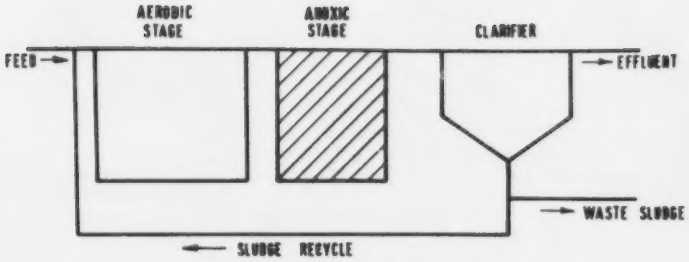

FIG. 1: The Wuhrmann process for biological denitrification

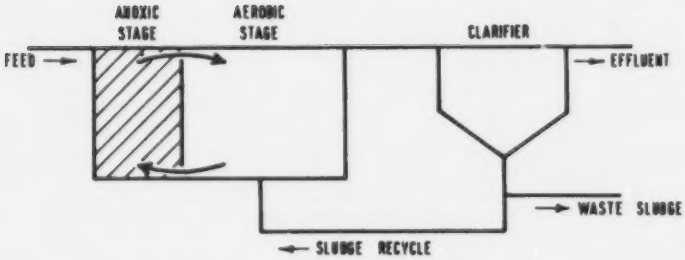

FIG. 2: The Ludzack-Ettinger process for biological denitrification

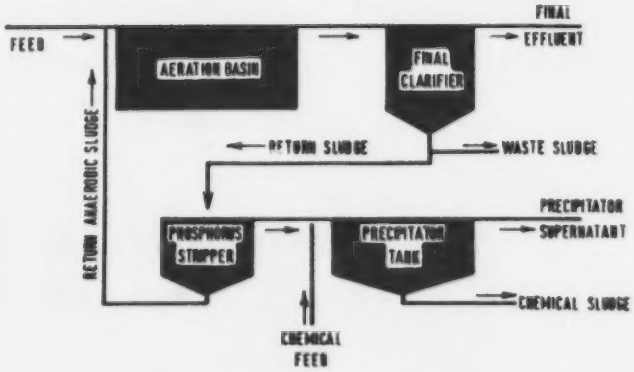

FIG. 3: Schematic flow diagram for the Phostrip process

concentrations, determined from sludge, which are in excess of this normal 2 % is caused by chemical precipitation of phosphate by the natural metal ions abounding in the carrier water mass. The pH of the mixed liquor was found to increase significantly from the point of entry to the point of exit, due to the stripping of carbon dioxide. This pH change was thought to be instrumental in causing the phosphates of calcium and magnesium to precipitate.

The researchers supporting the biological or 'luxury' uptake theory, were not able to propose a basic concept of the mechanisms of removal, but reported that when there was significant phosphate uptake during aeration, there were frequently higher concentrations of phosphate in the effluent from the secondary clarifier. This increase in phosphate concentration was thought to be caused by oxygen deficiency or low redox potential during settling. (Shapiro, Levin and Zea, 1967).

The publication of the chemical precipitation hypothesis prompted further research into the possible mechanism of phosphate removal and Yall, Boughton, Knudsen and Sinclair (1970) reported, after having used radio-active phosphorus (^{32}P) and also an inhibitor (2,4-dinitrophenol) to biological oxidative phosphorylation, that there was no doubt that the uptake of phosphate was mostly biological in nature. The authors concluded that much of the phosphate taken up by the sludge is associated with a mechanism involving the synthesis of adenosine triphosphate (ATP). More recently Carbury and Tenney (1973) re-examined the possibility of biological uptake, using much the same techniques as the previous researchers, and reported that their findings indicated that the removal of phosphate occurred by biological uptake. The authors indicated that the two possible mechanisms by which phosphate could be transported into the cell could be either a diffusion-controlled mechanism driven by a positive concentration gradient between the outside and inside of the organism cell, or an active transport mechanism in which energy derived from metabolic processes inside the cell drives the transport into the cell against a negative concentration gradient. Morgan and Fruh (1974) ran experiments using synthetic substrates which precluded chemical precipitation and reported that their results indicated that a 'luxury' uptake of phosphorus by activated sludge is not the exception, but the rule.

Further evidence supporting the biological uptake theory was provided by Fuhs and Chen in 1975. These authors used sludge taken from Baltimore, Maryland, to conduct a number of microbiological laboratory experiments from which they concluded that the opinions of Levin and Shapiro (1965) were valid but that the biological uptake of phosphates was caused essentially by a single strain of micro organism, namely *Acinetobacter* although uptake by other organisms was not ruled out. The role of the anaerobic stage was examined and they concluded that this stage supported the growth of organisms which tend to produce components such as ethanol, acetate and succinate which serve as a carbon source for *Acinetobacter*.

Barnard, in 1973, reviewed the available technology for biological nitrification and denitrification and as a result of this work proposed a four-stage reactor based on the principles originally introduced by Ludzack and Ettinger (1962) and Wuhrmann (1957). This proposed process was tested on pilot plant scale under ambient temperature and variable sewage composition conditions. The Council for Scientific and Industrial Research was granted patent rights (72/5371, 1973) for this treatment process, which has subsequently become known as the Bardenpho process (Figure 4). The system, as patented, consists of four stages – primary anoxic, primary aerated, secondary anoxic and secondary aerated, followed by a clarifier. During further studies there emerged one necessary precondition to the removal of phosphates in the activated sludge system. This condition is that the mixed liquor or the return sludge from the clarifier underflow must go through a period of anaerobiosis such that phosphate is released to the liquid, followed by a period of aeration during which the phosphates would be either precipitated or adsorbed by the sludge mass (Barnard, 1975). Both laboratory and pilot plant scale work was undertaken to substantiate this postulate and from this work has developed the Phoredox process, a process which is specifically designed to remove both nitrogen and phosphate from sewage. This modified process consists of five stages – the Bardenpho sequence with

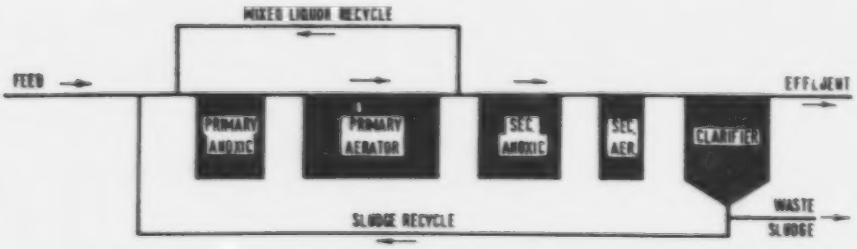

FIG. 4 Schematic flow diagram for the Bardenpho process

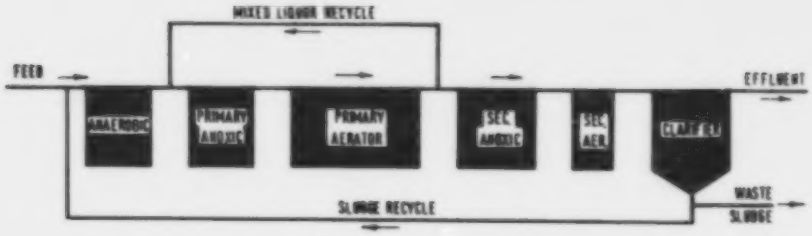

FIG. 5: **Schematic flow diagram for the Phoredox process**

an additional stage, the anaerobic stage, placed at the head of the process (Figure 5). Into the anaerobic stage is fed the influent sewage feed and the sludge recycled from the clarifier underflow. The outflow from the anaerobic stage is passed into the primary anoxic stage into which also flows the mixed liquor recycle. The mixed liquor recycle is drawn from either a position within the primary aeration stage, which is the third stage of the process, or from the outflow from this aeration stage. The remainder of this outflow enters the secondary anoxic stage which is followed by the secondary aeration stage and finally the clarifier, from which the supernatant liquor is discharged and the settled solids are returned to the head of the process.

CHAPTER 3

THE PHOREDOX PROCESS

The Phoredox process is a five-stage process (Figure 5) designed to remove nitrogen and phosphorus by biological means. The functions of nitrification-denitrification and phosphate release-phosphate uptake, are two entirely separate reactions which proceed side by side in the same reactor. In order to achieve optimum performance in a plant it is most important to have a clear understanding of these reactions and the conditions which best support them. To this end the process will be considered stage by stage and the reactions occurring in these stages will be described as far as present day knowledge allows. The concentrations quoted in the following explanation are typical for a plant which is operating well. Since the feed quality is usually found to vary under normal operating conditions, there are factors which may render the process less efficient. These will be outlined later.

ANAEROBIC STAGE

The activated sludge underflow from the clarifier is pumped into this, the first stage of the process, together with the influent sewage feed (Figure 5). It is of great importance that the concentration of dissolved oxygen should be kept as low as possible in this recycle, preferably less than 1 mg/ℓ. Since the sludge leaving the clarifier has either no dissolved oxygen, or in any event a very low concentration, the concentration of dissolved oxygen entering the anaerobic stage is entirely dependent on the design of the recycle and its inherent ability to avoid oxygen entrainment. When the recycled sludge and the feed are mixed on introduction into the anaerobic stage, any dissolved oxygen present is first utilized followed by the reduction of nitrates principally to nitrogen gas. As soon as the nitrates have been reduced conditions described as 'anaerobic' exist, and soluble phosphate is released into the aqueous phase (Figure 6).

This observed release of phosphate is a basic requirement before successful phosphate uptake in the third stage (Figure 5) of this process can occur. There is, apparently, a lower limit of phosphate release below which the subsequent uptake progressively deteriorates. It is, therefore, most important that sufficient retention time be provided, to allow for the minimum phosphate release to be attained under the most adverse conditions, that is either high nitrate input in the sludge recycle or low feed COD input. A high nitrate (as N) concentration is considered to be above 6 mg/ℓ while a low COD is below 250 mg/ℓ. The retention time for this basin is empirically related to the primary anoxic rate of denitrification. The anaerobic retention time should be sufficient for the reduction of the influent dissolved oxygen and nitrate concentrations and provide for an additional period equivalent to at least 15 mg/ℓ of nitrate. This extra period amounts to about 1¼ to 1½ hours nominal retention time at 20 °C.

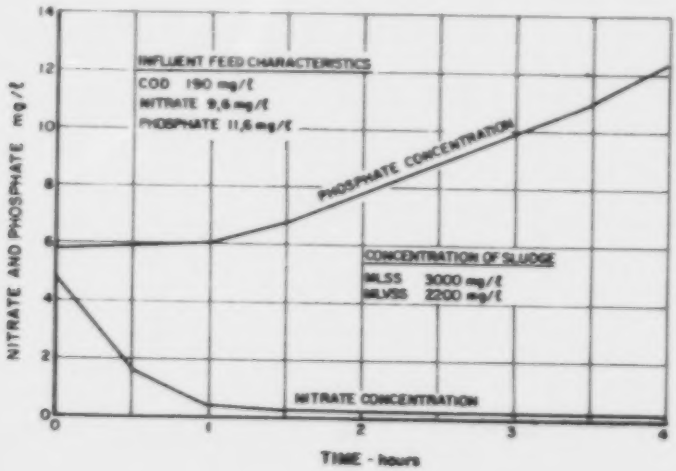

FIG. 6 Denitrification and phosphate release in the anaerobic stage

PRIMARY ANOXIC STAGE

The mixed liquor discharged from the anaerobic stage usually contains 0,5 mg/ℓ nitrate (as N) or less, and a high concentration of phosphate, depending on the influent COD concentration, phosphate concentrations between 10 mg/ℓ and 25 mg/ℓ (as P) may be expected. These values are approximately 1,5 to 3 times greater than the influent feed total phosphate concentration. The concentration of soluble COD is usually of the order 25 mg/ℓ to 35 mg/ℓ. This mixed liquor is passed into the second stage which is known as the 'primary anoxic' stage, the principal purpose of which is the denitrification of nitrates in the recycled mixed liquor from the primary aeration stage. The mass of nitrate reduced by denitrification is proportional to the rate of recycle, up to the point when nitrate starts to appear in the effluent leaving this anoxic stage. The mass of nitrate removed is also influenced by the dissolved oxygen introduced into this stage in the mixed liquor recycle drawn from the primary aeration stage. Denitrification will commence only after the dissolved oxygen concentration has been reduced to zero, and the process will then continue either until the available nitrate has been depleted or until the mixed liquor leaves this stage and enters the primary aeration stage. If denitrification is complete within the anoxic retention time, anaerobic conditions will be created in which phosphates will further be released. Experience has shown that this additional release is not detrimental to efficient phosphate uptake and is therefore not a condition which has to be prevented. If denitrification is not complete before the mixed liquor leaves this stage, the remaining nitrate will be re-introduced into the primary aeration stage, generally leading to higher concentrations in the effluent. The concentration of phosphate (as P) in this stage is greatly influenced by the magnitude of the mixed liquor recycle. Due to the dilution effect of this recycle, values of between 5 mg/ℓ and 10 mg/ℓ (as P) are usually measured. These values range from 1 to 1,5 times the concentration of total phosphates found in the influent feed.

PRIMARY AERATION STAGE

The primary aeration stage is the principal site for the oxidation of biodegradable nitrogen and carbonaceous matter. The reactions are supported by providing surface aerators or submerged diffusers of sufficient capacity to deliver the required mass of oxygen. This stage is designed to provide a retention time long enough to ensure the required reduction in organic nitrogen concentration. If there is any unoxidized carbonaceous matter in the mixed liquor leaving this stage, it is to the benefit of the denitrification which occurs in the fourth stage, namely the secondary anoxic stage. It is during this aeration stage that the reduction in phosphate concentration occurs. Diurnal peaks in carbonaceous, nitrogenous and phosphorus loading as well as the phosphate released in the anaerobic stage occur together. Since the capacity of the aerator is designed for an average value, it may be found that during the periods of these peaks the concentrations of unoxidized organic nitrogen, ammonia and phosphates will be increased in the mixed liquor leaving this stage. The dissolved oxygen concentration should be maintained in the vicinity of 2 mg/ℓ, even though concentrations below 1 mg/ℓ are sufficient to indicate that there is enough oxygen to support the oxidative processes. It has been found experimentally that the dissolved oxygen concentration can be limiting if maintained too low. With submerged diffusers it has been found that, at dissolved oxygen concentrations of approximately 1 mg/ℓ, the uptake of phosphates was not satisfactory, while at the suggested concentration of 2 mg/ℓ the removal was good.

The rate of the mixed liquor recycle, from the primary aeration stage to the primary anoxic stage, is controlled to obtain the desired reduction in nitrates. The recycle rate is calculated from the denitrification potential of the primary anoxic stage. It is desirable to provide capacity to vary this recycle rate from the design value, in order to cater for sewage characteristics which differ from those originally considered, an eventuality which may well occur during the useful life of the plant. When designing the primary aeration stage, the possibility of being able to increase the primary anoxic retention time, at the expense of aerated retention time should be considered. If the daily sewage feed concentrations vary significantly, (a situation which occurs when industrial effluents form part of the sewage feed) the primary denitrification efficiency may decline. Under these circumstances it is very useful to be able to extend the anoxic retention time, in order to maintain a satisfactorily low concentration of nitrates in the effluent. Under these conditions, the reduction of aeration capacity is unimportant since the process requires a reduced oxygen input. This procedure may be adopted up to the point where the growth of the nitrifying organisms is inhibited. To reduce the aerobic retention time further than this point will cause an increase of ammonia in the final effluent.

SECONDARY ANOXIC AND AERATED STAGES

The mixed liquor entering the secondary anoxic stage contains approximately 25 mg/ℓ soluble COD, 1 mg/ℓ phosphate (as P), usually less than 1 mg/ℓ organic nitrogen (as N) and zero, or nearly zero, ammonia concentration. The concentration of nitrates, depending on the mixed liquor recycle, will usually be between 6 mg/ℓ and 10 mg/ℓ (as N). The main purpose of this stage is to reduce the nitrate concentration to as low a value as possible, bearing economics in mind. The rate of denitrification in the fourth stage is low as the energy supporting the process is derived from the decay of organisms which release carbonaceous matter that can be utilized by the surrounding surviving cells. Since the rate of denitrification is low, a long retention time is required before a significant decrease in nitrate concentration is achieved. In general there is no change noted in the phosphate concentration as a result of this stage.

The secondary aeration stage is included in order to reaerate the mixed liquor prior to its entry into the clarifier. The introduction of this stage provides an additional safeguard to prevent the onset of anaerobic

conditions in the clarifier which would cause phosphate release, resulting in unnecessarily higher phosphate concentrations in the plant effluent. The concentrations of phosphates and nitrates are generally not altered in the secondary aeration stage where the retention time is both short and selected empirically. If there is a residual ammonia concentration leaving the primary aeration stage it will be oxidized to nitrate in this stage, causing a small increase in the nitrate concentration.

CLARIFIER

The separation of solids from the treated aqueous phase is as important an aspect of the treatment operation as the activated sludge reactor. If the separation is poor the final effluent will have a high concentration of suspended matter and as a consequence the concentrations of phosphate and COD will be proportionately higher. Without an efficient recycle of solids back to the activated sludge reactor a breakdown in the system is certain. It is, therefore, essential that the phase separation should produce an effluent low in suspended solids and a thickened solids mass which can be recycled. The separation process may be achieved by using any suitable phase separation process, with the exception of dissolved air flotation which would cause the solids recycle to the anaerobic stage to contain large concentrations of dissolved oxygen causing serious operational problems. The sedimentation type of clarifier is usually selected and in the design of this unit it is important to consider the quality of sludge produced by the Phoredox process.

The relatively long time that the mixed liquor is maintained in anaerobic or anoxic conditions may be responsible for the production of a sludge which has variable settling characteristics. Sludge volume indexes (SVI) determined from unstirred settling tests are usually in the range 300 – 400, at times decreasing to 150. These values would normally indicate a sludge that is quite unacceptable. However, experience has shown that this test does not provide a true reflection of the sludge characteristics. Pitman (1978) examined sludges produced by biological nutrient removal plants and when comparing them with sludges produced in different processes, concluded that the sludge age and the degree of aeration are very important considerations in generating a sludge with good settling properties.

In Pretoria, the pilot plant sludge was found to be rather filamentous, a state which seems to be common with the Phoredox process. Consequently it is advised that clarifiers should be designed with a view to poor settling properties. If, in operation, sludge loss occurs, the matter can be counteracted by increasing the limiting flux condition which is achieved by increasing the sludge recycle rate. This procedure is effective only when sludge thickening is the problem. If clarification cannot be obtained, increasing the recycle rate will achieve nothing and solids will be lost until the reactor mixed liquor solids concentration is sufficiently reduced to achieve an improved settling velocity. It is important to provide reserve pumping capacity in order to allow operational flexibility.

WASTE SLUDGE HANDLING

Sludge wasted from the Phoredox process may be applied directly to drying beds, or as is more usual, it may first be thickened. Pilot plant tests indicate that mixed liquor wasted from the primary aeration stage can be thickened from approximately 3 000 mg/ℓ to approximately 18 000 mg/ℓ in 5 to 6 hours. The thickened sludge required between 3 and 5 days to dry on a bed of coarse river sand. A full scale application of this method of sludge handling, at Windhoek, Namibia, produced results very similar to those found in Pretoria.

When designing a waste sludge drying bed system, there are two important factors to consider. Firstly, the supernatant from the thickener and secondly, the water percolating through the drying bed, must receive special attention. In the thickener, due to the extended retention time, anaerobic conditions will occur leading to the release of phosphate, resulting in a supernatant with high concentrations of phosphate. The water percolating through the drying beds will have very high phosphate concentrations and therefore an efficient sealed drainage system is required.

The water containing high phosphate concentrations must then be handled such that the phosphate is denied access to natural waters. A possible solution is to remove the phosphate by chemical precipitation. With the volume of water to be treated being relatively small, the required size of the treatment facility will be minimal.

CHAPTER 4

PILOT PLANT EXPERIENCE OF BIOLOGICAL NITROGEN AND PHOSPHORUS REMOVAL

The operating criteria outlined in the following paragraphs were obtained by operating a pilot plant designed for biological nitrogen and phosphorus removal, using the principles outlined in the previous chapter. The initial design of the process was not altered significantly for a period of over two years, thereby allowing a long-term analysis to be made of the efficiency of the Phoredox process. The results of this analysis are included to indicate, in real terms, what can be achieved with this process and, probably of greater importance, some of the problems encountered under near practical conditions.

TABLE 1
Volumes of the stages

Stage	Volume
Primary anaerobic	10.08 m³
Primary anoxic	10.56 m³
Primary aerated	26.58 m³
Secondary anoxic	20.88 m³
Secondary aerated	5.28 m³
Total	73.38 m³

PILOT PLANT SPECIFICATIONS

The pilot plant (Figure 7) consisted of 16 corrugated iron tanks and a settlement type rim flow clarifier of 12 m³ capacity. The effective volumes of the various tanks (or basins) were accurately determined under operating conditions (Table 1).

Positive displacement pumps were used for the feed, and the sludge recycle from the clarifier, and a centrifugal pump for the mixed liquor recycle. These three flows were controlled by means of separate penstocks (Figure 7). The feed was metered through an orifice while the sludge recycle and the mixed liquor recycle were controlled through triangular weirs. Both the weirs and the orifice were calibrated, practically, in order to determine their respective discharge coefficients. The measurements showed that the flow was determined to within an accuracy of 1,5 %.

Every basin was stirred with the exception of the secondary aerated basin (2N). Air was supplied by means of a blower through a pattern of submerged porous dome diffusers. The dissolved oxygen concentration was controlled between 2 mg/ℓ and 3 mg/ℓ by connecting an oxygen-sensitive probe, in the first basin

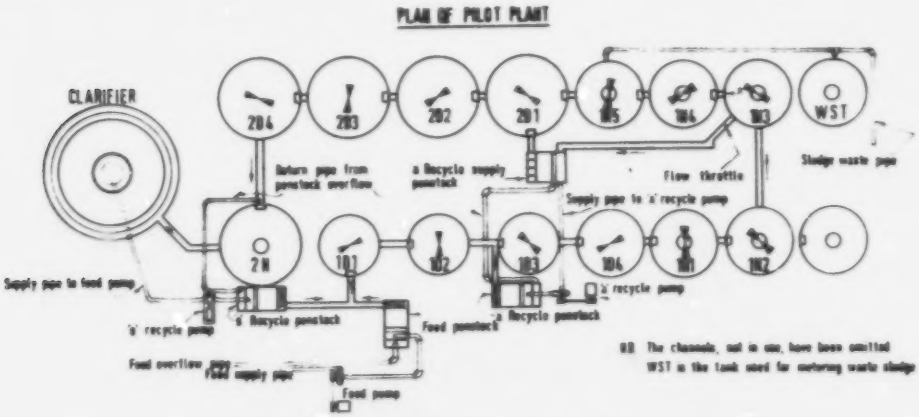

FIG. 7 Pilot plant (100 m³/day) used to study biological phosphate removal

of the primary aeration stage (1N1), to a meter which was set to activate a relief valve in the blower air line. The dissolved oxygen in the other aerated basins was controlled by butterfly valves in the air supply pipes.

The volume of sludge wasted was drawn off the last basin of the primary aeration stage (1N5) and allowed to flow into the waste tank under gravity, through a partially opened valve. This ensured a very slow flow rate which did not upset the plant flow unduly. The waste tank filled to the hydraulic level of 1N5 and thus a precise volume of 4,93 m^3, was wasted each day. Sludge wasting was performed every day except on rare occasions when the feed had been off for a long time or sludge was lost because of a breakdown.

The sludge age, defined as:

$$R_s = \frac{\text{Volume of mixed liquor in the reactor}}{\text{Volume of mixed liquor wasted per day}} \quad \ldots\ldots 4.1$$

was therefore maintained at an average value of:

$$R_s = \frac{73,38}{4,93} = 14,9 \text{ days.}$$

PILOT PLANT OPERATION

The pilot plant was designed to treat 100 m^3/d of feedstock, with a sludge return recycle rate of 100 m^3/d, the mixed liquor recycle from the primary aeration stage to the primary anoxic stage being 400 m^3/d. This latter recycle was later reduced to 200 m^3/d.

From the volumes of the stages (Table 1) and the flow rates given above, the nominal and actual retention times may be calculated and are given in Table 2.

TABLE 2

Pilot plant nominal and actual retention times for sludge recycle ratio (s) = 1, and for mixed liquor recycle (a) = 4 or 2

Stage	Retention time (min)		
	Nominal	Actual at 4:1	Actual at 2:1
Anaerobic	145	73	73
Primary anoxic	152	25	38
Primary aerated	380	113	133
Secondary anoxic	300	151	151
Secondary aerated	76	38	38
Total	1056		

The pilot plant was operated for a little more than two years of which the first 16 months were spent treating settled sewage obtained from the Pretoria Municipal Treatment Works, Daspoort. The settled sewage was piped from the primary clarifiers and introduced into the pilot plant without any further processing. The wastewater treated comprised approximately 80 % domestic sewage and 20 % from industrial contributors, including the municipal abattoir, a brewery and a dairy. In order to simplify the control of the feed pump, the sewage feed rate to the plant was kept constant. There were, however, diurnal variations for chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and total phosphate (Figure 8). The decision to use settled sewage was made because it was thought that the process conditions would be made more difficult due to the less favourable COD:TKN and COD:(total phosphate) ratios in settled sewage, while maintaining a relationship to practical treatment conditions. At the same time

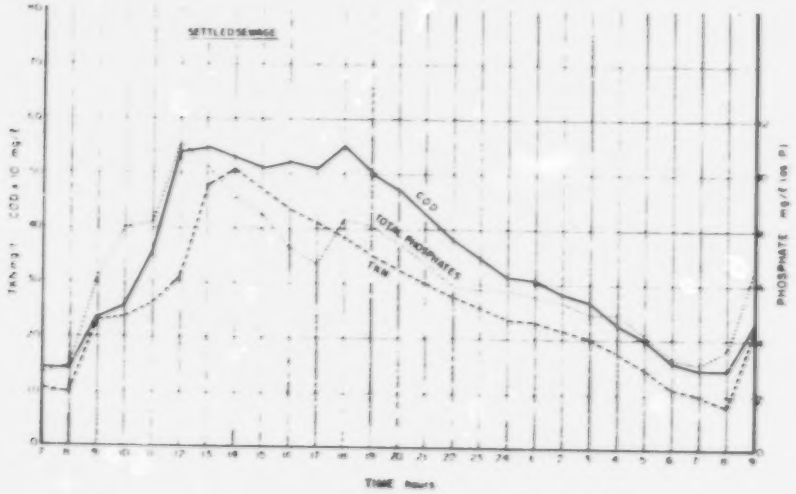

FIG 8 Diurnal variations of COD, TKN and total phosphate concentration

operational reliability was assured by eliminating the problem of pump blockages due to large particulate matter. Following this period of treatment the feed was altered and settled sewage was replaced by raw sewage. The sewage received from the municipality was screened through a wedgewire screen, the gaps between the screen wires being 0,2 mm, in order to protect the feed pump from rags, paper and other solid particles which would have caused damage. The introduction of this screen was very successful in removing solids but the collection of grease and oil from the sewage caused the screen to become less and less efficient. The problem was relieved by introducing a compressed air blower, and by chemically cleaning the screen once a week. The plant was operated for six months using raw sewage after which the feed was changed back to settled sewage.

The monthly mean feed concentrations for COD, TKN and total phosphate (as P) are given in Table 3.

TABLE 3
Monthly average feed concentrations for settled sewage and raw sewage (mg/ℓ)

	Settled sewage				Raw sewage			
	COD	Total phosphate	TKN	NH_4-N	COD	Total phosphate	TKN	NH_4-N
Maximum	359	6.6	36.6	24.5	394	5.4	35.6	22.2
Minimum	148	3.3	16.8	12.4	338	4.9	31.5	22.6
Mean	271	5.4	28.5	19.9	369	5.4	33.4	21.4

ANALYTICAL PROCEDURES

A comprehensive programme of sampling was introduced. The samples taken from the clarifier (effluent) and the various basins were filtered, using Whatman No. 2 filter paper and analysed using auto-analytical methods. The feed samples were not filtered and analysed by manual procedures.

All samples taken for chemical analysis were preserved with mercuric chloride as soon after sampling as possible, or with sulphuric acid where the former method might have interfered with the required chemical determination.

OPERATIONAL RESULTS

COD Removal

The daily composite COD values for the influent are given in Figures 9 and 10. A weekly cyclic pattern emerged with low values on Sunday or Monday and considerably higher values for the remainder of the week (Figure 11). The removal of COD remained consistently good whether settled or raw sewage was treated. The average effluent COD concentration was 23 mg/ℓ, representing an overall removal efficiency of greater than 90 %. Filtered samples taken from the last basin of each stage indicated that the COD concentration did not vary from after the first stage – the anaerobic stage – indicating that the biologically degradable COD had been accepted into the solid phase of the mixed liquor. The removal of COD in the anaerobic

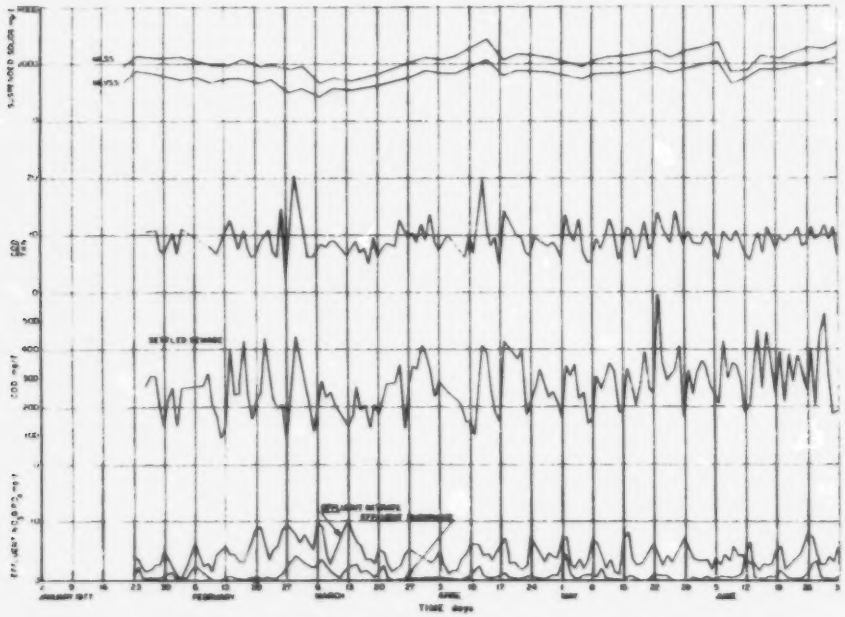

FIG. 9: Phoredox pilot plant performance

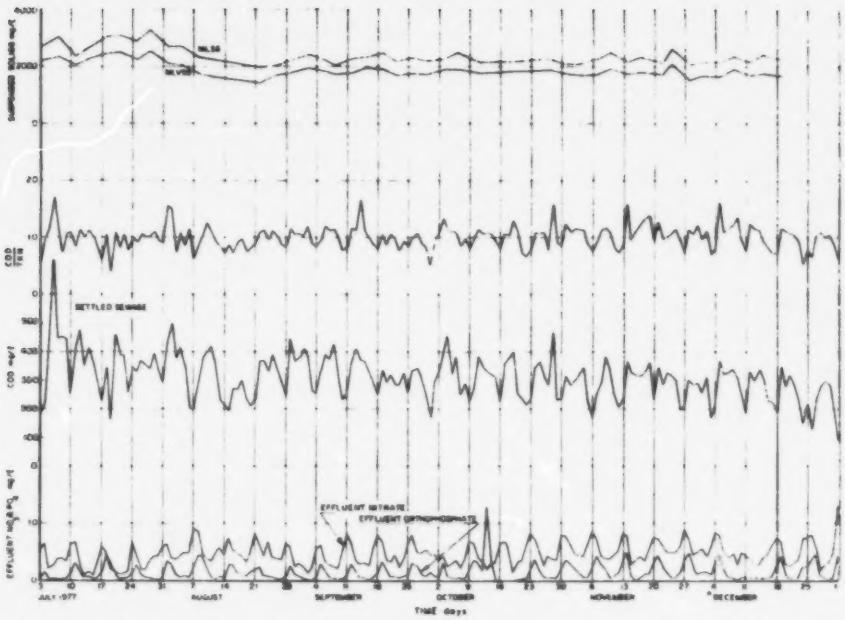

FIG. 10: Phoredox pilot plant performance

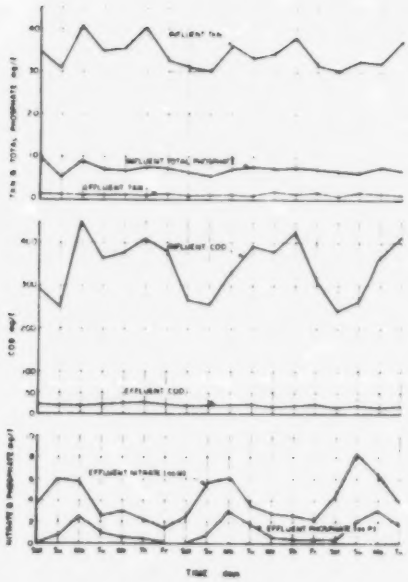

FIG. 11: Daily variations of influent and effluent COD, nitrogen and phosphate concentration

stage is thought to be due to adsorption. This process is very rapid to the point that samples taken immediately after contact between feed and return sludge averaged to give a filtered COD concentration of 32 mg/ℓ.

Nitrification — Denitrification

The daily effluent nitrate concentrations are presented in Figures 9 and 10, while the overall mean values for the period using settled sewage and raw sewage are given in Table 4.

The average concentration of total nitrogen in the effluent for the two periods was 6,1 mg/ℓ (as N) and 5,2 mg/ℓ (as N) for settled sewage and raw sewage respectively, of which approximately 1 mg/ℓ was organic nitrogen. These figures indicate that overall, more than 95 % organic nitrogen was oxidized to nitrate or utilized in cell synthesis and of the nitrate formed approximately 80 % was reduced by denitrification. The additional 36 % COD energy available in raw sewage reduced the effluent nitrate by a further 30 %, thereby providing conditions which should have been excellent for phosphate removal.

Phosphate Removal

The orthophosphate concentrations in the effluent are given in Figures 9 and 10, where a close relationship between nitrate concentration and phosphate concentration in the effluent is evident. These concentrations

TABLE 4
Monthly mean effluent concentrations for settled sewage feed and raw sewage feed (mg/ℓ), analysed from filtered samples

	Settled sewage feed					Raw sewage feed				
	COD	Ortho PO_4 P	NO_3 N	TKN	NH_4 N	COD	Ortho PO_4 P	NO_3 N	TKN	NH_4 N
Maximum	34	2.4	8.9	1.0	0.2	27	2.0	4.5	1.2	0.2
Minimum	15	0.5	3.9	0.7	0	24	1.0	4.2	1.0	0.1
Mean	23	1.2	5.2	0.9	0.1	23	1.7	4.0	1.2	0.1

rose regularly over weekends coinciding with the drop in COD (Figure 11). The process treating settled sewage was able to produce an effluent with an overall average of 1,2 mg/ℓ (PO_4-P) which included the high peaks experienced during the few breakdowns that occurred during the test period. However, the average value for the period when raw sewage was used was 1,7 mg/ℓ or 42 % higher. The poorer removal efficiency is also revealed when calculating the factor $\frac{P}{COD}$ (Table 5). This factor is calculated by dividing the difference between the mass of phosphate in the feed and in the effluent by the mass of COD removed. The resultant factor represents possibly the most accurate assessment of phosphate removal efficiency.

TABLE 5
Phosphate removal efficiency

Period	$\frac{\Delta P}{\Delta COD}$	% Removal of PO_4 P
Settled sewage feed	0.017	78 %
Raw sewage feed	0.011	58 %

No reason can yet be forwarded to explain this apparent paradox, but it would seem that primary clarification introduces a significant improvement in the phosphate removing process efficiency. The mean PO_4-P values would be greatly reduced if the weekend peaks, caused by poor denitrification, were removed. A method which seems to offer a satisfactory solution, is to increase the primary anoxic retention time by switching off aerators at the beginning of the primary aeration stage, thereby increasing the primary anoxic stage retention time but at the same time reducing the primary aeration retention time. This reduction is unimportant as the reduced COD input, causing poorer denitrification, itself requires less oxygen for its oxidation. However, as mentioned previously, if this process is taken too far, the growth of nitrifiers — which are obligate aerobes — will be inhibited causing the appearance of ammonia in the effluent. A further danger is the creation of suitable conditions for the proliferation of filamentous organisms. These organisms cause the solids to settle poorly in the clarifier, which may lead to sludge loss.

The relationship between COD, effluent nitrate and phosphate release can be seen in Figures 12 and 13. With a low effluent nitrate concentration (Figure 12) the release of phosphate closely follows the influent COD, and after an effective release the effluent phosphate is virtually absent. However, with high effluent nitrates (Figure 13) the release is suppressed, resulting in a marked increase in effluent phosphates.

Temperature

The liquid temperature ranged between 15 °C (winter early morning) and 26 °C (summer day) while ambient temperatures varied between 0 °C and 36 °C. Although the temperature range was 11 °C there was no apparent effect on phosphate removal. Since this test was run under natural conditions, it is not possible, at this stage, to report what effect temperatures lower than 15 °C might have on the pilot plant's efficiency to remove phosphate. The temperature dependencies for nitrification and denitrification had been established previously. During the period of operation of this plant the processes of nitrification and denitrification were satisfactory throughout, due to the fact that sufficient reaction time had been allowed for minimum temperature conditions.

Mixed Liquor Suspended Solids Concentration

The suspended solids concentration was relatively steady throughout the test. From Figure 9 two periods of instability are evident, the first was in March 1977 when lower average weekly COD values occurred due to rainfall; the second, in June 1977, was the result of faulty operation and mixed liquor was accidentally lost. In both cases the sludge concentrations returned to normal in approximately 1 sludge age, that is two weeks.

During the periods of recovery the volatile suspended solids (MLVSS) represented as much as 83 % of the mixed liquor suspended solids (MLSS), while normally it was of the order 75 %, indicating the presence of a greater proportion of new cells. After the change to raw sewage the MLSS reflected the rise in COD concentration by immediately increasing, and after a period

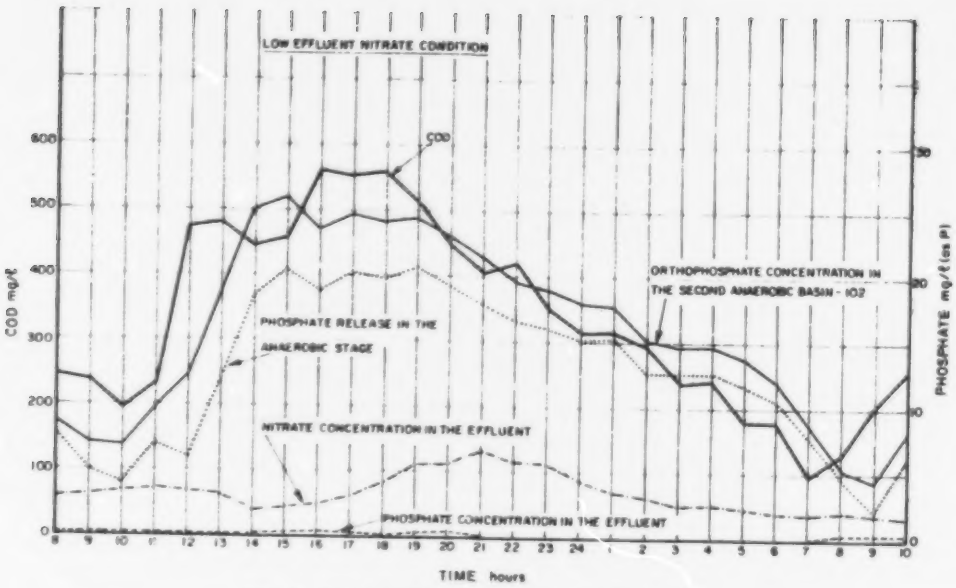

FIG 12 Diurnal influent COD and phosphate concentration in the anaerobic stage

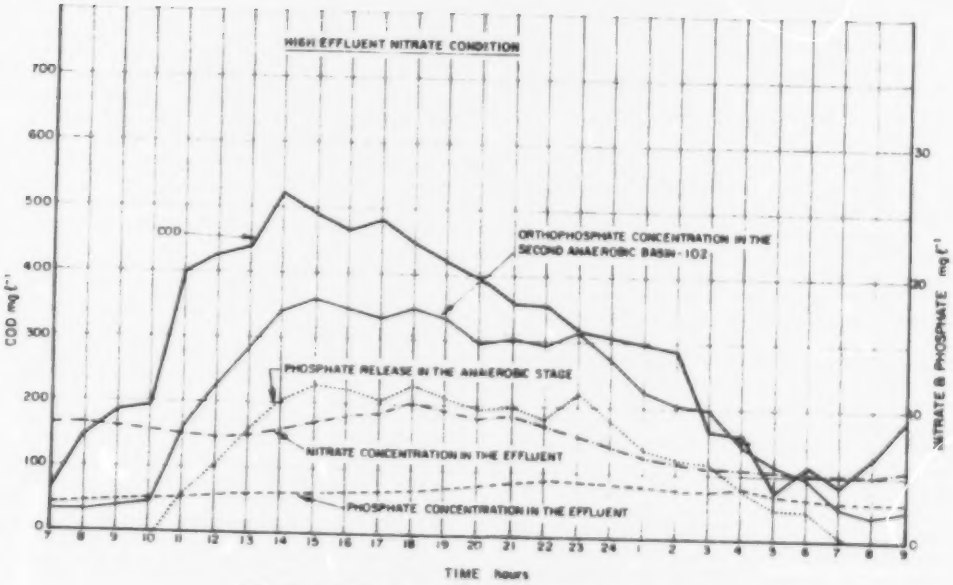

FIG 13 Diurnal influent COD and phosphate concentration in the anaerobic stage

equal to approximately two sludge ages reached its maximum value. This was followed by a period of variability after which the concentrations of MLSS and MLVSS became very stable until the feed was changed back to settled sewage. The mean values for MLSS and MLVSS were:-

	MLSS	MLVSS
Settled sewage feed	2150	1648
Raw sewage feed	3167	2440

CHAPTER 5

DESIGN AND OPERATIONAL CONSIDERATIONS

The success of a Phoredox process does not depend on the process design only. In fact the translation of the process design into practical reality and the correct operation of the constructed plant are equally important.

DESIGN CONSIDERATIONS

In the layout of a reactor it is important to bear in mind that operational flexibility is a major asset to the plant operators. The recycle pumps should be sized such that there is reserve pumping capacity. It has been found that the settling characteristics of the sludge changed, resulting in a sludge which settled badly. In order to prevent sludge loss, experience has shown that by increasing the sludge recycle, and therefore the total flux in the clarifier, the sludge loss can be minimized. However, if the settling characteristics are so bad that clarification cannot be obtained, increasing the total flux will not make any difference. In this case solids loss will continue until the MLSS concentration in the reactor is sufficiently reduced to achieve improved settling characteristics. The design of the clarifiers, therefore, demands particular attention.

The method of aerating the mixed liquor in the primary aerator deserves careful consideration. With the use of surface aerators it is possible that anoxic, and possibly even anaerobic zones may result in the aeration basin due to the hydraulic flow patterns created by the aerators. If these conditions become widespread, the aerobic uptake of phosphate might be less efficient. Indeed, in some instances no uptake was measured at all in plants which in every other respect should have supported phosphate removal. Phosphate removal in these circumstances took place in the secondary aeration stage, especially when the dissolved oxygen concentration was high. Experimentation has shown that even with submerged diffusion aerators, the dissolved oxygen concentration is limiting to successful phosphate uptake if maintained at approximately 1 mg/ℓ near the surface of the mixed liquor. Successful phosphate removal was measured with dissolved oxygen concentration controlled between 2 mg/ℓ and 3 mg/ℓ.

The Phoredox process is designed to provide a fully nitrified effluent and consequently depends on efficient denitrification to allow the implementation of the phosphate cycle. Due to the variable nature of the influent feed it is necessary to provide for changes in the primary anoxic retention time. Usually high nitrate concentrations in the effluent coincide with low feed COD concentrations. In these circumstances it should be possible to increase the anoxic retention time by switching off aerators at the head of the primary aeration stage. This action will correspondingly reduce the aerated retention time, but since the lower COD concentration requires less aeration time the effluent COD concentration will be unaffected. An undesirable result of this action might be the decline in nitrification efficiency if the process is left in this reduced aeration state too long.

A matter of great importance is the limiting of oxygen entrainment in the sludge recycle. Anaerobic conditions, in the anaerobic stage, can only develop after the nitrate concentration has been depleted. This denitrification will not take place until the available dissolved oxygen is utilized. The time required to reduce entrained oxygen and the recycled nitrate will increase with the increase in the concentration of either or both of these parameters. Therefore these concentrations must be limited in order to ensure successful phosphate release.

In a similar manner high dissolved oxygen concentration inputs to the primary anoxic stage will result in poorer nitrate reductions. Consequently oxygen uptake from atmosphere must be avoided in both the anaerobic and anoxic basins. Gentle stirring is necessary, since without it the mixed liquor solids will settle. Ideally the stirring provided should be sufficient to maintain a homogeneous mixed liquor without creating surface disturbances which cause oxygen entrainment. Some guidance on the power requirements necessary to provide sufficient scour is offered by Kalbskopf (1972).

OPERATIONAL CONSIDERATIONS

The biological process of phosphate removal is not an unnatural phenomenon, and if a nutrient removal plant is not functioning it is not the fault of the process. Every reactor is unique and in order to obtain the best results from it, it is necessary to have experienced operators who understand the theory of the process and the operational options available to them. In general, when the operational procedure has been developed for a given plant, it becomes a matter of routine to keep it running at its optimum efficiency. But there are times when operational adjustments become necessary and in order to allow the operator the best chance of making a correct decision instrumentation is essential. The instruments to be provided in addition to the usual electrical switching and power measurement boards, are flow measuring and recording devices as well as devices for dissolved oxygen concentration determination. Minimally, the influent feed flow should be measured, but if the two recycles are also metered it becomes very much easier to control the plant.

LIST OF SYMBOLS

Symbol	Description	Units
a	Mixed liquor recycle ratios	
COD	Chemical oxygen demand	mg COD/ℓ
MLSS	Mixed liquor suspended solids	mg/ℓ
MLVSS	Mixed liquor volatile suspended solids	mg/ℓ
$\triangle P$	Phosphate concentration removed	mg/ℓ
Q	Average influent flow	ℓ/d
R	Total nominal retention time of the reactor	hours
R_s	Sludge retention time for the reactor	days
$\triangle S$	Substrate concentration utilized	mg/ℓ
s	Sludge recycle ratio	
t	minimum temperature	°C
TKN	Total Kjeldahl nitrogen (as N)	mg/ℓ

LIST OF NUTRIENT REMOVAL PLANTS

1. Driefontein Water Pollution Control Works, City of Roodepoort

   Mr CC Strydom, Works Superintendent
   City of Roodepoort
   Private Bag X30
   ROODEPOORT
   1725 011-672-6641 x 368

2. Units 53 and 2/53, Sasol II, Secunda

   Mr JJ Brand, Assistant Works Manager
   Sasol II
   PO Box 1
   SECUNDA
   2302 01363-40111

3. Meyerton Sewage Purification Works

   Mr CJ Esterhuizen, Municipal Chemist
   Meyerton Town Council
   PO Box 9
   MEYERTON
   1960 01612-3683

4. Goudkoppies Sewage Purification Works, City Council of Johannesburg

   Mr G Keay
   Assistant Chief Sewerage Engineer, Wastewater Reclamation
   City Engineer's Department
   PO Box 4323
   JOHANNESBURG
   2000 011-725-6030 x 2107

5. Unit 3 of Northern Sewage Purification Works, City Council of Johannesburg

   Mr S Deacon
   City Engineer's Department
   Sewerage Branch
   PO Box 4323
   JOHANNESBURG
   2000 011-725-6030 x 2087

6. Baviaanspoort Sewage Purification Works, City Council of Pretoria

   Mr N Thirion, Assistant Chief Chemist
   City Council of Pretoria
   PO Box 1409
   PRETORIA
   0001 012-268788

7. Rynfield Purification Works, Town Council of Benoni

   Mr JP Marais, Chief Chemist
   Town Council of Benoni
   Private Bag X014
   BENONI
   1500 011-845-1650

8. Randfontein

   Mr Odendaal, Town Engineer
   Mr A McLaren, Consulting Chemist, Krugersdorp

9. Standerton Sewage Purification Works

   Mr N Vermaak, Works Superintendent
   Municipality of Standerton
   PO Box 65
   STANDERTON
   2430 01331-4103

10. Klerksdorp Sewage Purification Works

    Mr JJ Smith, Deputy Town Engineer
    Town Council of Klerksdorp
    PO Box 99
    KLERKSDORP
    2570 018-28515

11. Stilfontein Sewage Purification Works

    Mr AT Killian, Senior Technical Assistant
    Town Council of Stilfontein
    PO Box 20
    STILFONTEIN
    2550 018-41471

12 & 13. Mitchell's Plain and Cape Flats

    Mr M Taljard
    Cape Town City Council
    PO Box 1694
    CAPE TOWN
    8000 021-679090 621721 (Mitchell's Plain)
    733150 (Cape Flats)

14. Gammams Sewage Works

    City Engineer's Department
    PO Box 59
    WINDHOEK
    9100
    SOUTH WEST AFRICA 061-21428

15. Rietspruit Sewage Works, Town of Vanderbijlpark

    Mr RW Colebank, Deputy Town Engineer
    Town Council of Vanderbijlpark
    PO Box 3
    VANDERBIJLPARK
    1900 016-312820

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WILE, et al. (?), BLACK (?), and HANNA (?) describe and discuss the effectiveness of marshland ecosystems in the removal of nutrients from sewage in an engineered system. Their work showed that during the ice-free period, phosphorus can be reduced to 0.2 mg/l in the marsh effluents. A 10-90% reduction in phosphorus levels were found due to the marshland treatment of sewage effluents. It was generally concluded that the results of large-scale tests were encouraging, but more work was needed to generate data suitable for use as engineering parameters.

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Volume

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.)	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon (U.S.)	0.05841
Milligrams per liter	Tons per acre-foot	.001360
Tons per acre	Metric tons per hectare	2.217
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Gallons (Imperial)	Gallons (U.S.)	1.2009
Acre-feet	Gallons	325,851
Acre-feet	Cubic feet	43,560
Cubic feet	Cubic meters	.028317
Cubic feet	Gallons	7.481
Cubic meters	U.S. Gallons	264.2
Cubic meters	Imp. Gallons	220.0
1,000 m^3/d	I gpm	152.8
1,000 m^3/d	U.S. gpm	183.6
U.S. gallon	Cubic meter	0.3785

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INTRODUCTION

Selenium compounds are very toxic to a wide range of organisms including algae, some bacteria, aquatic microorganisms, and animals as well as land mammals and humans. Some of these, however, adapt to a selenium-rich environment. Selenium deficiency in animal diets is also very harmful.

Selenium enters the environment primarily through the weathering and erosion of rocks containing selenium-enriched mineralization. Other sources are in stackgases and ash from coal-fired power plants and in industrial effluents including those from some copper, lead, and zinc metal refining operations. Some coal spoils piles are also enriched in selenium.

Selenium is a particularly nasty element because of the way it concentrates in the food chain. One particular example is its concentration in certain plants that grow in selenium-enriched soils. Selenium in highly seleniferous plants can reach levels of 1,000

ug/g or more, and such plants are harvested for use as a food additive in selenium-deficient areas. Some aquatic bacteria also cause an accumulation of bottom sediments with enriched selenium levels which can prove toxic to fish.

Not all that much is known about selenium pathways into the environment nor about precisely what levels can be tolerated in water without damage. Analytical techniques and determination of the speciation of selenium also leaves much to be desired.

OCCURRENCE OF SELENIUM IN MINE-MILL ENVIRONMENTS

Selenium and selenium compounds are enriched in soids in large areas of the southwestern U.S.A. It also occurs with base sulfide metal ores and in coals.

Selenium occurs as selenide Se^{2-} in metal sulfide ores as discussed by HUTCHINSON (1959). When sulfide concentrates are roasted, selenium is oxidized to selenium dioxide which is released with SO_2 in the flue gases. When the flue gas is quenched and scrubbed, the SeO_2 reacts with the quench water to form selenious and H_2SeO_2. A selenium level of 0.7 mg/l has been reported in the wastewaters of copper smelting and electrolytic refining by HALLOWELL, et al. (1973). The selenite SeO_4^{2-} appears to be the most common from of selenium in wastewaters except for pigment and dye wastes which contain selenide (e.g., yellow cadmium selenide). Other forms decompose to yield the selenate SeO_4^{2-} ion.

Selenium may, therefore, be present in effluents from base metal refining operations and also in drainage from wasterock and mill tailings in these areas. Selenium may even be present in overburden and soils disturbed in the mining process. In base metal (Cu, Pb) smelting and refining, selenium in roaster and smelter gas quench and scrubber solutions will be much more concentrated than in the final effluent.

Selenium can also be present in rainwater, possibly introduced via coal-fired powerplants to the atmosphere. LYMBURNER and KNOLL (1973) reported analyses of coal, bottom, and flyash at 2 ppm, 3.4 ppm, and 41.3 ppm respectively, which are atypically high.

PATTERSON (1976) reported on the basis of limited data that industrial wastes often contain 1-10 mg/l selenium.

At a minewater settling pond at a New Mexico uranium mining complex, selenium was found by BRIERLEY, et al. (1980) to be removed from water to some extent. Bacterial and algal populations present in the pond system are considered to actively help remove selenium along with some other contaminants as discussed below.

Disposal of effluents and precipitate sludges containing selenium may, in fact, create new sources for future contamination.

OCCURRENCE OF SELENIUM IN NATURE

Selenium occurs in the earth's crust quite commonly at an average level of 7×10^{-5} percent. It is usually present as heavy metal selenides (together with sulfide minerals), but it also occurs as selenates and selenites. In soils around the Great Lakes region, selenium is present at levels ranging from 0.1 ug/g to less than 2 ug/g according to COOPER, et al. (1974). Elevated levels of selenium formations and their derived soils occur in central Canada and the U.S.A., particularly in the desert southwestern U.S.A.

There are no known mining activities for selenium, and its production comes mostly as a by-product of copper and lead refining.

Commercial use of selenium was about 500 tpa in 1968, mostly in the elemental form as red crystals or grey powder. It is used in electronics for rectifiers, photocells, and xerography. It is also used in steel and in pigments for paints, glass, and ceramics according to COOPER (1967) and LYMBURNER and KNOLL (1973).

Selenium is usually present in water as selenate and selenite; the elemental form is insoluble but may be carried in suspension. The weathering of rocks and soil erosion are major sources of selenium in water. An estimated 10,000 metric tons of selenium are annually weathered and carried downstream to the sea. Of this, an estimated 140 tons is in solution, but only 16 tons remains dissolved in the sea--the rest ends up in sediments according to SCHROEDER (1974).

Sewage in California (both raw and treated) was found to have only 10-60 ppb selenium except for a high value of 280 ug/l in an industrial area as reported by FELDMAN (1974).

The increasing interest in the use of incineration for garbage disposal in large municipal sanitary disposal operations near major metropolitan areas leads to some concern about selenium release as an air pollutant on incineration of paper products. For incinerator fly ash quench, water soluble selenium was measured at 5-23 ug/l while incinerator residue quench water contained 3 ug/l soluble selenium at an incinerator which handled a solid waste containing 55-70% paper according to JOHNSON (1970).

Concentrations of selenium in water are usually low. Several literature reviews are available including one by NAS/NAE (1973), but most older estimates of selenium are probably too high because of the limitations of older chemical analytical methods. However, some wells probably exceed the drinking water standard of 10 ppb in the U.S.A. and 50 ppb in Ontario.

According to ONTARIO (1979), most uncontaminated surface waters contain less than 50 ug/l Se, and most drinking waters contain less than 10 ug/l (APHA, et al., 1971).

Surface waters in a part of Germany averaged 4 ug/l according to HEIDE and SCHUBERT (1970).

In seawater, the normal concentration of selenium is only 0.4 ug/l (CHAU and RILEY, 1975). Even seepages from seleniferous areas do not contain more than 500 ug/l, and this content is lost when the seepages discharge into ponds or lakes, apparently by coprecipitation with ferric hydroxide (APHA, et al., 1971).

Selenium concentrations in the Great Lakes are below 1 ug/l offshore, and mean concentrations are 0.2 ug/l or less.

Lake sediments seem to act as sinks for selenium; in the northern U.S.A., they contain 1.0-3.5 ug/g dry weight of selenium, considerably more than the usual concentration in soils (WIERSMA and LEE, 1971). Small ecosystem experiments showed that of the total amount of selenium in rain which fell on soil, 75% stayed in the soil, and 25% ran off into an aquatic system. 36% of the selenium that entered the aquatic system ended in the sediments, and most of the remainder was in the biota according to HUCKABEE and BLAYLOCK, 1974.

Deficiency of selenium in soil and in grass eaten by livestock leads to "white muscle disease." The dietary needs of livestock are in the range of 0.1-0.2 mg/d according to NAS/NAE (1973). The daily needs of selenium in the human diet is not precisely known and appears to be in the range of 0.1-0.2 mg/d according to LEVANDER (1975). Adequate diets normally contain that much selenium according to NAS/NAE (1973).

Selenium is highly toxic to animals, but poisoning generally results from eating selenium-concentrating plants. A concentration in water of 0.4-0.5 mg/l was reported by

McKEE and WOLF (1963) to be non-toxic to cattle. HEM (1970) commented that water with selenium concentrations higher than 0.5 mg/l but satisfactory in other respects for livestock watering may exist, but that it would be unusual. Toxic substances of other kinds may be present in polluted water, and incidents of poisoning of animals by drinking polluted water in the U.S.A. are not unusual.

In the 1930's it was discovered that a disease of livestock in parts of the western U.S.A. was caused by an excessive intake of selenium. The agricultural significance of selenium has been summarized by ANDERSON, et al. (1961).

Some plant species of the genus Astralagus are particularly notable for their selective concentrating ability of selenium from the soil, and some plants have been found with several thousand mg Se per Kg dry weight.

Usually, water draining from seleniferous soils--which may contain up to 1 mg/l Se--also contains such high TDS that it is rendered unsuitable for drinking water by other constraints.

Selenium poisoning of livestock is divided into two classes: The acute type called "blind staggers;" and the chronic type called "alkali disease."

The accute type is caused by ingestion of highly seleniferous plants containing 1,000 ug/g or more of selenium, whereas chronic selenium toxicity is associated with grains and plants containing 5-20 ug/g selenium according to MOXON (1958). There is extensive literature on livestock poisoning due to selenium in food plants which indicates that 5 ug/g or more can lead to death in a herbivore, and that such levels can result in plants from soil concentrations of 0.5-6 ug/g according to ONTARIO (1979). A diet containing only 3 ug/g selenium in selenite form killed rats according to SCHROEDER (1967).

ONTARIO (1979) reviews numerous examples of selenium toxicity tests to fish in which levels of 2-20 ug/l were toxic in various degrees to a variety of fish. Concentrations of selenium in fish tissue in Canada ranged from 0.16-0.6 ug/g wet weight which is a comparable level to Se in fish tissue in New York and Finnish water. In the Great Lakes, however, Se concentrations in fish from the North Channel of Lake Huron, Georgian Bay, Lake Erie, and Lake Ontario ranged at 0.56-2.0; 0.42-1.14; 0.10-0.75; and 0.06-0.96 ug/g respectively.

BARNHART (1958) reported fish mortality in a Colorado reservoir as being caused by selenium from bottom deposits which has passed through the food chain to accumulated levels of 300 ug/g in an isolated case.

Fish absorb selenium principally from food and show little uptake from inorganic or organic selenium forms in water. Some species of aquatic invertebrates take up organic selenium while others seem to be able to take up selenium from inorganic forms too.

The livers of some seals contain 46-134 ug/g selenium according to KOEMAN, et al. (1973) which is much higher than the 0.5-1.3 ug/l level found in the livers of land animals. Tissue from a northern Canadian beluga whale contained 14.3 ug/g selenium.

Because the difference between optimal and toxic intake levels in the food is comparatively narrow, 25-40 times according to HOFFMAN, et al. (1973), the possibility exists that fish-eating birds and mammals may be subject to a dangerous accumulation of selenium.

ONTARIO (1979) recommended more stringent limits for selenium in drinking water than for aquatic biota.

Selenium is biologically methylated and CHAU, et al. (1976) demonstrated methylation of sodium selenite, soldium selenate, selenocystine, selenourea, and seleno-DL-methionine by microbial action in lake sediments. All sediments which demonstrated microbial action were capable of methylating selenite and/or selenate. Mono and dimethylselenide were produced.

RODEN (1982) reported what may be a useful technique for the determination of inorganic selenium species in groundwaters containing organic interferences by ion chromatography and hydride generation/atomic adsorption spectrometry.

REGULATORY LIMITS FOR SELENIUM

The 100 ug/l Se level considered safe to protect the aquatic environment by ONTARIO (1979) may be too high if bioaccumulation effects are to be taken into account.

The U.S. EPA (1980) freshwater criteria is 35 ug/l total recoverable inorganic selenite as a 24-hour mean concentration. Maximum permissible concentration of total recoverable inorganic selenite is 260 ug/l.

ENVIRONMENT CANADA (1979, 1979a) set a freshwater criteria of 10 ug/l total Se.

The U.S. EPA (1980) marine criteria for total recoverable inorganic selenite as as 24-hour mean concentration is 54 ug/l with 410 ug/l as total recoverable inorganic selenite maximum permissible concentration.

Industry observers concluded that the above objectives for Se in fresh water may be on the lenient side if bioaccumulation effects are to be taken into account.

There is not enough information about the toxicity of selenium in the marine environment to be able to establish a reliable objective and/or criterion.

The maximum permissible limit for selenium according to the U.S. EPA (1980) is 260 ug/l with a 24-hour mean maximum of 35 ug/l.

None of the operating mine-mill discharge permits encountered in the course of this investigation included a specific limit for selenium. However, several NPDES permits, including that for the HOMESTAKE MINING COMPANY's McLaughlin project in California would cover selenium in the following catch-all paragraph:

Se (ug/L) SELENIUM

Summary of North American Water Quality Criteria for Selenium

Compiled by NORANDA

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	B.C.[9*]	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	.01 of the 96-h LC50	24-hr mean 35	10 (until further research has been done)	<100	N.D.	--		--	--
MAX. PERMISSIBLE LIMIT		--	--	260	--	100	10	10		10	.01 of the 96-h LC50
PROTECTION OF MARINE LIFE											
OBJECTIVE		.01 of the 96-h LC50 <5	.01 of the 96-h LC50	24-hr mean 54.0	<10*	--	--	--		--	--
MAX. PERMISSIBLE LIMIT		10	--	410	--	--	--	--		--	--
PUBLIC WATER SUPPLY		10	10	10	50	10	N.D. (obj) 10 (limit)	(10)		--	50
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	50	(10)	--	20 (Min.) 50 (Max.)	50	--	(10)		--	50
	IRRIGATION	20	(10)	--	20	20	--	(10)		--	20

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/9-76-023.
3. United States Ambient Water Quality Criteria for Selenium, EPA 440/5-80-070.
4. * Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada 1979. Guidelines for Surface Water Quality. Vol.1. Inorganic Chemical Substances, Selenium.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Gouin, D. et Malo, D. 1977. Rapport Technique No. 11. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
9. British Columbia - Receiving water quality objectives not available.
10. Environment Saskatchewan. 1975. Water Quality Objectives - Water Pollution Control Branch.
11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

"5. The discharge shall not cause sedimentation or concentrations of any materials in the receiving waters which are deleterious to human, animal, aquatic, or plant life." CRWQCB (1983)

On August 27, 1971, the New Mexico Water Quality Control Commission enacted a state-wide regulation that effluents of any sort in New Mexico must contain less than 0.01 mg/l total selenium.

The South African Bureau of Standards' Revision 241 of 1971 sets a recommended and maximum allowable limit for selenium in any public water supply of 0.02 and 0.05 mg/l selenium. The South African Government Notice R553 of 1983 proposed a new standard for effluents which would not be permitted to contain more than 0.05 mg/l Se.

Although Se is not specifically mentioned in most effluent discharge permits, RANDOL INTERNATIONAL LTD. believes that in the event of Se contamination of groundwater and/or surface water by an operation in most industry centers to the extent of environmental damage or impairment of the use of the water, litigation would result against the owners of the cause of the contamination. In the U.S.A. there is little question about this given the present status of CERCLA and state regulations.

The public water supply limit for selenium in the U.S.A. is 10 ug/l which is the same as in Ontario; however, the federal Canadian limit is 50 ug/l Se.

PATTERSON (1979) listed the following industries as major industrial sources of metal containing wastewaters: paint, pigment and dye production, electronics and glass manufacturing, pulp and paper production, and nonferrous metals smelting.

Selenium was listed as a regulated metal for direct dischargers under BPCTCA, BATEA, or NSPS by the following industries:

Inorganic Chemicals
Nonferrous Metals

These are the only two of a host of industry catagories. The regulations governing nonferrous metal smelting were not encountered during this investigation.

PATTERSON (1979) listed a range of concentration limits for metals in effluent limitations under BPCTCA, BATEA, and NSPS.

	Average (30-Day mg/l)	Maximum (24-Hour mg/l
Se	0.5-5.0	1.6-10.0

The Illinois Effluent Standards Advisory Group, as part of the Illinois Institute for Environmental Quality, published an "Evaluation of Effluent Regulations in the State of Illinois" in which they recommended achievable effluent limits for a variety of metals. For selenium, no conventional control technology was recommended nor was an achievable limit reported.

TREATMENT FOR SELENIUM REMOVAL

Selenium may occur as selenium metal, selenides, selenite, and selenate. Its chemistry in this respect is somewhat analagous to sulfur.

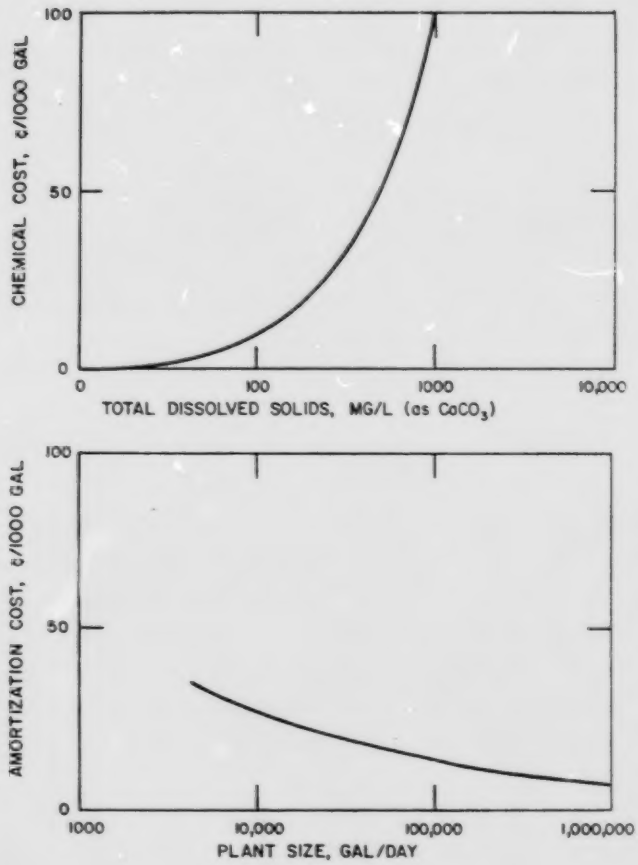
SO_2 REDUCTION AT ACID pH

One difference between selenium and sulfur is that selenium compounds or ions can be removed by the addition of SO_2 and by the addition of soluble sulfide ions in some cases. The mechanisms for this were not found during this investigation. However, it was indicated by John Shafer of EXXON Production Research that selenite is easily reduced to selenium metal by SO_2 at an acid pH. However, reduction of selenate requires the presence of high concentrations of chloride ions. Even where equilibrium diagrams indicate that selenate should be reduced, the kinetics can be very slow.

The logical method to be selected for selenium removal from solutions or effluents would depend on the nature and volume of the solution to be treated, the end-use destination of the treated solution, i.e., recycle or discharge as effluent, and the concentration of selenium in the solution to be treated.

Considering the low levels of selenium that must be achieved in an effluent to meet an environmental protection objective of 10 ug/l (the U.S.A. is currently 100 ug/l but subject to change), it would seem logical to find the main source of selenium in the operaton and to isolate a smaller flow of more concentrated solution for treatment rather than trying to treat the total plant effluent which would have a much larger volume and a lower, more difficult to treat concentration of Se.

Methods for Se and Se compound/ion removal include:



Chemical and amortization costs for a weak-base ion exchange system. [From Ahlgren (9), courtesy of *Industrial Water Engineering*.]

1) SO_2 Treatment
2) Settling
3) Lime Precipitation
4) Coagulation/Settling Using Fe Salts
5) Sulfide Treatment
6) Biological
7) Ion Exchange

It has been reported (PATTERSON, 1975) that selenium dioxide is readily reduced, which precipitates, finely-divided elementary selenium. He indicates that it is probable that the same reaction might occur for selenious acid H_2SeO_3 at acidic pH. In fact, a selenium by-product is believed to be recovered by sparging SO_2 into acidic roaster/smelter fluegas scrubber water at a base metal smelter-refinery in El Paso, Texas (NEWMONT or ASARCO?) Adsorption of slenite and selenate clearly plays an important role in its removal from solution which also appears to be pH dependent.

Selenide may be precipitated as the metal salt which, according to HUTCHINSON (1979) is also very sparingly soluble.

ACTIVATED CARBON

Secondary municipal sewage treatment plant effluents containing 2-9 ug/l selenium have been reported by ARGO and CULP (1972). Tertiary treatment by a sequence of lime addition to pH 11, sedimentation, mixed media filtration, activated carbon, and chlorination yielded selenium removal of 0% up to 89%. Best selenium removal was obtained at higher selenium concentrations. Activated carbon treatment of secondary treated municipal wastewater reduced selenium from 9.32 to 5.85 ug/l or a 37% reduction in a case cited by CULP and CULP (1974). LOGSDEN, et al. (1974) reported less than 4% removal of selenite ions from well water. This suggests that species in the treated municipal sewage may have been formed which are more easily removed by activated carbon than selenite ions. Possibly, organo-selenium compounds or chelated selenium compounds are present in the sewage.

LOGSDEN, et al. (1974) reported pilot plant test results.

ANION EXCHANGE

LINSTEDT, et al. (1971) concluded that selenium removal from effluents could be achieved with a strong acid-weak base ion exchange system. The capital and operating costs of such dual-bed ion exchange systems is strongly dependent on the dissolved solids content

as shown in the curves below. Although their actual costs per 1,000 gal. will be out of date, the relative influence of dissolved solids on cost will have remained unchanged.

REMOVAL OF SELENIUM BY BENCH SCALE ADVANCED WASTEWATER TREATMENT PROCESSES: LINSTEDT, ET AL. (1971)

Original Se Concentration: 2.3 ug/l.

Process Tested	Percent Removal
Lime Coagulation - Settling	16.2
Cation Exchange	0.9
Cation plus Anion Exchange	99.7
Process Sequence (Cumulative Removal)	
- Step 1 - Sand Filtration	9.5
- Step 2 - Activated Carbon	43.2
- Step 3 - Cation Exchange	44.7
- Step 4 - Anion Exchange	99.9

LINSTEDT, et al. (1971) did not report the efficiency of straight anion exchange without the other pretreatment steps. It must also be remembered that these results relate to the treatment of secondary sewage effluent which may have completely different removal properties compared with metallurgical effluents which have not been in contact with organics which demonstrated that neither ferric sulfate nor alum coagulation are very effective and that removal efficiency improves with increasing coagulant dosages and decreasing pH.

PILOT PLANT SELENITE REMOVAL BY COAGULATION

Initial Concentration: 0.09-0.10 mg/l Se as Selenite.

	pH	% Removal
Ferric Sulfate Coagulation		
- 25 mg/l	7.0	60
	5.5	78
- 60 mg/l	7.0	75
	5.5	83
- 100 mg/l	7.0	81
	6.0	84

		SELENIUM
Alum Coagulation		
- 25 mg/l	6.0	10
- 100 mg/l	6.0	27
- 200 mg/l	6.0	45

LINSTEDT, et al. (1971) measured 2.3 ug/l selenium in the effluent from a secondary sewage treatment plant. These workers investigated the efficiencies of removal of selenium as SeO_3^{-2} by several advanced wastewater treatment processes. His results were shown on the previous page as reported by PATTERSON (1975).

LIME PRECIPITATION

A major mineral company recently tested selenium precipitation with lime on a pilot scale. Reputedly, selenium was effectively precipitated, and the sludge could be settled efficiently. The settled sludge, when fresh, also passed the EP leach test. However, after standing for some months, the EP leach test could no longer be met as selenium became soluble as the precipitate aged. This phenomenon is possibly due to conversion to the carbonate due to action with CO_2 in the atmosphere or the resulting reduction in pH. Although selenium and selenium anions do not form carbonates, possibly calcium selenites are converted to calcium carbonate and free selenite ions in an analagous way to arsenate resolubilization from lime precipitate sludges as described by ROBINS in the section on arsenic. Certainly pH effects on resolubilization of selenium have been noted.

SULFIDE ADDITION

At a North American base metal processing facility which prefers not to be identified, selenium occurs in a sulfuric acid waste stream with a volume of 50-75 U.S. gpm. When this stream is neutralized with lime, gypsum precipitates and settles and carries the selenium with it. However, the gypsum sludge does not pass the EP leach test and would be classed as a hazardous waste. The answer is to precipitate selenium first by the addition of NaHS or H_2S and thereafter to neutralize the acid stream. In this way, the precipitated and settled sludge passes the EP leach test. It is not known whether the sludge is stable when in contact for months with water in equilibrium with atmospheric CO_2, nor in what form the selenium is removed by sulfide addition. Adsorption?

BHATTACHARYYA (1979) reported that precipitation with Na_2S is a highly effective method to obtain a high degree of separation of metal cations such as Cd, Zn, Cu, and Pb, and of the oxyanions of arsenic and selenium from complex wastewaters. The metal separation characteristics are evaluated with a dilute synthetic mixture and with an actual copper smelting plant wastewater. The overall separation of arsenic and other heavy metals and precipitate settling rates were found to be optimal at sulfide dosages about 60%

of the theoretical values and at a final pH greater than 8.0. The removal of Cd, Zn, and Cu from the actual wastewaters are greater than 99% and As and Se removals are 98 and more than 92% respectively. These data are of interest because they indicate that sulfide addition is somewhat less effective for Se removal than for most other base metals, although this may be due to the much lower levels of Se in solution.

WILMOTH, et al. (1979) tested lime neutralization, reverse osmosis, and ion exchange for their effectiveness in removing various trace elements including selenium from acid mine drainage. They found that all three processes removed Se as well as As, Cd, Cu, Hg, Ni, and Zn from acid mine drainage but not B and P. R.O. and IX were slightly more effective overall than neutralization, but the chemical requirements and need for subsequent waste treatment to handle and dispose of the concentrates offset their advantages.

Jim W. Kauffman of KERR-McGEE's technical center in Oklahoma City was quoted in C&EN, September, 1984, page 45, as saying that the selenium levels were then too high in minewater from Ambrosia Lake, New Mexico, uranium mines to be environmentally acceptable. However, preliminary laboratory and field tests showed dynamic removals of contaminants including selenium by soil-supported bacteria. The effectiveness of the process was found to be influenced by temperature, flow rate, and the presence or absence of cometabolite nutrients such as sucrose, lignosulfonate, and refining sludges. KAUFFMAN (1984) indicated the belief that the bacteria reduce minewater selenate to insoluble red amorphous selenium metal which is retained in the cell.

BRIERLEY, et al. (1980) and BRIERLEY and BRIERLEY (1981) reviewed contamination of ground and surface waters due to uranium mining and milling at the Ambrosia Lake district of New Mexico. This wastewater contains uranium, selenium, radium, and molybdenum. The KERR-McGEE CORPORATION has a novel treatment process for water from their mines 35 and 36 to reduce the concentrations of the trace contaminants. Particulates are settled by ponding, and the waters are passed through an ion exchange resin system to remove uranium. Barium chloride is added to precipitate radium as barium radium sulfate. The mine waters are subsequently passed through three consecutive algae ponds prior to discharge. Water, sediment, and biological samples were collected over a four-year period and analyzed to assess the role of biological agents in the removal of inorganic trace contaminants from the mine waters.

BRIERLEY, et al. (1980) refer to bacterial and algal populations present in the pond system which are considered agents which actively assist in the removal of the pollutants in the water. Pond-bottom sediments maintain a reducing zone and a large population of sulfate-reducing bacteria of the genera Desulfovibria and Desulfotomaculum. Uranium, molybdenum, and selenium accumulate in the pond sediment. Stimulation of the microbial sulfate-reducing activity resulted in a decrease of soluble concentrations of these elements in laboratory systems. Predominant components of the treatment ponds' algal flora are

the filamentous Spirogyra and benthic Chara. Laboratory study indicates that spirogrya is more active than Chara in the removal of uranium and molybdenum from solution, but their paper does not mention the effects of the algae on selenium removal. Nonetheless, sulfate-reducing bacteria at the pond bottom are likely to generate sulfide ions which are known to remove selenium from solution although the mechanism for this is not yet clearly understood.

More information is available in the referenced reports, the excerpt from BRIERLEY and BRIERLEY (1981) below, and publications or from:

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SELENIUM

The Chemistry of Selenium in Water

Selenium has five valence states: -2, 0, +2, +4, and +6. Only the +2 state has not been reported in nature. The higher valent oxides of selenium are powerful oxidizing agents, having a redox potential close to that of water: Se(VI/IV) 1.15 V; O_2/H_2O 1.23 V. The +6 oxide of selenium, selenate, is stable under acid and alkaline conditions. At alkaline pH values selenate is very soluble (Cotton and Wilkinson, 1972; Downes et al., 1979; National Research Council, 1976). Selenite, the +3 oxidation state, is much less soluble than selenate and is only weakly acid. At pH values from 3.5 to 9 biselenite ion would be the expected ion. Selenite is readily reduced to elemental selenium under acid conditions by mild reducing agents. In nature selenite is usually rendered insoluble by reduction to elemental selenium or formation of insoluble selenide compounds (National Research Council, 1976). Elemental selenium is extremely insoluble and can be considered a "sink" for selenium in the environment. The -2 oxidation state, selenide, occurs as inert, metal selenides. These are also considered "sinks" for selenium in the environment. There is some evidence, however, that metallic selenides may be oxidized to selenates by microbes (Downes et al., 1979; National Research Council, 1976).

The selenium content of surface waters is a function of the water's ionic content, pH (Lakin, 1973) and Eh (National Research Council, 1976). At pH 6.3-6.7 selenium is precipitated as basic ferric selenite (Howard, 1971; Lakin, 1973; Measures and Burton, 1978; Trudinger et al., 1979). In natural waters ferric hydroxide adsorbs one to two orders of magnitude more selenite per weight than kaolinite or montmorillonite; adsorption of selenium by humate is negligible. Removal of selenite by iron hydroxides concentrates selenium in sediments where the action of sulfate-reducing bacteria convert the material to a seleniferrous pyrite (Howard, 1971). If the pH of the aqueous system is about 8, selenite may be oxidized to soluble selenate (Lankin, 1979; Measures and Burton, 1978). Organic selenium species are not likely to be present in natural waters since these species would probably be hydrolyzed into selenide and then oxidized biologically (Robberecht and Van Grieken, 1980).

The Chemistry of Selenium in Biological Systems

The organic chemistry of selenium and sulfur is quite similar. Selenium may be concentrated in organic matter by substituting for sulfur in sulfur-containing amino acids (Lakin, 1973) to form selenocysteine and selenomethionine. Selenium in biological systems is usually as a selenol, RSe-H, or as a selenium ether, R_2Se. Because the selenols will be anionic in biological matter, they make good nucleophiles and good leaving groups. Consequently, selenium in these systems has an advantage over sulfur because it is more reactive. RSe^- is a strong binding agent of heavy metals

(William, 1978). In addition to being incorporated into amino acids, selenium can be methylated by biological systems to form dimethyl selenide ($(CH_3)_2Se$) and dimethyl disenlenide ($(CH_3)_2Se_2$) (Dence, 1973). The volatile organo selenium compounds are characterized by their unpleasant and strong, garlic-like odor (Downes et al., 1979).

Selenium Accumulation by Microorganisms

Groups of microorganisms, including bacteria, actinomycetes and fungi were examined for their ability to accumulate selenium. All of the groups accumulated from 0.03 to 0.18% selenium on a dry weight basis. The concentration in the cells exceeded that of the medium by factors of 60-430. Accumulation was proportional to the selenium content of the medium (Koval'skiy et al, 1968). During a study of trace element contamination of a drainage from a coal basin it was observed that bacteria had accumulated the greatest amount of selenium of all of the organisms examined from the different trophic levels of the drainage system (Guthrie and Cherry, 1979). Fungi have been noted to accumulate large concentrations of selenium. The yeast, Saccharomyces uvarum, was able to accumulate selenium from a medium containing 10 ppm SeO_2. Dried cell preparations contained 2000 ppm selenium (Yamada et al., 1978; Yamada et al., 1979). Filamentous fungi were found to accumulate selenium most rapidly during the period of intensive mycelial growth. The transport of selenate through the mycelia of the filamentous fungi, Penicillium and Aspergillus, occurs via a permease enzyme which is common for the anions, sulfate, thiosulfate, selenate, and molybdate. This permease is energy-, temperature-, pH-, and concentration-dependent (Tweedie and Segel, 1970; Downes et al., 1979; Stadtman, 1974; Stadtman, 1977).

In organisms which perform "assimilatory sulfate reduction", i.e. organisms which reduce small amounts of sulfate for sulfur-containing cellular components, selenium probably follows the same path as sulfate. Selenate can react with ATP to form 5'-adenosine phosphoselenate (APSe):

$$SeO_4^{2-} + ATP \rightleftarrows APSe + \text{pyrophosphate}$$

This reaction is catalyzed by the enzyme adenosine triphosphate-sulfurylase. APSe is less stable than APS, probably because the enzyme-bound APSe has more of a tendency to transfer the selenate to the enzyme or to water. The APSe is thought to form 3'-phosphoadenosine-5'-phosphoselenate as follows:

$$APSe + ATP \rightleftarrows PAPSe + ADP$$

PAPSe would be the presursor of selenite. This reaction has only been demonstrated indirectly, and it is not known whether APS kinase, the enzyme that catalyzes the formation of PAPS from APS, can react with APSe to form PAPSe. The six electron reduction of sulfite to sulfide is catalyzed by the enzyme sulfite reductase. This enzyme has been highly purified from some microbes, and analyses have shown the enzyme to have many components. Sulfite reductase is relatively non-specific in terms of its electron

acceptor and will reduce hydroxylamine and sometimes nitrite. Although it has never been specifically examined, sulfite reductase may reduce selenite. Once sulfide is formed it is introduced into the synthetic pathway by the enzyme cysteine synthase. If this enzyme can use selenide, this would be the mechanism for the formation of selenocysteine (Stadtman, 1974).

It has not been demonstrated whether organisms such as Desulfovibrio, which perform "dissimilatory sulfate reduction", i.e. sulfate reduction which is associated with the energy metabolism of the organism and is quantitatively significant, will use selenate as an electron acceptor. If such a reaction does occur it would involve the enzyme APS reductase which would reduce selenate to selenite (Stadtman, 1974).

Toxicity of Selenium to Microorganisms

The toxicity mechanism of selenite differs from that of selenate. The toxicity of selenite may be directly related to the reactivity of the ion since selenite is a strong oxidizing agent (Tilton et al., 1967). Selenite is thought to inhibit growth by the oxidation of sulfhydryl enzymes (Prakash et al., 1972). Through this action, selenite is reduced to elemental selenium (Kumer and Prakash, 1971). Selenite may also become incorporated between two sulfur atoms in an enzyme to form intramolecular selenotrisulfide bridges. This renders the enzyme inactive by disrupting the native structure of the enzyme (Diplock, 1976). The toxic action of selenite probably differs from that of other selenium compounds, but these mechanisms have not been clearly elucidated (Kumar and Prakash, 1971; Silverberg et al., 1976). The toxicity of selenate may result from the competitive inhibition of sulfate transport by selenate. Selenate may also be toxic because of the instability of adenosine 5'-phosphoselenate (Tweedie and Segel, 1970) and other selenium-containing species such as selenoproteins and 4-seleno-uracil in tRNA (Downes et al., 1979). In the green alga, Chlorella, selenate and selenomethionine block the metabolic uptake of methionine and the production of methionine, respectively (Shrift, 1954; Shrift, 1958).

Selenate at a concentration of 100 μg $m\ell^{-1}$ was found to be inhibitory to the growth of the fungus, Penicillium sp., but this inhibition could be reversed by the addition of sulfate. At 0.1 M sulfate the fungus grew in the presence of 1000 μg selenate per $m\ell^{-1}$. It is thought that sulfate competitively inhibits selenium entrance to the cell (Tilton et al., 1967; Kumar and Prakash, 1971). It is not known whether this protection occurs at a metabolic level or whether adsorption of selenium is affected.

The Adaptation of Microorganisms to Selenium

Organisms isolated from seleniferous soils were found to be more resistant to selenium than microorganisms isolated from soils having low selenium content (Koval'skii et al., 1968a). However, even microbes isolated from soils with little selenium adapted to

the element when placed in media containing higher concentrations of the element (Koval'skii et al., 1971).

Microbes in general are adaptable to metal concentrations, however, metal speciation is a factor in microbe adaptation. Some selenium species can be more toxic than other species. The blue-green algae, Anacystis nidulans and Anabena variabilis, exhibit a definite lag-time when cultured in sub-lethal concentrations (<200 ppm) of selenate, selenite, selenomethionine and selenopurine (Kumar and Prakash, 1971). However, both blue-green algae genera are more tolerant to selenate than selenite. Selenium, as 10 ppm of aqueous solution of SeO_2, was found to inhibit oxygen consumption by organisms in a soil/litter microcosm. The effect was immediate; however, a delay in inhibition of several hundred hours was noted if both aqueous SeO_2 and $CdCl_2$ were applied to the microcosm. This delay was not explained (Lighthart and Bond, 1976), but could be attributed to the protective effects that some heavy metals demonstrate (Allaway, 1975; Downes et al., 1979; Ganther et al., 1972; Oldfield, 1972; William, 1978; Wood et al., 1975). Selenite was found to inhibit nitrification in some soils. In these experiments 3 mℓ of a 50 μmole solution of H_2SeO_3 was applied to 10 g of soil. It was found that chemical and physical properties of soils as well as the nature of the nitrogen in the soil affected the inhibition of nitrification by selenium and other trace elements. Selenite has little effect on nitrification in calcareous soils (Liang and Tabatagai, 1977). Studies with diatoms showed that these organisms grew well at selenite concentrations of 1, 10, 40 mg ℓ^{-1}, but the diversity of the species was reduced at the highest concentration tested (Patrick, 1978). In another experiment selenate concentrations from 1-10 mg ℓ^{-1} were all toxic to diatoms; however, the blue-green alga, Schizothrix calcicola, was common even at the highest selenate concentration. There is one report that microbial nitrogen fixation and carbon consumption were enhanced by 25-100 μM selenium as SeO_2 (Jaiswal and Bahadur, 1974).

The Oxidation and Reduction of Selenium by Microorganisms

Reduction:

The reduction of selenite to elemental selenium by microorganisms is well documented. Whether this reaction is catalyzed by a specific enzyme is not positively known (Summers and Silver, 1978), although an induced adaptive enzyme, conditionally termed selenium reductase, has been proposed through studies with Bacillus megaterium (Koval'skii et al., 1968b). Reduction of selenite by Bacillus megaterium occurred at selenite concentrations of 10-100 μg mℓ$^{-1}$ and a pH of 6.4. Divalent cations, such as calcium, magnesium, manganese and cobalt, at low concentrations (0.2-6.0 mg mℓ$^{-1}$) acted as activators of selenite reduction but at higher concentrations these cations were inhibitory to the reductive process. The role of these cations is not known (Koval'skii et al., 1968a).

Work with Candida albicans also indicated that selenite

reduction to elemental selenium is an enzymatic process. Enzymatic activity disappeared upon dialysis. The coenzyme source included a quinone, a thiol compound, a pyridine nucleotide, and an electron donor (Koval'skii et al., 1968a).

The reduction selenite has been used as a differential test for the separation of members of the enterococcus group of bacteria, but the physiological implications of this capacity for selenite reduction have not been elucidated (Tilton et al., 1967). It is known that the growth of the organisms is not coupled to selenite reduction (Tilton et al., 1967).

Escherichia coli also reduces selenite to elemental selenium. When this occurs the broth cultures turn brick red. Observation of electron micrographs revealed that the elemental selenium was deposited on the cell membrane and cell wall rather than in the cytoplasm of the organisms (Gerrard et al., 1974). In other studies, using the transmission electron microscope and energy dispersive x-ray analyses, opposite results were obtained. Elemental selenium formed by the reduction of selenite by Pseudomonas sp. and Escherichia coli appeared as electron dense inclusions in the cytoplasm, and no deposits were observed in the cell wall (Silverberg et al., 1976). The selenium inclusions were distributed randomly throughout the cytoplasm. When elemental selenium inclusions were observed in Aeromonas and Flavobacterium, large fibrillar formations and spherical granular deposits were seen (Silverberg et al., 1976).

Oxidation:

Elemental selenium has been reported to be oxidized to selenate by soil microorganisms. Micrococcus selenicus reportedly oxidized selenide to selenate (Ehrlich, 1978). Both of these reactions are energetically favorable for microbial growth:

$$Se^{\circ} + H_2O + {}^{3}/_{2}O_2 = H_2SeO_4 \qquad \Delta G^{\circ} = -67.83 \text{ kcal}$$

$$Se^{2-} + O_2 = SeO_4^{2-} \qquad \Delta G^{\circ} = -142.62 \text{ kcal}$$

Thiobacillus ferrooxidans has been shown to oxidize copper selenide to cupric ion and elemental selenium (Sakaguchi et al., 1978):

$$CuSe + {}^{1}/_{2}O_2 + 2H^{+} + Cu^{2+} + Se^{\circ} + H_2O \qquad \Delta G^{\circ} = -33.26 \text{ kcal}$$

CuSe is an insoluble material, so oxidation of the selenide must occur by a mechanism similar to that used by T. thiooxidans for the oxidation of sulfur (Ehrlich, 1978).

Methylation of Selenium by Microbes

Methylation Processes:

Biological methylation was first reported by Challenger in 1945 (Challenger, 1945). He noted that, through the action of molds, organometals and organometalloids could be formed. It was proposed that methylation processes were a mechanism that organisms

used for detoxification of their environment (Lakin, 1972).

Methylation of selenium is carried out by a number of organisms including fungi, bacteria and higher plants and animals (Lakin, 1972). Methylated selenium compounds are volatilized from soil, and this activity is attributed to microbial methylation processes (Abu-Erreish et al., 1968; Barkes and Fleming, 1974; Doran and Alexander, 1976; Doran and Alexander, 1977; Francis et al., 1974; Hamdy and Gissel-Nielsen, 1977; Lakin, 1972).

Gases produced through methylation of selenium include dimethylselenide, $(CH_3)_2Se$, dimethyl diselenide, $(CH_3)_2Se_2$ and other unidentified volatile compounds. Like other methylated metals, organoselenium compounds are more toxic and have longer retention times than inorganic selenium salts (Lakin, 1972; Wong et al., 1975).

The production of methylated selenium compounds results from the alkylation of selenite or selenate (Barkes and Fleming, 1974; Wong et al., 1975), elemental selenium, selenomethionine, selenocystine, and methaneseleniate (Doran and Alexander, 1977). In studies using Corynebacterium S- adenosylmethionine was used as a cofactor to transfer methyl groups to the selenium (Doran and Alexander, 1977). From this study there was evidence that the organism first reduced inorganic selenium before methylation. Both stereoisomers, D- and L- methionine will serve equally as well as methyl donors for the methylation of selenium (Dransfield and Challenger, 1955).

Challenger has proposed a mechanism for the biological methylation of selenate (Challenger, 1978). This mechanism is outlined below:

$$SeO_2(OH)_2 \rightarrow CH_3SeO(OH) \rightarrow (CH_3)_2SeO_2 \rightarrow (CH_3)_2SeO \rightarrow (CH_3)_2Se$$

The scheme involves ionization, reduction and the coordination of a positive methyl group. L- and D-methionine is believed to be the methyl donor for reactions occurring in microorganisms (Challenger, 1978).

The formation of dimethyldisulfide has also been proposed to be analogous to the production of dimethyl sulfide from methionine. In this case methane thiol is cleaved from the amino acid, methionine, and the methane thiol is oxidized to dimethyl sulfide (Doran and Alexander, 1977).

Selenium Methylation in Water:

Methylation of selenium occurs not only in soil but in aquatic environments as well (Chau et al., 1976; Thompson, 1977).

Dimethylselenide was generated from raw sewage, and this was thought to be the result of the activity of the fungus, Penicillium (Fleming and Alexander, 1972).

Sediments enriched with selenite, selenate, selenourea, and seleno-DL-methionine produced dimethyl selenide and dimethyldiselenide. Pure cultures of organisms, believed to be species of Aeromonas, Flavobacterium and Pseudomonas, isolated from the sediments, were responsible for the methylation. The methylation process was observed to occur under both aerobic and anaerobic conditions (Chau et al., 1976).

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CHAPTER 49

SILICA SiO_2

Silica is present in almost all minerals and occurs in fresh water in a range of 1-100 mg/l according to NALCO (1979). Surface waters are often affected by seasonal diatom blooms, and diatom skeletons consist of pure silica. Silica behaves like a colloid in its reaction with adsorbents like MgO and $Fe(OH)_3$. At high concentrations, over 50 mg/l, the adsorption isotherms no longer apply, and silica behaves as a chemical precipitate. KEMMER (1979) postulates that there is probably an equilibrium between silica in colloid form and the bisilicate ion $HSiO_3^-$. In acid metallurgical solutions, silica may be in the form of H_2SiO_3. Because of this complexity, it is difficult to predict the conditions at which silica is kept in solution as water concentrates during evaporation.

Silica is objectionable at high concentration in cooling tower makeup because of this uncertainty about its solubility limits.

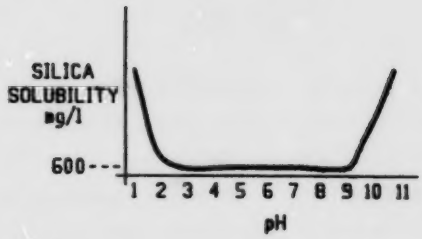
Silica is objectionable in feedwater makeup because it may form a scale in the boiler itself, and also because it volatilizes at high temperatures and redeposits on turbine blades. Treatment processes that remove silica are:

- Adsorption on magnesium precipitates in the lime softening operation.
- Adsorption on ferric hydroxide in coagulation processes using iron salts.
- Anion exchange in the demineralization process.
- Precipitation/adsorption from acid solutions onto fluidized limestone containing alumina.
- Seeded slurry R.O. and evaporation.

In mining and mineral processing environments, silica enters the scene in several ways, including the following examples:

1. At a Chilean copper recovery operation, silica can build up to 500 ppm in acidic recirculating process water also containing copper. At this level, H_3SiO_3 (silicic acid) is close to saturation. The pH of the solution is around pH 3.

   Straightforward lime addition to a high pH will not do much good because the solubility of silica appears to have reached a minimum at pH 2 to pH 9, and pH increase from 3 to 8 or 9 will not reduce silica below this minimum. Above pH 9, silica solubility starts to increase again.



At the Chilean copper plant in point, a flow of 8,000 gpm is treated for silica removal. A fluid bed crushed limestone system is employed using limestone with a relatively high $Al(OH)_3$ content. The Al content of this limestone is critical and if the available limestone has a very low Al content, $Al(OH)_3$ can be added separately to the slurry. In the same process, Cl^- is reduced from 100 ppm to 50 ppm. SiO_2 removal from solution appears to occur where the aluminum hydroxide hydrolizes at around pH 3.5. Limestone neutralizes acid at around pH 4.5. Alumina in the limestone dissolves in the acid mine drainage at about pH 3 and then reprecipitates in an active form at pH 3.5 as the limestone dissolution increases the pH. The alumina precipitated in this way is an active adsorbent for SiO_2.

If inadequate alumina is present in the limestone slurry, then silica will pass through the system.

More information on silica removal from acid solutions by fluid bed limestone slurries containing alumina may be available from:

HAZEN RESEARCH, INC.
4601 Indiana
Golden, CO 80403
(303) 279-4501
Paul Queneau

2. <u>ELLIOT LAKE URANIUM - See Appendix I</u>

At Elliot Lake, underground uranium mining operations are not permitted to recycle minewater underground. Water is used in sprays to supress siliceous dusts generated by underground operations, and recirculation of water underground would save pumping costs and also would lead to higher tenor uranium levels in the minewater which constitutes a secondary recovery. At first glance, the Ontario Ministry of Labor disallowment of water recycling because of an enhanced silicosis risk to mineworkers was construed as being due to an increased level of silica building up in the recirculated water. In fact, however, silica levels in the

minewater remain below 10 ppm. The increased $CaSO_4$ levels in recycled solutions, however, could result in fouling of the water sray nozzles which would choke off the supply of water for dust suppression. Another problem could result if mineworkers were to drink the water with elevated gypsum levels resulting from water recycling. The "silicosis risk" due to water recycling underground has nothing to do with silica levels in the water. More definition of the rules may be available from:

MR. J. L. CHAKRAVATTI
Senior Environmental Engineer
Denison Mines Ltd.
Post Office Box B-2600
Elliot Lake, Ontario P5A 2K2
(705) 848-9111

3. RÖSSING URANIUM - See Appendix I

Dissolved and colloidal silica level buildup in acid and alkaline uranium leach solutions present a problem in uranium extraction circuits. It is believed that silica levels have an influence on the degree of CRUD formation in SX circuits. Silica also builds up on filter cloths and on ion exchange resins in uranium plants. Every so often, remedial measures must be applied at many operations to remove silica from filter media and resins. The usual process is to apply hot solutions of caustic soda to dissolve silica. Such processes, however, result in osmotic shock to the resin which results in an increased resin degredation rate.

CIX barren solution tenor of 5-15 ppm U_3O_8 and a 1984 recovery into eluate of around 92% is poor by comparison with most plants around the world. The performance of the IX plant has been under scrutiny ever since the operation started, and some of the factors that have been examined are TDS buildup in the preg solution, SiO_2 fouling, ore type, and manganese levels in solution.

SiO_2 in the preg solution has increased steadily since 1980.

	March 1979	February 1984
SiO_2 (ppm) in Preg Solution	427	950

Resin regeneration frequency has been increased to keep SiO_2 levels on resin below 2,000 ppm. The cost of regeneration with 4% and 1% NaOH solutions is high, and the regeneration frequency had been relaxed without serious impact on silica loading. In this way, the cost of regeneration had been cut by 40% since 1983 by optimizing frequency and procedure. The SiO_2 level in pregnant solutions has increased as a result of the increased use of recycled solutions at Rössing as a water saving device. It is likely that some of this SiO_2 passes through the CIX system in the eluate to the SX plant where it may end up in CRUD.

Rössing ore contains variable amounts of cordierite gneiss containing phrrhotite which seems directly related to barren loss of uranium and SiO_2 levels in the pregnant solution. Certainly, the recycling of return dam solution has an influence on SiO_2 in the pregnant solution and, therefore, on the relative merits and costs associated with different resin types.

It is believed that the rate and degree of SiO_2 pickup from solution varies from resin to resin and that in the case of an operation such as Rössing, the effect of SiO_2 uptake on U_3O_8 recovery and on the cost of resin regeneration is significant enough to become a factor in resin selection.

4. JABILUKA URANIUM, NORTHERN TERRITORY, AUSTRALIA

LEVINS (1979) reported 30-150 ppm Si in acid tailings/raffinate from Alligator Rivers-type uranium ore in Northern Territory, Australia. It is not known whether this was a laboratory-derived test or whether the sample analyzed was collected from an actual operation which was recirculating tailings solution to the process.

5. COCA MINES HOG HEAVEN FLOWSHEET

LITZ and SEETON (1984) described testwork of a refractory siliceous silver ore from the Hog Heaven mine district of Coca Mines in Montana. By pretreating ore with 5 Kg NaOH/t in a hot solution, a remarkable improvement in cyanidation recovery of silver resulted. This is believed to be largely due to the unlocking of silica and jarosite encapsulated silver in the ore, possibly by dissolution of silica by the hot NaOH solution and possibly due to alteration of the jarosite structure or liberation of silver locked in alunite. When using two-hour 40°C pretreatment by NaOH solution, the most critical variable found in tests was the consumption of added sodium hydroxide. When all the data points for pretreatment of East Zone oxidized composite ore are plotted against NaOH consumed, it is found that when the consumption of NaOH during pretreatment exceeds 20 kg/t, the residual silver will be less than 30 g/t and in excess of 80% dissolution achieved in the cyanide leach step.

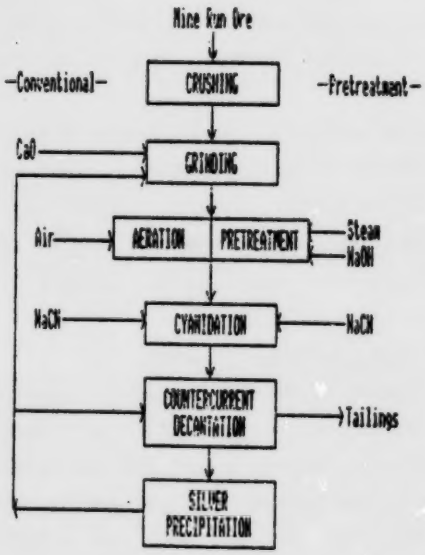
An interesting phenomenon in treating the East Zone test composite is that if NaOH is added in the grind, silver leach recoveries remain poor even when additional NaOH is subsequently added and the pulp heated. Could this possibly have anything to do with thiosalt generation?

Although it is somewhat of a wild speculation, one factor to consider in the flowsheet proposed by LITZ and SEETON (1984) is the fate of dissolved solids and especially, dissolved silica which could likely build up in recirculating solutions in the proposed flowsheet. It is not known whether the effect of solution recirculation was tested, but the chances are good that they were not since this is seldom the practice in

most precious metal bench scale testwork. Not all of the Hog Heaven ores responded positively to hot sodium hydroxide pretreatment.

If scrutiny leads to the conclusion that silica is in fact taken into solution by the proposed process, some consideration will have to be given to how it can be prevented from building up to levels that eventually interfere with metallurgical recovery.

Hog Heaven Flowsheet



Source: LITZ and SEETON (1984)

More information may be available on the effects of hot NaOH ore pretreatment from:

FRANK A. SEETON
1815 Union Drive
Denver, CO 80215
(303) 237-6522

JOHN E. LITZ
Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80401
(303) 279-4501

CHRIS MITCHELL
Coca Mines
1776 Lincoln Street
Denver, CO 80203
(303) 861-5400

6. Although, in the above cases, the ill effects of silica in ores and in process solutions have been discussed, it is noted that the Rand Water Board doses sodium silicate (waterglass) to Vaal Dam water as a coagulant for the removal of suspended metal precipitate and suspended solids. Silica is likely to help remove aluminum from solution, too, at the appropriate pH range as an alumino-silicate.

7. The NALCO Water Handbook (1979) discusses the removal of colloidal materials such as silica from water. The charge of colloidal materials (1 micron to 0.01 microns in size) is influenced by pH, so for adsorption processes to succeed, careful control of pH may be needed. It is possible for a sudden increase in pH to cause colloidal matter to desorb, rendering a poorer effluent quality than the influent.

   Although some silica in water exists as the bisilicate ($HSiO_3^-$) anion, it is likely that it is for the most part present as a negatively charged colloid. It can be removed by anion exchange in a demineralizing system, suggesting that is ionic; it can also be adsorbed on precipitated iron hydroxide and magnesium hydroxide following an adsorption isotherm which suggests that SiO_2 is colloidal.

8. UNDERGROUND HYDROPOWER, WITWATERSRAND

   In South Africa, the Chamber of Mines Research Laboratories has developed, in conjunction with a major engineering company, a hydraulically powered rockdrill that is considerably more productive than conventional pneumatic rockdrills. 95% water and 5% additives are used as the hydraulic fluid, and hydraulic pressure is provided by the head between the mine working face and the surface. The recirculated water can also be refrigerated on the surface to aid in mine cooling. In order to reduce abrasion on these hydraulic tools, it is important to remove quartz particles which could get into the hydraulic fluid as it is recirculated in the mine environment. Some of the abrasive quartz is present in extremely fine angular particles in suspension in the fluid, and these cannot readily be settled in a clarifier. RANDOL INTERNATIONAL LTD. has identified several cross-flow filtration devices that likely can remove this silica from the aqueous hydraulic fluid, although no such application has hitherto been identified either in bench scale tests nor in commercial use. RANDOL would be pleased to discuss this new idea and possibly arrange for test equipment and consulting expertise to carry out tests for sponsors of this study.

RANDOL INTERNATIONAL LTD.
21578 Mountsfiled Drive
Golden, CO 80401
(303) 526-1626
Hans von Michaelis

REFERENCES

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LEVINS, DESMOND M. (1979) Environmental Impact of Uranium Mining and Milling in Australia. Canadian Institute of Mining and Metallurgy, Ninth Annual Hydrometallurgical Meeting, Toronto, November 11-13, 1979.

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NALCO (1979) The NALCO Water Handbook. McGraw-Hill Book Company, New York, NY, pp6-7 to 6-8.

CHAPTER 50

SILVER

The concentration of silver in an unfiltered water sample should not exceed 0.1 ug/l to protect aquatic life according to ONTARIO (1979).

Silver occurs in the native state and as a sulfide as a constituent of a great variety of minerals with sulfur, antimony, arsenic, tellurium, and selenium. The average silver content of soils is about 0.1 ug/g, and certain coal ash contains 2-10 ug/g Ag.

Silver halides such as silver iodide and silver chloride are relatively insoluble in water in contrast to silver nitrate. A comprehensive review of the sources, use, distribution, losses to the environment, and human health aspects of silver have been prepared by CARSON and SMITH (1975).

Sources of silver to the environment include photographic processing, industrial electronics, cloud seeding with silver halides, municipal effluents, and mining and milling effluents and wastes. CARSON and SMITH (1975) indicated that effluents from various municipal wastewater plants indicated silver concentrations of 0.05-45 ug/l.

SILVER IN MINE-MILL POND LIQUIDS
PEDCO (1983) SUMMARY
mg/l

Mining District	No. of Samples	Average	Minimum	Maximum	Sample Source
Uranium, New Mexico	5	LT 0.007	LT 0.002	LT 0.01	Mine Water Pond
Uranium, Wyoming	4	0.009	0.005	LT 0.01	Mine Water Pond
Uranium, Other	2	0.014	LT 0.002	0.025	Mine Water Pond
Phosphate, Florida	6	0.004	LT 0.002	0.01	Tails Pond
Phosphate, Idaho	3	0.018	LT 0.002	0.041	Tails Pond
Phosphate, Other	2	LT 0.002	LT 0.002	LT 0.003	Tails Pond
Copper, Southwest	6	0.05	LT 0.01	0.15	Tails Pond
Copper, Southwest	3	0.347	LT 0.181	0.64	Leach Liquor
Copper, Other	3	0.031	LT 0.003	0.053	Tails Pond
Lead/Zinc, West	1	0.013	-	-	Tails Pond
Lead/Zinc, East	4	0.026	LT 0.01	0.072	Tails Pond
Lead/Zinc, Missouri	2	LT 0.002	LT 0.002	LT 0.002	Tails Pond
Molybdenum	3	0.003	LT 0.002	0.005	Tails Pond
Gold/Silver, Nevada	2	0.066	LT 0.01	0.121	Tails Pond
Gold/Silver, Other	4	0.087	LT 0.002	0.21	Tails Pond

Ag (us/L) SILVER

SUMMARY OF NORTH AMERICAN WATER QUALITY CRITERIA FOR SILVER

WATER USAGE		EPA[1] 1972	EPA[2] 1976	EPA[3] 1980	CANADA[4,5] 1979	ONTARIO[6] 1978	QUEBEC[7]	ALBERTA[8] 1977	BRITISH COLUMBIA[9]	SASK.[10] 1975	MANITOBA[11] 1979
PROTECTION OF FRESHWATER AQUATIC LIFE											
OBJECTIVE		--	.01 (96-h LC50)	--	0.1	<0.1	50	--	--	--	--
MAX. PERMISSIBLE LIMIT		--	--	$e^{(1.72(\ln(hard))-6.52)}$	--	0.1	--	50	--	50	.01 (96-h LC50)
PROTECTION OF MARINE LIFE											
OBJECTIVE		<1.0	.01 (96-h LC50)	--	5.0*	--	--	--	--	--	--
MAX. PERMISSIBLE LIMIT		5.0	--	2.3	--	--	--	--	--	--	--
PUBLIC WATER SUPPLY		100	50	50	50	50	50	(50)	--	50	50
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	--	(50)	--	--	--	--	--	--	--	--
	IRRIGATION	--	(50)	--	--	--	--	--	--	--	--

Compiled by NORANDA

1. Environmental Studies Board, 1973. Water Quality Criteria 1972. Environmental Protection Agency, Washington, D.C., EPA-R3-73-033.
2. United States Environmental Protection Agency, 1976. Quality Criteria for Water. EPA-440/5-76-023.
3. United States Ambient Water Quality Criteria for Silver, EPA 440/5-80-071.
4. Environment Canada. 1979. Water Quality Source Book - A Guide to Water Quality Parameters. (Values are extracted from other documents and are not guidelines established by the Federal government).
5. Environment Canada 1979. Guidelines for Surface Water Quality. Vol.1. Inorganic Chemical Substances, Silver.
6. Ontario Ministry of the Environment. November 1978. Water Management. Goals, Policies, Objectives and Implementation Procedures.
7. Gouin, D. et Nelo, D. 1977. Rapport Technique No. II. Etude de la Qualité générale de L'eau. Comité d'étude sur le Fleuve St. Laurent.
8. Alberta Environment. 1977. Alberta Surface Water Quality Objectives.
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11. Manitoba Clean Environment Commission. 1979. Report on A Proposal Concerning Surface Water Quality Objectives and Stream Classification for the Province of Manitoba.

The greatest concentration of silver was in the Colorado River basin where it was observed in 18% of the samples at a mean concentration of 5.8 ug/l. In the St. Lawrence River, concentrations in water from inshore intake pipes range from non-detectable to 6 ug/l with a mean of 2-6 ug/l, the latter levels considered by ONTARIO (1979) to be possibly suspect, i.e., possibly faulty analyses.

Both the U.S.A. (EPA) and the Canadian Government recommend a limit of 50 ug/l for domestic water supplies based on various human symptoms including blindness, lung malfunction, and skin discoloration due to prolonged ingestion.

Bacteria and fungi growth is inhibited, depending on type between 10-500 ug Ag/l.

Silver is very toxic to plants, even at levels below 1 mg/l.

Invertebrates are also sensitive to silver. Daphnia magna LC50 (24 hours) was 19 ug/l silver and, after 60 hours, 50 percent of Daphnia magna were immobilized at a concentration of 3.2 ug/l silver.

96-hour LC50's for shellfish, e.g., hard clams and the New England oyster Crassostrea Virginica, were 21 and 5.8 ug/l respectively.

Rainbow trout exposed from the egg stage over a two-month period resulted in total mortality of all fish at 2.5 ug/l and greater silver levels and even at 0.6 ug/l, there was a reduction in growth.

It is clear that many natural silver compounds are relatively insoluble, but that concentrations below the solubility limit are toxic to fish. Because of the extreme toxicity to fish over long-term exposures, an objective of 0.1 ug/l total silver for protection of aquatic species was recommended by ONTARIO (1979).

This investigation did not examine silver removals to such ultra-low levels from mine-mill effluents.

A review of silver levels in effluents and leachates from mine-mill wastes undertaken by PEDCO ENVIRONMENTAL, INC. (1983) for the EPA showed:

The PEDCO (1983) study did not flag any mine-mill effluents or solid waste leach tests as not passing the EP toxicity test. For silver, the lowest level category used was 0.05 mg/l Ag which is the primary drinking water standard.

An examination of the PEDCo results indicates that silver in tailings pond effluents ranges from LT 2 to 346 ug/l. Caution should be exerted in discharging solutions with typical tailings pond silver concentrations to fishery-supporting streams if the ONTARIO (1979)

objective of LT 0.1 ug Ag/l is to be met. However, nearly all the samples were, without dilution, below the primary drinking water standard of 50 ug/l.

In disposing of barren bleeds and cyanide leach tailings from silver and gold-silver operations, clearly silver may be a greater environmental problem than generally recognized.

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SULFATES, THIOSULFATE, SULFIDE AND POLYTHIONATES

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At mine-mill operations which treat sulfide ores or even "oxidized" ores with some sporadic sulfide content, it is not uncommon for soluble sulfides and a range of oxidation products of sulfides to occur in mine and process waters. The whole range of sulfur oxidation products from sulfide, sulfur, sulfite, thiosulfate, polythionates, and sulfate have been encountered in mine-mill environments. Of course, all of these except sulfur occur in solution, and sulfate and sulfide may form precipitates with metal cations. Elemental sulfur may be formed from sulfates and sulfide species and may occur as an aqueous suspension.

A most common source of sulfate in water is acid mine drainage which is a common phenomenon in underground mines as well as open pit mines. Sulfates are also generated from sulfide minerals in waste-rock and tailings ponds as described in the section on acid mine drainage.

Generation of thiosulfate, sulfide, ions, polythionates, and elemental sulfur in mine-mill waters and pulps is an area about which operators still know far too little. Very often, metallurgical problems are encountered which are not understood and which may be the direct or indirect result of these species which can be present in solution or in pulps without the operator being aware of their presence. Knowledge of how to inhibit or modify their formation or of practical ways to remove these species when their presence is found to be detrimental is still sadly lacking, as is quantitative knowledge of how they affect many metallurgical processes.

Of course, it is known that cyanide-soluble base metal and iron sulfide minerals in gold and silver ores result in higher cyanide consumption and may interfere with the carbon adsorption of gold and silver and may deplete oxygen levels in cyanidation pulps. On the other hand, soluble sulfide addition to pregnant solutions containing gold, silver, and base metals is advocated as one way to enhance gold adsorption on carbon by removing silver and troublesome base metals such as mercury as a sulfide precipitate before the solution comes into contact with carbon.

Sulfur dioxide is a common conditioning reagent in complex sulfide ore flotation operations, but how well are the reasons for its use known and the requirements for optimum results quantified? Does it contribute to downstream thiosalt problems in effluents?

Thiosulfate is generated in mineral processing plants when ores containing certain types of sulfide minerals are milled at a high pH. Thiosulfate and polythionates formation may be enhanced when SO_2 is added at certain eH conditions at a high pH. Polythionates are simply the polymerised form of thiosulfate.

As far as understanding the chemistry, generation, and treatment of thiosalts in milling effluents, the best summary has been provided by WASSERLAUF and DUTRIZAC (1982). Their report summarizes an extensive evaluation program by CANMET in conjunction with NORANDA MINES LTD. with emphasis on thiosulfate generation at BRUNSWICK MINING AND SMELTING CORP. LTD. in New Brunswick. One of the authors of this report who was deeply involved in the investigation, Mark Wasserlauf, has recently relocated to a consulting company, so three prominent sources of knowledge on thiosalts who have huge volumes of information and experience on the subject are:

CANMET
Energy, Mines, and Resources Canada
555 Booth Street
Ottawa, Ontario
Canada K1A 0G1
(613) 995-3117
Telex: 053-3117
John E. Dutrizac

NORANDA RESEARCH CENTRE
240 Hymus Blvd.
Point Claire, Quebec
Canada H9R 1G5
(514) 697-6640
Ken Wheeland
Head, Department of Environmental Technology
Paul Spira

GIONET, MELLOR, AND LIEBICH ASSOCIATES
(GML Associates)
2125 Boul. Industrial
Chambly, Quebec J3L 4C5
(514) 283-2462
Mark Wasserlauf

Their paper also describes methods for thiosulfate determination.

CANMET found that generation of thiosalts in milling circuits depends mainly on:

1. pH of the pulp and the type of alkalinity reagent used.
2. Sulfide content of the ore.
3. Residence time during flotation.
4. Temperature.

Mass balances were conducted at two New Brunswick mills to define the thiosalt production during various investigations by NORANDA (1977). COTTON, et al. (1977) indicated that some thiosalts in a ground pulp may originate from oxidized surfaces in the ore. Within the range of size distributions normally produced in grinding circuits, fineness of grind was found to have a small effect on thiosalt generation during the grinding operation itself and subsequent flotation. The relative amounts of thiosalts originating from grinding and from flotation in a concentrator apparently depend largely on the pH of the two steps. Other factors found by NORANDA to contribute to thiosalt formation were:

- Sulfide content of the ore; with five times the thiosalts generated by ores with 80-90% sulfides compared with 25-30% sulfides ore.
- Thiosalt generation more than doubles from 25 to 40°C'.
- Increased agitation in flotation results in greater thiosalt formation.

ROLIA and BARBEAU (1979) studied the generation of thiosalts in a continuous process development (pilot) mill at CANMET. The total amount of thiosalts generated was 959 g/t of ore which was comparable with 1021 g/t ore generated in the No. 3 flotation line at BMS before upgrading. A breakdown of thiosalt generation was as follows:

Operation	% of Total
Grinding	17.6
Conditioning	37.0
Scavenging	45.5
TOTAL	100.0

STEGER (1979) investigated the effect of pH, particle size, and airflow on the formation of thiosalts in aqueous suspensions of pyrrhotite, pyrite, chalcopyrite, galena, and sphalerte and found that an increase in temperature or pH of a suspension resulted in increased sulfate and thiosalt generation. A decrease in particle size of mineral also resulted in an increase in sulfate and thiosalt generation. Changes in airflow had a marginal effect.

ROLIA (1980) tested the generation of thiosalts during agitation of pulps on a variety of samples in a flotation cell and found a correlation between sulfur content and thiosalt production. No evident correlation was found between iron content and thiosalt generation.

ROLIA (1977) investigated the production of thiosalts during grinding of pyritic ore from the Brunswick Mining and Smelting No. 12 mine and found that:

1) Thiosalts are produced during mixing of coarse ore (minus 10#) with water prior to any grinding. The amount generated increased directly with mixing time.

2) Thiosalts diminished by two thirds during grinding with steel balls and billets at the natural pH 8 of the ore but increased during grinding with pebbles. This is probably due to either scavenging of oxygen by abraded iron or the reduction of thiosalts by iron.

3) There is an increase in the production of thiosalts with pH over the interval 9.4-10.7.

4) Less thiosalts are produced per unit weight of ore during grinding at higher pulp densities than at lower pulp densities.

5) A direct logarithmic relationship was found between the amount of thiosalts generated during grinding and the grinding time.

6) Significantly, reduced thiosalt generation (86%) occurred during grinding at pH 10.7 in a solution deaerated with nitrogen gas indicating that production of thiosalts was depressed by exclusion of oxygen. Sulfite appeared as the principal sulfur species in the deaerated solution.

Typically, when calcium is present, the gypsum level in solution before it precipitates out is around 2,000 mg/l. However, gypsum has a habit of forming supersaturated solutions and when appropriate "sequestering agents" are added, it is possible to increase the $CaSO_4$ level that a solution will carry to perhaps three times that level. This requires additions of chemical reagents, however. In flotation mills, seldom does the $CaSO_4$ level build up to saturation levels.

It has been found in acid mine drainage occurrences that the presence of magnesium in solution will inhibit the precipitation of gypsum, and much higher levels of sulfate can be held in solution in the presence of calcium ions--way in excess of the solubility product of gypsum.

HOFFMAN (1984) described one such case at the Shullsburg, Wisconsin, zinc mining district on which more information is included in Appendix I. In addition, it is rumored that several years ago a Na_2SO_4 effluent from a base metal recovery plant at Rustenburg seeped from a pond into the pyroxenite rocks below during which it leached magnesium from brucite, talc, and aragonite minerals. It is also believed that high magnesium levels in the underground minewater resulted in metallurgical recovery interference in the flotation plants that recover a copper-nickel sulfide concentrate which carries the platinum group metal primary products.

Even though the Na_2SO_4 seepage occurred from an operation outside the jurisdiction of any of the platinum producers in the area, the platinum mining and recovery companies were unwilling to discuss or confirm this interesting phenomenon due to the proprietory nature of their technology.

Polythionates are not uncommon in sulfuric acid uranium leach liquors and even at relatively low concentrations; these cause a problem by adsorbing onto ion exchange resins resulting in the blinding of resin pores. In some ion exchange systems, occasionally downtime has been attributed to rapid corrosion of stainless steel internal screens by "polythionates." Difficulties also arise when these polythionates convert to elemental sulfur on the resin beads which would clog the pores of the resin. This sometimes occurs when chemical processes are used to try and remove polythionates from resins.

Experts on ion exchange technology that are familiar with polythionate problems include:

ANTON R. HENDRIKSZ
Bechtel Civil and Minerals
Fifty Beale Street
San Francisco, CA

High concentrations of thiosalts in recycled tailings decant solutions are believed to interfere with the efficiency of the separations in the flotation plant. But where are the quantitative insights into the mechanisms for this?

At least one major new complex sulfide flowsheet was based on the belief that hexavalent chromium can safely be used as a flotation reagent because all excess Cr^{VI} would be reduced to Cr^{III} in the tailings and tailings decant solution due to the presence of thiosulfate in the pulp. NEWMONT MINING COMPANY's experience in Colorado at their Idarado Mine, which is a subject of CERCLA (Superfund) litigation, would suggest otherwise. Groundwater downstream from the Idarado tailings was found to contain hexavalent Cr in excess of safe drinking water standards.

Addition of soluble sulfides may sometimes be used to form a sulfide coating on oxidized base mineral particles rendering them amenable to froth flotation recovery by making them behave relative to collectors and frothers as a sulfide mineral particle.

It has been speculated that the presence of excessive sulfate in process solution can coat lead mineral particles with a thin layer of insoluble lead sulfate which makes these particles less amenable to flotation as a sulfide.

In tailings dumps containing sulfide mineral particles, usually the ubiquitous pyrite, pyrrhotite, or marcasite, oxidation of sulfides continues steadily for many years after the tailings pile has been deposited. When a cut is made through such tailings ponds after they are drained, be they sand or slimes, it is clearly evident that they contain zones with a wide variety in degree of oxidation and pH across the exposed cross-section of these tailings. Reclamation and retreatment of such tailings, for example, for gold cyanidation recovery may present metallurgical surprises.

Acid mine drainage is becoming recognized as a much more serious and common problem which is a feature of tailings and wasterock piles from just about every mine-mill operation that treats materials containing sulfides. The huge uranium recovery operations around Elliot Lake generate vast tailings impoundments containing 2-4% sulfide. In time these become a major source of acid which will require neutralization before seepage and runoff can legally be discharged for centuries to come. The massive sulfide ore deposits that occur across the Canadian shield and also in the western part of Canada yield tailings and wasterock that will also generate acid and sulfate for hundreds of years to come unless a better answer to their permanent disposal can be developed. The South American copper mines and Witwatersrand gold-uranium tailings all generate AMD containing sulfate as the most common anion. Of course, considering the widespread distribution and magnitude of coal mining and the ubiquitous presence of pyrite and other sulfur species in the coal waste, this industry presents the largest AMD problem.

The presence of sulfate in mine-mill effluents is used to advantage in the removal of radium from uranium mill effluents. Addition of barium chloride results in precipitation of $BaSO_4$ which coprecipitates radium as $\underline{BaRaSO_4}$.

When sulfate is present in solutions, e.g., reclaimed railings dam water recycled from tailings ponds containing sulfide-bearing materials, or from gypsum waste disposal sites (e.g., at Florida phosphoric acid plants), then where calcium is introduced to the system (as lime for pH control or as a constituent of the ore), a serious gypsum scale problems can result. The inhibition of gypsum scale formation by addition of reagents is a significant business opportunity for companies such as:

- NL Industries, Barochem Division
- Nalco
- Calgon Corp.
- Drew Chemicals

A wellknown gypsum scale inhibitor is sodium hexa meta phosphate, but there are others (cresylic acid?).

ENVIRONMENTAL IMPACT OF SULFATE AND THIOSULFATE

Sulfates, per se, are not generally considered detrimental to the environment unless their level exceeds a certain threshold which is in the thousands of mg/l range. At extremely high levels of sulfate, the water is rendered unsuitable for public water supply use and for livestock watering. The reason is that high sulfates cause humans and livestock to get the "trots."

Examples where this has occurred, for example, include the initial operation of the water treatment plant at Kromdraai Coal Mine, near Witbank, Transvaal. High density sludge decant water product was used to supply a nearby army base and soon had the army "on the run." Sulfate levels are around 2,000 ppm.

HOFFMANN (1984) described the Shullsburg, Wisconsin, water quality changes in well water after Eagle Picher closed down their zinc mines in Wisconsin.

Apart from the sensitivity of certain plant species to high sulfates in water and the catharsis effects mentioned above, the environmental impact of sulfides up to say 1,000-2,000 ppm is not known to be of major concern. Livestock can survive (not optimally perhaps) on water with TDS up to 10,000 if the TDS is mainly Na and Cl^-. When levels of other ions are high, e.g., $SO_4^=$, etc., perhaps the TDS level is reduced to 5,000 ppm, but no firm data was found.

REGULATORY LIMITS: SULFATE, SULFIDE, AND SULFUR COMPOUNDS

During the course of this investigation, no direct regulatory limits were encountered for sulfate and thiosalts, e.g., thiosulfate, thiosulfate and sulfur. However, there are indirect water quality limits that can be impacted by the presence of sulfides and thiosalts. For example:

1) At very high concentrations of sulfide ions, certain metal ions will become solubilized as sulfide complexes and may be difficult to precipitate.

2) Most effluents must meet certain pH limits before they can be legally discharged. When thiosulfate is present in an effluent, it may oxidize downstream to the extent that the pH of the receiving waters is lowered below permissible limits. A wellknown example where thiosulfate oxidation results in pH reduction is in the New Brunswick massive sulfide flotation operations in eastern Canada.

In drinking water, (SOUTH AFRICA, 1971), the recommended and maximum allowable limits for sulfate (as $SO_4^{=}$) are 250 ppm and 400 ppm respectively. Recommended tds and maximum allowable limits are 500 and 2,000 ppm respectively.

The South African Water Act (Act 54 of 1965) has recently been ammended. The Dept. of Water Affairs has been renamed the Dept. of the Environment, and it has promulgated a series of measures to protect water quality, several of which will have a major impact on mining operations in South Africa. Although sulfate concentration is not directly impacted, the new regulations are believed to have included an upper limit for TDS expressed in milliSiemens per m at 300 mS/m. This is the equivalent to aboout 2,000 ppm TDS.

Section 22 of the Water Act has been amended as follows:

> "Any person who has control over land on which anything was or is done which involves a substance capable of causing water pollution, whether such substance is a solid, liquid, vapor, or gas, or a combination thereof, shall take such steps as may be prescribed by regulation under Section 26 in order to prevent:
>
> - Any public or private water on or under that land, including rainwater which falls on or flows over or penetrates such land, from being polluted by that substance, or if the water has already been polluted, from being further polluted by that substance."

The new amendments also make provision for potentially very onerous forfeiture of profits and compensation to others who have suffered a loss on account of a polluting activity.

THIOSALT DETERMINATION METHODS

CANMET, in 1976 when they became involved in the thiosalt program, found that there are difficulties in taking reliable samples and storing them for thiosalt analysis. This is due to chemical degradation and natural oxidation of thiosalts by thiobacteria. Also, then available analytical techniques were cumbersome and largely unproved, especially on actual mill effluents.

These problems in sampling and analysis led to the conclusion that much existing chemical data on thiosalt levels in mine-mill effluents were questionable.

CANMET has developed adequate sampling procedures and simple but accurate analytical methods. These are simple titrimetric and colorimetric methods capable of determining thiosulfate, trithionate, and tetrathionate separately. Tests by CANMET indicated that freezing offered the best means of sample preservation.

Carbonate, sulfide, and sulfite were found to interfere with simple titrimetric methods as employed by NORANDA (1976) which were simple and rapid and able to measure between 50-5,000 mg/l total thiosalts but were unable to distinguish between individual polythionates.

WASSERLAUF and DUTRIZAC (1976) discuss the following determination methods:

TITRIMETRIC METHODS

Acidimetric Titrations: This is based on the oxidation of thiosulfate and polythionate with mercuric chloride as originally proposed by FELD (1911). After various modifications, the method was further improved by NORANDA (1976), and the method is described in detail by WASSERLAUF and DUTRIZAC (1982). Interferences may be caused by several components of mill waters, e.g., sulfide ions which will react with mercuric chloride to produce acid, but there is an analytical procedure around this. Ferrous iron also leads to high results which can also be avoided. Sulfate also interferes.

Iodometric Titrations: Thiosulfate and sulfite can be determined by classical methods. Two titrations are made: one in the absence of formaldehyde to determine the sum of thiosulfate plus sulphite; and one after addition of formaldehyde to mask the sulfite to determine only the thiosulfate. Sulfite is then calculated by difference. Polythionates are not titrated and do not interfere. Precautions must be taken to avoid air oxidation of the sulfite, especially in alkaline solution if accurate results are needed.

Spectrophotometric: Most spectrophotometric met' ods for polythionates and thiosulfate have been based on measuring the amount of thiocyanate produced after addition of suitable reagents. The thiocyanate is then determined as its iron(III) complex.

Colorimetric analytical methods for thiosulfate, trithionite, and tetrathionate in mill effluents were defined by CANMET. Several other techniques, including titrimetric methods using EDTA and excess barium, were investigated. Also, methods for determination of thiosulfate below 50 mg/l were investigated, but they were subject to large uncertainties. IR and UV thiosalt spectra were measured but in all cases, these methods were found to be unsuitable for routine determination of thiosalts in milling effluents.

TREATMENT FOR REMOVAL OF SULFIDE, THIOSULFATE, SULFATE, AND THIOSALTS

CANMET and NORANDA MINES LTD. have undertaken more work than any other mining company to our knowledge on the thiosalt removal process. WASSERLAUF and DUTRIZAC (1982) "evaluated fourteen methods of thiosalt destruction on technical and economic grounds. Some of these methods, e.g., electrodialysis, were the subject of paper studies only, but most of the techniques were extensively examined at the laboratory level and those such as biological oxidation were tested at pilot scale." They concluded that, "when all aspects are considered, thiosalt destruction costs become very high; furthermore, none of the methods has yet been proved to be continuously effective for the large-scale treatment of actual thiosalt effluents." Numerous reports, technical memoranda, and other documents describing the results of CANMET and NORANDA's six-year program have been issued and may still be available from CANMET. These are listed in Appendix 3A, B, and C of WASSERLAUF and DUTRIZAC (1982).

Natural oxidation of thiosalts occurs relatively rapidly at high temperatures, and all that is needed is a tailings pond and a large holding reservoir for decant solutions in summer and a location with a warm climate. Thiosalt removal becomes a problem mainly in cold climates, particularly where precipitation exceeds evaporation, and discharge of an effluent cannot be avoided.

The methods for thiosalt removal that CANMET evaluated include:

- Chemical Oxidation (Including H_2O_2, Cl_2, O_3)
- Membrane and Electrochemical Processes (Reverse Osmosis, Electrodialysis, and Electro-oxidation)
- Air Oxidation (Alkaline Oxidation, Cu-Catalyzed Air Oxidation, SO_2-Air Oxidation)

SULFUR

- Biological Oxidation (Biological Contactor, Activated Sludge; NORANDA Packed Ponds)

- Other: (Reduction by Metals; Disposal to the Sea)

Estimates of capital and operating costs were developed for most of the methods considered, but the reports urge caution in their use due to the very preliminary nature of the studies.

A summary of the CANMET project results as reported by WASSERLAUF and DUTRIZAC (1982) is inserted below together with a list of pertinent references, again with a caution that the 1982 capital and cost data in Canadian dollars are considered tentative estimates by the authors.

SULFIDE

When ores contain cyanide soluble sulfides, these will consume cyanide and add expense to a gold and silver recovery operation. The pH may also be lowered, and lime consumption will also be increased.

It is standard practice in several gold recovery operations to add lead nitrate or lead acetate to the ore to inhibit dissolution of the sulfide minerals. Examples of operations where a lead salt is added during leaching include:

ECHO BAY MINES
Lupin Project
Northwest Territories
Canada

NEW CONSORT GOLD MINE LTD.
Post Office Noordkaap 1304
South Africa
(01314) 3031
Piet Ferreira
Plant Superintendent

Often ores containing cyanide-soluble sulfide also contain ferrous iron. Such ores are best treated by pre-aeration prior to leaching to achieve better gold leach recoveries. This is particularly important if the pulp is to be treated by CIP because the presence of ferric iron and/or sulfides in solution seems to alter the way in which gold adsorbs on activated charcoal.

Additional lead nitrate is added prior to zinc precipitation as when soluble residual amounts of sulfides are present, and they have been found to inhibit zinc precipitation. The lead salts seem to remove any residual sulfides from solution. A typical dose of lead salt could be as high as 0.30 Kg/t solids as in the case at the NEW CONSORT GOLD

MINE. Sulfide addition in the presence of iron ions will effectively precipitate cyanide from pulps and solutions. This is, in fact, a way of removing cyanide from effluents which was patented by COMINCO.

SULFATE

Sulfate removal is generally not considered necessary or justifiable except for boiler feedwater production or to make a low TDS water for the AARL carbon elution process.

On the Witwatersrand (Johannesburg-Pretoria), currently there is serious concern about the steadily increasing TDS in water pumped from the Vaal Dam. This has been described by KEMPE (1983) who pointed out that about 30% of the dissolved solids reaching the Vaal Dam from point source discharges did so in 13% of the point source discharge volume contributed by acid mine drainage from underground mines. A further undetermined amount of acid mine drainage containing sulfate ions is generated by the many large mill tailings dumps.

Sulfate levels of 3,300 ppm $SO_4^=$ have been measured in the effluent discharged from the ERPM mine on the eastern Witwatersrand according to KEMPE (1983). Seepage from sand dumps are reported at 3,400-26,000 mg/l $SO_4^=$. These levels of sulfate and TDS are higher than those typically encountered in drainage from South African coal mines.

The removal of sulfates may soon become mandatory in South Africa in the context of meeting the limit on TDS. To date, reverse osmosis and electrodialysis reversal have been tested at the Hercules Shaft of the ERPM mine on the eastern Witwatersrand as described in Appendix I.

DESALINATION

REVERSE OSMOSIS

NORANDA and CANMET tested a pilot R.O. unit for thiosalt and sulfate removal from Brunswick Mining and Smelting effluent. The results were rather impressive as far as sulfate removal was concerned, but recovery efficiency does not seem to have been mentioned. One major problem with treating $CaSO_4$ containing water by membrane processes is that as the TDS concentration increases in the concentrate, so a point is reached where gypsum becomes saturated and precipitates onto the membrane resulting in fouling. This would normally occur at around 2,000 ppm $CaSO_4$ in acid mine drainage but by addition of additives, gypsum precipitation can be inhibited, perhaps to 6,000 ppm $CaSO_4$. Concentrates would exceed this level after only 80% recovery from AMD containing 1,500 ppm $CaSO_4$. This would also result in a relatively large volume of concentrate to dispose of.

MALAIYANDI and SASTRI (1981) investigated reverse osmosis separation of sulfate, nitrate, and ammonia from mining effluents. Cellulose acetate membranes were characterized in terms of pure water permeability constant, solute transport parameter, and mass transfer coefficient with NaCl solution as the reference system. R.O. behavior of several anions including sulfate were studied in the range 100-300 psi which constitutes a relatively low pressure as far as R.O. systems are concerned, and product water of suitable quality for use in recycle operations was obtained.

A major advantage of R.O. is that if several deleterious contaminants must be removed to render the water reusable in the metallurgical process or suitable for discharge as an effluent, then R.O. can very likely remove all of them with a single processing step.

MALAIYANDI and SASTRI can be reached as follows:

M. MALAIYANDI
Environmental Health Directorate
Health Protection Branch
Ottawa, Ontario
Canada

V.S. SASTRI
Mineral Sciences Laboratories
Ottawa, Ontario
Canada

MALAIYANDI and SASTRI (1981) subjected a sample of Quirke tailings effluent (a uranium mine at Elliot Lake), to reverse osmosis at 300 psig. The product water was analyzed for a series of common pollutants, and the following results were achieved:

QUIRKE TAILINGS EFFLUENT AFTER R.O.

Constituent	Feed Water (ppm)	Product Water (ppm)
Ca	100.0	5.0
Zn	2.0	0.09
Fe	10.2	0.10
Cu	2.0	0.09
Mg	18.0	1.00
NO_3	110.0	47.0
SO_4	1170	88.5
NH_3	22.6	9.1

The metal ion concentrations are within acceptable levels as far as environmental limits are concerned. A comparison of the average concentrations of sulfate and nitrate (1,400 ppm SO_4 and 110 ppm NO_3) in the tailing and levels in the product water (88.5 ppm $SO_4^=$ and

47 ppm NO_3^-) indicate that there is a respective reduction of about 16 and 2.6 times of these species. The sulfate level in the product water is lower than that drawn from the lake (142 ppm $SO_4^=$).

However, the nitrate level in the R.O. permeate is higher than the average level in the lake of 7.4 ppm NO_3^-. The product water was subjected to a second stage R.O. treatment and analyzed at 19 ppm Sulfate, 20 ppm NO_3^-, and 4 ppm NH_3. This water was suitable for recycling purposes. It is interesting to note how difficult it is to remove ammonia and nitrate to below regulatory limits by R.O. using a cellulose acetate membrane. Nonetheless, $SO_4^=$ and metals are very effectively removed.

MALAIYANDI and SASTRI did not show the recovery achieved in their R.O. tests. Considering that feedwater $SO_4^=$ concentration was 1,170 ppm, it would seem that $CaSO_4$ saturation would be reached after recovery of only 50% of the water and if $CaSO_4$ is sequestered after recovery of only 85% of the water in the feed leaving a large volume of effluent with concentrated salt levels to be disposed of. As recovery increases, so the volume of concentrate will decrease, and its level of salt concentration will increase correspondingly. As this occurs, so osmotic pressure will rise, and higher pressures are needed to yield more product. This can be largely overcome by applying a seeded slurry tubular R.O. configuration as discussed below.

BHATTACHARYYA, et al. (1979) described the use of low-pressure charged non-cellulosic membrane ultrafiltration which simultaneously remove dissolved metals and sulfate as well as suspended solids from acid mine drainage water. Of commercially available membranes evaluated, membranes of initial water flux 8.2-17.3 x 10^{-4} cm/s at 5.6 x 10^5 N/m² were most suitable. At the optimum operating pH of 4.0, a channel velocity of 200 cm/s minimized membrane fouling, and concentrated acid mine water containing 16,000 mg/l TDS caused a flux drop of less than 30%. For an acid mine water flow rate of 3,800 m³/d, 90% water recovery was achieved with a membrane having a surface area of 3.0-6.0 x 10^3 m². Ca, Mn, Fe, and Al removals were 50, 73, 98, and 85% respectively.

It was not established where the 3,800 m³/d facility referred to was located. D. Bhattacharyya can, however, be reached as follows:

PROF. D. BHATTACHARYYA
Chemical Engineering Dept.
University of Kentucky
Lexington, KY 40506-0046
(606) 257-2798

Results of the EDR and R.O. test demonstration plants at the EAST RAND PROPRIETORY MINES LTD. operation in South Africa (see Appendix I) have not yet been announced. However, it has been established that R.O. using a new configuration known as slurry seeding can achieve in excess of 95% water recovery from gypsum-bearing acid mine water

yielding the following product and a waste concentrate consisting of precipitated solids and a brine concentrate.

	Feedwater	Concentrate Brine	Concentrate Solids	Product
Ca	333 mg/l	440	24.7%	10.9 mg/l
Mg	120 mg/l	1,025	496 ppm	9.3 mg/l
Cl	88 mg/l	380		50 mg/l
SO_4	1,645 mg/l	8,250		112 mg/l
SiO_2	44 mg/l	92	5.4%*	13 mg/l
pH	4.24	4.4		5.22
Conductivity	2,650 ms/cm	12,200 ms/cm		545 ms/cm

* Acid Insoluble (Siliceous)

A flowsheet arrangement describing a seeded slurry reverse osmosis water recovery operation is shown below. The seeded slurry approach employs a recirculating slurry of solids that precipitate from the concentrate which cause supersaturated salts to precipitate preferentially on the solids particles rather than on the membrane surface.

The unit capacity of tubular R.O. modules is much smaller than for other systems such as holofine fiber and spiral wound systems. Consequently, more modules are required when employing the tubular R.O. system to treat a given flowrate. However, by using the seeded slurry process, the need for pretreatment of the feedwater can be dispensed with, and a much better overall water recovery can be achieved, as well as smaller concentrate volumes.

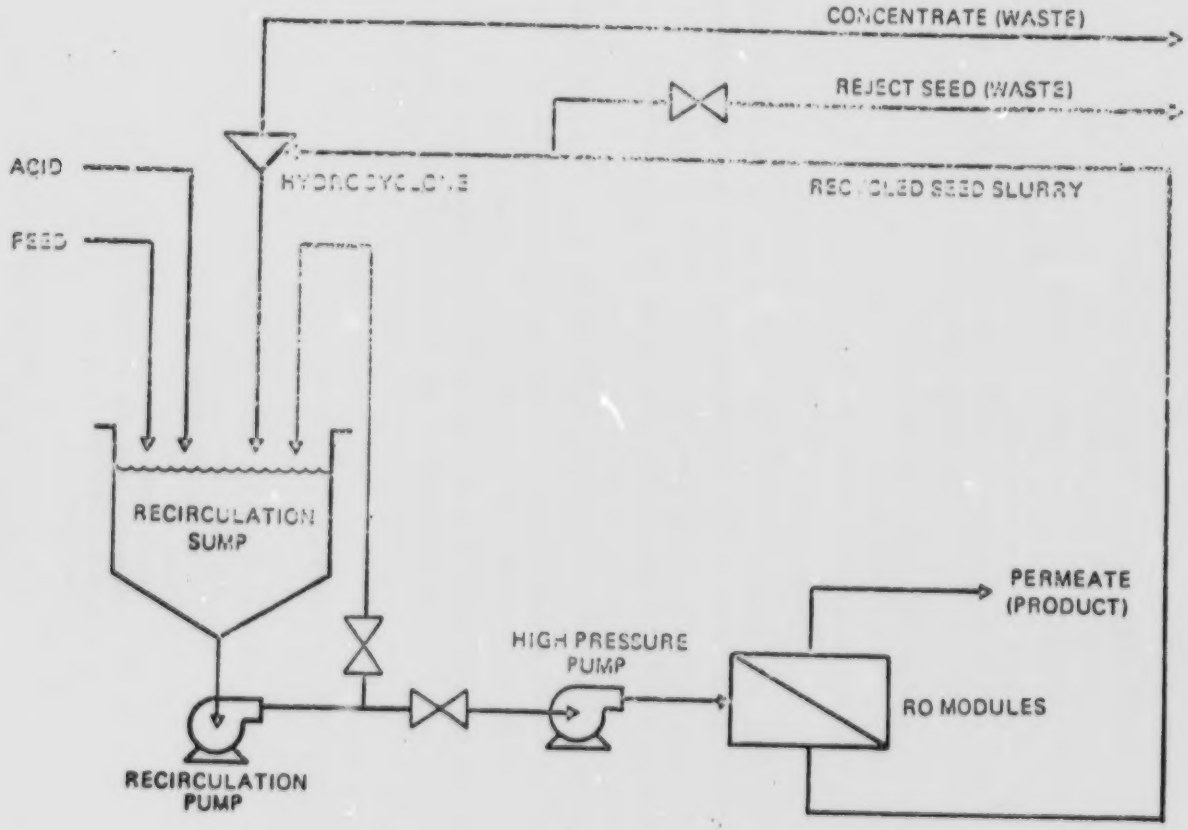
Seeded slurry technology is offered by:

RESOURCES CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, WA 98004
(206) 828-2400
Telex: 350166
Russell Vandenberg
Reams Goodloe
Tom Wolf

RESOURCES CONSERVATION COMPANY
INTERNATIONAL
Post Office Box 784561
Sandton 2146
(011)783-7121
Pat di Benedetto

RANDOL INTERNATIONAL LTD. predicts that seeded slurry technology will revolutionize the application of membrane technologies for applications such as acid mine drainage

SYSTEM SCHEMATIC
SEEDED REVERSE OSMOSIS PROCESS



treatment. Another factor in making seeded slurry R.O. economically feasible is the recent development of an improved low-cost tubular R.O. system by BINTECH (PTY) LTD., Paarl, South Africa.

EVAPORATION

At RUSTENBURG, a Na_2SO_4-rich effluent generated in the metallurgical leaching of copper, nickel, and cobalt from a matte is now treated by a multi-effect evaporating cyrstallizer to recover sodium sulfate and water as products.

The sodium sulfate is generated when a sulfuric acid waste stream is neutralized with NaOH. About 50% of the evaporated water is recovered and returned to the process water system. It is of excellent quality with a conductivity typically of 20-30 ms/cm.

When excess evaporator capacity is available, the evaporator is used to treat effluent that accumulated over several years in a nearby pond after it is first treated by lime/soda softening.

In addition, the crystallizer-evaporator treats runoff from the plantsite that contains Na_2SO_4.

The Na_2SO_4 crystallizer plant consists of a Swensson three-stage multi-effect evaporator followed by a centrifuge and air drier which yields a dry crystalline product.

Additional information might be available from:

RUSTENBURG REFINERS (PTY) LTD.
Post Office Box 483
Rustenburg 0300
South Africa
(01421) 91141
Bruce I. Dewar
Site Manager

It should be borne in mind that almost all technology related to platinum recovery is closely guarded and regarded as proprietory.

BIOLOGICAL - BACTERIA

Several biological processes have been proposed for sulfate removal from effluents. This is, after all, one of the ways nature purifies water containing metals and sulfates. It must always be borne in mind that numerous biological processes may be occurring at the same time in the same solutions--some may be generating sulfate while others are reducing it.

In discussing biological methods for sulfate and metal removal for treatment of effluents or as a final polishing step, invariably the idea is dismissed on the grounds of, "What assurance is there that metal sulfides generated in the process will be stable and will not reoxidize to produce a contamination problem in years to come?"

There really is no proof or assurance yet that this cannot happen. Nonetheless, biological systems have not been thoroughly investigated to see whether such safeguards can be engineered into a system. EDISON S. BASTIN (1926) reviewed the natural reduction of sulfates in a paper, in which he refers to sulfate depletion in soils and waters of the Black Sea and certain canals in Holland. The reason for this is the presence of sulfate-reducing bacteria which have converted sulfate to sulfide which has precipitated as FeS on the sediments in the lake and canal beds. In fact, the reason for the name Black Sea is the color of these sulfide sediments on its shores.

The reduction of sulfates in natural waters through the action of sulfate-reducing bacteria with the generation of hydrogen sulfide has been observed by many workers dating back to 1886. The situations in which such bacteria have been found include river muds, brackish canal muds, sewage, soils, lake sands, dune sands at depths to 37 meters, black muds of the ocean bottom to depths of 16 fathoms, and bottom muds of the Black Sea to depths of 2,118 meters. Three species of sulfate-reducing bacteria have been isolated and described by the early workers. These include Microspira aestuarii which is strictly anaerobic and was described by VAN DELDEN (1903-1904). Another sulfate-reducing bacteria is Microspira desulfuricans described by KUHR (1921).

Water drained from blue muds taken from the ocean floor by MURRAY and IRVINE (1895) were found to be higher in $CO_3^=$ and depleted in $SO_4^=$ than the normal seawater from which the muds were derived. The gain in carbonate is due to reduction of sulfate by organic matter in the muds and the subsequent decomposition of the alkali earth sulfides by the carbonic acid thus formed to yield alkali and alkalic earth carbonates. Sulfides formed in the process are deposited as FeS.

A thermophilic bacteria, Vibrio thermosulfuricans that flourishes at 55°C' and which grows more rapidly than Micorspira desulfuricans and M-aestuarii, has been identified by ELION (1924-1925). Vibrio thermosulfuricans is morphologically indistinguishable from the other two bacteria and, therefore, is probably an aclimated strain of the other two. A supplementary source of organic carbon may be needed for energy by these bacteria.

STARKEY (1956) reviewed the transformations of sulfur by microorganisms. He found that diverse microorganisms participate in transformations of sulfur, many of which command attention as they result in compounds having objectionable odors or causing destruction of industrial equipment. Incompletely oxidized inorganic sulfur compounds and elemental sulfur are oxidized principally by photosynthetic and chemosynthetic bacteria, but certain heterotrophic microorganisms can also bring about some of the

reactions. Two principal sulfur products are formed--under anaerobic conditions, sulfide is the stable product whereas under aerobic conditions, sulfate is the stable one.

Certain bacteria can oxidize thiosulfate, tetrathionate, and sulfite as well as sulfide and elemental sulfur. The green bacterium Chlorobium thiosulfatophelum, for example, oxidizes sulfide, sulfur, thiosulfate, and tetrathionate to sulfate, whereas Climicola oxidizes only sulfide and sulfur. All the purple and green sulfur bacteria can develop in the absence of petrified organic matter, meeting their energy requirements from light, with carbon dioxide as their only source of carbon, and oxidizing reduced sulfur materials.

The significance of this is that although bacteria do reduce sulfate and thiosalts to sulfur or sulfides, other bacterial processes can reverse the reaction and convert sulfur, sulfite, and thiosalts to sulfate, as do the wellknown thiobacillus ferrooxidans and thiobacillus sulfoxidans.

Inorganic sulfur compounds are oxidized by various heterotrophic microorganisms that develop equally well with or without these compounds. ARMSTRONG (1921) reported oxidation of thiosulfate by several fungi. TRAUTWEIN (1921) described certain cultures that oxidized thiosulfate to tetrathionate. These were found to be heterotrophic bacteria, and this transformation can, according to STARKEY (1956), be brought about by various bacteria, actinomycetes, and filamentous fungi growing on organic substrates.

GUITTONEAU (1927) and GUITTONEAU and KEILLING (1932) found that elemental sulfur was similarly oxidized to thiosulfate and tetrathionate by many heterotrophic bacteria, actinomycetes, and filamentous fungi during development on organic media.

WASSERLAUF and DUTRIZAC (1982) refer to the pilot scale work carried out by NORANDA at Brunswick Mining and Smelting with a view to oxidizing thiosalts to sulfate. Although the process works well on a bench scale, Brunswick Mining and Smelting has not been able to make this process work economically on a commercial scale in the New Brunswick climate. However, possibly a similar system (pebble bed substrate for bacterial support) could be developed for bacterial sulfate removal from effluents. Potential problems include the clogging of pores by accumulations of sulfur° or iron sulfides if the process is operated under anaerobic conditions or if suspended solids settle out in the open spaces of the pebble bed.

To date, there has been no sign of any testwork to develop the use of rotating biological contactors for biological SO_4 removal from solution although an RBC has successfully been demonstrated for oxidation of ferrous to ferric ions in acid mine drainage. To date, not much need has been noted for $SO_4^{=}$ removal in North America where RBC technology has developed. RBC's might prove useful in the context of South Africa's need to remove sulfate from Witwatersrand effluents.

Several other bacteria types are also known to reduce sulfate including Desulfovibrio desulfuricans and Desulfotomaculum. However, to date, no engineered system to use these has been tested to our knowledge.

SPISAK (1979) reviewed current research of the sulfur metabolic symbiosis of Desulfovibrio desulfuricans and Chlorobrium thiosulfatophilum, which sheds some light on the chemistry changes of solutions in contact with these bacteria.

John Spisak can now be reached as follows:

JOHN F. SPISAK
Anschutz Minerals Corp.
555 Seventeenth Street
Denver, CO 80202
(303) 298-1000

Another worker in this field is HERRICKS (1982) who evaluated two biological methods for the treatment of acid mine drainage. The first was the treatment of impounded AMD through the addition of a mixed microbial community and C sources appropriate for their maintenance. In the second method, an anaerobic digestor provided waste liquors high in organic acids. AMD was mixed with the digestor effluent in an anaerobic reactor which

maintained SO_4^{2-} reduction. The utility of a pilot plant design incorporating anaerobic digestion, SO_4^{2-} reduction, and final clarification and settling was demonstrated.

CORK (1985) described a two-step bioprocess for converting gypsum to sulfur. The bioprocess is completely aerobic and consists of an immobilized whole cell reactor coupled to a light efficient bioreactor. The first step of the single-stage reduction, single stage oxidation process is catalyzed by an acetate degrading, sulfate reducing microorganism. The second stage "gas to liquid" phase biocatalysis converts H_2S and CO_2 to acetate. The acetate from the second step is used to reduce sulfate in the first step. An economic analysis by the author indicates that the cost of the sulfur produced is dependent on the price of efficiently utilizing electrically generated light and establishing other marketable bioproducts. More information may be available from:

DR. D. J. CORK
Illinois Institute of Technology
#348, Life Science Building
3105 South Dearborn Street
Chicago, IL 60616
(312) 567-3492

Once again, a careful examination of the economics of innovative processes such as this is called for as little data is currently available to provide a frame of reference.

WAKAO, et al. (1979) described a process for treatment of acid mine water using sulfate-reducing bacteria at the abandoned Matsuo sulfur and iron sulfide mine in Japan. The acid mine water containing sawdust was used as a basic culture medium. Vigorous sulfate reduction and neutralization of the acid mine water occurred in the batch cultures supplemented with an organic nutrient, either peptone, sodium formate, sodium lactate, or sodium pyruvate. Sulfate reduction evidently did not occur below pH 4 but started only when the pH of the culture rose to the range 4-5.2, possibly through the activity of other heterotrophic microflora. Neutralization of the acid minewater (pH 4) by sulfate reduction was also possible in the continuous flow system if organic nutrients usable by bacteria were supplemented, and the flow rate of effluent was properly controlled.

TUTTLE, et al. (1968, 1969) showed that mixed cultures of sulfate-reducing bacteria could reduce sulfate ions and increase the pH of acid mine water when supplied with wood dust, degradation products of which served as carbon and energy sources for the bacteria. DECKER and KING (1973) also showed that the introduction of an organic energy source (waste water sludge) into an acid strip mine lake will substantially hasten the recovery of the lake.

SISLER, et al. (1977) showed that the rate of neutralization of acid mine water by sulfate reduction would increase electrobiochemically if electrodes connected with an external conductor were placed in the bottom sediment and also near the surface in the overlying water at pH 3 or above.

WAKAO, et al. (1979) concluded that sulfate-reducing bacteria are obligate anaerobes, and therefore their growth and activity are significantly influenced by the oxidation-reduction potential of the environment. Sulfate-reducing bacteria have been reported to require an environmental Eh value of below-200 mV for the initiation of growth (ZOBELL and RITTENBERG, 1948; ZOBELL, 1959; and POSTGATE, 1959).

Hydrogen ion concentration is a limiting factor of bacterial sulfate reduction in acid mine water because the growth and activity of sulfate-reducing bacteria were favored by neutral or slightly alkaline conditions pH 6.5-7.5 but were retarded by acidic conditions according to ZOBELL (1957), KIMATA, et al. (1955); TEZUKA (1965); and ABD-EL-MALEK and RIZK (1963). WAKAO, et al. (1979) found that sulfate reduction failed to occur below pH 4 and started when the pH of the culture reached 4-5.2, irrespective of the initial pH. The initiation of sulfate reduction in acid mine water requires an increase of pH to the threshold value of 4-5.2 either by the activity of other heterotrophic bacteria or by the addition of neutralizing agents. A higher initial pH increases the sulfate reduction rate by decreasing the lag period. Once started, progress of sulfate reduction in the acid mine water results in an increase in pH to neutral or alkaline values, probably due to the formation of alkaline species such as bicarbonate in addition to the formation of sulfides from sulfate (ABD-EL-MALEK and RIZK, 1963; and ABD-EL-MALEK and RIZK, 1963a).

It is also wellknown according to WAKAO, et al. (1979) that only a few compounds such as lactate, pyruviate, malate, and formate are utilized by sulfate-reducing bacteria as carbon and energy sources for sulfate reduction (TEZUKA, 1965; SATO and HATTORI, 1961; CAMPBELL and POSTGATE, 1965; and POSTGATE and CAMPBELL, 1966). Sulfate reduction works in cultures supplemented by peptone, wheat bran, or glucose because of synergisms between sulfate-reducing bacteria and other heterotrophs. WAKAO, et al. (1979) point out that sulfate-reducing bacteria commonly occur in close association with other hetrotrophic bacteria, and the latter decompose a wide variety of organic compounds, including carbohydrates, amino acids, peptone, organic acids, and alcohols with the formation of essential nutrients for the growth of sulfate-reducing bacteria (TEZUKA, 1966; TEZUKA and KITAMURA, 1963; TEZUKA, et al., 1964; TEZUKA, 1964; KIMATA, et al., 1955; and WAKAO and FURUSAKA, 1976). Therefore, the addition of sufficient amounts of readily decomposable organic compounds to acid mine water enables the sulfate-reducing bacteria to develop and reduce sulfate in the presence of a mixed bacterial population. This may prove to be a limiting factor unless a large quantity of low cost organic materials suitable for the purpose can be found near the location of the acid mine drainage treatment need.

It has been generally thought that various metal ions inhibit the sulfate-reducing bacteria, but very little is known about this. At the Matsuo Mine in Japan, described by WAKAO, et al. (1979), there is some Cu^{2+} in the acid mine water. WAKAO, et al. (1979)

found that Cu and Zn do not suppress the sulfate reduction by bacteria contrary to the findings of others (KIMATA, et al., 1955; POSTGATE, 1965; and DOWA MINING (1974).

WAKAO, et al. (1979) conclude, however, that the inhibitory effects of various metallic and inorganic ions (Cd, Pb, Hg, Mn, Al, As, etc.) which occur in minewater should be investigated to learn more about the sensitivity of sulfate-reducing bacterial processes to metal contaminants.

WAKAO, et al. (1979) attempted to establish sulfate reduction on a continuous flow basis. The pH of the effluent solution after it had passed through the sawdust culture remained neutral, and virtually all iron was removed as a black sulfide. When the pH was kept at four in the influent mine water, sulfate levels were significantly reduced. Once the pH was allowed to drop to three, however, a steady sulfate reduction was not established, and the sulfate levels in the effluent increased while pH dropped with time.

The continuous flow experiment in which organic nutrients were added to the water showed that sulfate can be reduced if adequate nutrients are supplemented.

WAKAO, et al. (1979) envisage a series of ponds supplemented with organic matter to treat acid mine water from the abandoned Matsuo Mine. However, they point out the need to solve the possible problem of iron sulfide re-oxidation to generate sulfate once the precipitates leave the anaerobic fermentation system. They feel that some treatment will be needed to remove excess hydrogen sulfide as well as FeS from the system. They suggest that this might be possible using anaerobic photosynthesis bacteria capable of oxidizing hydrogen sulfide to sulfur as proposed by CORK, et al. (1978) and CORK (1985).

WAKAO, et al. (1979) indicated that they will further investigate the applications of bacterial sulfate reduction and sulfide oxidation by photosynthetic bacteria to a purge process for acid mine water in the field. More information may now be available from:

NORIO WAKAO, TAEKO TAKAHASHI, ET AL.
Laboratory of Applied Microbiology
Dept. of Agricultural Chemistry
Faculty of Agriculture
Iwate University
Morioka 020, Japan

It is known that CANMET, Ottawa, has an ongoing experiment in which acid mine water is percolated through sawdust and in which the pH of the effluent increases presumably for the same reason. More information may be available from:

CANMET
Energy, Mines and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1
(613) 995-4124
Telex: 053-3117
Gordon M. Ritcey
A. Jongejan

In Colorado, an interesting, possibly related phenomenon has been observed in which a mountain stream in its upper reaches is polluted by base metal acid mine drainage. However, after being filtered through a series of beaver dams, the lower reaches support native trout. This observation was made by one of the engineers employed by the Colorado Dept. of Health who advocated research into the development of passive treatment systems.

In seeking expertise on biological processes and their applicability for mining industry effluent treatment, sponsors are referred to the following consultants:

ADVANCED MINERAL TECHNOLOGIES, INC.
Post Office Box 1339
Socorro, NM 87801
(505) 835-0207
Corale L. Brierley, Ph.D.,
President

In addition to examining bacteria, possible development of the algae Oscillaria and Ulothrix may have potential in sulfate removal. These attached filamentous algae have, for a long time, been recognized for their ability to decompose calcium sulfate to sulfur and H_2S, but very little is known about the conditions under which this process is optimized.

CONCLUSIONS: BIOLOGICAL PROCESSES

In conclusion, it must be emphasized that biological sulfate, thiosulfate, and thiosalt removal processes are still in the early stages of conceptualization. There are numerous technical aspects to be resolved and, most importantly, to date none seems to have quantifiable data on the economics of these processes. For example, what size ponds are needed, how much organic nutrient supplement is required and at what cost, and how much electric power is needed for photosynthetic processes? No doubt the economics and applicability of biological processes will vary greatly with location and site-specific conditions, including climatic constraints.

CHEMICAL PROCESSES

SOIL GEOCHEMICAL ATTENUATION

CRONCE, et al. (1980) described a test in which acid water was applied weakly at three levels (0, 12.5, and 25 m^3/week) to an unlimed and a limed (20 t/hr) floodplain soil. Soil water samples were collected weekly at soil depths of 25, 75, and 130 cm. The soil water samples and the acid water were analyzed for pH, total acidity, Al, Fe, Mn, K, Ca, Mg, Na, and $SO_4^=$. The effect of liming, levels of acid water irrigation, and depth in soil profile on the soil water quality were determined. Initially, both the unlimed and limed areas had a considerable capacity for renovating the applied acid water. However, with time, lower pH values and higher levels of Al, Fe, and Mn were found at 25- and 75 cm soil depths in the unlimed areas. When the soil was limed, the soil water at 25 cm depths was nearly neutral or alkaline throughout the study and practically devoid of Al, Fe, and Mn. At the 130 cm depth on both unlimed and limed areas, the pH, total acidity, Al, Fe, and pH of the soil water remained relatively unchanged, even after 525 m^3 of acid water had been applied. The growth of ryegrass and tall fescue was not adversely affected by irrigation with the acid water but was significantly increased by liming. The tall fescue yield was significantly increased by increased levels of acid water irrigation.

Geochemical adsorption and attenuation of contaminant migration by natural soils and rock can be an extremely powerful tool when the correct conditions exist. Geotechnical and geochemical expertise in these areas are available from:

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CHEMICAL PRECIPITATION

ALUMINA-LIME-SODA PROCESS

The alumina-lime-soda process has been shown to be able to reduce high $SO_4^=$ concentrations to 250 ppm without difficulty through a two-stage process in which raw water is treated with aluminate and lime to pH 12.0-12.1 to precipitate calcium sulfoaluminate $2CaSO_4.Al_2O_3.3CaO.XH_2O$. Effluent from stage 1 is pH-adjusted by adding CO_2 to pH 7.

The principles, performance, and economics of the alumina-lime-soda process are described by NEGBEN, et al. (1976), and a copy of their paper was inserted in Chapter 24 on treatment of acid mine drainage.

More information and possibly updated economics may possibly be available from the authors:

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PEREDERII (1979) in the U.S.S.R. published a description of a two-step process for the removal of Cu^{2+} and $SO_4^=$ from Cu mining wastewaters. In the first stage, the wastewaters were stirred at 700 rpm with a lime suspension at pH 12.35 (optimum condition). After settling, the clear liquor still contained 2,000 mg/l $SO_4^=$. In the second stage, the clear liquor was treated with Al(OH)5Cl and $Ca(OH)_2$ at pH 11.9 to precipitate $.3CaO.Al_2O_3.2CaSO_4.31H_2O$. The clarified wastewater was then discharged. The neutralization step gave a precipitate of $CaSO_4$ containing entrained Cu and Zn. The precipitate after drying could be used as a metallurgical flux.

A second U.S.S.R. application described by SAL'NIKOVA, et al. (1981) also involves the removal of calcium sulfate from wastewater by chemical precipitation. Ca and $SO_4^=$ concentrations of tailing leachate were reduced from 800 and 2,140 ppm to 180 and 300 ppm respectively by precipitation with aluminous cement to give insoluble non-toxic "ettringite" cement. The concentrations in minewater were also reduced from 310 and 3,470 ppm to 100 and 300 ppm respectively in a second application. The smaller amounts

of Cu, Fe, Zn, and Mg present in solution were also reduced. Not much more information was provided on this process other than the above from Chemical Abstracts.

The economics of the above chemical processes would likely depend on the cost of acquiring lime to reach high pH's in excess of 12 which, in the case of some solutions, would be expensive, and the cost of $Al(OH)_3$, Al(OH)5Cl, or aluminous cement. A further cost to take into account is that of safely disposing of the precipitated solids in a way that complies with the regulations. It is likely that these processes would cost no more than the treatment of water by R.O. which is estimated for large operations (5,000 m^3/d or more) to be around \$0.30-\$0.60/m^3 as a rule of thumb.

CHEMICAL REMOVAL OF SULFIDES

In straighforward metallurgical solutions, an obvious way to remove soluble sulfides from solution would be by adding a cation, e.g., Fe^{++} which forms an insoluble sulfide that also settles easily. In cyanidation pulps, when cyanide-soluble sulfides are present, it is common practice to add a soluble lead salt such as $Pb(NO_3)$ or $Pb(Ac)_2$ which then precipitates dissolved sulfides and also coats the surface of sulfide minerals thereby inhibiting the further dissolution of sulfide in the pulp solution. In so doing, sulfide dissolution is inhibited, and sulfide already in solution is precipitated. The alternative chemical method for removal of sulfide is through oxidation to a sulfate.

CHEMICAL REMOVAL OF THIOSALTS

No convenient way was encountered for chemical removal of thiosalts and thiosulfate. If thiosalts come in contact with cyanide solution, they usually consume cyanide and form thiocynate. Thiosalts can possibly be oxidized to sulfate by intense aeration at high pH, but this is an expensive, time consuming route.

ELECTROCHEMICAL

An unusual innovation was described by ANISIMOV, et al. (1978), another Soviet author, who treated mine pit water in a small rectangular plastic vessel equipped with a graphite anode and a metallic screen cathode separated by an asbestos diaphram. The wastewater contained Ca^{2+}, Mg^{2+}, K^+, Na^-, Cl^-, HCO_3^-, and SO_4^{2-}. The total salt concentration was about 14 g/l. In the reaction, Ca^{2+}, Mg^{2+} precipitated as hydroxides; K^+ and Na^+ formed KOH and NaOH; Cl^- yielded NaClO and $KClO^-$, H_2 evolved on the cathode, and clay particles were collected in the anodic compartment which was acidic. The cathodic compartment contained colloidal matter and gave an alkaline reaction. The processed water was used for flotation of coal sludges. Their paper does not describe what

happens to the sulfate. Presumably, it migrates to the acid anode compartment and probably remained as sulfate at a concentration that was higher than in the feedwater.

The description sounds as though it describes a bench-scale test. No commercial scale operations employing this process are known, and the economics are also not defined.

SISLER and SENFTLE (1977) described a biogeochemical neutralization of acid mine water in which biological processes are enhanced by applying an electric field. Not much is known about this still new branch of technology or its performance or economics.

Additional information on the nature of permeate, concentrate, and the recoveries possible by conventional R.O. systems from acid mine drainage may be contained in a report by the U.S. EPA written by WILMOTH (1973).

CANMET

REPORT 82-4E

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

THE CHEMISTRY, GENERATION AND TREATMENT OF THIOSALTS IN MILLING EFFLUENTS - A NON-CRITICAL SUMMARY OF CANMET INVESTIGATIONS 1976-1982

M. WASSERLAUF AND J.E. DUTRIZAC

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES

MARCH 1982

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

2973

Canada

Table 9 - Generation of thiosalts in the mill circuit at Brunswick Mining and Smelting*

Operation	Thiosalts generated g/min	% of Total
Adding internal reclaim water to lines 1 & 2	1363	5.6
Grinding (lines 1, 2, & 3)	3215	13.2
Aeration (lines 1 & 2)	3290	13.6
Flotation (lines 1, 2, & 3)	4316	17.8
Flotation (primary upgrading)	5193	21.4
Flotation (secondary upgrading)	4144	17.0
Adding SO_2 (primary upgrading)	454	1.9
Adding SO_2 (secondary upgrading)	1049	4.3
Heating 85°C (primary upgrading)	818	3.4
Heating 85°C (secondary upgrading)	445	1.8
Total	24287	100.0

*As determined during Sept. 19-30, 1977.

Table 10 - Generation of thiosalts in the mill circuit at Heath Steele Mines*

Operation	Thiosalts generated g/min	% of Total
Grinding	423	15.5
Aeration	322	11.8
Conditioning for Cu-Pb flot.	85	3.1
Bulk Cu-Pb flot.	693	25.3
Cu-Pb Scav and Cu-Pb Cl	162	5.9
Conditioning for Zn flot.	267	9.7
Primary Zn flot. and Cl	209	7.6
Second. Zn flot. and Cl	441	16.1
Zn thick O/F	80	2.9
Cu thick O/F	12	0.4
Pb thick O/F	46	1.7
Total	2740	100.0

*As determined during June 5-16, 1978.

Table 11 - Comparison of mill process parameters at Heath Steele Mines and at Brunswick Mining and Smelting

Size	Heath Steele			Brunswick Mining		
Ore milled, TPD	3500			10 000		
Sulphides in ore, %	75			80		
Grind	65% - 400M			68% - 400M		
Fresh water used, U.S. gal/min.	1832			2950		
Retention of ore in mill	1.5-2 h			3 h		
Metallurgy						
	Cu%	Pb%	Zn%	Cu%	Pb%	Zn%
Mill feed	1.0	1.5	4.5	0.3	3.0	7.0
Copper conc. grade	29	5	4	20.0	8.0	5
Lead conc. grade	2	30	4	0.3	36.0	6
Zinc conc. grade	<1	1.2	50	0.2	1.0	52
Bulk conc. grade	-	-	-	0.8	21.0	33
Recovery	68	50	74	40.0	60.0	80
Total thiosalts generated						
Thiosulphate ($S_2O_3^{2-}$), g/min	1800			12 000		
Trithionate ($S_3O_6^{2-}$), g/min	1100			10 000		
Tetrathionate ($S_4O_6^{2-}$), g/min	100			2 000		
Total thiosalts, g/min	3000			24 000		
Flotation lines						
				Line 3	Line 2	Line 1
Ore processed, TPM	2.43			2.43	2.25	2.25
Fresh water/ton, ore, U.S. gal	754			525	367	367
Thiosalts generated in:						
Grinding, g/min	423			1705	755	755
Aeration, g/min	322			-	1645	1654
Cu-Pb Rgh, g/min	778			776	1007	1007
Prim Zn Rgh, g/min	476			-	136	136
Prim Zn Upgr, g/min	135			2010	2010	2010
Sec Zn Upgr, g/min	441			1880	1880	1880
Cu-Pb separation, g/min	165			921	921	921
Total thiosalts, g/min	2740			7292	8354	8354

place at the natural pH of the ore. Only the zinc circuit is alkaline.

(2) Upgrading of concentrates at BMS is done by cleaning only, whereas SO_2 is used for Cu-Pb separation and to improve grade and recovery of Zn concentrate at BMS.

Rolia and Barbeau studied the contribution of sulphur dioxide to thiosalt generation in the flotation circuit at BMS (78). Their results indicated that bisulphite is formed initially upon addition of SO_2 to pulp slurries; the bisulphite then reacts with mineral particles, other thiosalts, and with air during flotation, resulting in more thiosalts.

LABORATORY STUDIES

To define the occurrence of thiosalts during beneficiation of sulphide ores, studies were conducted at CANMET from 1977 to 1980.

Rolia investigated the production of thiosalts during the grinding of pyritic ore from the BMS No. 12 mine (79). His findings were as follows:

(1) Thiosalts are produced during mixing of coarse ore (minus 10 mesh) with water, prior to any grinding. The amount generated increased directly with mixing time (Fig. 14).

(2) Thiosalts diminished by two-thirds during grinding with steel balls and tillets at the natural pH of the ore (pH 8), but increased during grinding with pebbles. This is probably due to either the scavenging ability of abraded iron for oxygen or the reduction of thiosalts by iron.

(3) There is an increase in the production of thiosalts with pH over the interval of 9.4 to 10.7, as indicated in Fig. 15.

(4) Less thiosalts are produced per unit weight of ore during grinding at higher pulp densities than at lower pulp densities (Fig. 16).

(5) A direct logarithmic relationship was found

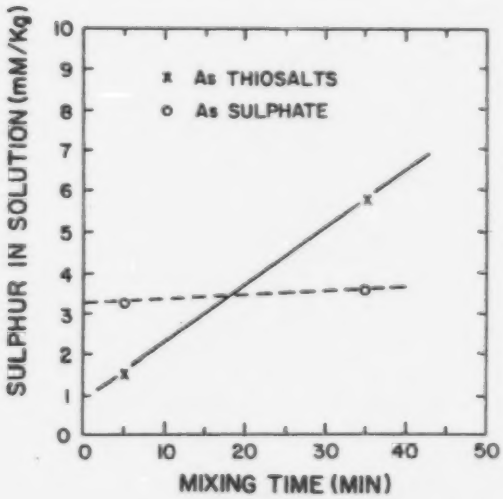

Fig. 14 - Effect of mixing time on the production of thiosalts from coarse ore in a closed circuit; 70 rpm, 30% pulp density, pH 11.2

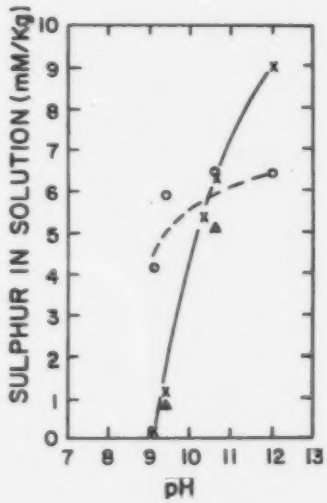

Fig. 15 - Effect of pH on thiosalt formation; closed circuit, 30 min, 60% pulp density, steel balls: X = thiosalts (Na_2CO_3-NaOH added); Δ = thiosalts (CaO added); o = sulphate

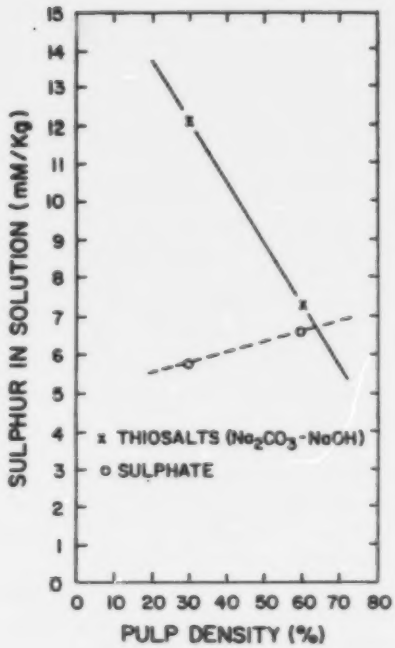

Fig. 16 - Effect of pulp density on thiosalt formation; closed circuit, 30 min, pH 10.7, steel balls

between the amount of thiosalts generated during grinding and the grinding time, as indicated in Fig. 17.

(6) Significant reduction of thiosalt generation (86%) occurred during grinding at pH 10.7 in a solution deaerated with nitrogen gas, indicating that production of thiosalts was repressed by exclusion of oxygen. Sulphite appeared as the principal sulphur species in the deaerated solution.

Investigations by the Noranda Research Centre indicated that some of the thiosalts in the ground pulp may originate from oxidized surfaces on the ore (80). Within the range of size distributions normally produced in grinding circuits, fineness of grind was found to have only a small effect on thiosalt generation during the grinding operation itself and subsequent flotation. The relative amounts of thiosalts originating from grinding and from flotation in a concentrator apparently depend largely on the pH in the two operations.

Other factors found to contribute to thiosalt formation were:

(1) Sulphide content of the ore; with five times the thiosalts generated in ores of 80-90% sulphides as with ores of 25-30% sulphides.

(2) Residence time during flotation; with the amount of thiosalts generated directly proportional to the residence time.

(3) Temperature; with thiosalt generation more than doubling from 25 to 40°C.

(4) Agitation rate in flotation; increased agitation promoted thiosalt formation.

Rolia and Barbeau studied the generation of thiosalts in a continuous process development mill at CANMET (Fig. 18) (81). The total amount of thiosalts generated was 959 g/t of ore; this compares with 1021 g/t of ore in the No. 3 flota-

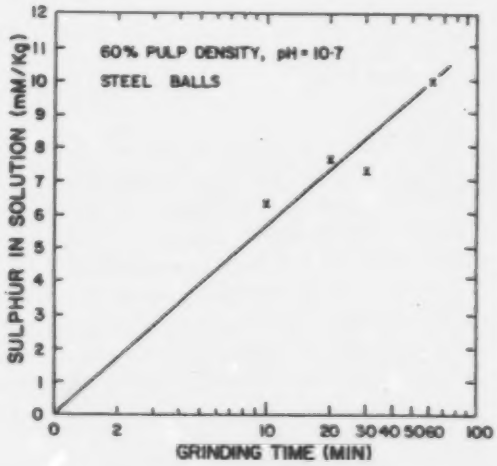

Fig. 17 - Effect of grinding time on thiosalt formation; closed circuit, 60% pulp density, pH 10.7, steel balls

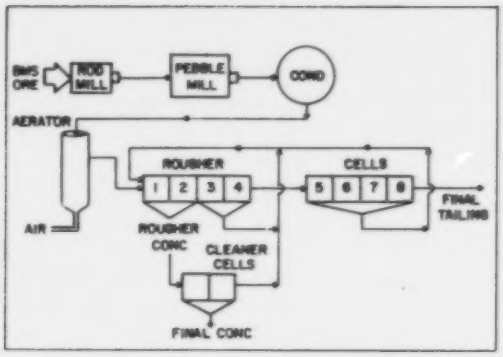

Fig. 18 - Continuous process development mill flowsheet at CANMET for the production of bulk concentrate

tion line at BMS before upgrading. A breakdown of thiosalt generation by operation was as follows:

Operation	% of Total
Grinding	17.6
Conditioning	37.0
Scavenging	45.5
Total	100.0

Steger investigated the effect of temperature, pH, particle size, and airflow on the formation and relative proportion of thiosalts in aqueous suspensions of samples of pyrrhotite, pyrite, chalcopyrite, galena, and sphalerite (82). An increase in the temperature or pH of a suspension resulted in an increase in sulphate and thiosalt formation. A decrease in the particle size of the mineral also resulted in increased sulphate and thiosalt formation. Changes in airflow had a marginal effect.

Rolia investigated generation of thiosalts during agitation of pulps on a variety of samples in a flotation cell (83). The results, presented in Fig. 19, indicated a clear correlation between the sulphur content and thiosalt production. No evident correlation was found between iron concentration and the amount of thiosalts generated.

THIOSALT TREATMENT METHODS

The CANMET thiosalt program evaluated a large number of thiosalt treatment alternatives. Most of these were limited duration bench-scale tests conducted inhouse. Two contracts were awarded - Noranda Research Centre evaluated pilot-scale biological removal of thiosalts using bacteria at Brunswick Mining and Smelting, Bathurst, N.B. and the University of Waterloo investigated catalyzed air oxidation of thiosalts using synthetic thiosalt solutions.

The following sections detail the studies which were conducted.

AIR OXIDATION

Solutions of thiosulphate and polythionates were aerated at pH 7 for 4 months under

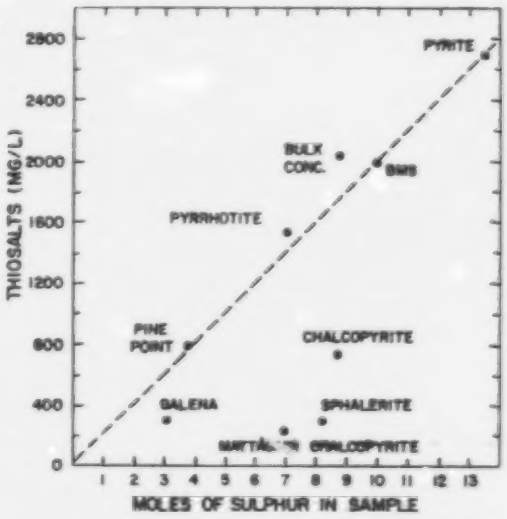

Fig. 19 - Influence of sulphide content of various materials on the amount of thiosalt production after 5-h aeration

sterile laboratory conditions at the Noranda Research Centre (80). During this time, minimal changes in the thiosalt concentration were observed (<10%). Thus, it was concluded that air oxidation alone was not suitable for the destruction of thiosalts.

CATALYZED AIR OXIDATION

Process Description

A process for the removal of thiosalts by copper catalyzed air oxidation was tested by Rempel and O'Driscoll of the University of Waterloo (84). In the process, the effluent passes through a two-stage continuous aerated reactor containing slurries of synthetic resins combined with copper. In the first stage, the thiosulphate and trithionate are oxidized employing quaternized polyvinyl pyridine-Cu (QPVP-Cu) catalyst. In the second stage polyvinyl pyridine-Cu (PVP-Cu) is used for tetrathionate oxidation. The pH in both stages is controlled at 3 to 4.

The two types of catalyst used in the oxidation stages (PVP-Cu and QPVP-Cu) both deactivate slowly with time. The cause of deactivation of the PVP-Cu catalyst and to some extent of the QPVP-Cu catalyst appears to be the continuous leakage (soluble loss) of copper from the polymer complex. Deactivation of the catalyst on prolonged use is also believed to result from a considerable amount of thiosalt adsorption (i.e., $S_2O_3^{2-}$ and $S_4O_6^{2-}$) as well as SO_4^{2-} adsorption on the polymer matrix. Hence, periodic catalyst regeneration is required that involves pretreatment of the spent catalyst consecutively with HCl and NaOH to remove adsorbed thiosalt species followed by recomplexing with divalent copper. A simplified flowsheet of the process is illustrated in Fig. 20.

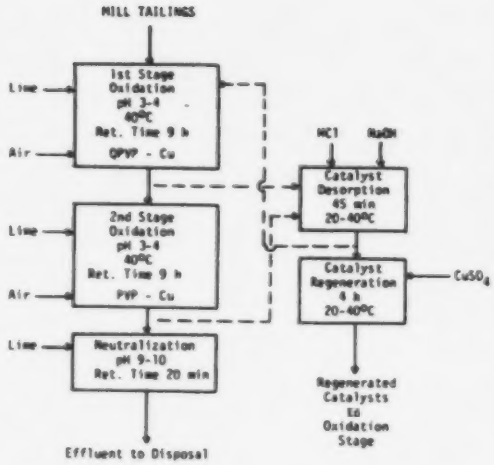

Fig. 20 - Simplified flowsheet for the copper-catalyzed air oxidation of thiosalts

Results of Tests

Tests of synthetic solutions containing 1680 mg/L S_2O_3 have been run at various temperatures and residence times using the catalyzed oxidation process. Based on these tests, optimum conditions appear to be pH 3 to 4, total residence time of 24 h (12 h per reactor), and temperatures from 35 to 40°C. To maintain an effluent quality of less than 100 mg/L thiosalts, desorption and regeneration of the PVP-Cu catalyst was required after 7 days of continuous operation. While desorption of the QPVP-Cu catalyst is also required after 7 days, regeneration is only necessary after 6 months. Typical results achieved during the tests are illustrated in Fig. 21.

Costs

Based on laboratory tests with synthetic solutions, Wong prepared preliminary capital and operating cost estimates for a plant capable of treating 1500 USGPM (5.67 m^3/min) mill tailings solution containing 5330 ppm $S_2O_3^{2-}$ (16 820 STPY or 15 255 MTPY) (85). The total fixed capital cost for this process in first quarter 1981 dollars is $17 495 000. The annual operating costs estimated for chemical reagents, catalysts and utilities only are $12 197 000 based on an assumed catalyst price of $2/lb with a life of one year. About 26% of the operating cost is for catalyst and 42% is for NaOH and HCl reagents. If the catalyst price is assumed to be $5/lb with

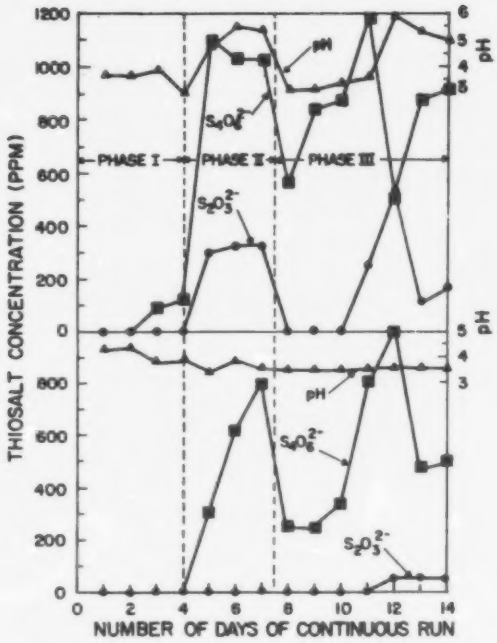

Fig. 21 - Continuous operating data for a two-stage copper-catalyzed reactor for thiosalt destruction: influent = 15 mM $S_2O_3^{2-}$ (1680 ppm); aeration rate = 1200 L/h; influent solution rate = 1.3 L/h (Day 1-4), 1.9 L/h (Day 5-7) and 1.5 L/h (Day 8-14). Reactor 1 (upper figure): QPVP-Cu (II) Catalyst (8.95% Cu (w/w), <75 μm); 2% (w/v) slurry; 12-L capacity; temp. 40°C. Reactor 2 (lower figure): Reilly-PVP-Cu (II) Catalyst (6.70% Cu (w/w) 50-500 μm); 2% (w/v) slurry; 12-L capcity; temp. 40°C (Day 1-5), 20°C (Day 6-7), 36°C (Day 8-14).

a life of one year, then the annual operating cost is $16 985 000 of which 47% is attributable to catalysts and 30% to NaOH and HCl reagents. On the basis of a catalyst life of 10 years, the estimated annual operating cost is from $9 324 000 to $9 803 000 for catalyst cost of $2 to $5/lb. However, the minimum possible operating cost is $8 253 000 if steam heating of the mill tailings solution is not required.

HYDROGEN PEROXIDE OXIDATION

Hydrogen peroxide is a strong oxidizing agent which is widely used industrially. Rolia investigated, in bench-scale tests, the oxidation of thiosalts utilizing hydrogen peroxide (86). He achieved complete oxidation of synthetic solutions (2.5 g/L thiosalts, as Na_2, S_2O_3 and $Na_2S_4O_6$) within 6 min using stoichiometric amounts of H_2O_2.

Reagent cost estimates (Dec. 1981), based on the treatment of 77 000 lb/d of thiosalts, amounted to $9.02 million per year. No capital cost estimates were provided.

CHLORINE OXIDATION

Rolia and Barbeau conducted laboratory tests to evaluate the kinetics and reagent requirements for the oxidation of synthetic solutions containing thiosulphate, tetrathionate, and trithionate using chlorine gas (87). They found that the oxidation rate depends directly on the rate of chlorine addition. The reaction required 2 moles chlorine for each mole of thiosalt sulphur. Reagent requirements for the destruction of 77 000 lb/d of thiosalts were estimated at $6 million per year (June 1979). No capital cost estimates were provided.

OZONE AND OTHER OXIDANTS

Environment Canada indicates that chemical oxidation of thiosalts may be achieved through the use of ozone, as well as chlorine sodium chlorate, sodium hypochlorite, and hydrogen peroxide (88). For ozonation, they propose the following reactions:

$$2\ S_2O_3^{2-} + 5\ O_3 + 2\ H_2O \rightarrow 4\ SO_4^{2-} + 3\ 1/2\ O_2 + 4\ H^+ \quad \text{Eq 86}$$

or

$$5\ S_2O_3^{2-} + 2\ O_3 + 7\ O_2 + 5\ H_2O \rightarrow 10\ SO_4^{2-} + 10\ H^+ \quad \text{Eq 87}$$

Their comparison of chemical treatment costs (Dec. 1975) is presented in Table 12.

SO_2-AIR OXIDATION

INCO has developed a process for the destruction of cyanide using SO_2-air oxidation. Preliminary tests carried out by INCO to evaluate thiosalt destruction using SO_2 and air were inconclusive due to a lack of analytical methods for thiosalt determination.

Rolia and Barbeau carried out tests to evaluate the effect of SO_2 and air on thiosalt solutions (87). They found minimal changes in thiosalt levels in tests of up to 48-h duration; in fact, in some tests, SO_2 combined with thiosulphate to produce more thiosalts. These tests were carried out without the addition of any catalysts (e.g., copper) which INCO utilizes for cyanide oxidation. In one of the tests, ferrous chloride was added, but it did not affect the results.

Oxidation of thiosalts by SO_2 and air and neutralizaton of acids thus produced probably occurs as follows:

(1) Formation of Caro's acid:

$$H_2O + SO_2 + O_2 \rightarrow H_2SO_5 \qquad \text{Eq 88}$$

(2) Oxidation of thiosulphate by Caro's acid:

$$S_2O_3^{2-} + H_2O + 4H_2SO_5 + 2H^+ \rightarrow 6H_2SO_4 \qquad \text{Eq 89}$$

(3) Neutralization of acid generated:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \qquad \text{Eq 90}$$

Similar equations can be derived for the oxidation of other thiosalt species. Since SO_2 is converted to H_2SO_4, the neutralization requirements are greatly increased over other chemical oxidation methods.

Based on the above reactions, reagent costs (SO_2 and lime) for the destruction of 77 000

Table 12 - Comparison of chemical treatments for thiosalts (based on treating a 2 mgd stream of 1000 mg/L S_2O_3)

Chemical	Quantity required per lb S_2O_3	Estimated cost/lb $	Daily cost $	Estimated relative capital cost of facilities	Neutralization
Oxidants					
Ozone	1.06	0.16	3800	High	Yes
		0.125	2500	High	Yes
Chlorine	3.16	0.03	1900	Low	Yes
Calcium hypoclorite	3.22	0.40	8000	Low	Questionable
Buffers					
Sodium bicarbonate	1.5	0.0465	1400	Low	-
Soda ash	0.95	0.075	1425	Low	-
Neutralizing agents					
Limestone	0.89	0.0001	18	Low	-
Lime	0.50	0.001	100	Low	-

lb/d of thiosalts can be estimated at $6.6 million per year (June 1982), assuming on-site generation of SO_2 gas from sulphur.

ALKALINE OXIDATION

Polythionates are unstable in alkaline solution, decomposing to elemental sulphur, thiosulphate and sulphite. Rolia studied the reaction kinetics for the decomposition of tetrathionate, trithionate and thiosulphate in alkaline solutions (89). He found that tetrathionate degraded rapidly to thiosulphate and trithionate at pH >10 and at 35°C. At higher temperatures (e.g., at 100°C), trithionate was found to decompose to thiosulphate and sulphate. The rate of hydrolysis of trithionate was not affected to any great extent from pH 5.5 to 12.

Thiosulphate was oxidized to sulphate by dissolved oxygen in alkaline solutions. The reaction was characterized by an induction period whose duration increases with increasing pH and decreases with rising temperature and pressure.

The oxidation of thiosalts in strongly alkaline media was studied by Rolia using slaked lime [$Ca(OH)_2$], sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH). Oxidation was always incomplete when [$Ca(OH)_2$] was used (90).

Complete oxidation was achieved using Na_2CO_3 but the oxidation rate was 80% of that obtained using NaOH. Other process variables were concentration of alkaline reagent, temperature, oxygen pressure, and thiosalt concentration. For an effluent solution containing 2500 mg/L thiosalts, two sets of preferred conditions were identified:

	1	2
Temperature, °C	150	100
Partial pressure of oxygen, kPa	2070	2070
Retention time, h	0.022	0.2
NaOH conc., g/L	1.92	1.92

Craigen estimated operating costs (June 1981) for the alkaline oxidation, using lime, of a 2000 U.S. gal/min stream containing 2000 mg/L S_2O_3 from $1 million to $2.4 million depending on the cost of steam (91). No capital cost estimates were provided. More recently, Weng calculated the annual operating cost at $5.2 million and the capital cost at $8.9 million (106) (Jan. 1982). Wong's cost were based on NaOH since lime lead to incomplete oxidation.

ULTRAVIOLET (UV) INDUCED OXIDATION

Haque evaluated UV oxidation of thiosalt solutions using a laboratory-scale reactor (UV source - 500 W Hanowa mercury vapour lamp) with air or oxygen bubbled through the solution (92). His results are presented in Table 13, and indicate:

(1) In the presence of gaseous oxygen, UV brought down the concentrations of thiosalt species to less than 2 mg/L.

(2) Results with air are similar to those achieved with oxygen.

No cost estimates, either operating or capital were provided.

REVERSE OSMOSIS (RO)

Reverse osmosis involves the forcing of water under pressure through a specially designed membrane which has the capability of allowing passage of pure water while rejecting impurities.

Sastri conducted laboratory RO tests using a static cell with a cellulose acetate membrane and tested both synthetic thiosalts and actual mill solutions (93). In initial experiments, he investigated separation of individual salts, and found that in each, maximum separation was achieved at 300 psig. Subsequently, he conducted tests with twelve different actual mill solutions at 300 psig. As indicated by the results in Table 14, effluent concentrations of less than 200 mg/L total thiosalt were achieved in most cases.

Dutrizac quotes capital cost estimates for an RO installation of 4000 U.S. gal/min at $5.4 million Can. and calculates operating costs from $0.63 to $1.02/1000 U.S. gal (94) (Dec. 1978). These costs do not include pretreatment for calcium removal or disposal of concentrated effluent.

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Table 13 - Results of UV experiments

Expt. No.	Initial pH	Reactions	Observations	$S_2O_3^{2-}$ mMole	$S_3O_6^{2-}$ mMole	$S_4O_6^{2-}$ mMole	Initial SO_4^{2-} mMole	Sulphur total g/L	Total S from SO_4^{2-} g/L
1	4-5	Irradiated in presence of bubbling oxygen for 2 h	Straw colored light ppt. settled at bottom of reaction vessel	<0.01 (5.5)*	<0.01 (4.7)*	<0.01 (0.2)*	(11.0)*	0.73	0.72
2	4-5	Thiosalt soln. & methanolic extract of chlorophyl (25 mL) irradiated for 3.5 h in bubbling oxygen	Straw colored light ppt. settled at bottom of reaction vessel	<0.01 (5.5)	<0.01 (4.7)	<0.01 (0.2)	(11.0)	0.83	0.69
3	4-5	Thiosalt soln. & 25 mL of methanolic extract of chlorophyl irradiated for 3.5 h in bubbling air	Light grey ppt. settled at bottom of reaction vessel	<0.01 (5.5)	<0.069 (4.7)	<0.01 (0.2)	(11.0)	0.81	0.69
4	4-5	Thiosalt soln. irradiated in bubbling air for 3.5 h	Light grey ppt. settled at bottom of reaction vessel	<0.01 (5.5)	<0.040 (4.7)	<0.01 (0.2)	(11.0)	0.85	0.85
5	4-5	Only air was bubbled through the thiosalt soln. (600 mL) for 18 h (dark reaction)	Light grey ppt. settled at bottom of reaction vessel	0.08 (3.3)*	0.020 (2.4)*	1.98 (0.3)*	(10.7)	0.88	0.67
6	4-5	Thiosalt soln. (600 mL) & methanolic extract of chlorophyl (25 mL) & oxygen gas bubbled for 3.5 h (dark reaction)	Light grey ppt. settled at bottom of reaction vessel	0.07 (3.3)	<0.01 (2.4)	2.03 (0.3)	(10.7)	0.85	0.67
7	7	Irradiated with 25 mL of methanolic extract of chlorophyl in bubbling oxygen for 3.5 h at pH 7.0	Whole reaction soln. turned milky and pH 5 to 6	0.22 (3.3)	0.01 (2.4)	0.01 (0.3)	(10.7)	0.85	0.67

* Initial concentrations

Table 14 - Results of reverse osmosis experiments

Sample No.		Species concentration - mg/L						
		SO_4^{2-}	Total thiosalts (as SO_4^{2-})	$S_2O_3^{2-}$	$S_4O_6^{2-}$	$S_3O_6^{2-}$	$S_2O_6^{2-}$	SO_3^{2-}
1	Feed	1085	3379	985	233	403	128	32
	Product	124	144	11	25	1	18	1
2	Feed	1344	3523	896	179	211	160	-
	Product	99	144	1	13	4	27	-
3	Feed	374	931	202	112	-	-	8
	Product	33	78	1	7	-	-	1
4	Feed	1450	2592	482	67	115	80	-
	Product	99	103	1	5	1	1	-
5	Feed	317	854	39	123	-	-	-
	Product	16	45	1	9	-	-	-
6	Feed	653	2362	426	314	192	160	88
	Product	54	54	1	9	1	1	1
7	Feed	1478	3715	616	1107	902	-	-
	Product	120	204	26	43	10	-	-
8	Feed	854	3005	750	1344	499	-	-
	Product	58	132	12	35	1	-	-
9	Feed	1344	4176	336	2137	1190	-	-
	Product	44	155	10	27	10	-	-
10	Feed	1642	4378	750	1250	1056	-	-
	Product	79	135	18	16	6	-	-
11	Feed	1325	3610	750	1004	749	-	-
	Product	81	156	27	9	6	-	-
12	Feed	1632	2918	370	1001	461	-	-
	Product	51	161	4	10	4	-	-

ELECTRODIALYSIS

Electrodialysis involves removing inorganic ions from water by impressing an electrical potential across the water, resulting in the migration of cations and anions to the cathode and anode, respectively. By alternately placing anionic and cationic permeable membranes, a series of concentrating and diluting compartments results with the solution between one pair of membranes becoming depleted in solute while the adjacent solutions become solute enriched. The amount of electric current required for the demineralization is proportional to the number of ions removed from the diluting compartments.

No experiments were conducted to evaluate electrodialysis for treatment of thiosalt solutions. Dutrizac indicates that industry spokesmen believe that membranes used for sulphate removal would also be effective for thiosalts, and quotes operating costs from $0.50 to $1.00/1000 U.S. gal (Dec. 1978) (94). This does not include costs for removal of calcium or disposal of concentrate. Capital costs of a recently-built 3 million U.S. gal/day plant to treat brackish water correspond to $4 million Can. (Dec. 1978).

ELECTROOXIDATION

Bartels evaluated the treatment of thiosalts using electrooxidation (95). He outlined the main anodic reactions which are presented in Fig. 22. These can be divided into four general groups:

(1) Oxidation of thiosulphate in neutral-acid media.

(2) Oxidation of thiosulphate in alkaline media.

(3) Oxidation of polythionates in acid or alkaline media.

(4) Oxidation of sulphite and bisulphite in neutral, acid, or alkaline media.

Based on calculations for the direct oxidation of thiosalts on platinum, a thiosalt loading of 50 000 lb/d, and power costs of $0.0350/kWh, Bartels estimated power costs at $4.9 million per year. No capital cost estimates were provided. Among factors contributing to the high costs are:

(1) Complex multipath chemical and electrochemical reactions occurring during electrolytic oxidation.

(2) Buildup of dithionate which cannot be further oxidized anodically.

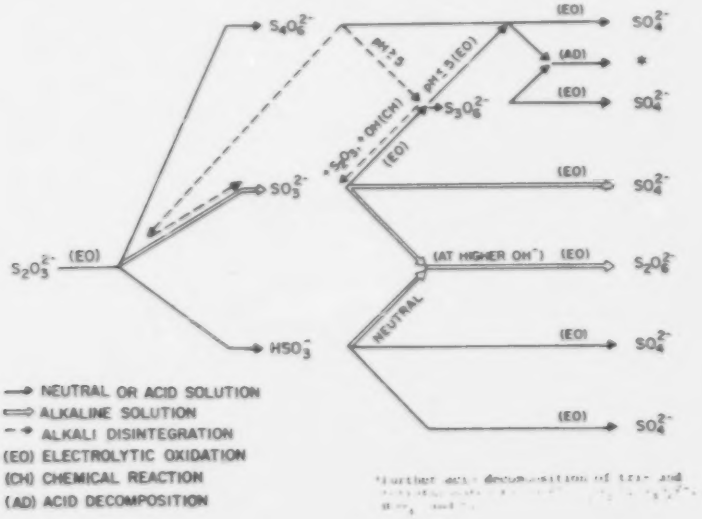

Fig. 22 - Anodic reactions occurring during electrooxidation of thiosalts

(3) Significant drop in current efficiencies below 500 mg/L thiosalt concentrations.

As of the date of the report (Sept. 1979), improved design of electrochemical reactors for thiosalt oxidation has not been proven. The carbon fibre anodes tested have evolved oxygen rather than oxidize the anions.

REDUCTION BY METALS

Based on observations of the disappearance of thiosalts following wet grinding of ore using steel balls, Rolia investigated reactions between metals and synthetic thiosalt solutions (96). His preliminary results, presented in Table 15, indicate that thiosalts could be completely destroyed in 24 h in the presence of nickel or iron; the fastest destruction occurring with iron.

Subsequently, he investigated the iron-thiosalt reactions more closely, concentrating on the effects of excess iron, temperature, and thiosalt concentration. Based on his experiments, he derived the rate expression governing the reaction. Qualitative tests indicated the evolution of H_2S gas and the generation of colloids consisting of Fe_2O_3, FeO and FeS.

Table 15 - Reduction of thiosalts by metals (Temp. = 80°C)

Metal/S mMole/mMole	Time h	$S_2O_3^{2-}$ mM	$S_4O_6^{2-}$ mM	$S_3O_6^{2-}$ mM
Absence of metal.	0.1	4.7	5.6	4.0
	2	4.5	6.3	1.7
	4	4.3	6.4	0.9
	6	4.3	5.7	2.1
	24	4.3	5.8	1.6
Ni/S = 25.5/22.5	0.1	5.1	5.2	4.6
	2	6.3	2.6	3.8
	4	7.2	1.4	2.9
	24	Nil	Nil	Nil
Fe/S = 26.8/22.5	0.1	6.3	4.4	4.6
	2	12.3	0.1	3.9
	4	9.3	Nil	2.8
	21	Nil	Nil	Nil
Cu/S = 23.6/22.5	0.1	4.5	3.3	7.5
	1	3.7	4.5	6.0
	3	1.3	6.1	2.5
	5	Nil	6.6	0.8
Zn/S = 22.9/22.5	0.1	4.9	5.9	4.3
	2	5.5	6.4	1.9
	4	6.1	6.3	1.0
	21	9.6	4.7	Nil
	47	11.7	1.8	Nil

Estimated operating costs for removing thiosalts by metallic iron was $7.1 million per year (January 1982) based on an effluent flow of 3000 U.S. gal/min, and a loading of 33 000 lb/d thiosalts. This does not include expenditures for the disposal of H_2S or FeS. The capital cost was estimated at $38.4 million, mainly attributable to using a ball mill as necessary contactor between iron sponge and the effluents (106).

ACTIVATED CARBON TREATMENT

Activated carbon is finding increased use in the treatment of municipal and industrial effluents. Removal of waste products from water by activated carbon involves the accumulation or concentration of substances at a surface or interface by adsorption, a process in which matter is extracted from one phase (i.e., liquid) and concentrated at the surface of another (i.e., solid carbon).

Rolia evaluated the removal of thiosulphate, tetrathionate and trithionate in synthetic solutions by activated charcoal (87). Essentially, no removal was achieved, despite varying pH from 6 to 12, temperature from 20 to 65°C, and residence time from 30 to 230 min.

Noranda Research tests of a number of adsorbents - activated carbon, bone charcoal, bituminous coal, peat, alumina, diatomaceous earth, clay - indicated that only activated carbon was able to retain significant quantities of thiosalts (80). Of the six commercial brands of activated carbon examined, Calgon Filtrasorb 200 appeared to be the best, having a loading capacity of 10 lb/100 lb of carbon in batch tests. Results of a column test indicated that a 5-ft deep bed having a total volume of 53 000 ft^3 (1 600 000 lb of carbon) would be required to treat 3000 Imp. gal/min of effluent containing 800 mg/L thiosalts at pH 2. Alkaline regeneration of the carbon bed was uneconomic. Alternatives such as biological regeneration may be possible but were not investigated because of the apparent high capital and operating costs of a carbon adsorption system.

BIOLOGICAL OXIDATION

Treatment of base-metal mine effluents containing thiosalts was first studied by Schmidt and Conn, who reported complete removal of 1000 mg/L thiosulphate in a bench-scale biological reactor at room temperature and a residence time of 18 h (97). The predominant bacterial species was Thiobacillus thiooxidans.

Laboratory studies by B.C. Research evaluated bench-scale Rotating Biological Contactors (RBC) and activated sludge units utilizing a synthetic feed (98). The unit achieved an oxidation rate of 70 mg/L/h, and the RBC achieved 1600 mg/L/h at room temperature and 120 L/h at 8.5°C.

Environment Canada carried out tests utilizing both bench- and pilot-scale RBC units (99). A flow diagram of the pilot-scale unit is presented in Fig. 23. Oxidation rates achieved using synthetic effluent and bench-scale units at 2°C were from 450 to 700 mg/L/h. At 30°C, rates as high as 1450 mg/L/h were achieved. Pilot-scale tests, carried out on site utilizing mill effluent from a metal mining operation in New Brunswick, achieved oxidation rates as high as 760 mg/L/h. Based on the results of the pilot-scale tests, Environment Canada provided cost data for an RBC facility treating 2.3 million Imp. gal/d of effluent containing 1250 mg/L thiosalts. Capital cost was estimated at $1.66 million and operating cost at $428 000 per year (May 1980). These costs do not include pre-treatment facilities such as primary clarification, flow equalization, or post-treatment facilities like lime neutralization, clarification, and possible supplementary chemical oxidation treatment, and the operating costs associated with such facilities. Also, the mechanical complexity of the system and the corrosive nature of the treated effluent (pH 2) would require close supervision of the process during operation and result in high maintenance costs. During the pilot tests, extensive corrosion problems were encountered, thus dependable continuing operation was difficult to maintain.

Meuller studied the oxidation of thiosulphate from the flotation waste waters of a base metal mine at Meggen, Germany, in bench- and pilot-scale packed towers (100). Packing materials tested included Raschig rings, quartz pebbles,

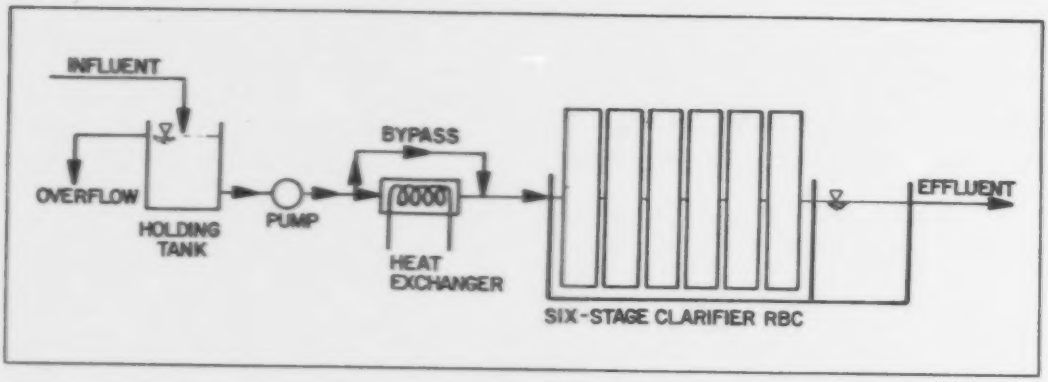

Fig. 23 - Flow diagram of the Environment Canada pilot-scale RBC

pilot-scale packed towers (100). Packing materials tested included Raschig rings, quartz pebbles, pyrite and native rock. The optimum thiosulphate oxidation rate was 470 mg/L/h in bench-scale tests and 200 mg/L/h in pilot-scale tests.

Noranda Research conducted bench-scale laboratory biological oxidation studies using a synthetic feed and on-site studies at Brunswick Mining and Smelting (BMS) using actual mill effluents (101). Two types of reactor were utilized: mixed aerated tanks (without packing) and extended surface packed reactors (using rock and foam packing). In addition, a rock packed column was evaluated.

Successful biological oxidation of thiosalt was achieved from 2.6 to 30°C, and the highest oxidation rates (about 1000 mg/L/h) were attained in the rock packed column and tank reactor. Lowering of the reaction temperature to 2.6°C resulted in an oxidation rate decrease of up to 50% over that achieved at room temperature. While the feed was generally pH 5 to 7, thiosalt oxidation resulted in the formation of sulphuric acid and subsequent pH depression. During optimal operation, the reactor effluent was pH 2.0 to 2.2.

It was noted that the packed reactors and columns were less sensitive to changes in feed composition and temperature than the mixed aerated tank. There was no evidence during the on-site tests of any toxic effect of components in the treated mill streams over a 5-month period. Colloidal sulphur, formed by acid decomposition of thiosulphate, was found to deposit on the packing material.

Dinardo carried out a literature review of thiosalt oxidation by thiobacilli species (102).

Silver and Dinardo studied the effects of temperature, initial pH, and concentration of ammonium, phosphate and heavy metals on the oxidation of thiosalts by an authentic strain of Thiobacillus thiooxidans (ATCC 8085) and by a mixed culture isolated from a base metal processing mill effluent pond (103). The optimum temperature was found to be 30°C and the optimum initial pH 3.75 for both cultures using thiosulphate and for the mixed culture using tetrathionate. T. thiooxidans ATCC 8085 did not oxidize tetrathionate. Highest rates of thiosalt destruction occurred at ammonium concentrations above 2 mg/L and in the presence of 1 mg/L of phosphate. Under optimal conditions, the pure culture oxidized thiosulphate at 55 mg/L/h; the mixed culture oxidized thiosulphate at 40 mg/L/h and tetrathionate at 50 mg/L/h.

Metal ions were found to cause inhibition in the kinetics of oxidation of thiosulphate by T. thiooxidans ATCC 8085, but only a slight additive effect was apparent in the presence of sev-

eral of the metal ions. The mixed culture of thiosalt oxidizing bacteria was less sensitive to heavy metal inhibition; the order of inhibition of thiosulphate oxidation was Cd < Zn < Pb < Ag < Cu and tetrathionate oxidation Zn < Cd < Pb < Ag < Cu.

Noranda Research is presently carrying out pilot tests of biological thiosalt oxidation using an aerated pond, a rock-packed aerated pond, and packed aerated columns. A flowsheet and layout schematic of the facilities are presented in Fig. 24 and 25. The study is partly funded by the federal Department of Supply and Services. Preliminary results indicate considerable variation, likely caused by the bacteria-inhibiting effect of lead in the feed. The maximum oxidation rate

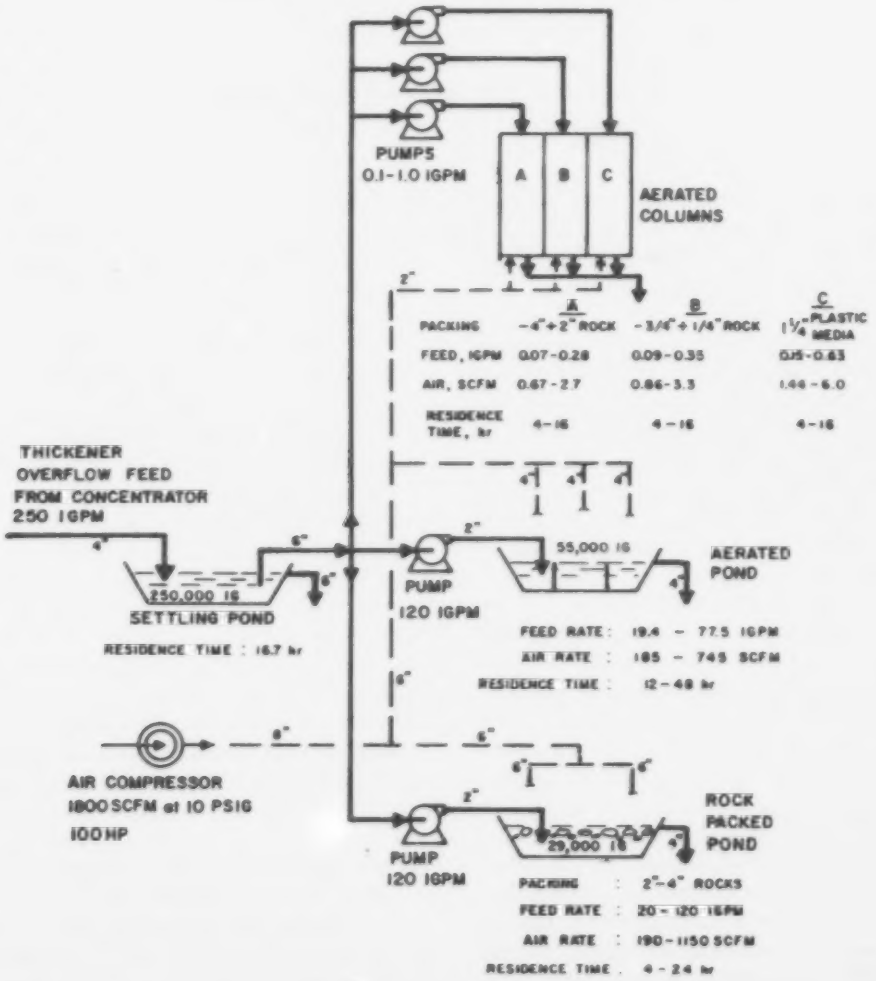

Fig. 24 - Flowsheet of the Noranada Research thiosalt pilot plant

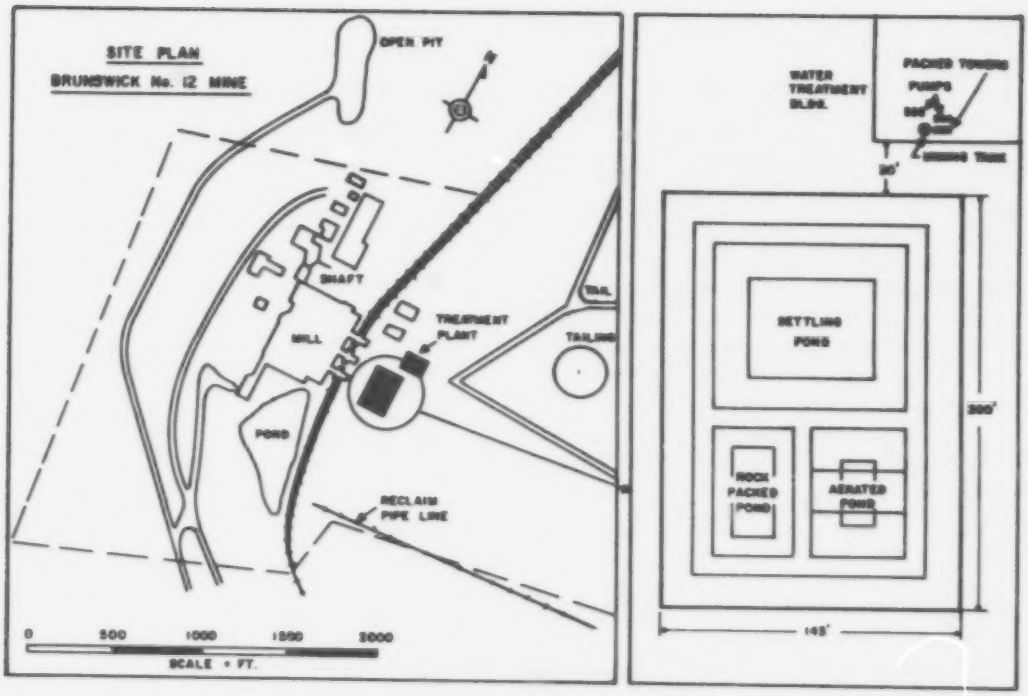

Fig. 25 - Schematic diagram of the Noranda Research thiosalt pilot-plant layout

achieved in the aerated columns was 160 mg/L/h and in the rock-packed aerated pond 70 mg/L/h. The process is also susceptible to fluctuations in the thiosalt concentration. Continuous operation was maintained during the winter months, with complete thiosalt removal being achieved at temperatures as low as 6°C.

Based on the results to date, it appears that a full scale system will require primary clarification, an auxiliary chemical oxidation system, lime neutralization, and secondary clarification facilities.

DISPOSAL TO THE SEA

Discharge of wastes to the sea is presently considered an acceptable disposal technique. In the U.S., the Environmental Protection Agency has designated more than 100 sites for ocean dumping of wastes (104). Generally, sea disposal methods involve careful control of discharge rates over sufficient discharge paths to ensure adequate dilution resulting in negligible changes in ambient seawater concentrations.

For mining operations located on or near a coastline and generating effluents containing significant levels of thiosalts, disposal of effluents to the sea may be a disposal alternative, if permitted by regulatory bodies. Francis carried out an assessment of a pipeline to carry effluents from a mine site near Bathurst, N.B., to Bathurst Harbour (105). A 75-cm O.D. pipeline fully powered with pumps and running a distance of 29 km including a 1.5 km long sea outfall would be required. A comparison of effluent thiosalt

and metal concentrations with background seawater levels is presented in Table 16. Francis estimated that the effluent would have to be diluted by at least 15 times to prevent significant changes in the seawater pH. The dilution factor would result in negligeable changes in the sulphate and metal levels of the seawater. A comparison with a similar size sewage pipeline near Pompano Beach, Florida, indicated dilution factors of 70 to 250:1 near the discharge point, and 1000 to 10 000:1 at a distance of 1.5 km from the discharge depending on wind and current velocity.

His estimates indicated capital costs of $5.5 million and operating costs of $50 000 per year (Jan. 1977).

COMPARISON OF COSTS

A summary of the methods reviewed above that indicated technical promise for the treatment of thiosalts is presented in Table 17. Where available, original costs presented by the authors are quoted. It should be emphasized that these costs in most cases are very preliminary estimates based on bench-scale test results. Also, in most cases, pre- and post-treatment facilities would be required to fully complete the teatment system to provide water which could be discharged to the water course.

Table 16 - Thiosalt effluent and seawater quality

	Effluent	Seawater
pH	5.5	not reported
SO_4, mg/L	1500	2800
Fe, mg/L	1.0	0.003 - 0.01
Cu, mg/L	0.03	0.003
Zn, mg/L	0.15	0.005 - 0.01
Pb, mg/L	0.1	< 0.001
Total thiosalt mg/L	2000	-

Table 17 - Summary of thiosalt treatment methods and costs

Method	Ref	Original estimate: Basis	Original estimate: Annual operating	Original estimate: Capital	Comments
1. Catalyzed air oxidation	85	1500 U.S. gal/min 5330 mg/L S_2O_3 96 000 lb/d S_2O_3 1st Q, 1981	$8.25 million	$17.5 million	Does not include pre- and post-treatment, test only with synthetic solutions
2. Hydrogen peroxide	86	77 000 lb/d S_2O_3, 4th Q, 1981	$9.02 million	NA	Does not include pre- or post-treatment
3. Chlorine	87	77 000 lb/d S_2O_3, 2nd Q, 1979	$6.0 million	NA	Does not include pre- or post-treatment
4. Ozone	88	2 million imp. gal/d 1000 mg/L S_2O_3 17 000 lb/d S_2O_3 1975	$1.4 million	NA	Does not include pre- or post-treatment
5. SO_2-Air oxidation	-	77 000 lb/d S_2O_3, 2nd Q, 1982	$6.6 million	NA	Does not include costs for copper catalysts
6. Alkaline oxidation	91	2000 U.S. gal/min 2000 mg/L S_2O_3 48 000 lb/d S_2O_3 2nd Q, 1982	$5.2 million	$8.9 million	Includes all neutralization costs
7. Ultraviolet oxidation	92	-	NA	NA	-
8. Reverse osmosis	94	4000 U.S. gal/min 1500 mg/L S_2O_3 72 000 lb/d S_2O_3 4th Q, 1978	$1 to $1.6 million	$4.3 million	Does not include costs for calcium removal and disposal of concentrated solution
9. Electrodialysis	94	4000 U.S. gal/min 1500 mg/L S_2O_3 72 000 lb/d S_2O_3 4th Q, 1978	$0.7 to $1.5 million	$4.0 million	Does not include costs for calcium removal and disposal of concentrated solution
10. Electrooxidation	95	50 000 lb/d S_2O_3, Power = 3.5¢/kWh 2nd Q, 1979	$4.9 million		Does not include pre- or post treatment
11. Reduction by iron	96	3000 U.S. gal/min 33 000 lb S_2O_3/d 1st Q, 1982	$7.1 million	$38.4 million	Does no include costs for disposal of byproducts of H_2S and FeS
12. Activated carbon treatment	80	-	NA	NA	-
13. Biological oxidation	99	2.3 million gal/d 1250 mg/L S_2O_3 24 000 lb/d S_2O_3 2nd Q, 1980	$430 000	$1.67 million	Does not include pre- and post-treatment
- NBC					
- Noranda Packed ponds			NA	NA	
14. Disposal to the sea	105	75 cm OD pipeline, 29 km long 189 000 lb/d S_2O_3 1st Q, 1977	$50 000	$5.5 million	Does not include pre-treatment costs

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CHAPTER 52

THALLIUM Tl

Thallium occurs occasionally in ores, particularly in some disseminated gold ores which are often associated with high arsenic and sulfide levels. A classic example is the Mercur Gold Deposit near Toelle, Utah, now operated by GETTY MINES.

The area around the Getty Mercur Mine has been used extensively for sheep grazing, and no known incidences of thallium poisoning to livestock in the area have been identified, neither due to grazing on plants that have accumulated thallium, nor due to drinking local water.

Not very much is known about precisely how thallium is distributed in gold ore minerals at Mercur or other locations.

Employees of the Mercur Mine and of GETTY MINES LTD. have found that if it is present in the ore, thallium does leach in alkaline cyanide solutions at pH 10-10.5. Thallium also adsorbs onto activated carbon with gold to 400-600g Tl/ton carbon and occasionally to 1,000g Tl/ton carbon. Thallium does not seem to interfere or, in fact, to have any effect whatever on the leaching or recovery of gold from an ore. In some cases, it is possible that thallium is present in gold ores and that operators are not aware of it.

In the case of the Mercur Mine, the presence of thallium in the ore was known for a very long time. In fact, during very much earlier gold recovery operations at Mercur, operators in the refinery were fatally afflicted, and thallium was believed to have been the cause.

Thallium in the thallous sulfate form, for example, is highly toxic, it having been used as rat poison in years gone by. Thallium in most other forms is said to be much less toxic.

Thallium salts are also contact poisons and should not be allowed to come into contact with the skin.

At GETTY's Mercur Mine, thallium leaches with gold and adsorbs onto activated carbon in the leach circuit. Thallium is loaded onto the carbon to, typically, 400-600 g/t and sometimes 1,000 g Tl/t carbon. It appears that, by no means, all the thallium in the ore is leached, and that not all of it is adsorbed onto the activated carbon.

Loaded carbon is next rinsed and then washed in ambient 2-3% HNO_3 which removes about 80% of the thallium. The HNO_3 wash also removes arsenic and calcium from the carbon and some mercury (but not much), iron, and base metals.

Tl (ug/L) THALLIUM

Summary of North American Water Quality Criteria for Thallium

WATER USAGE		EPA[1]. 1972	EPA[2]. 1976	EPA[3]. 1980	CANADA[4,5]. 1979	ONTARIO[6]. 1978	QUEBEC[7].	ALBERTA[8]. 1977	B.C.[9.**] 1979 For Final Effluent	SASK.[10]. 1975	MANITOBA[11]. 1979
PROTECTION OF FRESHWATER AQUATIC LIFE						Undefined Tolerance Limit					
OBJECTIVE		--	--	<40 (recommendation only)	--	<10,000 (96-hr LC50) Rainbow Trout	--	--	--	--	50
MAX. PERMISSIBLE LIMIT		--	--	1400 (recommendation only)	--		--	--	--	--	--
PROTECTION OF MARINE LIFE											
OBJECTIVE		<50	--	--	50	--	--	--	--	--	--
MAX. PERMISSIBLE LIMIT		100	--	<2130 (recommendation only)	<100	--	--	--	--	--	--
PUBLIC WATER SUPPLY		--	--	13.0	--	--	--	--	--	--	--
AGRICULTURAL WATER SUPPLY	LIVESTOCK WATERING	--	--	--	--	--	--	--	--	--	--
	IRRIGATION	--	--	--	--	--	--	--	--	--	--

Compiled by NORANDA

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pH of the acid wash solution is maintained at pH 2.

The acid rinse solution used to wash the loaded carbon is collected in a separate tank at pH 2. The concentration of thallium in this neutralization tank is around 1,000-1,200 mg/l at times, but more typically 800-900 mg/l. Next, NaOH is added to pH 9 or 10. As the pH is increased, Tl precipitates with the other metals. Then, a small amount of Na_2S is added to stabilize the hydrolized thallium precipitate and to make sure that any residual thallium is precipitated from solution with base metal sulfides. Caution is taken not to add Na_2S until after the solution has been neutralized to avoid the obvious dangers of H_2S generation.

Thallium is not quantitatively removed from the carbon by the cold HNO_3 rinse. Some stays adsorbed on the carbon but, to date, no problems have been identified that could be ascribed to the thallium in the circuit.

The sulfide-hydroxide precipitated metals are collected as a decanted sludge from the neutralization tank and bled into the tailings stream to be disseminated and lost in the lined tailings pond which is designed for zero discharge.

Not much is known about thallium distribution in rocks. It appears to occur reasonably often in disseminated gold ore deposits and may even be useful as a pathfinder element in mineral exploration for gold, although there is considerable debate on this.

The BUREAU OF MINES Bulletin 650 by Arthur Greenspoon is believed to contain a discussion to thallium distribution in ores. Mineral Facts and Problems 1970 mentions thallium in rocks and refers to levels of thallium up to 1,500 g/t at Mercur. It is believed that thallium may substitute for rubidium and potassium in sericite particles. Thallium, like rubidium, is a large, light ion.

The removal of thallium from gold metallurgical process solutions appears to be routine and easy as practiced at the GETTY Mercur Mine. It has been mentioned by WICKS and BREWER (1984).

More information may be available from the authors:

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(801) 263-3850
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Robert E. Brewer
Chief Metallurgist

Also involved in the thallium washing process and disposal design was:

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Kilborn Engineering
1199 West Pender Street
Vancouver, B.C.
Canada V6E 2R1
(604) 669-8811

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CHAPTER 53

URANIUM U, RADIUM Ra, AND OTHER RADIONUCLIDES

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This investigation included visits to several gold-uranium operations in South Africa and trip reports on DENISON MINES LTD. at Elliot Lake, KEY LAKE URANIUM LTD. in Saskatchewan, QUIVIRA MINING CO. at the Ambrosia Lake District of New Mexico, RØSSING URANIUM LIMITED, Swakopmund, South West Africa-Namibia, and the COTTER CORP.'s Schwartzwalder Mine, Colorado.

In this review it was also possible to draw from past RANDOL reports; for example, RANDOL (1978) and RANDOL (1979, 1980).

The five uranium operations described in Appendix I reflect a very wide diversity of geographic location, climate, and environmental as well as regulatory sensitivities. This diversity could be further extended by including examples of in situ leaching. Four additional trip reports on the KLOOF GOLD MINING CO., RM-3, VAAL REEFS, and ERGO describe gold-uranium recovery operations on the Witwatersrand from deep ore and from reclaimed tailings. Uranium recovery does not have to be the "hot" issue it has become in the U.S.A., Canada, and Australia.

A typical uranium leach extraction circuit is portrayed in a flow diagram for Jabiluka Uranium in Australia from LEVINS (1978). There are several variations on the theme to choose from.

Uranium decay gives rise to a chain of radioactive daughter products (illustrated below) that either accumulate in the ore or escape as a gas. The chain of elements, each decaying to the next, ends with Pb-210 which is radioactively stable. ITZKOVITCH and RITCEY (1979) provided an excellent summary review of radionuclides in uranium mill tailings; this review could likely be obtained by writing to:

GORDON M. RITCEY
CANMET - Energy, Mines Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1
(613) 995-4124

When uranium ore is mined and milled, these daughter products may leach together with uranium in the extraction process, or they may be rendered water and/or acid soluble in the process, but they leach so slowly that these elements proceed to the tailings disposal area with the tailings pulp. Radionuclides may therefore occur in minewater, mill tailings, seepage from wasterock, and ore stockpiles and in effluents from the milling process.

Uranium mine wasterock and mill tailings, as well as minewater and mill effluents, can build up considerable concentrations of these daughter products as well as other soluble species, especially where process water and tailings decant solutions are recycled which is typically the case.

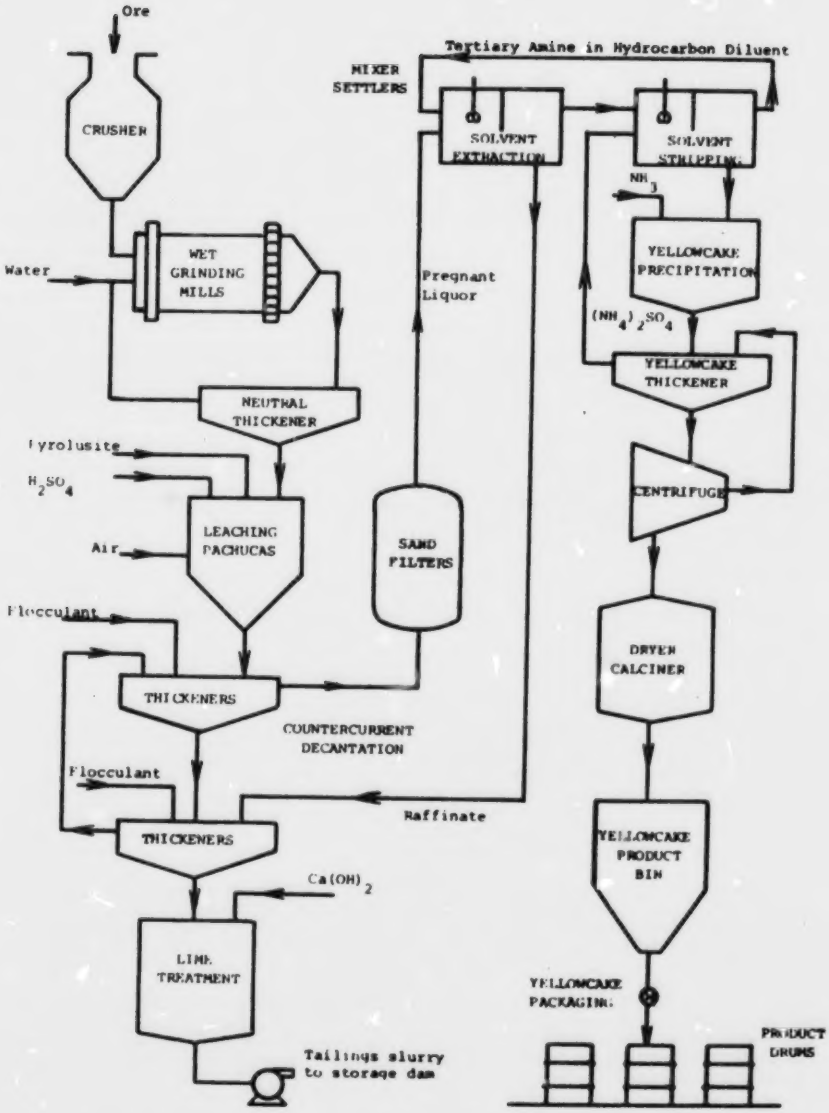

FIGURE 1. ACID LEACH FLOW DIAGRAM FOR ALLIGATOR RIVERS ORES

to prevent such radionuclides from entering the environment in water runoff or seepage from tailings and wasterock dump sites.

Radionuclides of concern are primarily uranium, thorium, lead-210, radium-226, and polonium-210. Frequently arsenic, molybdenum, and selenium, which are not radioactive, must also be taken into account in tailings. TAYLOR and ANTOMMARIA (1978) reviewed the natural geochemical attenuation of migration by these species from uranium tailings at a Wyoming site.

URANIUM - HEALTH EFFECTS

Apart from generating radioactive daughter products, uranium is in itself not particularly hazardous. Ingestion of high levels of uranium can result in liver damage.

ENVIRONMENTAL AND HEALTH IMPACTS OF RADIUM AND RADIONUCLIDES RELATED TO MINING AND MILLING ACTIVITIES

The U.S. NRC (1979) has outlined what is known about the health effects of radium and radionuclides released in uranium mining and milling as shown in the following excerpt.

The U.S. NRC Generic Environmental Impact Statement for Uranium Milling includes the following text on the hazards of radionuclides in uranium milling wastes:

> In ore bodies which have been undisturbed for many years there are equal amounts of radioactivity of each radionuclide. The common unit of quantity of activity is the curie (Ci), defined as 3.7×10^{10} disintegrations (or decays) per second (the SI unit is the becquerel, or Bq, equal to one disintegration per second). In ore containing 0.1% natural uranium (U_3O_8) there are 2.8×10^{-7} Ci of U-238 (10,000 disintegrations/second) per kilogram of ore. If nothing has occurred to remove any decay products, a condition known as secular equilibrium exists and there would also be present 2.8×10^{-7} Ci each of Th-234, Pa-234, U-234, Th-230, and Ra-226 per kg of ore. This does not imply that an equal weight of each isotope is present per unit weight of ore. The mass, or number of atoms, per curie is inversely proportional to the half-life.
>
> In Figure C.1, the disintegrations, or decays, by alpha particle emission are those which result in a decrease of 4 in mass number and 2 in atomic number (such as Po-210 to Pb-206) and are indicated by a line directed down and to the left at a 45° angle. These nuclides represent a negligible radiological hazard as long as they remain outside the body, but are serious health hazards once inside the body.
>
> It may be seen from the figure that radium-226 decays by alpha emission to radon-222. Radon, being an unreactive gas with a 3.82-day half-life, may escape from its immediate environment, whether that environment is an ore body, a tailings pile, or a bone in which radium has deposited. If a significant amount of radon escapes, then the decay chain will not be in a state of secular equilibrium from that point onward.
>
> Radon does escape into the atmosphere continually and outdoors is present in concentrations ranging from about 0.1 to 1 picocurie per liter of air (pCi/L). Radon is inhaled with each breath, but it is likely to be exhaled again without irradiating the respiratory tissues. When radon undergoes alpha decay, there follows within a short time a series of four more decays (two by alpha emission) before relatively stable Pb-210 (half-life of 21 years) is reached. The longest half-life among the intervening nuclides is only 27 minutes. The radon daughters are

not gases, but heavy metals, and rapidly become attached to available surfaces, usually to small airborne particles or aerosols. These aerosols, unlike radon gas, are easily deposited when breathed into the respiratory tract. Experience has shown that the bronchial epithelium (the lining of the bronchi) is an especially critical tissue, and that the total concentration of radon daughters, rather than the concentration of radon itself, is the parameter which best predicts the potential hazard. For this reason, in 1957 the U. S. Public Health Service introduced the concept of working level. One WL is any combination of short-lived radon daughters (meaning Po-218, Pb-214, Bi-214, and Po-214) in one liter of air that will result in the ultimate release of 1.3×10^5 MeV of alpha ray energy.[1] This amount of energy is the amount that will be released by the daughters in secular equilibrium with 100 pCi of radon. Unfortunately, radon and its daughters are almost never found in equilibrium, so a simple measurement of radon concentration will not reflect the potential inhalation dose.

When originally proposed, 1 WL was considered to be an acceptable maximum concentration for miners working a normal 40-hour week (170 hours per month). Exposures were described in "working-level months" (WLM). Thus 17 hours in an airborne concentration of 10 WL constitutes an exposure of 170 WL-hours or 1 WLM. The current EPA recommended maximum occupational exposure limit is 4 WLM per year, or 40 hours each week in a concentration of 1/3 WL.

Because the dose to lung tissue depends on respiratory parameters as well as on WL concentration and duration of exposure, it is not appropriate to determine continuous, nonoccupational exposure in WLM per year simply by multiplying WL by (24 × 365/170) to give about 52 WLM/year at a concentration of 1 WL. Instead, in this document it is assumed that a concentration of 1 WL yields 25 WLM/year for exposure that is continuous and nonoccupational. This reduction by about a factor of two reflects the difference in respiratory parameters appropriate for a worker engaged in physical activity and these parameters averaged over periods which include rest and other sedentary activity. To convert WLM of exposure to dose equivalent to the bronchial epithelium, it is necessary to make a number of assumptions about which there is not complete agreement among scientists. In this document a factor of 5 rem/WLM, based on the BEIR report, has been used in calculating doses and developing risk estimators (Appendix G).

Source: U.S. NRC (1979), Page C4

ONTARIO (1979) has set water quality objectives for radionuclides in receiving waters as follows:

Gross Beta Emitters, 100 pCi/l
Radium, 3 pCi/l

The rationale for these water quality objectives for radioactivity were established for protection of aquatic life and recreation.

It has been assumed by ONTARIO (1979) that if water is good enough for human consumption, then the radioactivity levels will not be harmful to other organisms. This assumption is supported by many reports in the literature, e.g.:

> "The doses that cause injury to plant and animal life are much higher than would be permitted under any circumstances in which human safety must be considered." (Environmental Radioactivity, 1973)

> "Compared with the experimental data available for warm-blooded animals, only a meagre amount of information is available on chronic dose-effect relationships for aquatic forms. The preponderance of available data indicates, however, that no effects are discernible on either individual aquatic organisms or on populations of organisms at dose rates as high as several rads/week." (EPA, 1973)

Both the levels listed above for gross beta emmiters and radium-226 are based on arbitrary considerations rather than firm evidence.

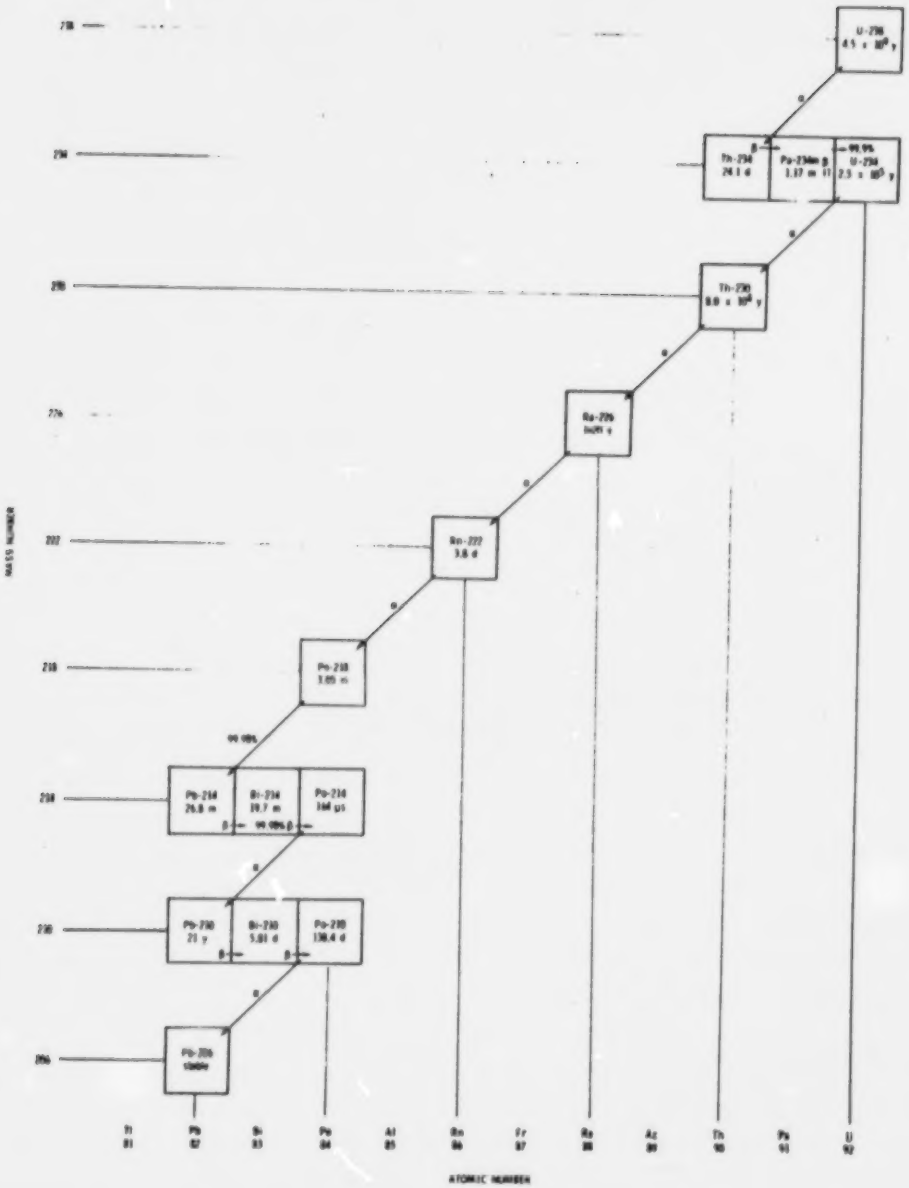

Fig. C.1. The Uranium-238 Decay Series.

3. RADON INHALATION

The concentration of Rn-222 at ground level depends on its rate of emanation from the ground and on the stability of the air near the ground. The emanation rate is extremely variable and is highly dependent on soil characteristics and meteorological conditions. The concentration of the parent Ra-226 and the grain structure and porosity both of the soil and of the cover material all affect the rate of radon emanation from soil. Barometric pressure has been reported to affect the radon flux from soil, a twofold increase in the radon emanation occurring when pressure drops by 1%.[10] Variation within 24-hour periods in Rn-222 concentration near the ground has been observed by many investigators.[11,12] Explanations for the concentration changes include effects of temperature, pressure, humidity, and air movement. However, the most significant cause for the fluctuations has been shown to be vertical exchange through eddy diffusion. Since radon concentration is highly variable, the dose from its daughter nuclides will also vary significantly. The dose values that are summarized here represent average values; the actual, short-term values can be expected to differ from the average.

The weather conditions at the model site are taken to be similar to those found in the western states. The concentration of Rn-222 in open air at ground level has been measured at different locations in the U.S. (Ref. 13 and Ref. 7, p. 79), including a site in New Mexico for which the average concentration over a six-year period was 240 pCi/m^3. Other studies (Ref. 18, 19) have measured outdoor Rn-222 concentrations in western areas ranging from about 60 pCi/m^3 to over 2000 pCi/m^3. A value of 240 pCi/m^3 is thought to be a conservative average value for outdoor Rn-222 concentrations in western regions. The concentration of Rn-222 in buildings is generally higher than in the open, depending on the Ra-226 content of the construction materials and the degree of ventilation of the building. Indoor concentrations as low as 5 pCi/m^3 (Ref. 14) and as high as 4800 pCi/m^3 (Ref. 7, p. 82) have been reported. George and Breslin have measured Rn-222 concentrations in homes in the New Jersey-New York area (Ref. 20). They have reported a geometric mean of the Rn-222 concentrations on the first floor of houses of about 830 pCi/m^3. The geometric mean for outdoor concentrations in the New Jersey-New York area is about 180 pCi/m^3. An indoor concentration of about 900 pCi/m^3 for western regions can be derived from George and Breslin's work by substituting the conservative outdoor Rn-222 concentrations for western regions (240 pCi/m^3) for the New Jersey-New York outdoor concentrations (180 pCi/m^3).

The average value (900 pCi/m^3) would result in a bronchial dose of 560 mrem/year (based on the dose conversion factor of 0.625 mrem/yr per pCi of Rn/m^3, which is used throughout this document). American Indians living in the region generally inhabit poorly ventilated huts with mud-lined walls. Houses made with sun-dried, unburnt clay have been found to have an indoor Rn-222 concentration of 1760 pCi/m^3 (Ref. 15). Since the huts are made of similar material, a dose of about 1100 mrem/year to the bronchial epithelium would result.

The air in a trailer-home could be expected to have about the same concentration as the outside air. Thus, an individual living in a trailer would breathe air with a concentration of 240 pCi/m^3 and would receive a dose to brochial epithelium of approximately 150 mrem/year.

4. TECHNOLOGICALLY ENHANCED RADIATION

The reader is referred to References 16 and 17 for a discussion of technologically enhanced radiation. The study described in Reference 17, which specifically addresses technologically enhanced sources of radon, was funded by NRC in support of developing regulations for the disposal of mill tailings.

APPENDIX K-2. COSTS OF ALTERNATIVE SPECIAL TAILINGS CONTROL PROCESSES

Costs of a number of special tailings control processes (described in Sec. 8.2) are considered in this appendix. Some of these processes are simple, involving as few as one piece of machinery, while others involve complex networks of machines and pipes. Also, the design and costs depend rather specifically on the exact purpose of the installation. Most of the processes described below are used only in tailings disposal Alternatives 7 and 8. The costs quoted are tailored to that use; however, the values cited should give general ideas of costs for other installations. Process numbers on the flow sheets in Appendix K-4 (Figs. K-4.1, K-4.3, K-4.4, and K-4.5) are keyed to the numbers given in the pertinent discussion in this section. Detailed descriptions and engineering cost evaluations of most of the mechanical processes are contained in Reference 1.

1. SANDS-SLIMES SEPARATION

Sands would be separated from the slimes in two cyclone separators costing (installed, 1978) $15,000.

2. DEWATERING FILTER BED

For open-air drying of slimes (by use of a dewatering filter bed), it is assumed that an area sufficient to hold three years' production of slimes in a one-meter-deep layer (about 40 ha) would be necessary. After two years of drying, the slimes would be recovered for processing or disposal and the vacated portion of bed prepared for reuse. The tailings drying area would be lined with Hypalon and protected by an earth or sand layer. Small berms would be needed to enclose the entire area and to form cells to separate fresh from dried tailings. Also, grading and drainage would have to be provided. Preparation costs are estimated at $2500/ha and installation and covering of the Hypalon liner at $40,000/ha.[2-5] Restoration costs at the end of operations are also expected to be about $2500/ha. Costs for total tailings are estimated as twice those for slimes (i.e., 80-ha bed).

3. FOSSIL-FUELED EVAPORATORS

The capital costs of evaporators and associated equipment with an evaporation capacity of 4.6×10^5 m^3 of water per year are estimated as $1.45 million (1978 costs).[1] With a 70% thermal efficiency, 90,000 MT of coal per year would be required, at a cost of $2.55 million.

4. EVAPORATION POND

The evaporation pond is assumed to have an area of 40 ha and to require a 5-m-high dam; the bottom would be lined with Hypalon. The costs are estimated as $70,000 for site preparation, $50,000 for the dam, and $1.6 million for the liner. After 15 years of operation, about 30 cm of soluble salts would be deposited on the pond bottom. It is postulated that these solids would be collected in a 6-ha area, then covered with a second Hypalon membrane and 2 m of earth. The cost to collect and cover these salts, then restore the entire 40-ha evaporation pond area is estimated to be $600,000. The total cost is thus $2,300,000.

5. HORIZONTAL VACUUM BELT FILTER

A horizontal vacuum belt filter probably could be used to filter and wash whole tailings or sands; however, the filtration of slimes alone probably would not be feasible. For the whole tailings from the model mill it is estimated that a filter of 64 m^2 area,[6] at a cost of $810,000,[7] would be required. For separated sands an 8 m^2 filter costing $210,000 would be used.[6,7]

6. LIME NEUTRALIZATION

The slimes and liquid would be neutralized with lime. Details of the equipment and cost estimates are given in Reference 1. The costs are estimated to be $670,000, including lime-handling and

Excerpt from: Generic Environmental Impact Statement on Uranium Milling, U.S. Nuclear Regulatory Agency, April 1979, Draft.

-mixing equipment, instrumentation, and auxiliary equipment. Each day 22 MT of lime would be used at a cost of $27/MT delivered.[1]

7. SLIMES FILTRATION (disc filter)

The neutralized slime slurry would be treated in thickeners and filtered in vacuum disc filters (200 m^2) at a total cost of $1.15 million (1978, installed).[1]

8. CEMENT FIXATION

Costs of equipment for cement fixation are also described in Reference 1. Materials-handling and mixing equipment, instrumentation, and associated apparatus would be required, at an estimated cost of $1.20 million (1978). To provide a sufficient degree of resistance to leaching by groundwater, a mixture of one part cement to five parts slimes (dry basis) would be required, or 110 MT of cement per day at $50/MT.

9. ASPHALT FIXATION

Costs of equipment for asphalt fixation are described in Reference 1. The capital costs would include materials-handling and mixing equipment, wiped film evaporators which combine mixing of asphalt with further drying of tailings, instrumentation, and associated equipment, for a total cost of $4.4 million (1978). About 750 kg of asphalt would be required per metric ton of dry slurry (420 MT/day) at a cost of $22/MT of asphalt. The equivalent of 50 MT of coal per day (cost, about $1,400) would be required for evaporation of water from the asphalt mixture carried out in the wiped film evaporator.

10. BARIUM CHLORIDE TREATMENT

The costs of barium chloride ($BaCl_2$) treatment are largely those of the material plus the costs of a series of lined settling ponds. The amount of $BaCl_2$ added can range from 0.03 to 0.1 g/L of tailings solution,[8] and about 1200 MT of tailings solution (Ch. 5) must be treated. The cost of $BaCl_2$, including transportation, is about $385/MT (1978) for a materials cost of $14 to $38 per day. A total load requirement for 40 ha in three or four plastic-lined settling ponds would cost about $2 million. Restoration would add about $100,000 more to the costs.

11. ION EXCHANGE

Although not considered in the alternative tailings disposal programs, the removal of radium from tailings solution using ion exchange is a potentially viable process.[9] To remove about 99.5% of the radium from the tailings solution, about 1200 kg/day of barite (natural barium sulfate) would be required as a disposable ion-exchange bed. The cost would be about $200/day ($76,000/year). The used barite would be relatively inert and could be disposed of in the tailings pile. Lime neutralization and filtration would be required pretreatment of the tailings solution.

12. NITRIC ACID MILL

The capital and operating costs of a nitric acid mill may be estimated by using the costs given in Reference 10 for a sulfuric acid mill and comparative costs for the two types of mills given in Reference 1. For equipment, the costs are about $7.1 million for the sulfuric acid mill and $37.7 million for the nitric acid mill. Additional capital costs include those for building and site development, utilities and connections, engineering costs, and contingencies. These items add $16.8 million to the costs of the sulfuric acid mill. The non-equipment items for the nitric acid mill probably would not be proportional in cost since a substantial fraction of the extra equipment costs are for similar items in stainless steel rather than wood or mild steel; furthermore, a larger plant area would be required for the equipment of the nitric acid plant. It therefore is assumed that the non-equipment costs for the nitric acid plant are about double those of the sulfuric acid plant, or about $35 million.

Operating costs for the sulfuric acid mill (including reagents) are given as $8.40 to $9.84 per ton of ore processed and for the model mill are assumed to be $9.00 per ton.[10] Total operating costs of $12.50 per ton are then obtained for the nitric acid mill. Annual operating costs for the model mill would be $5.6 million if sulfuric acid were used and $7.7 million for the nitric acid version. Lifetime (15 years) costs are $108 million and $189 million for sulfuric and nitric acid mills, respectively. Tailings disposal costs for the nitric acid mill are discussed in Section 10 of Appendix K-4. The costs of the two types of mills are summarized in Table K-2.1.

Table K-2.1. Costs of Nitric and Sulfuric Acid Mills (in millions of dollars)

	Nitric Mill	Sulfuric Mill
Equipment (including piping and instrumentation)	37.7	7.1
Construction and building	35	16.8
Lifetime (15-year) operating costs	116	84
TOTAL (rounded)	189	108

References

1. M. B. Sears et al., "Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluent in the Nuclear Fuel Cycle for Use in Establishing as Low as Practical Guides--Milling of Uranium Ores," Oak Ridge National Laboratory, ORNL-TM-4903, May 1975.

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5. Letter from R. E. Williams, University of Idaho, to Fred Vaslow, Argonne National Laboratory, March 1978.

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9. M. S. Peters and K. D. Timmerhaus, "Plant Design and Economics for Chemical Engineers," 2nd edition, McGraw-Hill, 1968.

10. "An Evaluation of the Cost Parameters for Hypothetical Uranium Milling Operations and Ore Transportation Systems in the Western United States," Dames and Moore report prepared for Argonne National Laboratory, July 1977.

LEVINS (1979) reviewed the environmental impact of uranium mining and milling in Australia. Australia has almost 20% of the western world's low-cost uranium reserves located mostly in the Alligator River Region of the Northern Territory. This area, subject to very dry seasons and monsoonal downpours of short duration, presents special problems in water management. More information can be obtained from:

AUSTRALIAN ATOMIC ENERGY COMMISSION
Research Establishment, Lucas Heights
NSW 2232, Australia
Desmond M. Levins

LEVINS (1979) points out that Alligator River ores contain very little natural thorium, but about 60% of the thorium-230 in the ore is dissolved during processing according to LEVINS, et al. (1978).

Only 0.1-0.3% of the radium 226 is released into solution during leaching.

Apart from acid raffinate, the only other process waste of importance is the ammonium sulfate effluent arising from yellowcake precipitation and solvent stripping. It is normally discharged with the tailings although, in some cases, it is first treated to recover ammonium for recycle as has also been practiced at KEY LAKE MINING in Canada.

REGULATORY LIMITS; URANIUM, RADIUM, AND RADIONUCLIDES

South Africa is one of the world's largest uranium-producing countries. Unlike other major producers, all of its uranium production is concentrated in one area, the Witwatersrand, where uranium is produced as a by-product of gold. It is in a way remarkable that there are no regulatory limits for uranium or radium and its daughter products in tailings and effluents from these operations. Despite careful investigations, no evidence of adverse health effects on miners, mill operators, or the public has been identified related to possible radioactive contaminants. In this area, where the city of Johannesburg and the major extensions to this metropolitan region have grown as gold mines opened up to the west and east, and later in the far west rand and Orange Free State goldfields, the urban population is often settled in very close proximity to huge mill tailing dumps and even on reclaimed mine, mill, and tailings sites.

This raises the question as to whether the attention radionuclides in effluents from uranium mines and recovery operations in other parts of the world deserve the, at times, paranoid attention that they have attracted in the recent past.

It is beyond the scope of this investigation to pass judgement on this question, and the health effects and environmental impact or non-impact of radionuclides are not reviewed here beyond a few cursory observations. It is, however, fair to note that the uranium

grade in Witwatersrand ores at around 0.1-0.2 Kg/t is much lower than in most other primary uranium mining districts.

The uranium supply is now becoming increasingly met by newer mines that treat very high-grade and low-cost ores such as in Saskatchawan around the Athabascar Basin, the Northern Territories of Australia, etc. where radionuclide concentrations are higher by an order of magnitude or two.

As far as a mining company is concerned, it matters not whether a regulation is logical or not--if one wants to operate, the regulation must be met (or changed).

One of the great problems that was faced by companies in the U.S.A. (and possibly Australia, too) was not so much the regulations, but the lack of them. During the uranium boom of the late 1970's, numerous applications were filed with the NRC for permits to open new uranium mines and mills. The regulations were in a formative stage of development and, as such, permits were held up for an inordinate length of time while the NRC went about its task of reviewing, evaluating, and creating new regulations. Eventually the uranium boom had come and gone by the time the NRC was ready to issue permits and firm up regulations and effluent limits.

In the U.S.A., regulation of uranium mines and mills at the federal level is the responsibility of the U.S. Nuclear Regulatory Commission.

U.S. NUCLEAR REGULATORY COMMISSION
Washington, DC 20555
(202) 492-7000
Ross Scarano

However, the regulation of uranium mining operations is increasingly left to the individual states provided they contract with the U.S. NRC to promulgate and enforce state regulations that are at least as stringent as the federal NRC regulations. It appears that the federal government is intent on delegating this responsibility as much as possible to the state authorities. New Mexico, Colorado, and Wyoming, where most operating underground uranium mines are located, are "agreement states," which means that they have entered this contract with the NRC. Texas, where much of the in situ leaching of uranium is carried out, is also an agreement state. Appropriate state authorities charged with regulation of the uranium industry are:

RADIATION CONTROL BRANCH
Division of Occupational Health and
Radiation Control
Texas Dept. of Health
Austin, TX

COLORADO DEPT. OF HEALTH
4210 East 11th Avenue
Denver, CO 80220
(303) 320-8333
Ken Weaver
Chief Radiation Control Division
Robert Shukle
Mining Water Quality

RADIATION PROTECTION SECTION
NM Environmental Improvement Division
State of New Mexico
Post Office Box 968
Santa Fe, NM 87503
(505) 827-5271
Theodore (Ted) A. Wolff
Program Manager

Anyone contemplating becoming a uranium producer in the U.S.A. will find that just about every aspect of his operation is subject to regulatory control and scrutiny and also exhaustive pre-permitting baseline study requirements and post-startup environmental monitoring and reporting needs. These are described by U.S. NRC (1979) and in summary by MARTIN (1978) who described the objectives and direction of the Nuclear Regulatory Commission uranium mill licensing program.

In in-situ leaching of uranium, the extent of licensing requirements will depend on whether the operation will produce uranium in slurry form or whether a yellowcake drying operation will be installed, in which case, careful air sampling requirements must be met.

The site of at least one former uranium recovery operation, namely the old COTTER CORPORATION millsite at Canon City, Colorado, has been designated as a "Superfund" site for cleanup under CERCLA regulations. It is likely that the owners of this site and others will have to defend themselves in litigation aimed at covering the cost of repairing environmental damage at this and several other uranium processing sites across the U.S.A.

REGULATORY LIMITS FOR Ra AND URANIUM MILL EFFLUENTS

Operaton	Date	State	Ra (p Ci/l)	U (ppm)
Key Lake Uranium	1984	Saskatchewan (Mo. Ave.)	10	0.50
Saskatchewan		(Max. Grab)	30	-
Quivira Mining	1984	Mine	3	1
New Mexico		Mill	Zero Discharge	

REGULATORY LIMITS FOR Ra AND URANIUM MILL EFFLUENTS (Continued)

Operaton	Date	State	Ra (p Ci/l)	U (ppm)
Denison Mines Ltd. Ontario	1984	Elliot Lake, Ontario (Mo. Ave.)	5.0	-
Cotter Corp. Minewater Colorado	1984	Colorado	5	0.06
Rössing Uranium Ltd. SWA-Namibia	1984	Mine/Mill	Zero Discharge	

It must be remembered that often acid and alkaline leach liquors and pulps in uranium extraction will contain several other metals in solution and that they are also likely to be regulated in effluents. Processes designed to remove, say radionuclides, should therefore take into account what other contaminants are present in a given operation which may simultaneously be removed.

LAKSHMANAN and ASHBROOK (1979) referred to a Canadian federal maximum permissible concentration (MPC) of 10 p Ci/l (0.37 Bq/l soluble Ra-226).

The AECB (1978) Joint Government-Industry Program in Canada suggested that 10 p Ci/l total Ra-226 be considered as an effluent guideline.

The province of Saskatchewan has a receiving water quality objective of 3 p Ci/l of total Ra-226.

LEVINS (1978) and HART (1974) showed the following water quality standards and derived aquatic standards in Australia:

AUSTRALIAN WATER QUALITY STANDARDS

	Drinking Water Standards		Derived Aquatic Standards		
	Max. Permissable (mg/l)	Max. Desirable (mg/l)	LC 50 (mg/l)	Application Factor	Standard (mg/l)
Cu	1.5	0.05	0.04	0.05	0.002
Pb	0.1	N/A	0.18	0.01	0.002
U	10	N/A	2.5	0.01	0.025
Zn	15	5	0.14	0.005	0.001
Mn	0.5	0.05	10	0.01	0.1

It is of interest to note that in Australia, water quality standards have been selected which are five thousandths to one twentieth of the LC 50 concentration for various metals.

According to RYAN and LEVINS (1979), in Australia uranium tailings cannot be disposed of in an unrestricted manner unless the radionuclide content is reduced to near background levels, say less than 0.2 Bq/g. To meet this criteria, over 99% of the uranium radium, and thorium must be removed from the average uranium ores mined in Australia. Even the impractical sodium chloride process to leach radium described in their paper results in 80-90% radium removal and a residual radium activity of 2 to 11 Bq/g which is still an order of magnitude above levels for unrestricted disposal.

TREATMENT OF URANIUM MINE/MILL EFFLUENTS

In mine/mill effluent and water management, several factors need to be taken into account:

- The effect on water quality when solutions are recycled. What effect does recycling have on the salt load, individual contaminants, and on metallurgical recoveries, corrosion, and scaling phenomena.

- If it is essential to discharge an effluent because of water and/or salt balance characteristics, it may be necessary to treat this water.

- The impact of seepage and runoff from the working area, ore, and wasterock stockpiles and mill tailings on groundwater and surface water quality must be determined.

- In dry areas where water is in short supply, water consumption must be minimized. This can have an effect on water quality. For example, Rössing consumes 0.39 m^3/t fresh water whereas QUIVIRA MINING in New Mexico consumes several times that amount.

- If water treatment is contemplated to remove, say, radium from effluents, it would be just as well to consider a process that would remove the other unwanted contaminants (radioactive and non-radioactive) at the same time.

- In removing uranium, radium, and other radionuclides from effluents, a suitable means of disposal of the precipitate sludges or concentrated solutions generated should be devised.

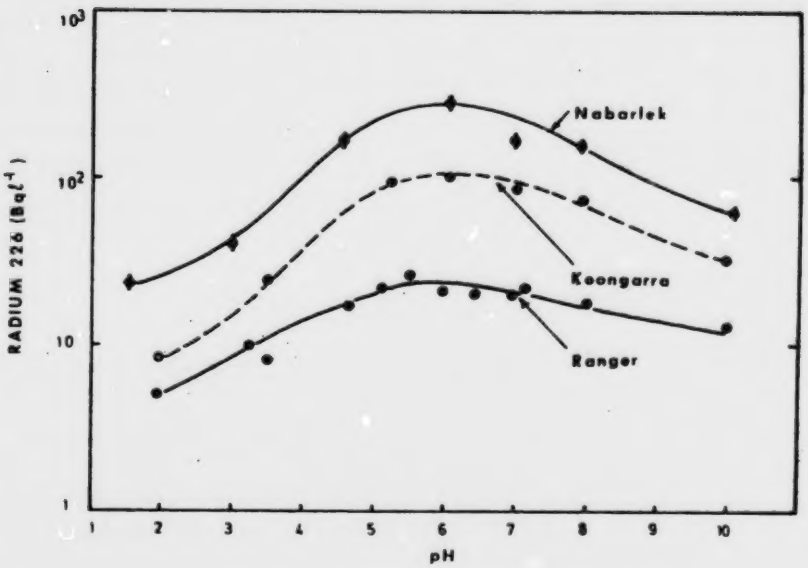


FIGURE 4. CONCENTRATION OF ^{226}Ra IN NEUTRALISED TAILINGS-RAFFINATE SLURRIES

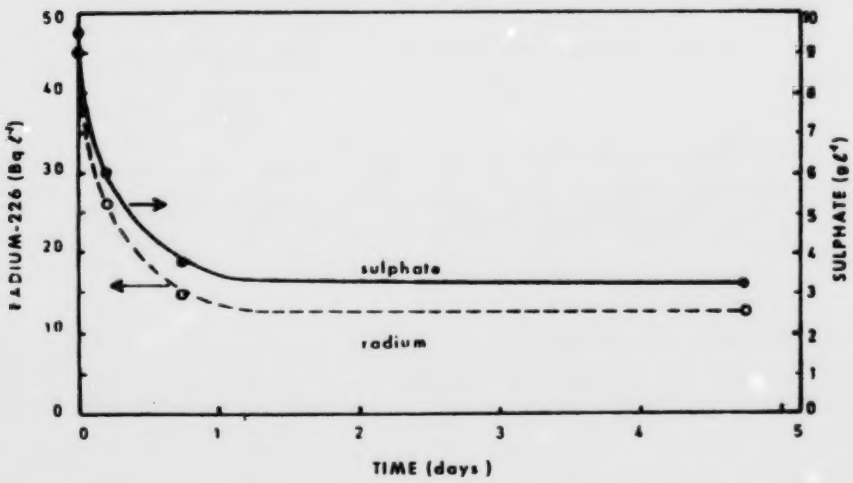


FIGURE 5. AGEING OF KOONGARRA TAILINGS - RAFFINATE SLURRY AFTER LIME-TREATMENT TO pH 8.0

According to LEVINS (1979), the behavior of radium during lime treatment is complex. According to his Figure 4 shown on the following page, during neutralization of Alligator River tailings-raffinate slurries, the concentration of radium-226 actually rises, reaching a maximum at pH 6. This effect is not completely understood but is believed to be related to the decrease in sulfate concentration as a result of precipitation of $CaSO_4$ (LEVINS, et al., 1978). This could lead to dissolution of radium sulfate held on the tailings in accordance with the common ion effect. Above pH 6, radium is removed from solution by adsorption, co-precipitation, and hydrolysis. His Figure 5 shows that further radium is removed from solution if the neutralized slurry is allowed to age at constant pH for several days. The concentration of sulfate in solution also decreases during this period. The net effect of all these factors is that the concentration of radium-226 in aged waste treated with lime to pH 8 is approximately the same as in acidic waste.

Several alternative approaches to radium and radionuclide removal from uranium mill tailings have been considered. Of these, only one has been applied in industry for both the removal of Ra from liquid mill effluents, minewater, and for precipitation of Ra for disposal in tailings. This process consists of the addition of $BaCl_2$ and settling. There are several variations on this theme including:

- pH adjustment to around 6-7 before $BaCl_2$ addition.
- Aging after $BaCl_2$ addition.
- $BaCl_2$ addition in stages.
- Addition of coagulants and flocculants to aid $BaRaSO_4$ settling, e.g., $FeCl_3$, $Fe_2(SO_4)_3$, and alum.

RADIUM PRECIPITATION WITH $BaCl_2$

At the request of the Abatement and Compliance Branch of the Environmental Protection Service, a bench-scale test project was undertaken at the Wastewater Technology Center at Burlington, Ontario, during 1976-1977 and is described by WILKINSON and COHEN (1977). The objectives of this project were to provide a better understanding of current physical-chemical methods of removing Ra-226 from uranium-mine effluents and to develop technology that would enable the uranium mining industry to comply with existing and anticipated effluent limits. The WTC bench-scale studies showed that total Ra-226 levels of less than 10 p Ci/l could be achieved using barium chloride as the precipitant and either ferric chloride or alum as coagulant.

MOFFETT and VIVYURKA (1979) in an independent study at the RIO ALGOM LTD. facilities investigated the effect of $BaCl_2$, $FeCl_3$, and superfloc additions on the rate of precipitation and settling of Ra-226 as a function of time from effluent solutions using settling columns 10 feet (305cm) tall and 24.8 cm in diameter. The total radium content, even after 72-hours settling time, did not meet the level of 10 p Ci/l.

LAKSHMANAN and ASHBROOK (1979) described testwork on $Ba(Ra)SO_4$ settling on Marie Lake overflow at the Beaverlodge operations of ELDORADO NUCLEAR LTD. Settling columns 305 cm high and 24.8 cm internal diameter were used. The test included investigations of the effects of temperature, mixing time, and addition of barium chloride, ferric chloride, and ferric sulfate on the precipitation and settling of $Ba(Ra)SO_4$.

These tests concluded that:

1) Total Ra-226 at less than 10 p Ci/l can be obtained under summer conditions after 72-hour settling when 15 ppm $BaCl_2$ and 25 ppm $Fe_2(SO_4)_3$ are used as precipitant and flocculant respectively.

2) Total Ra-226 at less than 10 p Ci/l after 72-hour settling could not be achieved in tests carried out at a simulated winter temperature of 4°C'.

The Beaverlodge tailings were generated using an alkaline uranium leach process whereas the Elliot Lake tailings tested by MOFFETT and VIVYURKA (1979) were acid leached uranium tailings.

LAKSHMANAN and ASHBROOK (1979) found that suspended solids containing finely divided $BaRaSO_4$ and fine tailings were responsible for the residual radium-226 in the treated effluent.

The sludges produced in these tests where ferric sulfate and $BaCl_2$ were used varied between 408-754 p Ci/g, whereas the normal Dorrclone overflow at Beaverlodge contains Ra-226 at 705-805 p Ci/g in suspended solids.

MOFFETT, et al. (1979) reported on a joint industry-government program to develop a more effective method of radium removal including development of physical/chemical treatment systems as an alternative to settling ponds. Target Ra-226 activities for treated tailings basin effluents were set at 10 p Ci/l total and 3 p Ci/l dissolved Ra-226. The program led to the selection of two physical-chemical processes which met the radium-226 target activities. The pilot plant was located at the Quirke Mine of RIO ALGOM LTD. at Elliot Lake, Ontario. The trailer-mounted plant was positioned below the main dam of the Quirke tailings basin and had a nominal capacity of 5 lgpm. The processes investigated included co-precipitation of $(Ba,Ra)SO_4$ with subsequent solid-liquid separation by flocculation/clarification or granular media filtration.

The mean Quirke tailings basin overflow prior to treatment by $BaCl_2$ addition had the following composition in 1977/1978 according to MOFFETT, et al. (1979).

QUIRKE TAILINGS BASIN OVERFLOW

Ra-226,	Total p Ci/l	820
	Dissolved p Ci/l	800
pH		9
$SO_4^{=}$	mg/l	1,330
Suspended Solids		2
TDS		2,480
NH_3,	(mg/l NH_3-N)	23
NO_3,	(mg/l No_3-N)	77
Calcium,	(mg/l)	480

Three continuously stirred tank reactors with a total residence time of 115 minutes were used for the $BaCl_2$ addition step to provide adequate contact time for continuous $BaCl_2$ addition.

Over a 12-month monitoring period, the tests showed that performance of the precipitation system varied and that special reactor designs would be needed to maintain acceptable performance under all conditions. The reactors can produce a dissolved Ra-226 activity of 3 p Ci/l, although some dissolved radium measurements exceeded 10 p Ci/l. MOFFETT, et al. (1979) concluded that the causes of the variability in the $BaCl_2$ precipitation of Ra-226 needed further investigation.

Laboratory and bench-scale tests showed that the settling rate of barium-radium sulfate could be markedly enhanced by the addition of ferric chloride as a coagulant. Tests by WILKINSON and COHEN (1977) established an optimum $FeCl_3$ dose as 4 mg/l (as Fe) although the settling rates achieved by coagulation were very slow compared with conventional clarifier hydraulic loadings. A hydraulic loading of 150 lgpd/ft^2 was selected for the pilot plant.

$FeCl_3$ (at 4 mg/l Fe) was added in the rapid mix step to the overflow from the precipitation reactors and subsequently flocculated in series connected flocculators with 80 minutes residence time. This achieved an overflow with 48 p Ci/l Ra-226 which formed a baseline for their further testwork.

Further improvements were achieved when precipitate sludges were recycled and an additional polymer was added after $FeCl_3$ addition in two flocculators in series. In this case at 150 lgpd/ft^2 hydraulic loading, the Ra-226 activity was reduced from 48 p Ci/l to 22 p Ci/l when sludge recycle was used. When an inclined plate clarifier was installed with a hydraulic loading of 600 lgpd/ft^2, the "once through" effluent had a total radium activity of 32 p Ci/l. With sludge recycle, this dropped to 14 p Ci/l.

A very significant reduction in the radium activity was achieved by increasing the sludge recycle rate to the flocculator until a suspended solids level in the flocculator reached 3,000 mg/l. This improved the settling rate of the iron/barium precipitate to give a reduction to 8 p Ci/l total Ra-226.

Ultimate improvements showed that at 10,000 lgpd/ft^2 and below it was possible to produce an acceptable effluent with 8 p Ci/l total and 3 p Ci/l dissolved Ra-226 in overflow from the plate clarifier while maintaining 3,000 mg/l solids in the flocculator and a sludge age of about four weeks. The schematic of this flocculation/clarification process is given in their Figure 5 which also notes an addition of an anionic polymer (0.4 mg/l AQUAFLOC 465) between the two flocculators.

MOFFETT, et al. (1979) also tested granular media filtration as an alternative to flocculation/clarification for the removal of the precipitated $BaRaSO_4$ which was investigated both with and without filter aids. Small doses of ferric chloride were found to act as an effective filter aid. If too much ferric chloride was added, however, the surface of the filter quickly clogged.

The MOFFETT, et al. (1979) paper very adequately describes a variety of experiments which ultimately led to filtration rates of 8 lgpm/ft^2 for 10-hour runs and 22 hours at 6 lgpm/ft^2 using 0.01 mg/l PERCOL 727 additions for one hour in every eight-hour cycle.

Dual media filters extended the filtration runs further for polymer-aided runs.

The ultimate configuration of the plate clarifier aided process with sludge recycle and the dual media filtration pilot plant arrangements are shown in their Figures 5 and 9 below.

These tests undoubtably formed the basis for the effective radium removal plant described in the KEY LAKE trip report in Appendix I.

ITZKOVITCH and RITCEY (1979) carried out a paper study on techniques for the removal of the radionuclides radium-226, lead-210, and thorium-230 from sulfate, carbonate, nitrate, and chloride streams produced in uranium ore processing. Detailed in a final report available from CANMET is the origin and control of radionuclide contamination of mill effluent streams from conventional and non-conventional milling of uranium ores. The basic chemistry of radionuclides of concern as it relates to potential alternatives along with published cost data are presented. Their paper summarizes the conclusions arrived at from the critical assessment of the published literature. ITZKOVITCH and RITCEY (1979)'s summary and the complete report are available from:

CANMET, Energy, Mines and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1
(613) 995-4124
Gordon M. Ritcey
Head, Solution Purification Section

These documents will be most useful to industry when environmental questions or challenges arise.

An important conclusion is that redissolution of precipitated barium-radium-sulfate in contact with water exposed to atmospheric CO_2 poses a potential long-term environmental problem. The KEY LAKE MINING operation resolved this question by returning the precipitate to the tailings pond where they employ a "dry" tailings technique which, with their ore type, yields an impermeable tailings material in which the Ba-Ra-SO_4 will not be exposed to water saturated with CO_2. This is described in Appendix I.

Conclusions arrived at with respect to alternative radionuclide control technology other than those based on either in situ precipitation of $(BaRa)SO_4$ or adsorption of radium onto barite include:

- Solvent extraction shows little promise of removing Ra-226 from process effluents.
- Reverse osmosis can reduce Ra-226 to below 3 p Ci/l, but it produces a concentrate requiring further treatment.
- Ion exchange shows the most promise for removing one or all of radium-226, thorium-230, and lead-210 from conventional uranium process effluents as well as from leach liquors produced from the non-conventional processing of uranium ores.
- For acid and carbonate process effluents, the use of solid ion exchangers, zeolites, or strong acid cation resins will probably reduce the level of the nuclides to environmentally acceptable levels.
- Strong acid cation exchange resins may also be effective in removing the radionuclides from chloride, nitrate, or EDTA non-conventional process liquors if acid and total anion levels could be maintained to give effective extraction.
- Separation and purification of radium-226, thorium 230, and lead-210 may be accomplished by the proper choice of resins and eluting resins.
- The cost of non-conventional leaching of radionuclides, e.g., EDTA or uranium plus radium by nitric acid, requires significantly greater capital and/or operating costs than the conventional processes for uranium extraction.

RADIUM LEACHING WITH NaCl

RYAN and LEVINS (1979) described a process to rapidly leach radium from uranium tailings using 3M NaCl solutions. The radium is rapidly leached at ambient temperatures by either multi-stage contact in agitated vessels or by washing on a tailings filter cake. Extraction efficiencies ranging from 80-94% have been measured for tailings derived from a number of Australian ores. Extraction of radium with sodium chloride offers the following advantages claimed by the authors:

- The low cost of chemicals.
- Extraction occurs at ambient temperature.
- Rapid kinetics of extraction.
- Low consumption of reagents by gangue minerals.
- The process is easily adapted to conventional mill flowsheets and to existing tailings piles.

COMPOSITION OF AUSTRALIAN TAILINGS

		Tailings						
Ore	% U In Ore	% U	Ra-226 (Bq/g)	Sulfate mg/g	Stages Required	NaCl Conc (M)	Radium Extracted	Residual Ra-226 (Bq/g)
Ranger	0.217	0.023	28.4	8.7	4	5	91	2.6
Jabiluka	0.44	0.021	52.4	8.9	5	3	90	5.2
MKU	0.12	0.010	11.4	19.9	6	3	80	2.3
Nabarlek	1.42	0.048	189.9	6.0	11	3	94	11.4
Koongarra	0.375	0.026	41.3	7.8	8	3	80	8.3

Several methods for radium recovery from the NaCl leach were tested:

- Ion Exchange (Dowex AG-50W; Dowex AG-1; Chelex 100)
  Chelex 100, a weak acid resin, was effective in either the sodium or barium forms for radium removal. Radium dissolved from one ton of tailings could be recovered onto 20 Kg of Chelex resin. The resin could be regenerated by passing three bed volumes of 1NHCl through the column.

  Sulfate removal was not satisfactory for all the resins tested. Only Chelex 100 in the barium form retained sulfate to any significant extent and even with this resin, there was some immediate breakthrough of sulfate.

- Barium Chloride

Sulfate removal was almost quantitative for barium chloride additions in excess of twice the stoichiometric requirement. The efficiency of radium removal decreased in excess barium chloride. The authors suggested this might be because the radium was leached from the precipitate by the barium ion. Kinetics of precipitation are quite slow, and residence in excess of one hour is needed for maximum sulfate removal. Radium and sulfate precipitation were not affected by pH in the range 3-8.

Close control of $BaCl_2$ addition is required in an extraction plant to preserve an optimum balance between radium and sulfate. In practice, multi-stage precipitation has proven more satisfactory. In the first stage, stoichiometric $BaCl_2$ additions precipitate most of the radium while in the second stage, additional barium chloride would complete the sulfate precipitation. Alternatively, RYAN and LEVINS (1979) suggested that the process could be optimized for sulfate removal and the residual radium removed by either ion exchange or adsorption.

An obvious disadvantage of extracting and recovering radium from uranium ores is that the precipitates formed now will be concentrated and require special handling and disposal considerations.

RADIUM ADSORPTION ON $BaSO_4$ BARITES

ARNOLD and CROUSE (1965) established that barium sulfate adsorbs radium from effluent waters. To determine the efficiency of radium adsorption from 3M NaCl solution, powdered barium sulfate was agitated for one hour with a solution containing 5,300 Bq/l of Ba 226. Maximum radium removal was 80%, and this required 0.01 moles $BaSO_4$ per liter of solution.

RADIUM ADSORPTION ON MANGANESE

MOORE and REID (1973) described the use of manganese impregnated acrylic fiber for the removal of radium from seawater. A sample of this fiber was obtained from the U.S. Naval Oceanographic Office and tested for radium removal from 3M NaCl solution. One hundred and twenty superficial bed volumes of solution were passed through a column containing the fiber without breakthrough. This method of radium removal appears promising for the removal of residual radium before leach liquor is recycled according to RYAN and LEVINS (1979).

In the late 1970's or early 1980's at one or another meeting called to discuss uranium mill tailings disposal technology, the observation was made in discussion that radium can very

efficiently be removed by adsorption on manganese oxides. No reference or further mention of this technology has been found, however.

If tests were to confirm the usefulness of manganese as a radium adsorbent, then some of the coated sand media applications mentioned in Chapter 43 on manganese could be of interest also in radium removal.

RÖSSING URANIUM LTD.

RÖSSING URANIUM LTD. is an example of a large uranium operation in an extremely arid location where fresh water availability is limited. Numerous measures are adopted to reduce the fresh water needs, mainly through a greater degree of solution recycling. RÖSSING has reduced its net fresh water consumption to 0.39 m^3/t ore in 1984 which is a truly remarkable achievement. There are, however, several metallurgical effects that result from this that are described in a trip report in Appendix 1.

The RÖSSING URANIUM LTD. tailings dam is unlined and is constructed by spigotting tailings as a pulp at the dam wall. The dam is porous, and there is a significant flow of seepage water which is intercepted by trenches around its base. It is noted, however, that the quality of this water after it has percolated through the carbonate-rich sub-strata is significantly improved in that the acid content is neutralized, and several contaminants are reduce, for example:

	Tailings Dam Solution	Collected Seepage Water
pH	1.6	6.6
TDS ppm	33,000	13,500
Cl^-	880	960
$SO_4^=$	21,000	8,100
F^-	100	40
Fe	1,800	0.1
Mn	1,900	1,100
K	260	70
Silica	320	27
U_3O_8	17	0.5
Radium-226 p Ci/l	230	21.0

Although the effect of calcerous substrate is wellknown, the above data has not been officially confirmed and should please be kept strictly confidential.

Groundwater quality is carefully monitored around the property, and data shows that deleterious elements are satisfactorily attenuated well within property limits to the satisfaction of the regulatory authorities.

Of interest in the crosscut sections of the calcerous rock strata that are exposed by the seepage collection ditches is to see manganese precipitating out in the fractures. This manganese also seems to act as a good adsorbent for radium although no quantitative data was available other than the excellent removal of uranium and radium from the solution as it seeps through the underlying rocks. Undoubtably, as the seepage migrates further from the sampling point referred to above which was very close to the toe of dam, further attenuation takes place.

The RØSSING URANIUM main plant IX plant has been under scrutiny ever since the plant was commissioned because the IX tails are higher in U_3O_8 than are most other CIX plants around the world. Increased use of recycle water results in a further deterioraton in uranium recovery efficiency. ROSSING URANIUM LTD. operates a second CIX plant to scavenge additional uranium from the tailings decant water before it is returned to the plant for reuse. It is emphasized that in the current depressed uranium market, this operation must tune for optimum economics rather than optimum recovery. Most of the uranium that escapes primary CIX adsorption and also escapes the tailings solution CIX plant returns to the plant, and there is a good chance of recovering it there.

Unquestionably, the use of RDS recycle results in TDS concentration with increase in concentration of ions competing for sites on the IX resin. Silica levels are also higher in the pregnant solution, but it does appear that RØSSING has learned to achieve results that would have been considered impossible in the uranium industry just a year or two before. Some data was previously published on the CIX performance on RDS solution but, since the amount of recycle has been increased, this would have changed. RØSSING has not released present performance data.

THORIUM REMOVAL

ITZKOVITCH and RITCEY (1979) concluded that:

- Neutralization of acid mill effluents to pH 5 or higher adequately controls soluble thorium-230.

- No added treatment is required to control thorium-230 in carbonate mill effluents.

COTTER CORPORATION, SCHWARTZWALDER MINE (SEE APPENDIX I)

Water quality limits set in COTTER CORPORATION's operating permit (NPDES through the Colorado Dept. of Health) for their Schwartzwalder Mine would appear at first glance to present an almost impossible technical task. Much to the embarresment of the technical experts who said that there would not be an economically viable solution, the permit conditions have been met and according to all concerned, reliably. These effluent discharge limits (30-day average) are shown in the following table along with the composition of the feedwater and the treated effluent that is discharged (PALMER, et al, 1984).

Element	Feed (mg/l)	Typical IX Effluent (mg/l)	Discharge Limits mg/l 30d Ave.
Uranium (Dissolved)	2-7	0.01-0.02	0.06
Cadmium	0.002	0.0004	0.0004
Copper	0.02	0.005	0.005
Lead	--	0.005	0.032
Zinc	0.0026	0.05	0.05
Radium 226+228 p Ci/l	50-100	5	5 Total
Sulfate	800	800	N/A
Chloride	60	60	N/A
Barium		1.0	1.0
Arsenic		0.05	0.05

The continuous downflow ion exchange system that has been installed to achieve these remarkable results at a flow rate of 500 U.S. gpm in which uranium is reduced from 3-3.5 ppm U_3O_8 to 10-20 ppb U_3O_8 is described in the trip report on the COTTER CORPORATION in Appendix I using two 10-12 foot high resin columns in series.

Radium is removed using the now conventional $BaCl_2$ dosing technique. Coagulants are added in a mixing tank downstream from the surge tank, and $BaCl_2$ is dosed directly to this surge tank. This is followed by clarification in a 35-foot outdoor conventional clarifier and indoor filtration through two deep-bed sand filters. Particulates are dropped at this stage to around 0.2 ntu's. To achieve this low suspended solids level, both anionic and cationic NALCO polymers are added. Clarifier underflow sludge is dewatered on a drum filter and added to the ore. Sandfilter backflush sludges are returned to the clarifier.

A unique feature of the CIX system is acidification of the loaded resin in a transfer vessel located between the loading and elution steps. The acid (spent eluate) washing of resin serves to dissolve any carbonates from the resin and vents CO_2 in the transfer

vessel. This avoids CO_2 generation in the elution column where gas bubbles would cause channeling and impair performance.

Another remarkable aspect of the CIX performance is that 12 g U_3O_8/l eluates are generated from feedwater of say 3 mg/l U_3O_8 yielding a product water with 10-12 ppb U_3O_8.

The main points on COTTER CORPORATION are therefore:

- Extremely tight limits for U_3O_8 in effluents that are discharged, especially for uranium and cadmium.
- Extremely low level U_3O_8 in treated effluent.
- Remarkable concentration ratio achieved by the HIMSLEY CIX system installed at COTTER CORPORATION. Elution grade is high enough for the concentrate to be shipped directly as preg solution to the uranium recovery circuit at Canon City.

More information may be available from:

COTTER CORPORATION
Water Treatment Plant
Ralston Creek Canyon
Golden, CO 80401
(303) 642-7888
Charles Palmer
Site Manager

Note: COTTER CORPORATION's head office declined to discuss the operaton. Most of the above information was published by PALMER, et al. (1984), but some details included here could be regarded as confidential.

Information on the CIX plant may be available from:

HIMSLEY ENGINEERING
250 Merton Street
Toronto, Ontario M4S 1B1
(416) 485-4441
Alec Himsley
President
Al Peterson

QUIVIRA MINING CO., AMBROSIA LAKE, NEW MEXICO

Despite the fact that the QUIVIRA MINING COMPANY is located in a very arid climatic region, water shortage is not a problem at Ambrosia Lake from a mill operating standpoint. In fact, the six mines must be dewatered, and excess water must be treated

to remove uranium, radium, and selenium before it can be discharged to a "creek" from which most seeps back underground in some kind of a macro-recycle loop.

Uranium is recovered from minewater by continuous ion exchange but as the TDS has built up in concentration over several years, e.g., $SO_4^=$ and Cl^-, so uranium loading on the two-stage fluid-bed KERR-MAC columns is depressed, and tail levels of U_3O_8 have been more difficult to keep down. To maintain 1 ppm U max. in the effluent, resin must now be eluted up to 100 times per month compared with about 16 times when the plant was first designed.

Water balance at the mill is regulated on the level of chloride in mill water. Cl^- is added to the system as 0.6 M NaCl used to elute the loaded solvent extraction SX organic phase.

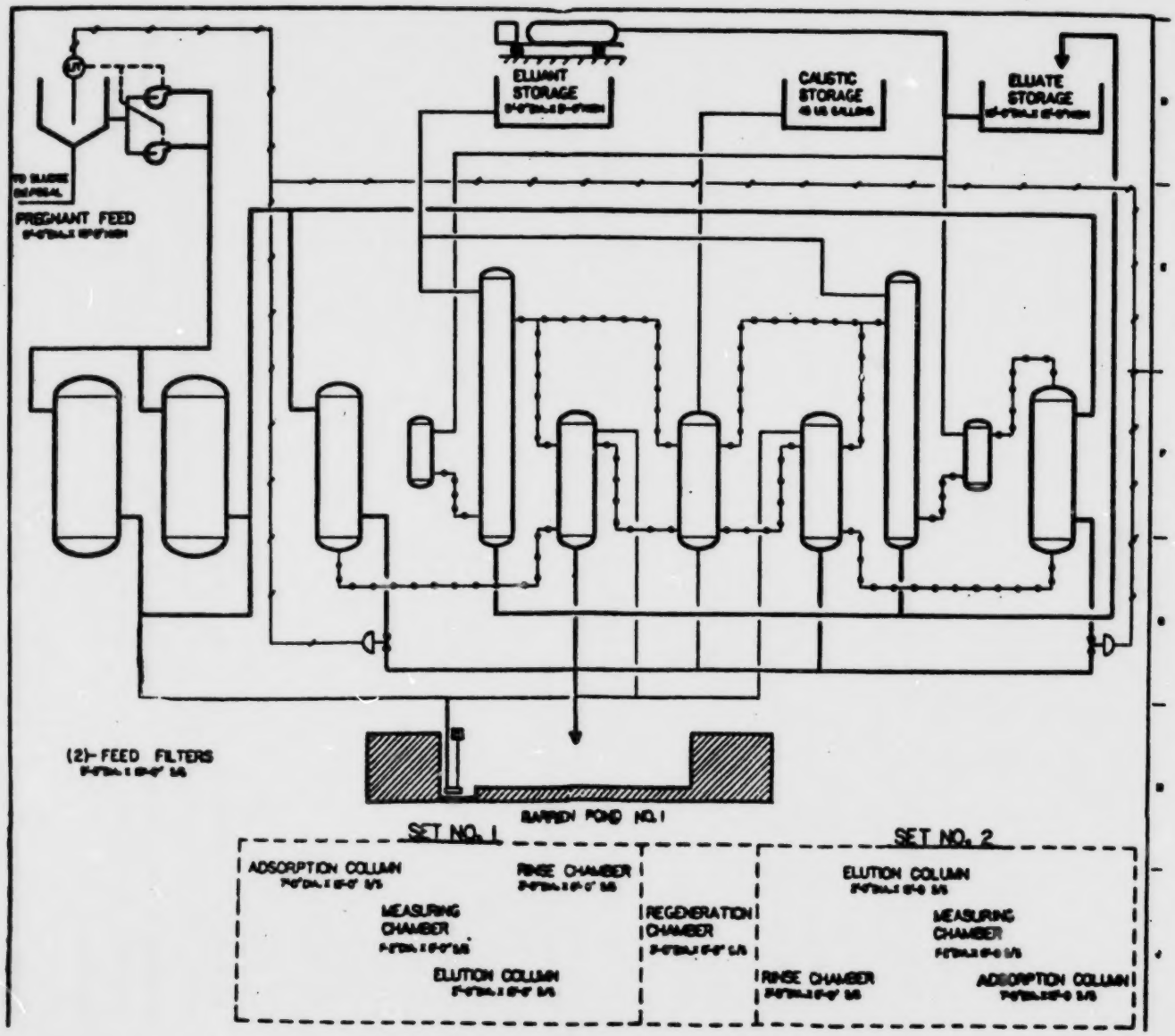
Excess mill water is evaporated so it does not have to be treated for discharge as an effluent. This is possible because the operation is located in a climate with significant net evaporation. This requires very large and expensive impermeable ponds, however.

Tailings pond solution is recycled to some extent. The tailings dam is relatively porous, and it appears that a considerable degree of water seeps into the mines ultimately to be pumped out again.

Minewater, after IX removal of U_3O_8 and radium precipitation with $BaCl_2$, is stored in a series of ponds where biological processes remove some U_3O_8, Mo, and Se as described by BRIERLEY, et al. (1980) and BRIERLEY and BRIERLEY (1980). Although in the non-engineered way these biological processes work in the ponds, they do not seem to be super efficient. Nevertheless, there is evidence that there are definite biological mechanisms for contaminant removal at work in these ponds. Filamentous spirogira and benthic chara, both algae, were identified as acting as biofilters for U, Se, and Ra. Death and decay of the algae was found in lab studies not to result in the return of cell-bound U and Mo to the water due to the reducing conditions in the pond sediments which precipitate U and other metals. The recirculating minewater in effect acts as an in situ leaching process, and the IX recovery system produces about 100,000 lbs. U_3O_8/year.

This is an example of where a multi-stage CIX recovery system would perform better than the one or two-stage KERR-MAC Systems employed here. Multi-stage systems achieve better uranium recovery from solutions with high competiting ion concentrations.

Additional information would be available from:



PROCESS FLOW SHEET FIG. 1

QUIVIRA MINING COMPANY
Ambrosia Lake Operations
Post Office Box 218
Grants, NM 87020
(505) 287-8851
Charles F. Stanley
Mill Manager
Johnathan Ma
Metallurgical Manager

BEISA MINE LTD., SOUTH AFRICA

The Beisa Mine located south of Welkom, South Africa, produces gold and uranium from Witwatersrand-type ores. Minewater at this mine is high in chlorides (up to 2,080 ppm CL^-) and has around 4,000 ppm TDS.

The gold mill employs carbon in pulp after cyanide leaching. The uranium plant employs sulfuric acid leaching followed by belt filtraton.

Operators find that the high chloride level allows a 20% faster rate of filtration than when the OFS Water Board fresh water is used.

The uranium plant IX recovery system is designed to operate at high Cl^- levels, and the operators claim that the plant is operating to design specifications which probably took the high Cl^- levels into account.

Rather than treat the large volumes of excess water pumped from underground at Beisa, evaporation has been found to be more cost effective as described by BENTAL and JAMES (1983).

DENISON MINES LTD.

At DENISON MINES LTD.'s Elliot Lake operations, minewater is used to encourage the leaching of uranium from the mine stopes. Low pH oxidizing solution is sprayed onto mine walls and collected for uranium recovery. 5,700 m^3/d of underground minewater is treated in the metallurgical operations to recover incremental uranium values. Minewater contains around 104 ppm U_3O_8 and 60 p Ci/l total radium-226. The uraniferous mine solution is used in the mill.

Excess precipitaton over evaporation at Elliot Lake requires that excess water decanted from their tailings pond must be discharged back to the lake system via Quirke Lake.

Data provided by DENISON MINES LTD. did not include a maximum value for uranium in discharged effluents, although there are regulated limits for radium:

	URANIUM, RADIUM Max. [Ra]
AECB Licence, Grab Sample	5.0 p Ci/l
Federal Metal Mine Regulations	
Monthly Average	10.0 p Ci/l
Annual Average	5.0 p Ci/l
Composite	10.0 p Ci/l
Grab Sample	15.0 p Ci/l

The Canadian federal limit on radium-226 in drinking water is 27 p Ci/l.

Radium is removed from tailings decant effluents at DENISON MINES LTD. by adding $BaCl_2$ to precipitate $BaRaSO_4$. DENISON has observed that the amount of radium in the final effluent is a function of the volume of the effluent. Radium dissolves in quantities that are a function of the amount of water in the mill. If ore is washed in fresh water, radium continues to leach from the ore.

At DENISON, it is found that the solids fraction of mill tailings contain an average of 256 p Ci/l. After neutralization, the liquid fraction in the mill tailings contains 1,411 p Ci/t, i.e., 1.4 p Ci/l, and 4,000 mg/l $CaSO_4$, mostly as $CaSO_4$.

Before addition of $BaCl_2$, soluble radium in the decanted tailings effluent runs around 370 p Ci/l. After a few weeks of aging, the dissolved radium in the pulp drops to 125 p Ci/l as the remainder attaches to solid particles. Even if aged another 20 years, if the tailings are not chemically altered, saturated pore solution stabilizes at around 120 p Ci/l.

At very high pH values, $BaRaSO_4$ flocs don't settle as well as at low pH. Also, the higher the sulfate concentration, the more effective radium removal is found to be. When adding $BaCl_2$, more gypsum and $SO_4^=$ is removed from the solution than would have been expected.

Concentration of radium in the settled sludge when precipitated at higher pH is diluted by gypsum that also precipitates, and radium may be present at hundreds of p Ci/g rather than thousands in the precipitate.

If $BaCl_2$ is added to a slightly acid effluent, radium precipitaton is said to work more efficiently than when $BaCl_2$ is added to high pH pulps and effluents.

Precipitation of $BaRaSO_4$ is also pH dependent like all sulfate precipitation reactions. When lime is added to an acid uranium leach effluent solution, a range of species such as $CaSO_4$, $BaSO_4$, and Ca-$BaSO_4$ will precipitate. The precipitation on addition of $BaCl_2$ at

pH 5-6 goes faster than at high pH's. When $BaCl_2$ is added to high pH solutions, the main species that precipitates is $BaSO_4$.

When $BaCl_2$ is added at a lower pH range, say 5-6, two results are noted:

- More radium is precipitated.
- Ba-Ra-SO_4 precipitates in a bigger volume of precipitate.

DENISON MINES adds $BaCl_2$ to their effluent at pH 8 and does not have a final pH adjustment like RIO ALGOM's Panel operation where provision is made for lime addition right before the $BaCl_2$ addition. Denison's final effluent averages about 3 p Ci/l Ra or less.

RIO ALGOM LTD., Elliot Lake

The behavior of radium in tailings pulps at Elliot Lake has been studied under various conditions by:

AL J. VIVYURKA
Senior Environmental Engineer
Rio Algom Ltd.
Post Office Box 1500
Elliot Lake, Ontario
Canada P5A 2KA
(705) 461-2518
Telex: 067-7338

Early work at RIO ALGOM LTD. dating to 1972 was reported by DUNN, et al. (1972) which may describe useful evaluations. Rio Algom Ltd. has installed a large effluent treatment plant at Elliot Lake, but this was not visited, and precise results were not obtained as the opportunity to return to Elliot Lake for a third time as planned did not materialize. Nonetheless, when considering alternative approaches for radium removal, the Rio Algom effluent plant should be considered.

After $BaCl_2$ addition to the tailings pulp, radium drops to 3.3 p Ci/l average. The ratio of total to soluble radium varies depending on conditions. Radium settles out as $BaRaSO_4$ precipitate in which the radium level typically falls in the range 500-5,000 p Ci/g.

According to CHAKRAVATTI (1984, personal communication), the amount of residual soluble radium in an effluent is virtually independent of the $BaCl_2$ dosage. More critical is how the $BaCl_2$ is added, e.g., contact time, settling capacity, pH, etc.

Multistage $BaCl_2$ additions to effluents are practiced at both RIO ALGOM LTD.'s Quirk uranium plant at Elliot Lake and at KEY LAKE MINING's operations in Saskatchewan.

RABBIT LAKE OPERATIONS, SASKATCHEWAN

Ra is removed from solution by $BaCl_2$ addition which precipitates $BaRaSO_4$.

A change in ore type from the original Rabbit Lake ore to Collins "B" zone required a whole new metallurgical process which is described in Appendix I.

More information on the effectiveness of the new process with respect to heavy metals, arsenic, radium, and uranium removal from effluents could be requested from:

ART CARINO
Metallurgical Manager
Eldor Mines Ltd.
Division of Eldor Resources
Post Office Box 2070
Saskatoon, Saskatchewan S7K 3S7
(306) 382-0505

KEY LAKE MINING CORPORATION, SASKATOON

Key Lake processes a very high grade uranium ore which also contains high levels of other contaminants such as nickel, arsenic, and radium.

KEY LAKE MINING LTD. operates an innovative water treatment plant to precipitate arsenic and nickel which employs an interesting approach achieving some of the same effects as a high density sludge process by adding lime in stages to flash mixers between each neutralization tank, ending at pH 11 and over.

Following bulk neutralization of the effluent using lime, the effluent is neutralized by adding H_2SO_4 to pH 7, and then $BaCl_2$ is added in stages and achieves in hours what at other uranium mines such as at Elliot Lake and Rabbit Lake takes days or weeks. The Key Lake radium precipitation plant arrangement is depicted in the following diagram. $BaCl_2$ addition has also been found to precipitate arsenic to 0.1 ppm As.

Following bulk neutralization and radium precipitation, KEY LAKE MINING retains the treated effluent in ponds where it can be tested to ensure that it meets effluent limits stated in their permit before it is released to the receiving waters. If not, it is recycled to the front of the treatment process.

KEY LAKE has employed a layered "dry" tailings disposal technique which, as the tailings dry out, results in a tailings material of extremely low permeability. This type of tailing provides a very effective encapsulation of sludges recovered after water treatment. More can be learned about this type of tailings disposal in the Appendix I trip report and from:

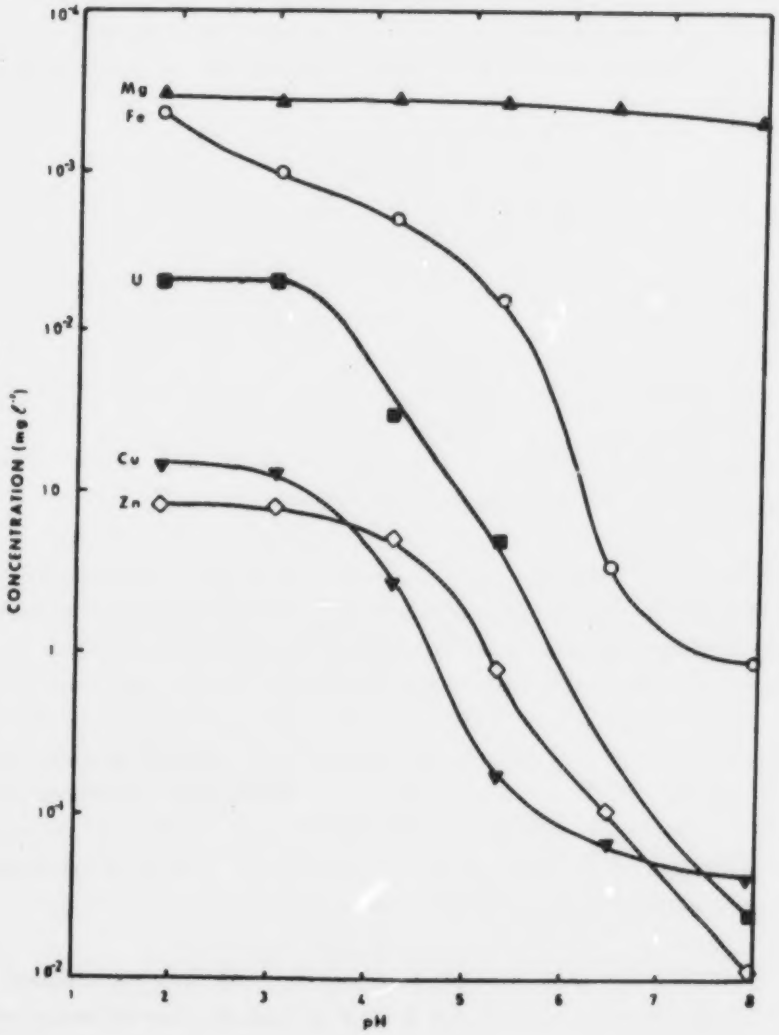


FIGURE 3. CONCENTRATION OF MAGNESIUM, IRON, URANIUM, COPPER AND ZINC IN LIME TREATED, JABILUKA TAILINGS-RAFFINATE SLURRIES

KNIGHT AND PIEZOLD
409 Granville
Vancouver, B.C. V6C 1TC
(604) 685-0543
R. Bruce Knight
Partner

STEFFEN ROBERTSON AND KIRSTEN
Post Office Box 8856
Johannesburg 2000
(011) 834-6061
Dr. O. Steffen

STEFFEN, ROBERTSON AND KIRSTEN
#801, 1030 West Georgia
Vancouver, B.C.
Canada V6E 2Y3
(604) 681-4196
Andrew McG. Robertson

Sludges of base metal and arsenic precipitates generated in the water treatment process may become unstable in time if simply disposed of in a pond. ROBINS and TOZAWA (1982) and ROBINS (1984a) pointed out that although barium arsenate is very unsoluble when freshly formed, it may be destabilized by CO_2 from the atmosphere in equilibrium with pondwater.

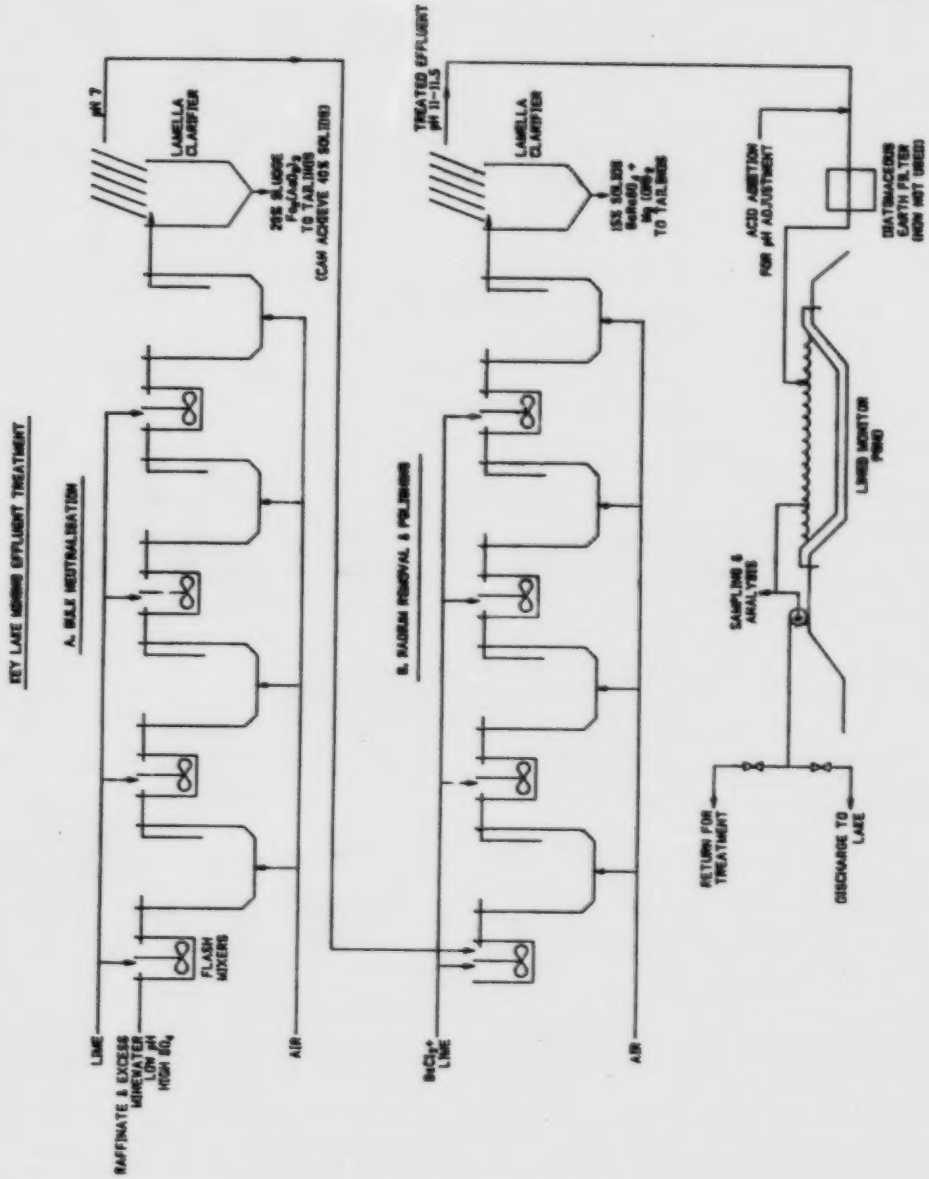
Encapsulation of sludges in the super-impermeable tailings using the sub-aerial technique mentioned above overcomes this possibility very effectively as neither CO_2 nor water can get to the sludge, nor can solutions seep from the tailings pond material once they have been decanted and dried.

This "semi-dry" or "subaerial" tailing disposal method works best in net precipitation climates, however, and the effectiveness in the field at Key Lake was not investigated firsthand, although simulated pilot scale testwork showed very promising results.

JABILUKA URANIUM OPERATION, ALLIGATOR RIVER AREA, NORTHERN TERRITORY, AUSTRALIA

Contaminant concentrations in a typical Alligator River ore treatment facility in Australia before and after lime treatment were reported by LEVINS (1979) for Jabiluka tailings-raffinate slurries.

Component mg/l	Acidic Waste mg/l	Lime Treated to pH 8 mg/l
Al	1,000-2,500	0.3
Ba	0.1-1	0.5


KEY LAKE MINING EFFLUENT TREATMENT
A. MILK NEUTRALIZATION
B. RADIUM REMOVAL & POLISHING
pH 7
LAMELLA CLARIFIER
TREATED EFFLUENT pH 11-11.5
LAMELLA CLARIFIER
ACID ADDITION FOR pH ADJUSTMENT
DIATOMACEOUS EARTH FILTER (NON WET USED)
LIMED MONITOR POND
SAMPLING & ANALYSIS
RETURN FOR TREATMENT
DISCHARGE TO LAKE
FLASH MIXERS
LIME
RAFFINATE & EXCESS MINEWATER LOW pH HIGH SO4
AIR
BaCl2+ LIME
AIR

Component mg/l	Acidic Waste mg/l	Lime Treated to pH 8 mg/l
Ca	100-600	500
Cr	10-50	0.3
Cu	15-100	0.04
Fe	2,000-5,000	1
K	20-500	20-500
Mg	2,000-5,000	1,500-3,000
Mn	1,500-4,500	100
Na	25-1,700	20-1,500
Pb	2-4	0.4
U	10-60	0.03
V	10-120	N/A
Zn	5-100	0.01 Cl 10-60 10-50
P	10-300	10
Si	30-150	5
$SO_4^{=}$	25,000-50,000	2,000-8,000
Ra (Bq/l)	5-25	3-15

It is clear that lime addition to pH 8 is effective in the presence of Fe and other co-precipitatants in reducing residual uranium values to below 0.1 mg/l. It is not, however, as effective in precipitating radium, even though the effluent contained only 0.1-1 mg/l Ba. The addition of 10 mg/l $BaCl_2$ before or after the addition of lime would undoubtably reduce radium further.

The following curve from LEVINS (1978) shows how several metals including uranium are effectively removed in lime-treated Jabiluka tailings-raffinate slurries.

EAST RAND GOLD AND URANIUM CO. LTD. (ERGO)

ERGO recovers gold, uranium, and pyrite by re-processing 1.6 million tons of slimes per month from tailings dams left by earlier gold mining operations on the East Rand.

This operation produces a significant amount of uranium by acid leaching the roasted pyrite concentrate recovered from the tailings by flotation.

Uranium, radium, and radionuclides in tailings and effluents are not amongst the several water balance and effluent treatment challenges and innovations at ERGO. These elements, at the low levels at which they occur in ERGO tailings and effluent, are not of concern to regulators after careful scrutiny.

VAAL REEFS EXPLORATION AND MINING COMPANY LTD.

A trip report describing Vaal Reefs is included in Appendix I to summarize water management practices and treatment technology employed at this huge multi-mine and multi-mill complex which treats close to ten million tons of mined ore per year.

As at ERGO, this major uranium producer experiences no problems with uranium and radium in its effluents and tailings. In fact, these elements do not even appear on the list of elements and ions to be monitored in the various effluent streams.

It is believed that this is because the levels are so low that they have been deemed, appropriately, non-detrimental to the environment.

URANIUM MINE, WASHINGTON STATE

A uranium mine subsidiary of a major mining house is currently shut down for economic reasons based on the price of uranium.

Ear Craig, who retired from DAWN MINING several years ago, recalls that multi-media filter containing a bed of anthracite coal was employed to clarify pregnant feed liquors ahead of the ion exchange plant.

A routine radioactivity survey many years ago found that this coal filter bed had become highly radioactive. It is possible that radium-226 in the pregnant solution had been building up for some time. This took place many years ago, and none of the professional staff working there when the plant shut down had any recollection of the anthracite filter. What is important about it is that anthracite coal may be worth testing as a means of removing radionuclides from effluents.

The DAWN MINING operation is located in an area with a net precipitation, and it is consequently not possible to operate on a zero-discharge basis. Before the tailings pond was lined in 1982, there was adequate leakage from the pond to bring their water into balance. This leak also provided an adequate bleed of salts so that these did not build up excessively. After the pond was lined, however, much more tailings decant water had to be recycled to avoid filling the dam to capacity prematurely. As a result, dissolved salts steadily built up in the water. This had a definite effect on the efficiency of uranium recovery on the ion exchange resin. This was partly due to competitive ions in the process water and, it is believed, partly due to silica buildup on the resin which caused fouling. These factors, combined with a reduction in uranium price, contributed to the decision to suspend operations. Although undoubtedly the tailings pond decant liquor contains some U_3O_8, no mention has been made of the need to discard excess water

as an effluent since the plant shut down or to remove uranium from effluents. If the plant starts up again, eventually an effluent will probably have to be treated.

RADIUM REMOVAL: LITERATURE SEARCH

A search of Chemical Abstracts and Waterlit produced the following:

HUCK, P. (1982) of the Engineering Dept., the University of Regina, reviewed effluent treatment from Canadian uranium mining and milling operations to remove Ra-226. Historically, treatment has been by adding $BaCl_2$ to form a finely divided precipitate of $(Ba,Ra)SO_4$ which is then settled in large ponds or lakes. He discusses improvements to conventional pond systems as well as a new mechanical solid liquid separation device incorporating co-precipitation and solids separation.

Ion exchange provides an alternative to systems based on co-precipitation by $BaCl_2$ addition.

Ra removal during mill processing is discussed as a potential long-term alternative to effluent treatment by HUCK but does not look too encouraging.

AVERILL, et al. (1981) of the Wastewater Technology Center of Environment Canada at Burlington, Ontario, established a data base for the design of two alternative wastewater treatment processes for the removal of Ra-226. Both of these processes achieved less than 0.37 Becquerel/l of total Ra-226 and dissolved Ra-226 of less than 0.11 Becquerel/l. The clarification process of Ba-Ra co-precipitation, rapid mixing of a chemical coagulant, flocculation, and solid/liquid separation in a clarifier could operate at a load of 490 m^3/m^2 day. The process using Ba-Ra sulfate co-precipitation and solid/liquid separation in a granular media filter could operate at a hydraulic load of 6.5 l/m^2s.

RYAN and ALFREDSON (1976) of the Australian Atomic Energy Commission at Lucas Heights, Australia, compared lime, limestone, caustic soda, and lime-soda ash mixtures as reagents for neutralizing raffinates and for removing amines and heavy metals including Ra from solution. All methods of neutralization reduced contaminant levels significantly. Two-stage neutralization with limestone in the first stage, followed by lime, usually gave the lowest residual Ra concentration, provided the solids from the first stage were not removed before adding lime. Ra can be further reduced from neutralized raffinates and from mine water conditioned with SO_4^{2-} by the addition of $BaCl_2$ to less than 3 p Ci/l by adding 10 mg Ba/l raffinate. For mine water containing 0.01 M SO_4^{2-}, Ba additions of 20 mg/l were required to attain the same Ra concentrations. Adsorption on barite was also effective in removing radium from conditioned mine water and neutralized raffinates.

SHERWOOD and CERN (1983) reviewed the treatment of uranium mill tailings and effluent in NUREG CR 2938, PNL 4453 of July 1983. The authors are employed at:

DIVISION OF HEALTH, SITING, AND
WASTE MANAGEMENT
U.S. Nuclear Regulatory Commission
Washington, DC 20555

CAMPBELL and SKEAFF (1982) characterized barium/radium sulfate sludges from uranium mining effluents. Based on bench-scale tests, they identified unexpected differences among the dewatering characteristics of several $BaRaSO_4$ sludges. Although these sludges resulted from the same basic waste treatment process (addition of $BaCl_2$ for precipitation of Ra-226) and the same minewater, the process configuration, i.e., settling pond, clarifier, sand-filter, etc., had a significant impact on the characteristics of the resulting sludge. This fact, in conjunction with the proposed ultimate disposal option, should play a major role in choosing a dewatering system. A freeze-thaw process resulted in the greatest degree of volume reduction for sludges with high specific resistances.

H. W. Campbell and J. M. Skeaff are employed at the Environmental Protection Service, Division of Environment Canada, at Burlington, Ontario.

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CHAPTER 54

WATER QUALITY AND MANAGEMENT IN FROTH FLOTATION

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WATER QUALITY AND MANAGEMENT IN FROTH FLOTATION

Water quality and water management has a significant impact on recovery, grade of concentrate, and effluent quality in flotation processes. Flotation of mineral particles from gangue, or one mineral from the other, makes the use of their different surface properties. These properties are modified or adjusted through the use of reagents. It is not surprising that water chemistry will influence the performance and selectivity of the flotation process since water is the suspension media with which the milled ore is in contact.

What is surprising is how little is generally known about the effect of various contaminants in water on the process and on the mechanisms for these effects.

Technical treatises on the flotation process rapidly become complicated and theoretical. In the end, the operator or researcher who is faced with a problem usually reverts back to empirical test results anyway.

FLOTATION OF MINERALS

Flotation is typically used in mineral processing to separate valuable sulfide minerals, e.g., chalcopyrite, galena, stibnite, sphalerite, pentlandite, native silver, silver sulfides, and molybdenite from gangue minerals such as quartz, limestone, dolomite, schist, and/or clay minerals, micas, etc.

These types of separations are typically employed in the treatment of copper porphyry and massive sulfide ore deposits in Chile, Zambia, Southwestern U.S.A., Canada, and South Africa.

Separation is also used to separate one sulfide mineral from another from bulk or semi-bulk concentrates, e.g., galena from copper minerals, molybdenum from copper minerals, or base metal sulfides from iron sulfides.

Separation of one sulfide from another by flotation is typically employed in the recovery of separate concentrates from complex sulfide ore such as occur across the Canadian Shield (Cu, Pb, Zn), in Sweden, Australia, and South Africa. Sulfide separations are also employed to separate copper-molybdenum bulk concentrates.

At Kidd Creek Mines, Timmins, Ontario, a flotation unit is installed in the secondary grinding circuit to float metallic silver particles which otherwise would be returned with clarifier underflow streams to the mill and would eventually be overground unless removed by this innovative flotation step.

Froth flotation is employed to recover non-sulfide minerals from gangue as, for example, in the recovery of Foskorite from carbonatite rocks at Phalaborwa or fluorspar from gangue, or in the recovery of Barytes.

Gold is recovered in free metallic from and/or in sulfide minerals, e.g., arsenopyrite or pyrite from a variety of ore types and/or from cyanided tailings.

Flotation can also be used to remove impurities, e.g., ferromagnesian minerals from silica sand where high purities are required for the glass and other industries.

There is clearly a very wide range of applications of flotation processes. All of these can be influenced by water quality effects.

Here there is room to refer to just some of these applications and to follow by inserting a few review papers which could provide useful insight into some of these effects. Clearly, a book could be devoted to this topic alone.

Brief comments on the following flotation applications follow:

Copper from Porphyry Deposits
Molybdenum
Copper-Molybdenum
Lead-Zinc
Copper-Lead-Zinc
Phosphate-Copper
Pyrite-Gold from Tailings

FACTORS INFLUENCING WATER QUALITY

Several factors influence the quality of water in flotation plants:

- Quality of available makeup water for use in the mill. Minewater, seawater, well, or lakewater.
- Dissolution of contaminanats from the gangue or mineral species.
- Flotation reagents or their degradation products.
- Tailings pond reactions and influence on recycled water quality.
- Degree of recycle water use and where it is used.
- Biological processes.

MOTIVATION AND EFFECT OF SOLUTION RECYCLING

Increasingly, strict effluent discharge regulations make it more or less mandatory in the U.S.A. to operate with zero discharge where climate allows. This means that water must be recycled or evaporated. Where climatic constraints do not allow zero discharge, effluents must be treated before they are discharged in order to meet the rigorous effluent contaminant levels that are required. This can be very expensive as well as difficult. The economic pressure of meeting these regulations is, therefore, also toward greater use of recycled solution.

When tailings decant solution is recycled, common contaminants that build up in the solution include:

Sulfate Ions
Sulfide
Thiosalts and Thiosalts
Alkaline Earth Elements Mg^{2+}, Ca^{2+}
Base Metals, e.g., Cu^{2+}, Zn^{2+}, Ni^{2+}
Reagents, e.g., Collectors, Frothers, Activators, Depressants, and their Degradation Products
Colloidal Materials, e.g., SiO_2, Clays $Fe(OH)_3$
Calcium, Magnesium, Sodium, Potassium
Fluoride and Chloride

Before solutions had to be recycled, it was common practice to use hexavalent chromium as sodium dichomate as a depressant in the separation of galena from lead-copper semi-bulk flotation concentrates. $Cr^{(VI)}$ is a powerful depressant for galena and, if even traces were to get into the main recycle water stream, this would result in loss in lead recovery in the primary concentrate.

Also, since hexavalent chromium is very soluble and toxic, its use would render tailings "hazardous" under the EP toxicity test which would require special disposal and management procedures. This is but one example of the need for a knowledgable use of a systems approach in managing water in mines and mills using flotation processes.

Another example of this is soluble copper in complex sulfide flotation flowsheets. For example, if water is recycled many times, small incremental levels of copper may dissolve from interaction with the ore until eventually a high enough level is reached to activate sphalerite in the primary semi-bulk float--just where, in the processing arrangement, depression of sphalerite is wanted. Soluble copper is used to activate sphalerite later in some circuits in the final zinc recovery step. If this soluble copper finds its way back to the front of the circuit, this could have the same undesired result. Copper can also get into mill process solutions if ores contain even small fractions of soluble oxide copper. This was a startup problem at the VAJASA concentrator on the Yukon border.

Similar considerations have to be taken into account for a host of ionic and organic species that are used or can find their way into solution.

The comminuted mineral surfaces first come into contact with water in the grinding circuit. In some cases, it has been found that even if the millwater is replaced with deionized water as it leaves the mill, the flotation characteristics will be affected by the composition of water in the mill. This, of course, is not usually the case, but some flotation separations are much more sensitive to water quality in the float cells than others. Another important aspect is the effect of water and air oxidation of surfaces on

flotation and water quality. For example, WASSERLAUF and DUTRIZAC (1982) and others showed that much of the thiosalt generation in flotation pulps occurs in the float cells and can be avoided if a nitrogen atmosphere is used. Aeration is often used as a preconditioning step in the separation of complex sulfides, however.

COPPER PROPHYRY FLOTATION

Copper sulfide minerals are recovered on a massive scale from porphyry deposits. All but one of the operations located in the southwestern desert region of the U.S.A. recycle as much water as they can recover from tailings as can be seen in the table below.

In these cases, scale control is important due to the use of lime for pH control and sulfate generation through oxidation of sulfides in the pulp and tailings..

Motivation to recycle water is due to to generally limited water availability in this region. Some operations, e.g., Phelps-Dodge at Morenci, recover 85% of the water calculated to be lost by seepage from their tailings pond via intercepter wells.

The simple metallurgical flowsheets used and the limited sensitivity of the single-component recovery process allows virtually 100% recycle of solution with the result that these operations consume only 80-105 U.S. gallons of net fresh water per ton of ore treated, i.e., 0.3-0.38 m^3/t. In these cases, over 85% of the total water used per ton of ore (2.3-2.7 m^3/t) is recycled.

On the other hand, where water is abundantly available or excess minewater must be disposed of in any case, a smaller percentage of water is recycled. The White Pine Copper Co. recycled no water. All decanted tailings water discharged lime-settling treatment.

Magma at Superior, one of the smallest copper recovery operations, delivers their excess water to local farmers for irrigation.

Before the Anaconda Co. shut down their operations at Butte, Montana, they were discharging 10 million gallons per day of decanted process water after pH adjustment with H_2SO_4.

Contacts in the copper industry with whom water quality and treatment aspects can be discussed include:

ADRIAN J. RODERICK
Superintendent of Mills
Phelps-Dodge, Morenci
Morenci, AZ

MAGMA COPPER COMPANY
San Manuel Operations
(602) 385-2201
Gayl Dopson

COPPER

Company	Concentrator TPD (1980)	Recycle Water	Discharge to Stream	Treatment of Reclaim Solution	Notes
The Anaconda Co. Butte, Mt	50,000	10,000 Gallons per Minute	10,000,000 Gallons per Day	Lime added to raise pH, then flocculant added, then to settling basin. The settling basin effluent is treated with H_2SO_4 to control pH. Water discharged to environment originates from tailings, middlings, and concentrate thickener overflows. Recycled water is treated as follows. Mine water and precipitation plant effluent is added to mill tailings underflow. Heavy metals from mine and precipitation plant waters are precipitated out by alkaline mill tailings underflow. Tailings dam water returned to plant barge pumps at pH 10.5.	Discharged water must not exceed the following PPM: Cu 1.0, Fe 2.0, Zn 1.0, Pb 0.1, As 0.05, Cd 0.1, Hg 0.002, suspended solids 30. pH must be between 7 and 11. Maximum discharge allowed is 19,000,000 gallons per day.
The Anaconda Co. Carr Fork, Ut	10,000	All	None	Recycled water is not chemically treated.	
ASARCO Sacaton	11,000	All	Nil	Hexametaphosphate for scale control.	
Cities Service Pinto Valley	47,500	All	Nil	Discharge water is put into a holding tank, and fresh water is added. Salts are allowed to settle out; water is recycled. No reagents used.	
Inspiration Christmas	6,000	All	Nil	Calgon reagent - scale control. Lime - pH control.	Hardness is main concern to avoid scaling.
Magma Superior	3,200	Part	Excess water is delivered to farmers for irrigation.	Phosphate chemical added for scale control. pH adjusted as needed with lime. Settling pond to remove particulates. Flocculant added to tailings thickener.	
Phelps-Dodge Tyrone	50,000	All	Known seepage loss from tailings (slight).	Calgon CL-50 (inorganic phosphate) and CL-95 (dispersant) in 5 to 1 ratio for scale control.	
White Pine Copper Company	25,000	None	All	Slaked lime - "lime and settle" treatment. Treated water is held 90 days for settling.	Cu, Pb, Zn is monitored in tailings pond.

COPPER - MOLY

Company	Concentrator TPD	Recycle Water	Discharge to Stream	Treatment of Discharge	Net Makeup Water (at Full Capacity)	Makeup Water at Partial Capacity	Gross Water Use	% Recycle	Notes
ANAMAX Twin Buttes	40,000	All	None	Mill tailings are passed through a cyclone, underflow to tailings pond, overflow to the tailings thickener. Thickener overflow water is recycled to plant. A phosphate chemical from N.L. Baroid dosed for scale control. Lime is added for pH control.	215 U.S. gpt (0.81 m^3/t)	390 U.S. gpt (1.47 m^3/t)	- -	- -	Scaling of pipes is major problem
ASARCO Mission	22,500	All	None	P_2O_5 - scale control.	205 U.S. gpt (0.77 m^3/t	250 U.S. gpt (0.93 m^3/t) at 50% Cap	N/A	N/A	--
ASARCO Silver Bell	11,000	All	None	Phosphate chemicals - scale control; particulate matter settles in a holding pond.	215 U.S. gpt (0.81 m^3/t)	275 U.S. gpt (1.04 m^3/t) at 50% Cap	N/A	N/A	--
Cyprus Bagdad	40,000	All	None	Water from tailings pond is pumped to a reclaim water reservoir. Fresh water is added and recycled with the reclaimed water. No reagents used.					
Cyprus Pima	57,500	All	None	Decant from tailings pond is mixed with fresh water. Sludge precipitates and settles.					
Duval	18,000	All	None	Mill tailings to thickener, underflow to tailings pond, overflow is recycled to plant. Tailings pond decant is recycled to plant. Water is chlorinated quarterly. Wells around tailings pond are monitored.					
Duval Esperonza	19,000	All	None	Mill tailings to thickeners (4), overflow to reclaim water reservoir, underflow to tailings pond. Tailings pond decant to reclaim water reservoir. Water from reservoir to a reclaim water thickener, overflow water recycled to plant, underflow to tailings thickener. Lime is added to thickeners to maintain on 11 pH. A phosphate chemical by Baroid is added for scale control.					Scaling
Duval Sierrita	92,000	All	None	Same as Duval - Esperonza	217 U.S. gpt (0.82 m^3/t)	225 U.S. gpt (0.85 m^3/t) at 75% Capacity			Scaling is major problem
Inspiration Inspiration	20,000	All	None	Tailings to hydroseparator, underflow to pond, overflow to thickener. Thickener overflow recycled to plant, thickener underflow to pond. Decant from pond mixed with fresh water, a Calgon reagent is added, and water is recycled. Lime is added occasionally for pH control.					
Kennecott Bingham Canyon	110,000				40,000 U.S. gpm 2.2 m^3/t		70,000 U.S. gpm 3.9 m^3/t		
Magma San Manuel	64,000	All	None	Polyphosphate for scale control.	234 U.S. gpt (0.9 m^3/t)	-	500 U.S. gpt 1.9 m^3/t	52%	

COPPER-MOLYBDENUM FLOTATION

Somewhat sketchy information was gathered about water recycling at copper-molybdenum recovery operations from porphyry ore deposits in the southwestern U.S.A.

Water is usually recycled in the bulk copper-moly flotation step but almost never in the copper-moly separation step which uses a lot less water, in any case, because the volume of primary concentrate treated is only a small fraction of the ore milled.

Results of a rough survey of a few operations as to how much water they use and how much is recycled are shown on the table overleaf.

According to this table, all the southwestern copper-moly operations recycle all the tailings decant water that they can from their tailings pond.

However, it is interesting to note that:

1) Net fresh water consumption per ton ore for Cu-Mo operations ranges between 0.77-0.92 m^3/t (200-235 U.S. gpt). This is two to three times as much new water as is used by straight copper flotation plants.

2) In the copper-moly separation step, recycle water is not used as this process is much more sensitive to water quality as described by FISHER and RUDY (1976) and HOOVER (Post 1979) inserted below.

HISCOX and BUZA (1975) described a new lignin sulfonate application as a moly depressant at Twin Buttes copper-moly recovery operation. An important aspect of this is that it illustrates the powerful depressing effects of lignin sulfonate on some minerals--in this case, molybdenum sulfide. This is important as it has impact on the decision as to whether or not to use lignin sulfonate as a binder for dust control on mine haulage roads. If the mine road is built on ore which will be mined at a later date, the use of lignin sulfonate would have a marked detrimental effect on molybdenum recovery.

Others have reported that even small amounts of naturally generated lignin sulfonate, when it gets into the plant water stream, can cause disastrous results on flotation plants. Lignin sulfonate generated by mine timbers in contact with minewater used in a mill reputedly caused uncontrolled frothing resulting in concentrate discharging to the floor sump at a copper-moly mill in the U.S.A.

FISHER and RUDY (1975) showed that the use of reclaimed sewage water results in significant reduction in molybdenite recovery and grade when used for flotation. They showed that activated carbon and foam fractionation treatment of the sewage water only partially improved the flotation performance compared with demineralized water. HOOVER

(after 1979) showed that the reduced recovery was largely due to the presence of colloidal solids rather than organic molecules. See his paper inserted below.

These workers at the time they wrote the papers were employed as follows:

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SCALE CONTROL

When water is recycled from tailings where it has been in contact with sulfide minerals, especially once the pH is allowed to drop requiring lime neutralization on return to the high pH process circuit, TDS builds up, principally consisting of $SO_4^{=}$, Ca^{2+}, and Mg^{2+}. These solutions can be highly scale forming. Scale must also be controlled in the powerhouse and steam plant. Copper and copper-molybdenum operations all depend on water treatment specialist companies who do this as a contracted service, e.g.:

NL Industries, Barochem Division

Drew Company

Nalco Chemical Company

Calgon Corp.

Betz Chemical Company

SOUTH AMERICAN COPPER-MOLY MILLS

It is known that high-TDS water with a poor quality must be used at some South American copper-moly producers. Seawater has been used for copper precipitate flotation operations. At the sulfide flotation mill of Codelco's Chuquiquamata operations, it is believed that poor quality water is used due to the need to recycle water on account of poor availability of good quality fresh water. It is believed that reclaimed sewage water is also used in the mill.

The 90,000 tpd (1966) operation at Chuquiquamata employed four 350' thickeners for water recovery from the surface of which evaporation was calculated at 2,000 m^3/d on account of the high altitude and wind effects. Apparently the highly recycled water has high TDS levels which cause scale problems.

COMPOSITION OF TAILINGS DAM RECLAIM WATER

Reclaim water from the Duval Sierrita operations typically contains 1,400 mg/l $SO_4^=$ and Ca, Mg, and Cl^- in the 100-150 ppm range.

KENNECOTT MINERALS COMPANY, BINGHAM CANYON, UTAH

The Bingham Canyon operation milled 110,000 tpd ore to recover copper and molybdenum. Total water used in the circuit is 70,000 U.S. gpm (3.9 m^3/t) of which 40,000 U.S. gpm is "new" water (2.2 m^3/t). Of this, half comes from deep wells which yield an excellent quality water. The remaining 50% comes by surface canals from Utah Lake located in the Salt Lake City Valley.

MoS_2 recovery has been recognized since the 1940's to be subject to seasonal variation. During the hot summer months, MoS_2 recovery is poor, and in the cold winter months, recovery improves significantly.

MoS_2 recovery to the bulk Cu-Mo concentrate is 80-85% in winter but only around 60% in summer. In order to determine the cause of this, all variables (ore, reagents, water quality, etc.) were analyzed weekly over a two-year period. Organic and inorganic constituents of water were analyzed including residual reagents, humic acid (a depressant for molybdenum), and fluvic acid.

It was found that during summer, biological decay on farms resulted in 4-5 mg/l humic acid in the water supply to the concentrator. Humic acids were analyzed by loading them onto a Rohm & Haas resin and then stripping them prior to liquid chromatography determination.

Contacts in the copper-moly flotation industry:

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THE ARIZONA BUREAU OF MINES
Circular 17
1976

UTILIZATION OF MUNICIPAL WASTE WATER FOR FROTH FLOTATION OF COPPER AND MOLYBDENUM SULFIDES

by
Walter W. Fisher, Assistant Metallurgist
and
Samuel Rudy, Assistant Metallurgist

INTRODUCTION

Water is becoming a more and more controversial subject in Arizona. The problem stems from the fact that the amount of water consumed far exceeds the ability of nature to replace it. In order to meet growing agricultural, industrial, mining and municipal demands, water is being mined from groundwater reservoirs at alarming rates. Statistics presented in Phase I of the Arizona State Water Plan recently released by the Arizona Water Commission indicate that for Arizona, taken as a whole, water is being withdrawn from groundwater storage at 1.7 times the rate at which it is being replaced by natural recharge. In Pima County, where essentially all water consumed is drawn from the groundwater supply, the depletion rate is 4.7 times the recharge rate. Such depletion of the groundwater supply cannot go on indefinitely. Alternatives must be found and implemented to narrow the widening gap between water use and water recharge.

One alternative that could result in a significant reduction in groundwater depletion near metropolitan areas is utilization of municipal waste water. This large source of water is presently used to a very limited extent. For example, in Pima County, the City of Tucson discharges about 33 million gallons per day of municipal waste water into the Santa Cruz River. Part of this water percolates into the ground and will ultimately enter the groundwater reservoir to the north of Tucson. However, a large portion of the water evaporates into the atmosphere. The City of Tucson is currently seeking alternative uses for this water. Of the many possibilities, the one that has received the most public exposure is utilization of the waste water by the four copper mining and processing operations located south of Tucson. This alternative would reduce the groundwater depletion in the area and at the same time provide the local copper industry with a reliable, long term source of water.

Municipal waste water is already utilized to a small extent in several copper processing operations in Arizona. However, the amount used is rather small when it is compared with the total water consumed by each operation and the adverse effects attributable to the waste water are not readily observed in these operations.

The proposed use of waste water by the operations near Tucson is considerably different. The water currently used by these operations would be almost completely replaced with waste water. The mineral processing techniques used by these companies are extremely sensitive to chemical contaminants, and therefore, large scale substitution of waste water could have serious detrimental consequences. Because there is not an industrial precedent for this type of municipal waste water utilization and since experimental studies on the effects of waste water in mineral processing have not been reported, there remains a large gap between proposed utilization and commercial acceptance.

The Arizona Bureau of Mines, under the sponsorship of the Office of Water Research and Technology at The University of Arizona, has for the past two years studied the feasibility of utilizing municipal waste water in mineral processing. The laboratory investigation has been aimed at first identifying potential problems, and then, seeking solutions that would be acceptable to the mineral processing industry. Since this work was prompted by a specific problem in the Tucson area, the investigation has been limited to utilizing City of Tucson municipal waste water in the mineral processing operations south of Tucson. The largest use of water in these operations is in the froth flotation recovery of copper and molybdenum sulfide minerals. Consequently, this entire report is devoted to the utilization of sewage effluent in the flotation process.

The work reported in this paper is by no means an exhaustive study of the problem. Rather, it is an exploratory study meant only to define the problem and point out areas for future concentrated investigation.

Background on Copper-Molybdenum Froth Flotation

Froth flotation is the principal process by which sulfide minerals are recovered from ores to form sulfide concentrates. The copper industry relies almost entirely on froth flotation for its feed to smelters and hydrometallurgical refining processes. The success of the flotation process lies in the carefully controlled addition of small quantities of specific chemicals to the processing system at the correct addition point. As a result, froth flotation is extremely sensitive to small amounts of chemical contaminants that may be present in water supplied to the processing system. Foreign chemical contaminants in the process water can have a significant effect on froth flotation metal recovery.

Flotation recovery of copper sulfide minerals and by-product molybdenum sulfide, as practiced in most copper concentrators, consists of many interdependent flotation stages. Raw ore, having been crushed and ground sufficiently fine, is subjected to the rougher flotation stage. A rougher bulk concentrate is produced which contains most of the copper and molybdenum sulfide minerals, along with other impurities. The rougher concentrate is ground finer, and cleaned two or three times by flotation to remove as much non-sulfide material or gangue as possible and produce a high-grade bulk copper-molybdenum concentrate. Molybdenum sulfide is then separated from copper sulfides by chemical treatment and differential flotation to produce a relatively low grade rougher molybdenum sulfide concentrate and a high grade copper concentrate. The rougher molybdenum concentrate is cleaned by several additional stages of flotation to further reject copper sulfides and gangue to produce a high-grade final molybdenum concentrate.

This report is devoted solely to the determination of the effects of sewage effluent on bulk rougher flotation. Therefore, the results presented serve only to identify the gross and most obvious effects of sewage effluent. Determination of the effects of sewage effluent on the integrated copper-molybdenum froth flotation processing scheme is beyond the scope of this report, and in fact, can probably only be determined with certainty in a pilot plant of sufficient size to allow scale up to commercial practice.

EXPERIMENTAL PROCEDURE

Ore, Water and Reagents

The investigation was conducted using an ore obtained from the Cyprus Pima Mining Company open pit mine located south of Tucson. Approximately 800 pounds of ore was collected in the concentrator from conveyors feeding three grinding mills in the primary grinding circuit. The ore was stage crushed in the laboratory to minus 10 mesh, mixed, split into 1000 gram dry test charges, and stored in plastic bags for later use. Since the ore samples were ground in a laboratory ball mill prior to each flotation test to produce an ore pulp containing about 47 percent finer than 200-mesh, oxidation of the sulfides in the minus 10-mesh ore during storage was not considered to be a significant problem. Chemical analysis showed the sample to contain 0.49 percent copper, 4.40 percent iron and 0.011 percent molybdenum. Chalcopyrite, pyrite, and molybdenite were identified microscopically as the main sulfide minerals present.

Demineralized water generated with a high-capacity Barnstead demineralizing column was used for the standard flotation tests. (Use of product or company names in this report is made for identification only and does not serve as an endorsement by the Arizona Bureau of Mines.) Water obtained by this procedure was designated standard water in subsequent flotation tests, and was used to establish a reference flotation response from which direct comparisons of flotation results could be made. Sewage effluent was obtained at the City of Tucson's Roger Road sewage treatment facility from one of the activated sludge units. All samples were collected from the same treatment unit between the hours of 8 and 9 A.M. so that the flow rate through the plant was essentially the same for each sample.

Flotation reagents used throughout the study were standard laboratory chemicals in general use by flotation laboratories. Potassium amyl xanthate (Z-6) and methyl iso-butyl carbanol (MIBC) were used as the primary collector and frother respectively. In some tests, American Cyanamid AERO PROMOTER 3302 was used as the collector. A mixture of 50 percent kerosene and 50 percent Number 2 diesel fuel constituted the fuel oil mixture. Hydrated lime assaying 93 percent $Ca(OH)_2$ was used as the pH modifying agent.

Flotation Procedure

Flotation tests were conducted in the following manner. One thousand grams of ore containing suitable additions of desired reagents were ground at 67 percent solids for 10 minutes in a 7.5 by 8-inch laboratory ball mill containing 30 pounds of steel balls of various sizes. The ground pulp was transferred to a Denver D-1 2.5 liter laboratory flotation cell and diluted to 2.2 liters or about 35 percent solids. The pH of the slurry was determined using a Corning Model 7 pH meter. The slurry was then conditioned for 2 minutes with the air valve of the flotation mechanism in the open position, after which time frother was added and the slurry conditioned another minute without introducing air. The conditioned pulp was subjected to rougher flotation with the impeller of the flotation machine rotating at 1800 RPM. Froth was drawn on 10 second intervals for 8 minutes. The sides of the flotation cell were washed on 2 minute intervals, and the pulp level was adjusted after 4 minutes by adding 100 milliliters of water. Rougher concentrate and rougher tailings were filtered, dried, weighed, and analyzed for copper and molybdenum using an atomic absorption method. Iron determinations were made by a standard volumetric method.

The procedure of conducting a standard flotation test with each series or set of sewage effluent tests was adopted to allow a direct comparison of results of the various test sets.

Experimental Approach

Most of the copper processing operations use complex reagent schedules that have been devised through several years of laboratory evaluation and plant operating experience. In general, each reagent schedule is tailored to fit the ore on which it is used with optimum flotation response as the goal. If an

optimum, multi-component reagent schedule was used in this investigation, some of the effects of sewage effluent might have been masked by the compensating ability of the reagent schedule. Therefore, a very simple reagent schedule was chosen for the initial flotation tests, so that the full effects of sewage effluent would be apparent.

RESULTS AND DISCUSSION

Development of the Standard Flotation Test

The development of a standard laboratory flotation reagent schedule and establishment of a standard flotation response was necessary to provide a basis from which comparisons could be made and metallurgical differences could be determined between sewage effluent and standard demineralized water flotation systems. Adequate liberation of sulfide minerals from host rock was the first consideration. Laboratory grinding studies indicated that a 10 minute grinding time provided adequate liberation and produced a particle size distribution that generally paralled that which mining companies in the area achieve. Table 1 shows the particle size distribution obtained for a 10 minute grind.

Table 1

Screen Analysis of Ground Ore

Tyler Screen Fraction	Weight Percent Retained	Cumulative Weight Percent Retained
+ 35	1.8	1.8
- 35+ 48	4.7	6.5
- 48+ 65	11.9	18.4
- 65+ 100	11.3	29.7
-100+ 150	10.4	40.1
-150+ 200	13.1	53.2
-200	46.8	100.0

Potassium amyl xanthate and methyl iso-butyl carbanol were chosen as the collector and frother respectively, because of their wide use in industry. Figure 1 shows copper and molybdenum recovery as a function of collector dosage at a pH of 11.5 with 0.04 pound per ton of frother. A collector addition level of 0.04 pound per ton was adopted as the standard collector dosage to be held constant throughout the study.

Flotation recovery for copper and molybdenum is shown as a function of pH for standard water and sewage effluent systems in Figures 2 and 3. These figures indicate that a pH in the range of 11.0 to 12.0 is optimum for copper and molybdenum recovery in both standard water and sewage effluent systems. A pH of 11.5 was thus selected as the pH at which the standard test would be conducted. Figures 2 and 3 also show that sewage effluent effects molybdenum recovery far more than it does the recovery of copper.

Iron in the rougher concentrate is contributed by both chalcopyrite and pyrite. Pyrite is generally an undesirable constituent of the concentrate and therefore flotation conditions are adjusted to reject as much pyrite as possible. A decrease in the iron content of the concentrate is an indication of pyrite rejection. Figure 4 shows the effect of flotation pH on the amount of iron contained in rougher concentrate for the standard water and sewage effluent systems. Pyrite depression is substantial but not complete at a pH of 11.5. In practice, a more complete depression of pyrite is generally achieved in the cleaner flotation section.

Table 2 summarizes the standard test reagent schedule developed during the initial stage of the investigation for comparing sewage effluent with standard water.

Table 2

Reagent Schedule for Standard Water and Sewage Effluent Flotation Tests

Addition Point	Reagents, pounds per ton					
	Standard Water			Sewage Effluent		
	Lime	MIBC	Z-6	Lime	MIBC	Z-6
Grind	3.5	----	0.04	4.0	----	0.04
Condition	---	0.04	----	---	0.03	----

The lime requirement necessary to attain a pH of 11.5 was greater for sewage effluent than for standard water. In addition, less frother was required to achieve optimum frothing conditions in the sewage effluent system than in the standard water system.

Standard Water and Sewage Effluent Test Results

Table 3 shows a comparative metallurgical summary for eight standard water and eight sewage effluent flotation tests conducted on different dates over a period of several months. The table illustrates the small but measurable detrimental effect on copper recovery, and a substantially larger detrimental effect on molybdenum recovery when utilizing secondary treated sewage effluent as process water in the systems studied. The percent recovery values have been calculated at the 95 percent confidence level. The magnitude of the losses attributable to sewage effluent can be dramatically reduced by the addition of certain supplemental flotation chemicals to the system, especially in the case of molybdenum.

In addition to the quantitative metallurgical differences between sewage effluent and standard water systems evident from Table 3, a very significant difference in frothing characteristics exists between the two systems. Sewage effluent causes a voluminous, dull grey colored initial froth (without the

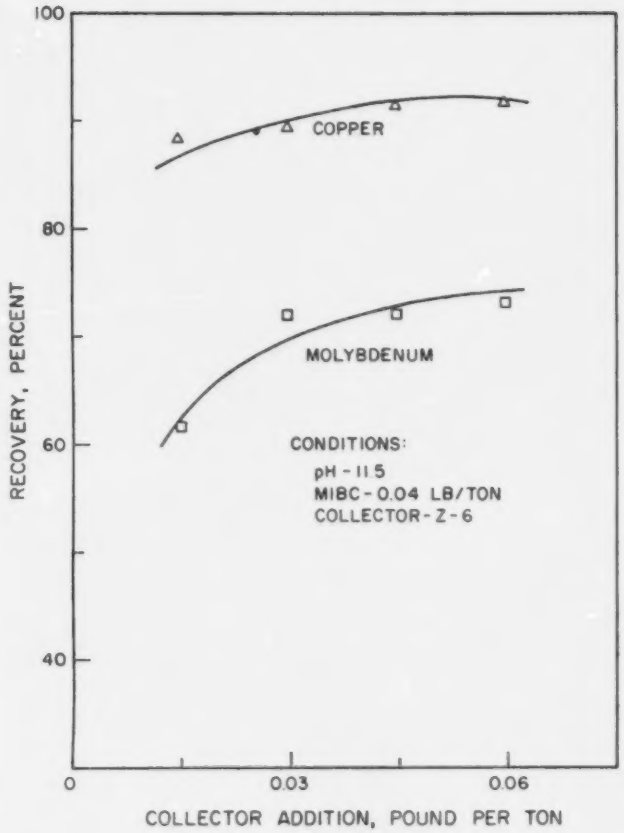

Figure 1. Copper and molybdenum recovery vs. collector addition in demineralized water.

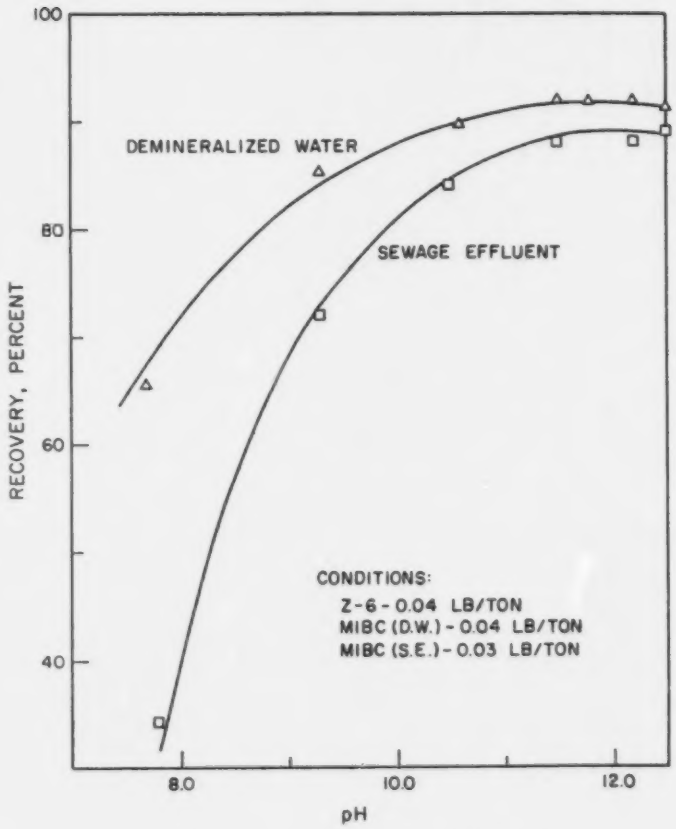

Figure 2. Copper recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.).

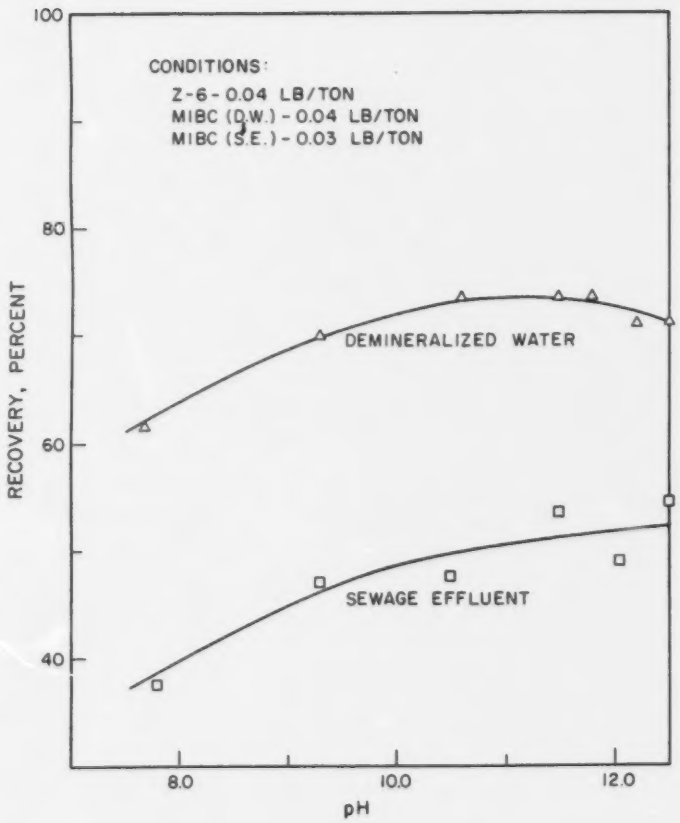

Figure 3. Molybdenum recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.).

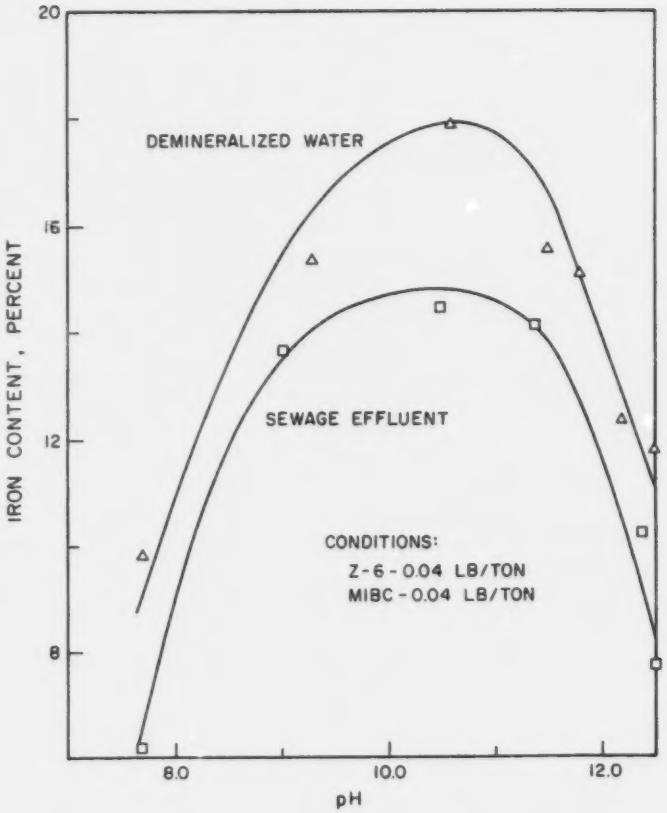

Figure 4. Percent iron in rougher concentrate vs. pH for demineralized water and sewage effluent.

Table 3

Comparative Metallurgical Summary for Standard Water and Sewage Effluent Flotation Systems

Water Type	Concentrate			Tail		% Recovery	
	Wt. %	% Cu	% Mo	% Cu	% Mo	Cu	Mo
Standard	6.8	6.52	0.120	0.055	0.0035	89.7 ± 1.2	71.7 ± 1.0
Sewage	8.5	5.09	0.078	0.069	0.0058	87.3 ± 0.9	55.5 ± 1.7

addition of frother) that has little mineral carrying capability and is difficult to control. The initial froth in the standard test is smaller in volume, and is heavily laden with a coating of bright, brassy chalcopyrite. As the standard test proceeds and the initial froth is removed, it is replaced by a froth of relatively uniform bubble size of smaller diameter than the initial bubbles. Occasionally, the larger bubbles reappear. The frequency of occurrence of the larger bubbles, the size of the smaller uniform bubbles, and the thickness and brightness of the mineral coating all diminish as the test proceeds. As the sewage effluent test proceeds and the initial froth is removed, the same gradual decrease in bubble size and mineral coating occurs. However, toward the end of the test the bubbles in the sewage effluent test give a wet, sudsy appearance and seem to contain more slime particles than the standard froth at the same point.

The first sections of this investigation, in addition to establishing a standard flotation test procedure, served to define the effects that secondary treated sewage effluent has on the flotation process when it is substituted for standard water. First, sewage effluent causes a substantial decrease in molybdenum recovery. It also causes a small but significant decrease in copper recovery. Finally, sewage effluent creates a voluminous froth, even in the absence of frother, that is difficult to control and has little mineral carrying ability. The remainder of this investigation was devoted to determining changes in the reagent schedule to compensate for the effect of sewage effluent and to examining methods of treating sewage effluent to make it more acceptable for flotation.

Dilution of Sewage Effluent with Demineralized Water

In the event that sewage effluent were utilized on a large scale by a copper concentrator, eventually the entire water inventory would be sewage effluent. It is likely, however, that the detrimental constituents of the effluent would be removed from the system by the flotation process. Therefore, the recycled water supply might consist of acceptable water and only sewage effluent added for makeup would create a problem. Consequently, the detrimental effects of sewage effluent under these conditions might not be as severe as those encountered with complete replacement with sewage effluent as practiced in tests previously reported. This possibility was evaluated by performing flotation tests using sewage effluent diluted with demineralized water.

Figure 5 shows the effects on copper and molybdenum recovery of diluting sewage effluent with standard demineralized water. Dilutions were made by mixing measured quantities of the two water types in a plastic container until a well blended solution was obtained. The data indicate a gradual, almost linear, increase in recovery for both copper and molybdenum with increasing percentages of standard demineralized water. In the case of molybdenum, however, small additions of standard water appeared to cause a disproportionate increase in recovery. In general, the improvement in recovery appears to be attributable to simple dilution of the deleterious constituents contained in sewage effluent.

Dilution of Sewage Effluent with Process Tailings Slurry

Process tailings discharged from a flotation concentrator might be used to remove some of the deleterious contaminants contained in sewage effluent. By mixing sewage effluent with process tailings slurry, the relatively high surface area of the ground ore particles might adsorb some of the undesirable contaminants contained in the effluent prior to its contact with fresh ore, and thus eliminate some of the detrimental effects that sewage effluent has on flotation recovery. A test series was conducted to determine the merits of this proposal. The tests involved establishing a reference curve using sewage effluent diluted with various quantities of clear process water, and then combining sewage effluent with samples of process tailings slurry and comparing the results thus obtained with the reference curve at the appropriate dilution. Samples used for these experiments were obtained from the Cyprus Pima concentrator. Tailings thickener overflow water was used where required, and tailings thickener underflow slurry was used where dilutions with slurry were required. Figure 6 shows the effects on copper and molybdenum recovery of diluting sewage effluent with clear process water

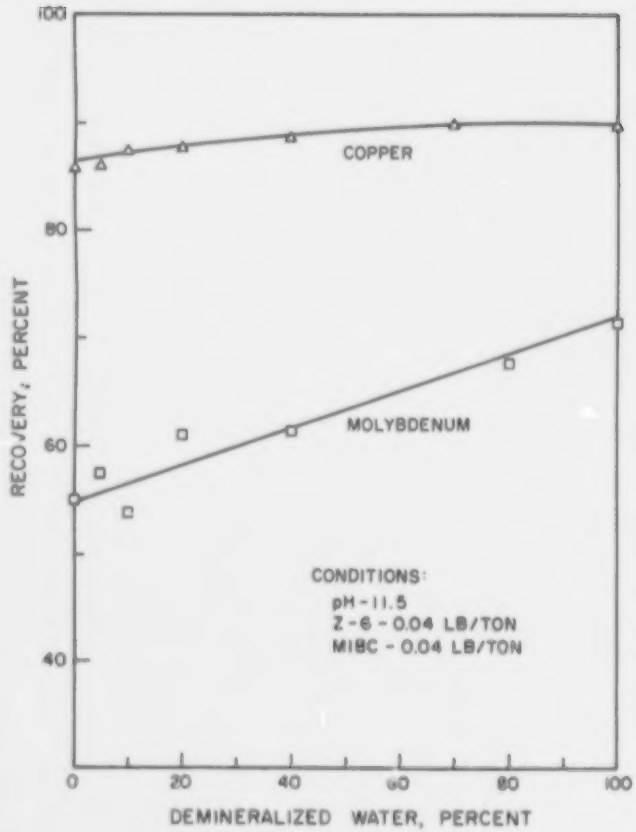

Figure 5. The effect of diluting sewage effluent with demineralized water.

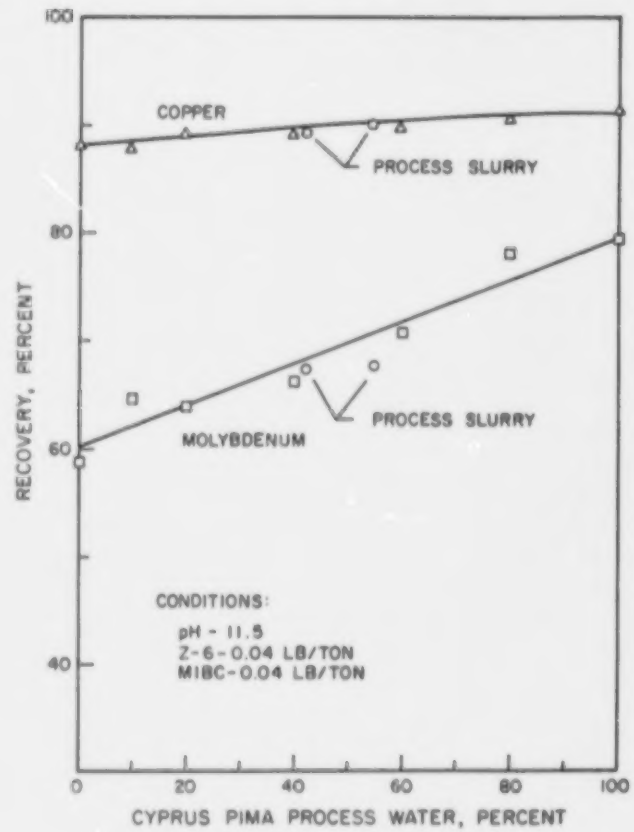

Figure 6. The effect of diluting sewage effluent with Cyprus Pima process water and process slurry.

Table 4

South Tahoe Public Utility District
Estimated Overall Plant Efficiency

Quality Parameter	Raw Waste Water Influent	Activated Sludge Effluent	Reclamation Plant: Separation Bed Effluent	Reclamation Plant: Chlorinated Carbon Column Effluent
BOD, mg/1	200-400	20-100	1	1
COD, mg/1	400-600	80-160	30-60	3-16
Suspended solids, mg/1	160-350	5- 20	0.5	0.5
Turbidity, units	50-150	20- 60	0.5	0.5
Phosphate, mg/1	15- 35	10- 30	0.4-2.0	0.2-1.0
Chlorine Demand, mg/1	Over 50	10- 50	5-10	1-3
Odor	Odor	Odor	Odor	Odorless

and process slurry. The addition of process tailings slurry to sewage effluent had no beneficial effect on flotation recovery, and the deleterious constituents contained in sewage effluent apparently do not adsorb on the surface of ground ore particles to any measurable extent. Furthermore, aging the slurry-sewage effluent solution for 2 days had no effect on water quality in terms of flotation response.

Activated Carbon Treatment of Sewage Effluent

A method sometimes employed to improve the quality of industrial and municipal waste waters is treatment with activated carbon. Granular activated carbon treatment of large quantities of waste water began in the early 1960s (Hager, 1974). The development of granular activated carbon with the capability of regeneration and reuse made adsorption an economic alternative for removal of dissolved organics and other contaminants from waste water. At Lake Tahoe, California, the South Tahoe Public Utility District uses activated carbon for tertiary treatment of more than 2.5 mgd of activated sludge effluent prior to discharge to the environment (McDonald, 1965). The water discharged from the plant has been characterized as being colorless, odorless, and crystal clear. The water reclamation plant's estimated overall plant efficiency is summarized in Table 4 (McDonald, 1965).

A laboratory activated carbon column was constructed and operated to determine the effect of activated carbon treatment of sewage effluent on flotation recovery. Table 5 summarizes the column operating conditions. Sewage effluent was pumped upward through the column at a controlled rate with a contact time of 2 minutes. No attempt was made to maximize the efficiency of the column and no chemical analysis of column influent or effluent was performed.

Figures 7 and 8 show the effect on copper and molybdenum recovery of treating sewage effluent with activated carbon. The results indicate a significant increase for both copper and molybdenum recovery when sewage effluent is treated with granular activated carbon. Further improvements in sewage effluent quality may be obtained with longer carbon contact times. Indeed, mining company personnel have indicated that they have generated water from sewage effluent using activated carbon treatment that is of a quality equal to their standard process water in terms of flotation response (Khan, 1975).

Table 5

Activated Carbon Column Operating Conditions

Carbon Description	6X16 mesh Pittsburgh Activated Carbon
Column Diameter, ft.	0.125
Area, sq. ft.	0.0123
Carbon Weight, lb.	0.77
Bed Depth, ft.	2.3
Flow Rate, gpm	0.074
Residence Time, min.	2.0

The detrimental frothing characteristics associated with sewage effluent appeared to be significantly reduced by activated carbon treatment. The initial froth generated on conditioning without frother was not as voluminous and unmanageable as with untreated sewage effluent. However, there did

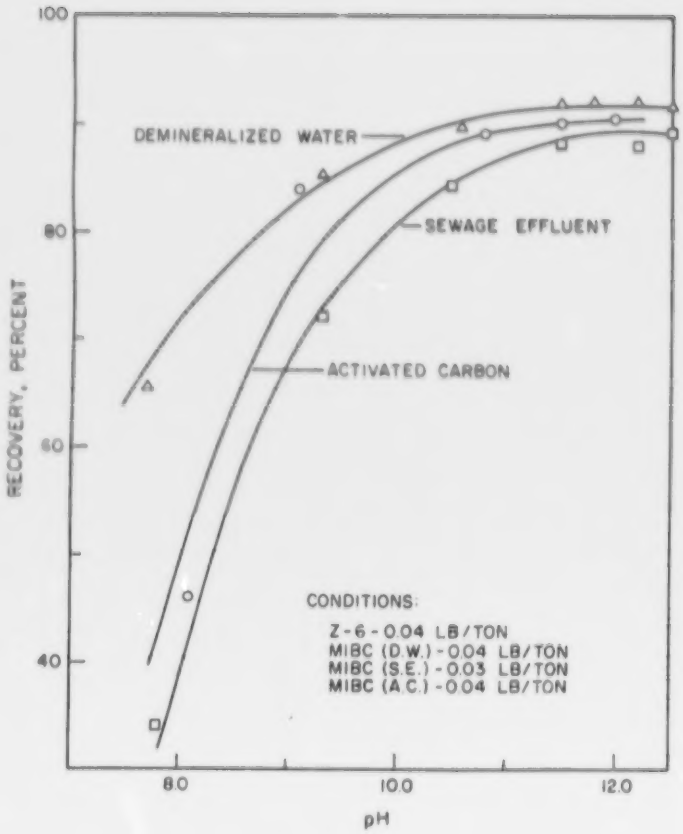

Figure 7. Copper recovery vs. pH for demineralized water (D.W.), sewage effluent (S.E.), and activated carbon (A.C.) treated sewage effluent.

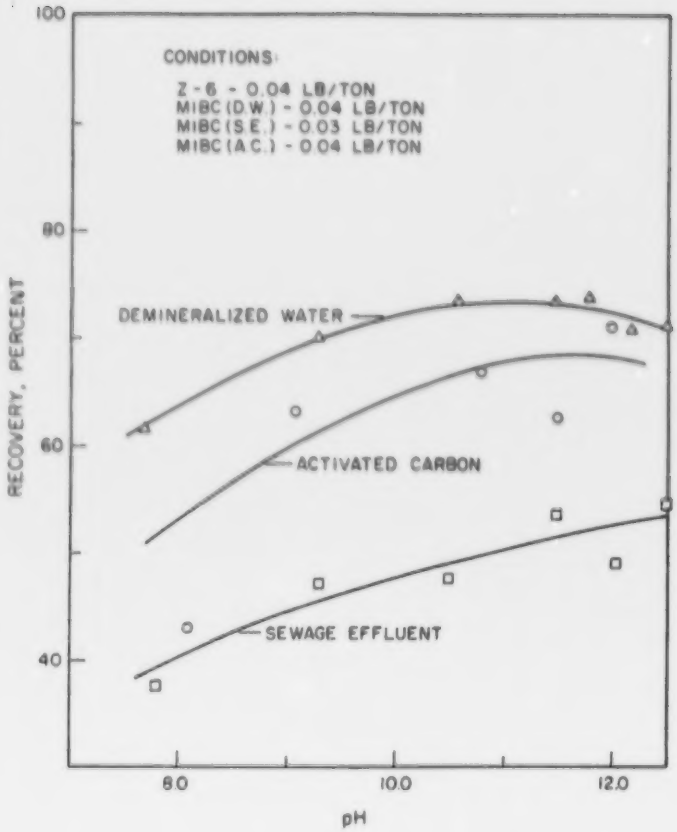

Figure 8. Molybdenum recovery vs. pH for demineralized water (D.W.), sewage effluent (S.E.), and activated carbon (A.C.) treated sewage effluent.

Table 6

Analysis of Plant Number 3 Effluent
for Fiscal Year 1974-75

Quality Parameter	Concentration, PPM	Quality Parameter	Concentration, PPM
Total Solids	656	NH_3-N	18.9
Suspended Solids	36	NO_2-N	0.2
Dissolved Solids	620	NO_3-N	0.5
Fixed Residue	469	Organic N	8.2
Volatile Residue	151	Calcium	66
Total Alkalinity ($CaCO_3$)	277	Magnesium	17
pH	7.7	Hardness	325
BOD	28	Chloride	92
COD	68	Bicarbonate	338
MBAS	0.9	Phosphate, ortho	28
Grease	9	Sulfate	146
		Sodium and Potassium	116

appear to be some minor residual frothing characteristics that are associated with untreated sewage effluent. A longer carbon contact time might eliminate most of the detrimental frothing characteristics associated with sewage effluent.

Ion Exchange Removal of Contaminants in Sewage Effluent

The number and variety of contaminants contained in sewage effluent is large. This fact is evident from viewing the typical sewage effluent analyses presented in Table 6 for plant Number 3 of the City of Tucson Roger Road treatment facility for fiscal year 1974-75 (Trueblood, 1975).

In an attempt to determine whether the deleterious constituent or constituents present in sewage effluent are cations, anions, or neutral molecules, a series of ion exchange tests were performed on sewage effluent samples. Amberlite 200, a cationic exchange resin with a sulfonic acid functional group, was loaded in the acid form and used to exchange cations in sewage effluent. Sewage effluent samples were first filtered through Whatman No. 50 filter paper, and then agitated with 250 milliliters of resin for 30 minutes in a 4 liter pyrex beaker. After cation exchange, the pH of the resulting solution was adjusted from 2.8 to 7.5 with sodium hydroxide. The water thus generated was then used in laboratory flotation tests to determine the effect of cation removal on flotation recovery. In a similar procedure, anions were removed from filtered sewage effluent using Amberlite IRA 900, an anion exchange resin with a quaternary ammonium functional group loaded in the hydroxide form. The pH of the anion exchanged sewage effluent was adjusted from 11.5 to 7.6 with sulfuric acid and the resulting effluent solution was used in laboratory flotation tests. Exchange of both cations and anions was accomplished by first exchanging cations with Amberlite 200, and then exchanging anions with Amberlite IRA 900. The pH of the resulting solution was adjusted from 10.7 to 6.7 with sulfuric acid. Table 7 shows a comparative metallurgical summary of the flotation results obtained with water generated by the foregoing procedures. Flotation results of ion exchanged sewage effluent are compared with standard water, as received sewage effluent, and filtered sewage effluent.

Table 7 illustrates that a significant increase in both copper and molybdenum recovery can be achieved by removing the anions from sewage effluent. Whether the deleterious ionic species is a simple inorganic ion, a more complex organic derivative, or a combination of both has not been determined.

Foam Fractionation of Sewage Effluent

Foam fractionation has been employed in a number of engineering applications (Kobe and McKetta, 1962 and Schoen, 1962). In one instance, alkyl benzene sulfonate and other organics analyzed as chemical oxygen demand have been removed from secondary sewage effluent (Rubin, 1963). The process of foam fractionation utilized the tendency of surfactants to accumulate at the air-aqueous interfaces formed when bubbles are generated in a liquid. This process deals with a two phase system: that is, a gas and a liquid, in contrast to froth flotation which deals with a three phase system involving one or more solid constituents.

A series of flotation tests utilizing foam fractionated sewage effluent was conducted to determine the effect on flotation of foam fractionation. Sewage

Table 7

Comparative Metallurgical Summary
for Ion Exchange Test Series

	Concentrate			Tails		% Recovery	
	Wt. %	% Cu	% Mo	% Cu	% Mo	Cu	Mo
Standard Water	6.8	6.52	0.120	0.055	0.0035	89.7	71.7
Sewage Effluent	7.5	5.80	0.085	0.069	0.0053	87.2	56.5
Filtered Effluent	6.7	6.40	0.091	0.068	0.0051	87.2	56.3
Cationic Exchange	6.6	6.58	0.115	0.067	0.0044	87.5	64.9
Anionic Exchange	7.5	5.90	0.111	0.056	0.0035	89.5	71.9
Cationic-Anionic Exchange	6.6	6.95	0.117	0.059	0.0036	89.2	69.6

Table 8

Comparative Metallurgical Summary for
Foam Fractionation Test Series

Water	Concentrate			Tails		% Recovery	
	Wt. %	% Cu	% Mo	% Cu	% Mo	Cu	Mo
Standard Water	6.8	6.52	0.120	0.055	0.0035	89.7	71.7
Sewage Effluent	7.4	5.86	0.093	0.065	0.0060	87.8	55.4
Foam Fractionated Sewage Effluent	7.2	5.96	0.098	0.060	0.0060	88.4	55.8

effluent was foam fractionated for 10 minutes in a laboratory flotation cell without frother. Table 8 shows a comparison of flotation results obtained for standard water, sewage effluent and foam fractionated sewage effluent.

The results indicate that foam fractionation did not improve the quality of sewage effluent in terms of flotation metal recovery. There was, however, a noticeable improvement of frothing qualities. The voluminous, unmanageable froth associated with sewage effluent appeared to be significantly reduced. Foam fractionation could be employed as one approach to froth control when utilizing sewage effluent.

Substitution of an Alternate Collector for Potassium Amyl Xanthate

A collector frequently employed in copper and molybdenum flotation is the allyl ester of amyl xanthate (S-3302). This water insoluble, oily collector is sometimes used in combination with a xanthate, fuel oil, and a frother, to give optimum copper and molybdenum rougher flotation results. Because this type of collector is also in wide use in industry, a series of flotation tests were conducted using the same procedure previously described with the exception that 0.04 pound per ton of S-3302 was added to the grinding mill in place of 0.04 pound per ton of Z-6. Figures 9 and 10 show the effect on copper and molybdenum recovery, respectively, of substituting S-3302 for Z-6 in demineralized water and sewage effluent flotation systems. Figure 9 indicates that copper recovery with S-3302 is less sensitive to pH change than is Z-6 in both standard demineralized water and sewage effluent. Above a pH of about 9 to 9.5, copper recovery is adversely affected by the substitution of S-3302 for Z-6 in both standard water and sewage effluent systems. Figure 10, on the other hand, shows that molybdenum recovery is increased dramatically over the entire pH range studied for both demineralized water and sewage effluent systems. In fact, the recovery versus pH curve for S-3302 in the sewage effluent system lies almost directly on the recovery versus pH curve for Z-6 in standard demineralized water. Figure 11 shows a comparison of the percent of iron contained in the rougher concentrate for Z-6 and S-3302 in demineralized water. Since S-3302 is already widely used by industry, the results of this test series are of fundamental interest.

Fuel Oil in Combination with Potassium Amyl Xanthate

A study of this nature could not be complete without determining the effect of fuel oil addition on molybdenum recovery in both the sewage effluent and demineralized water flotation systems. Fuel oil is almost universally used in commercial molybdenum flotation as a molybdenum promoter. Table 9 summarizes the results of a test series (using Z-6 as the collector) to determine the effect of fuel oil addition on copper and molybdenum recovery.

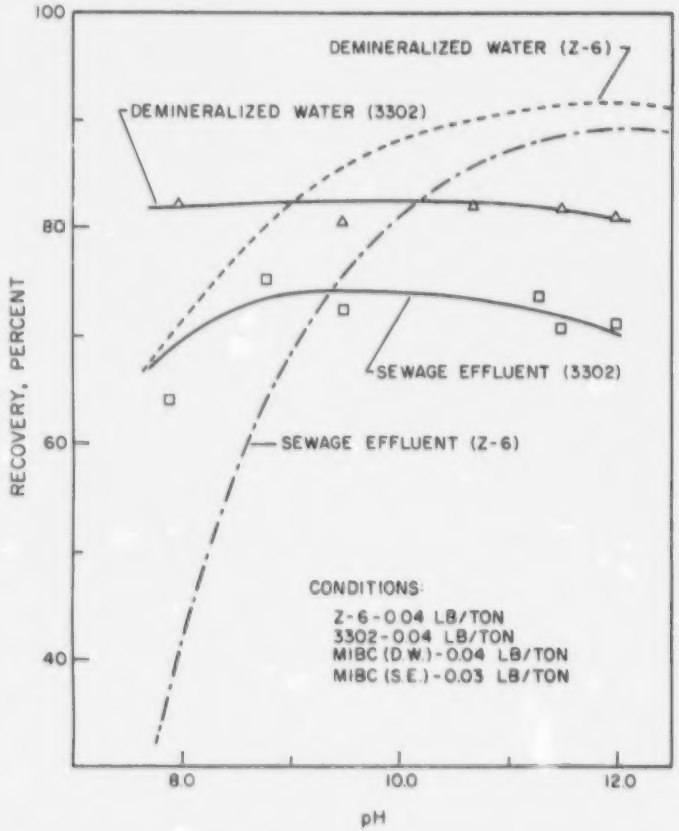

Figure 9. Comparison of copper recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.) using Z-6 and 3302 as collectors.

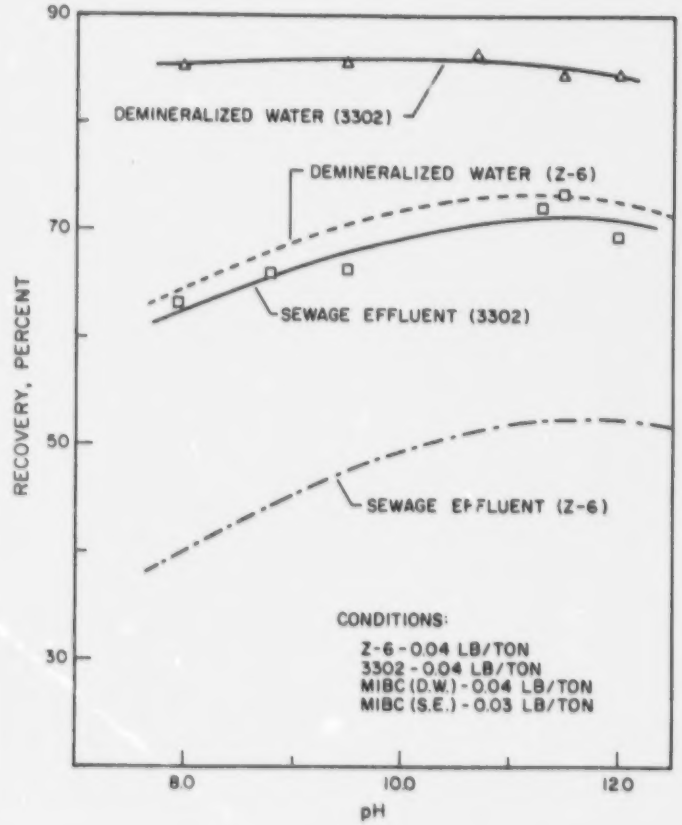

Figure 10. Comparison of molybdenum recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.) using Z-6 and 3302 as collectors.

Table 9

Effect of Fuel Oil Addition on Copper and Molybdenum Recovery in Demineralized Water and Sewage Effluent Flotation Systems

Fuel Oil, Lb/Ton	Water Type: Demineralized % Recovery Cu	Demineralized % Recovery Mo	Sewage Effluent % Recovery Cu	Sewage Effluent % Recovery Mo
0	89.2	68.7	89.1	52.8
0.025	89.7	70.8	90.3	59.5
0.05	90.0	75.7	88.8	63.1
0.10	90.0	78.4	89.0	68.3
0.20	91.2	81.0	90.2	73.9
0.40	--	--	89.9	69.3

This table clearly indicates the beneficial effect of fuel oil addition on molybdenum flotation in both standard water and sewage effluent systems. The magnitude of molybdenum losses attributed to sewage effluent are substantially reduced by the addition of fuel oil to the system. However, the molybdenum losses attributable to sewage effluent are still significant. There appears to be no appreciable effect on copper recovery by the addition of fuel oil to the systems studied.

A Multicomponent Reagent Schedule

Most concentrators in the vicinity of Tucson employ a flotation reagent combination consisting of a primary collector, a supplemental collector, fuel oil, and a frother for the recovery of copper and molybdenum sulfides. A single "optimum" reagent combination that works equally well for all copper-molybdenum ores does not exist, and consequently, reagent schedules differ from concentrator to concentrator. The metallurgical staff for a particular operation may have invested years developing and refining a reagent combination that satisfies their operating requirements most of the time. With the foregoing in mind, an attempt was made to establish the effect of sewage effluent on copper and molybdenum recovery using a multicomponent reagent system. The emphasis in this test series was placed on reducing the large detrimental effect that sewage effluent has on molybdenum recovery.

Table 10

Multicomponent Reagent Schedule

Reagent	Quantity, Lb / Ton
Z-6	0.013
S-3302	0.027
Fuel Oil	0.025
MIBC	0.03

Previous testwork in which S-3302 was substituted for Z-6 established that a very significant increase in molybdenum recovery could be obtained by using S-3302. Since this reagent is widely used by the copper industry, it was chosen as the supplemental collector.

In the development of the multicomponent reagent schedule, the effect of S-3302 addition level on flotation response was determined. Figure 12 shows the results obtained from a test series devoted to this end. The most significant features of this figure are the large increases in molybdenum recovery accompanied by corresponding decreases in copper recovery.

To determine the interaction of Z-6 and S-3302 when both are used simultaneously as collectors, a series of tests using various combinations of these flotation reagents was conducted. The results of this series are shown in Figure 13. All tests were carried out in standard water at a pH of 11.5, with 0.04 pound per ton total collector addition, using MIBC as the frothing agent at a level of 0.04 pound per ton. Since the objective of this section of the study was to increase molybdenum recovery, a ratio of S-3302 to Z-6 of 2:1 was chosen as an acceptable collector combination. This choice was obviously a compromise between the desired higher molybdenum recovery and reduced, but reasonable, copper recovery.

The reagent schedule listed in Table 10 was selected on the basis of the cumulative experience gained in this investigation with the emphasis on minimizing molybdenum losses.

Table 11

The Effect of Sewage Effluent on Copper and Molybdenum Recovery in a Simple Reagent System and a Complex Multicomponent Reagent System

Water Type	% Recovery: Simple System Cu	Simple System Mo	Cu	Mo
Standard	89.7 ± 1.2	71.7 ± 1.0	83.1 ± 0.6	77.3 ± 1.2
Sewage	87.3 ± 0.9	55.5 ± 1.7	80.1 ± 1.0	71.9 ± 1.3

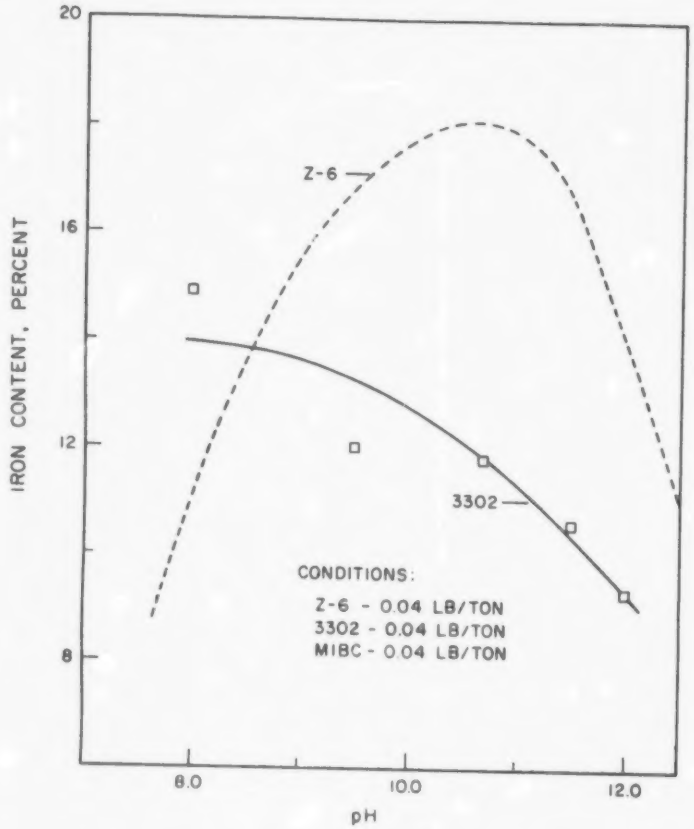

Figure 11. Comparison of percent iron in rougher concentrate vs. pH for demineralized water using Z-6 and 3302 as collectors.

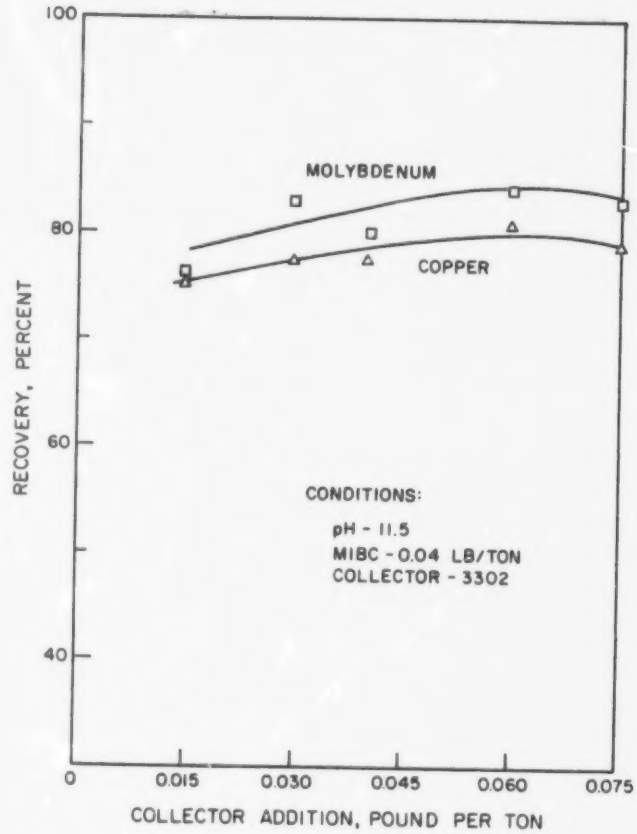

Figure 12. Copper and Molybdenum recovery vs. collector addition in demineralized water.

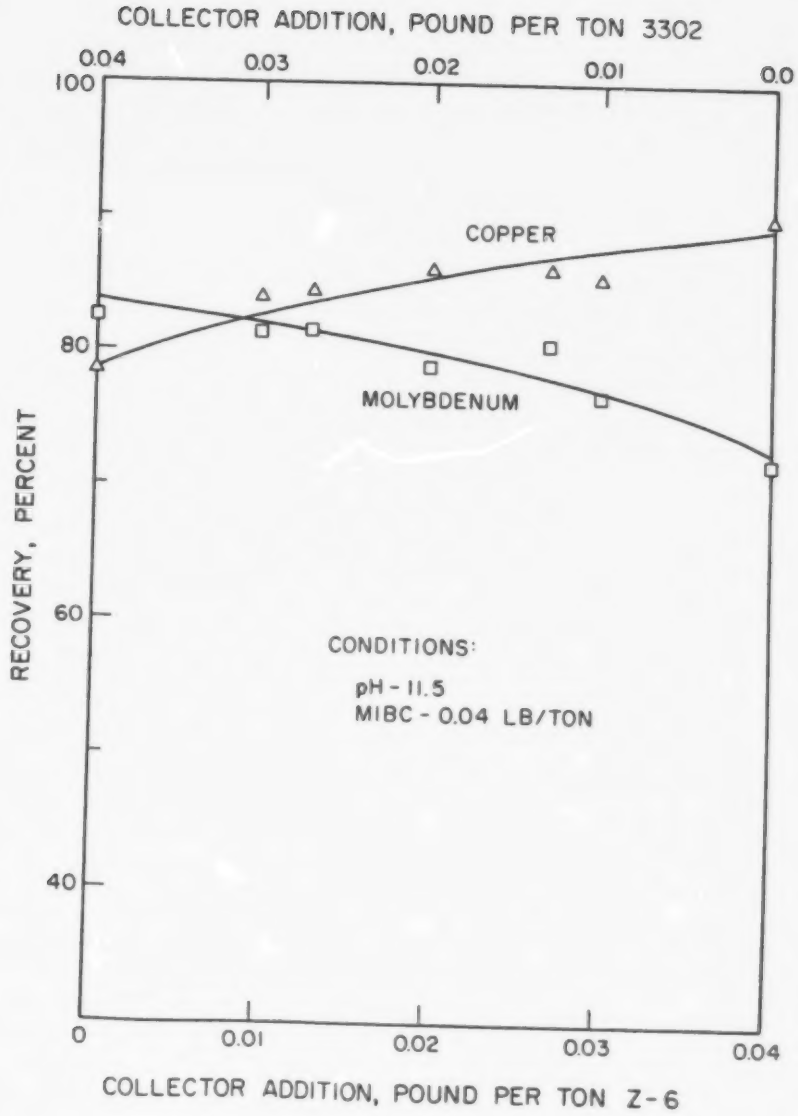

Figure 13. Copper and molybdenum recovery as a function of combined Z-6 and S-3302 at a total collector addition of 0.04 lb/Ton.

Table 11 shows a comparison of recoveries at the 95 percent confidence level obtained in standard water and sewage effluent systems for the simple Z-6 reagent schedule and the multicomponent reagent schedule described above. All tests were conducted at a pH of 11.5. Although the multicomponent reagent schedule is effective in improving molybdenum recovery, the loss of molybdenum in the sewage effluent system remains significant and the reduction in copper recovery is unacceptable.

CONCLUSIONS

The conclusions drawn from this study are intended to serve as a guideline and reference from which future investigations can proceed. They are not intended to serve as a definitive prediction of operating results for commercial scale utilization of City of Tucson sewage effluent in mineral processing. The following conclusions can be drawn from the experimental results generated in this investigation.

1. Secondary treated sewage effluent caused a small but measurable decrease in copper recovery and a substantially larger decrease in molybdenum recovery when used in place of demineralized water. In the simple reagent system used as a basis for this study, sewage effluent caused a reduction in recovery on the order of 2.4 and 16.2 percentage units respectively for copper and molybdenum.
2. Secondary treated sewage effluent creates a voluminous froth, in the absence of frother, that is difficult to control and has a reduced capacity to carry minerals.
3. Dilution of sewage effluent with demineralized water results in a proportionate reduction of the detrimental effects associated with the effluent.
4. Combining process tailings slurry with sewage effluent has no beneficial effect on sewage effluent quality in terms of flotation metal recovery. Deleterious constituents contained in sewage effluent are apparently not adsorbed on particles of ground ore.
5. Tertiary treatment of sewage effluent by activated carbon results in a significant improvement in water quality measured in terms of flotation metal recovery. Detrimental foaming characteristics of sewage effluent are significantly reduced by activated carbon treatment.
6. Ion exchange removal of anions contained in sewage effluent results in a significant improvement in water quality in terms of both copper and molybdenum recovery. In addition, the foaming attributed to sewage effluent is significantly reduced. This result indicates that the species detrimental to metal recovery are anions.
7. Foam fractionation does not improve the quality of sewage effluent in terms of flotation metal recovery. There is, however, an improvement in the deleterious frothing characteristics associated with the effluent.
8. Use of a multicomponent reagent schedule results in a significant improvement in molybdenum recovery using both demineralized water and sewage effluent. However, this reagent system causes an unacceptable loss in copper recovery.

ACKNOWLEDGMENTS

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Water chemistry effects in the flotation of sulphide ores—a review and discussion for molybdenite

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Synopsis

The steadily rising consumption of water and an increased usage of recycled mill waters presently constitute important problems for the mineral industries throughout the world. The detrimental effect of waste water impurities in the flotation recovery of sulphide ores is presently recognized. The objective of the present study is to bring together the information on water chemistry effects as it relates to the flotation of sulphide ores. Molybdenite has been selected for illustrative purposes. From the published literature the effect of colloid: inorganic cations, inorganic anions and organic species on the floatability of molybdenite is reviewed. The experimental data provide a clear picture of the effect of cations and colloidal material on the molybdenite surface. In general, we can postulate that inorganic cations are not detrimental for MoS_2 flotation. Precipitated colloidal hydroxides (especially aluminium and iron) have a strong depressant action on MoS_2 flotation, due mainly to a 'slime coating' phenomenon. The deleterious effect of inorganic anionic species is experimentally known, but very limited specific information is available. A method to overcome the detrimental effects of 'slime coatings' is discussed, and recommendations are made for systematic research in the area of water chemistry effects in the flotation of sulphide ores.

In most parts of the world, because of increasing energy problems and the resurgence in the care for the environment in which we live, a continuous drive towards a more efficient recovery of minerals and decreasing or eliminating the discharge of waste water from minerals processing plants into streams or other waters where it can become environmentally harmful has been mounted. This has resulted in increased usage of recycled mill waters and other waste water products for the processing of ores.

The effect of water impurities on the flotation recovery of sulphides has been under investigation by several researchers since the introduction of the flotation process. Published information has been compiled since the late 1930s, when the discovery was made that flotation in fresh water and recycled mill water often produced different recoveries. We generally accept now that recycle mill water actually gives lower recoveries.

Published data are highly divergent in their interpretation of the causes for the loss in recovery attributed to 'bad water'. The objectives of this paper are to bring together information on water chemistry effects as it relates to flotation of sulphide ores with specific collector systems and pulp mineralogy in various stages of the concentration process and to establish the basis for a systematic investigation. The data presented in this publication are derived from published scientific literature and from the personal experience of the author. Since it was not possible to include all the information for all the commercially important sulphide minerals, one mineral—molybdenite—was selected for illustrative purposes.

Background

Occurrence

The only molybdenum mineral of commercial importance is molybdenite (MoS_2), although small deposits of molybdenum-bearing minerals, such as wulfenite, powellite and ferrimolybdite, occur throughout the world. Molybdenite occurs in four generic deposits. These include: (1) porphyry or disseminated deposits, including stockworks and breccia pipes, in which metallic sulphides are dispersed through relatively large volumes of altered and fractured rock (examples include Climax, Urad and Henderson, U.S.A.); (2) contact-metamorphic zones and tactite bodies of silicated limestone adjacent to intrusive granite rocks (examples include most of the western United States porphyry copper–molybdenum deposits and the Pine Creek tungsten–molybdenum deposit in California); (3) quartz veins and stringers (an example is Questa, U.S.A.); and (4) pegmatites and aplite dykes (examples are Val d'Or and Preissac, Canada).

Most of the world's molybdenum reserves coincide with copper reserves and are located in the western mountain regions of North and South America, extending from Alaska and British Columbia through the United States, Mexico and Central America to the Andes Mountains of Chile. These regions roughly border the western margin of the Pacific Basin and are regarded as most promising for the discovery of additional reserves in the future. In the U.S.A. 70% of reserves occurs in large porphyry or disseminated deposits, such as Climax, Henderson and Questa, in which molybdenum is the major resource. The remaining 30% is contained in porphyry copper deposits and is recovered as a by-product of copper mining. In Canada 30% is contained in a single primary deposit (Endako), 70% being associated with copper–molybdenum porphyry deposits in British Columbia. On the other hand, in Central and South America and in the U.S.S.R. molybdenum is primarily contained in several large copper porphyry deposits.

Processing

Most molybdenite-bearing porphyries contain copper, iron, lead, zinc and other minor quantities of complex sulphide minerals that require rejection during processing to produce a final marketable molybdenite concentrate.

The general flowsheet for a primary ore consists of rougher flotation at a coarse primary grind followed by multiple-stage regrinding and cleaner flotation of a relatively low-grade rougher concentrate to produce a final concentrate of specification grade. For by-product molybdenite from a copper–molybdenum porphyry the general flowsheet consists of bulk flotation of molybdenite and copper sulphides followed by selective flotation of molybdenite in repeated countercurrent flotation circuits to depress the copper and iron sulphide

minerals by addition or pretreatment with specific reagents.

Water chemistry effects in molybdenite processing

In a recent publication[1] the results of tests to determine which constituents of waste water, such as secondary treated sewage effluent, were detrimental to the flotation of molybdenite and copper sulphides were reported. These tests included treating the waste water in Barnstead cartridges to remove specific groups of ions and assessment of the effect on the flotation metallurgy of the treated water.

Some of the experimental results obtained from the flotation tests are presented in Figs. 1 and 2. These results are summarized below.

(*a*) The use of sewage effluent caused a decrease in recovery of 16.2% for MoS_2 and 2.4% for copper sulphides.

(*b*) Dilution of the sewage effluent with distilled water resulted in a proportionate decrease in the detrimental effects associated with the use of waste water effluent.

(*c*) Removal of cations from the sewage effluent resulted in a slight improvement of the recoveries.

(*d*) Removal of anions from the sewage effluent resulted in the most significant improvement in copper and molybdenum recovery.

(*e*) Foam fractionation to remove surface-active material did not improve the quality of sewage effluent, and hence the recoveries were at the same level as that of untreated sewage effluent.

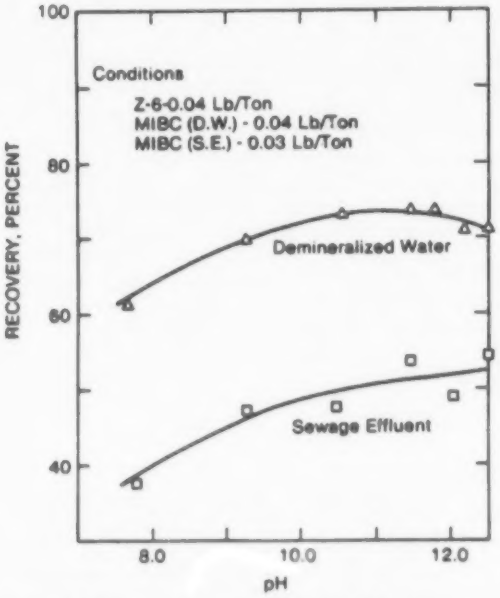

Fig. 1 Molybdenite recovery versus pH for demineralized water (D.W.) and sewage effluent (S.E.). After Fisher and Rudy[1]

(*f*) Tertiary treatment of the sewage effluent by activated carbon resulted in a significant improvement in water quality measured in terms of recovery of metals,

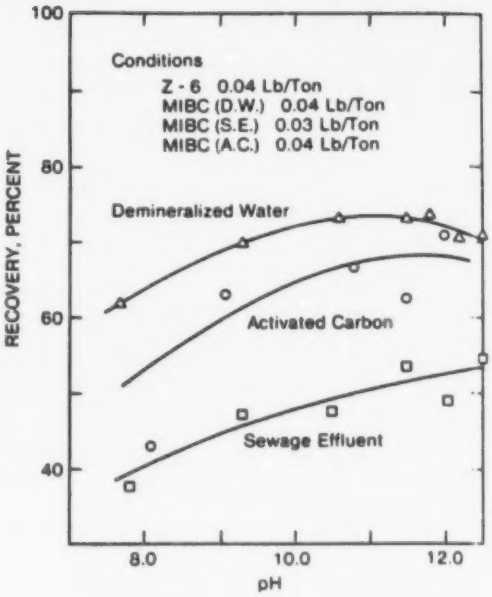

Fig. 2 Molybdenite recovery versus pH for demineralized water (D.W.), sewage effluent (S.E.) and activated carbon (A.C.). After Fisher and Rudy[1]

but not to the level achieved by removal of anionic species.

Similar results have been reported by many concentrators that have attempted to recycle process water, but published data on the effects of recycle water are scarce. Essentially, all the known data demonstrate a strong influence of soluble water constituents on the recovery of molybdenite and provide the basis for a more detailed review and discussion.

This paper includes a literature review on the mechanism of interaction between water components, cations, anions, colloids and organic species, and molybdenite surface, followed by a detailed discussion on ways to overcome detrimental effects of water components. Also included are recommendations for research programmes to gain a full understanding of water chemistry effects on sulphide minerals flotation.

Review of published literature

Interaction of inorganic and organic ions and colloids with molybdenite

Effect of hydrogen ion (pH)

Arbiter and co-workers[2] found that the relationships (1) zeta-potential versus pH in the absence of ionic species besides pH modifiers and (2) flotation recovery versus pH do not correlate well for molybdenite. On the other hand, Chander and Fuerstenau[3,4] found a definite qualitative correlation between zeta-potential and Hallimond tube flotation for molybdenite. As shown in Fig. 3, the higher the MoS_2 zeta-potential, the lower the MoS_2 flotation recovery. A similar correlation to that reported by Chander and Fuerstenau has been

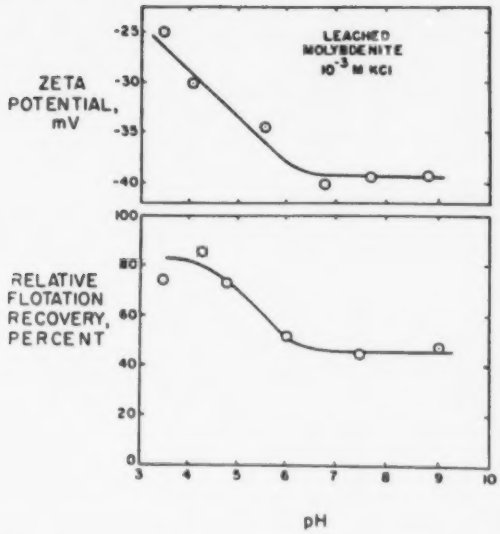

Fig. 3 Zeta-potential and flotation recovery of leached molybdenite as a function of pH. After Chander and Fuerstenau[3,6]

observed and reported by Hoover and Malhotra.[8] Chander pointed out that theoretical calculations with DLVO theory[9] predict that no flotation can occur unless the potentials are about −0.1 V, assuming the potential of an air bubble to be −0.055 V.[7] In practice, however, MoS_2 flotation takes place at much lower potentials. To explain the experimental results, several investigators[3,4] have postulated that the faces and edges of the anisotropic molybdenite crystals have different contributions to the measured zeta-potential, the zeta-potential of the faces being small (probably about −0.01 V) and the potential at the edges being large. Thus, edges control the observed zeta-potential. Chander and Fuerstenau[3,6] postulated the existence of charged surface of thiomolybdate species to explain the observations. The following equilibrium reaction, assumed to occur mainly on the edges of the molybdenite particles, might explain the pH-dependence of the zeta-potential:

$$[MoS_XO_Y]^{-n} + H^+ = [MoS_XO_YH]^{-n+1}$$

A special case for $X = 0$, $Y = 4$ and $n = 2$ is

$$MoO_4^{-2}\ (\text{surface}) + H^+\ (\text{solution}) = HMoO_4^-\ (\text{surface})$$

This reaction in homogeneous solution has a pK of 5.95.[4]

The presence of negatively charged surface ions explains the negative zeta-potential of molybdenite, and the equilibrium between these species and hydrogen ions explains the pH-dependence of the zeta-potential as shown in Figs. 4 and 5. The zeta-potentials of Chander and Fuerstenau for samples 1 and 2 and the reported values[2,8] support this hypothesis. Sample 1, which was obtained by crushing molybdenite crystals in a roll crusher, has more uniform surface in comparison with the particles in sample 2, which were obtained by grinding molybdenite in a jet mill.[8] The data reported by Hoover and Malhotra[8] and also by Arbiter and co-workers[2] represent coarser particle-size ball-mill products and are presented in Fig. 4 according to their edges/faces ratio. Higher edges/faces ratios have a higher density of charged surface species and, as a result, their zeta-potential is always more negative. Fig. 5 shows[9] the relationship between the zeta-potential of MoS_2 and pH, and the zero point of charge (zpc) of MoS_2 is about 2.4. In this study slightly higher potentials were observed above the zpc in the presence of H_2SO_4 than in the presence of HCl. When NaOH and Na_2CO_3 were used for pH adjustment the zeta-potential became quite negative (about −60 mV at pH 10) and then turned less negative above pH 10, probably because of the adsorption of Na^+ at these higher pH values.

Additional evidence on qualitative correlation between zeta-potential and flotation response for molybdenite will be presented later.

Effect of calcium ion (Ca^{++})

The effect of Ca^{++} on the floatability of molybdenite is probably the best understood and most thoroughly

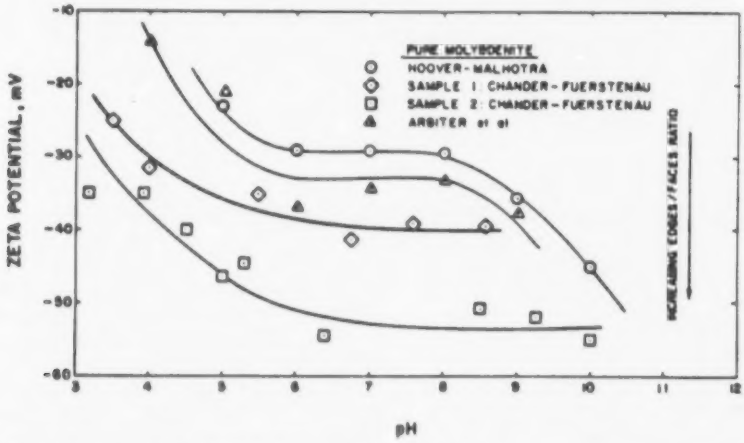

Fig. 4 Zeta-potential of molybdenite in water as a function of pH

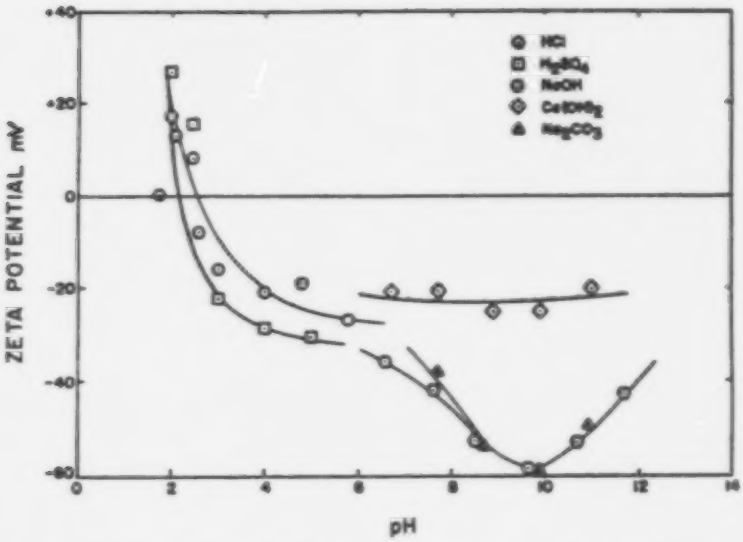

Fig. 5 Relationship between zeta-potential of MoS_2 and pH with various reagents for pH adjustment. After Fuerstenau[9]

studied. Chander and Fuerstenau[4,8] studied the influence of Ca^{++} on zeta-potential and the flotation of molybdenite. The zeta-potentials of leached molybdenite in the presence of Ca^{++} are shown in Fig. 6.[8] The zeta-potentials became less negative with an increase in Ca^{++} concentration, but the shape of the zeta-potential–pH curve remained unchanged. As was suggested by Chander and Fuerstenau,[3,8] $HMoO_4^-$ and MoO_4^{--} ions are strongly specifically adsorbed on molybdenite and thus may serve as potential-controlling surface species. In

The zeta-potential of molybdenite as a function of Ca^{++} concentration is shown in Fig. 7. At Ca^{++} concentrations less than 10^{-3} M, virtually no change occurs in the zeta-potential, but the potential becomes less negative in the presence of Ca^{++} than in the presence of K^+. At larger concentrations of KCl no indication exists of a change in the sign of the zeta-potential. On the other hand, the zeta-potential becomes positive at large Ca^{++} concentration because of the specific adsorption of Ca^{++}. The concentration at which

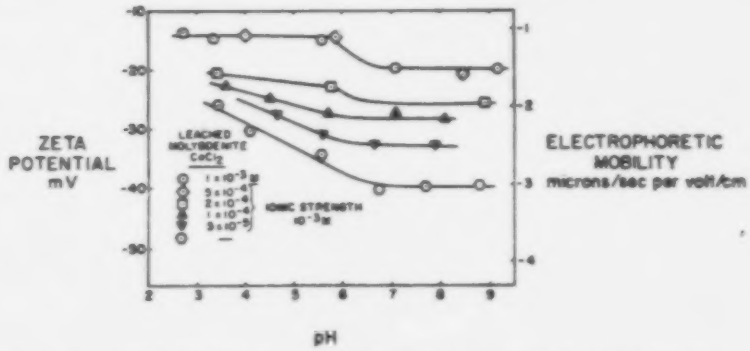

Fig. 6 Zeta-potential of leached molybdenite as a function of pH in presence of calcium ions. After Chander and Fuerstenau[3,8]

the presence of Ca^{++} the surface charge may well change because of the reaction

$$MoO_4^{--}\text{ (surface)} + Ca^{++}\text{ (solution)} \rightleftharpoons CaMoO_4\text{ (surface)}$$

The corresponding reaction in homogeneous solution has $pK = 7.38$.[10] Adsorbed Ca^{++} neutralize an equal amount of MoO_4^{--} ions, thus decreasing the surface charge and the zeta-potential.

the zeta-potential reverses sign increases with an increase in the pH of the solution. This is an expected change because at higher pH all the surface species are present as MoO_4^{--} ions, whereas at lower pH values some surface species are $HMoO_4^-$ ions. The concentration of Ca^{++} required for reversal of the zeta-potential is designated as the pzr, i.e. the point of zeta reversal. The decrease in zeta-potential on further increase in Ca^{++} at pH 3.8

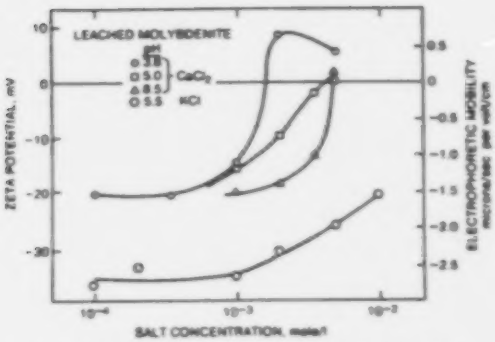

Fig. 7. Zeta-potential of leached molybdenite as a function of salt concentration. After Chander and Fuerstenau[3,4]

probably results from the competition between compression of the double layer and specific adsorption of the Ca^{++} on the crystal faces.

Lenkovskaya and Stepanov[11] measured the adsorption of calcium on molybdenite by using a radioactive tracer technique (^{45}Ca isotope). Their data (Fig. 8) indicate that adsorption of Ca^{++} on molybdenite increases with pH and concentration of free $Ca(OH)_2$ in the system.

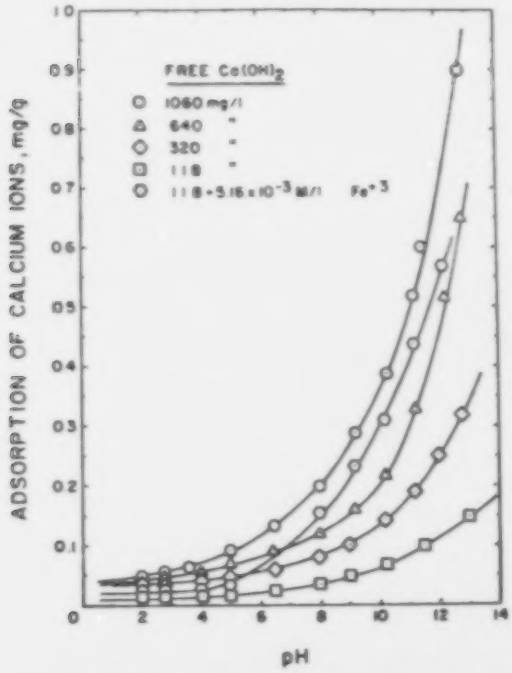

Fig. 8. Adsorption of calcium ions as a function of free $Ca(OH)_2$ content in slurry (mg/l) and pH (pH adjusted with H_2SO_4 and NaOH). After Lenkovskaya and Stepanov[11]

The flotation recovery curves for molybdenite as a function of calcium chloride concentration as reported by Chander and Fuersteanu[3,4,8] in Fig. 9 show good accord with the zeta-potential measurements. This is additional supporting evidence to the qualitative observation of correspondence between zeta-potential and flotation response of molybdenite. Flotation recovery is maximum at pzr, as shown by the dotted vertical line in Fig. 9. The flotation recovery first increases with increase in Ca^{++} concentration; this recovery increase may be attributed to the decrease in electrical layer repulsion between the particle and the bubble. At higher Ca^{++} concentrations than those which correspond to maximum flotation recovery the adsorption of Ca^{++} may make the faces more hydrophilic because of an increase in the dehydration energy or the corresponding disjoining pressure; consequently, floatability is decreased. Also, Lenkovskaya and Stepanov[11] found that as the pH of the medium increases, the floatability of molybdenite decreases for all types of pH modifiers, with the possible exception of Na_2CO_3. As is shown in Fig. 10, frother and xanthate were used in this case. Xanthate, however, has been proved[22] to be non-surface-active on MoS_2; consequently, the experimental results presented in this review are compatible.

The results of Chander and Fuerstenau[3,4,8] have been corroborated by Malhotra and co-workers[12] with Climax Molybdenum Co. ore. These data showed that Ca^{++} is beneficial for flotation of MoS_2 up to a certain point, above which it becomes detrimental to MoS_2 recovery.

Effect of ferric (Fe^{+3}) and ferrous (Fe^{+2}) ions

In general milling practice 40–90% of the steel consumption is due to electrochemical corrosion[13] according to the reaction

$$Fe^0 + 2H^+ \rightleftharpoons Fe^{+2} + H_2$$

In a laboratory study[13] a major difference has been detected by grinding with mild steel, stainless steel or porcelain media. The concentration of Fe^{++} was ten times greater in pulps ground with mild steel versus stainless steel and 25 times more by grinding with mild steel than with porcelain. In commercial plants Fe^{++} oxidizes and precipitates as ferric hydroxide, as indicated by a very low Fe^{++} concentration in the discharge of the ball-mill grinding circuits[14] according to the reactions

$$Fe^{+2} + \tfrac{1}{4}O_2 + H^+ = Fe^{+3} + \tfrac{1}{2}H_2O$$
$$Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^+$$

In the sealed laboratory mills sufficient oxygen may not be available for this reaction to go to completion. Thus, the Fe^{+2} oxidation reaction and the resulting $Fe(OH)_3$ precipitate represent a plant condition that is not easily reproduced in the laboratory.

Lenkovskaya and Stepanov,[11] who used 200 different samples, have shown (Fig. 11) that Fe^{+3}, present as finely divided $Fe(OH)_3$ particles (colloids), has the greatest negative effect on the floatability of molybdenite. These investigators studied the effect of several inorganic salts on the floatability of pure molybdenite at pH 7.5 ± 0.3, which corresponds, according to the authors, to the optimum flotation pH for the treatment of primary molybdenite ores, and in a strongly alkaline medium at pH 11.3 ± 0.2, which corresponds, again according to the same investigators, to the optimum pH in the upgrading of rougher molybdenite concentrates. Also, the effect of salts on a molybdenite concentrate (54% Mo) produced from a

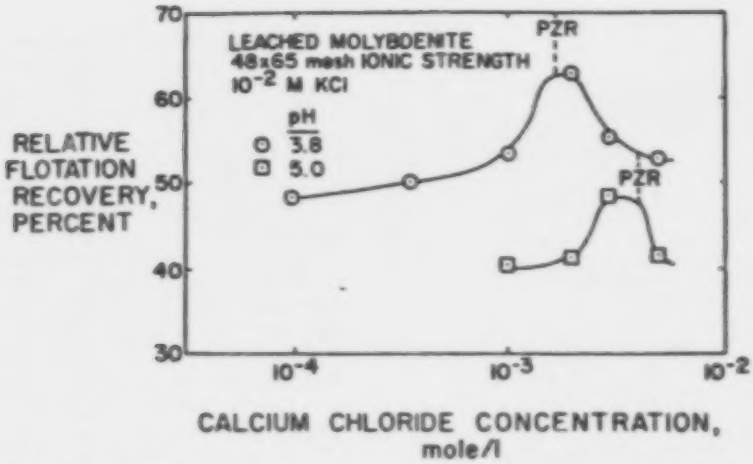

Fig. 9. Flotation recoveries of molybdenite as a function of calcium ion concentration at ionic strength of 1.0×10^{-2} M KCl. After Chander and Fuerstenau[3-6]

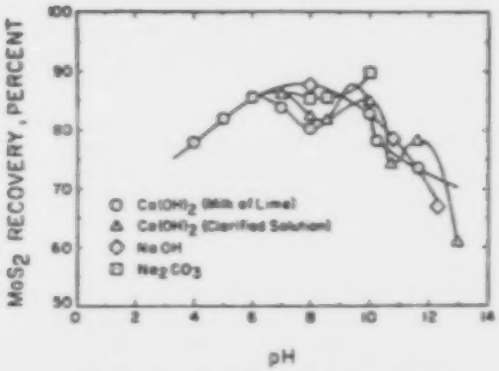

Fig. 10. Effect of pH on floatability of molybdenite with xanthate (25 mg/l) and several pH modifiers. After Lenkovskaya and Stepanov[11]

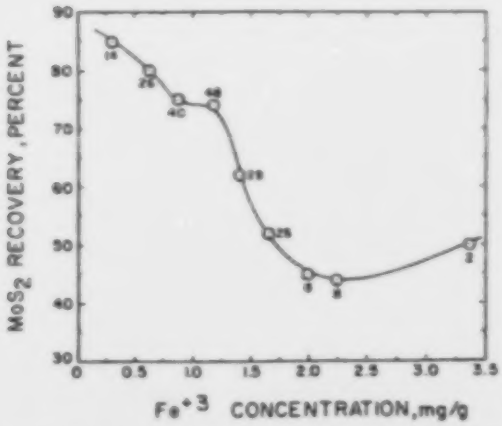

Fig. 11. Dependence of molybdenite extraction on concentration of trivalent iron in flotation feed. Numerals indicate cases out of total of 200. After Lenkovskaya and Stepanov[11]

copper sulphide–MoS_2 separation process with Na_2S was studied at pH 10.3 ± 0.3. This pH corresponds to the optimum pH for the separation of a bulk copper–molybdenite concentrate. In these experiments the inorganic salt was added before the pH modifier.

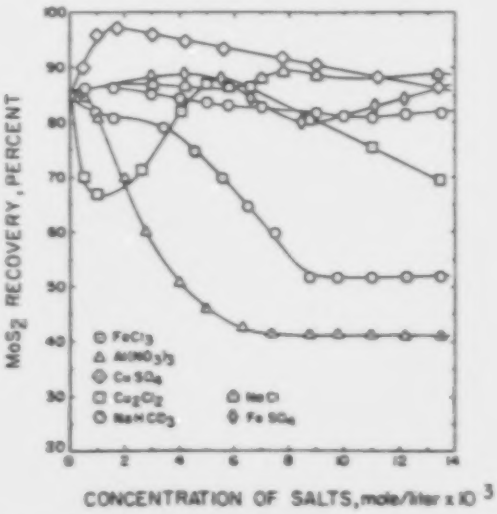

Fig. 12. Effect of soluble salts on floatability of molybdenite by xanthate (25 mg/l) at pH 7.5 ± 0.3. After Lenkovskaya and Stepanov[11]

The results on the effect of inorganic salts on the floatability of MoS_2 at pH 7.5 ± 0.3 shown in Fig. 12 demonstrate that the salts of trivalent iron have a highly depressant effect on the floatability of molybdenite. The effect of the same inorganic salts at pH 11.3 ± 0.2 is given in Fig. 13, which shows the adverse effect of the ferric and ferrous iron salts; the effect of these inorganic salts on molybdenite concentrate at pH 10 ± 0.3 gave the same results as those obtained at pH 11.3 ± 0.2.

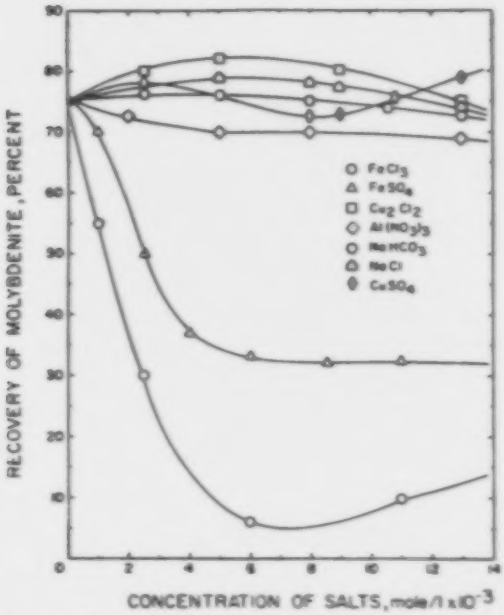

Fig. 13. Effect of soluble salts on floatability of molybdenite by xanthate (25 mg/l) at pH 11.3 ± 0.2, adjusted with $Ca(OH)_2$. Soluble salts formulas represent chemical compound added to system—not ions in solution. After Lenkovskaya and Stepanov[11]

To identify the effect of the individual inorganic salts that can be used as pH modifiers additional tests were carried out by Lenkovskaya and Stepanov[11] over a wide range of pH values with various alkaline reagents. The experimental results presented in Fig. 8 show that if trivalent iron salts are present in the system, the adsorption of calcium ion on molybdenite is substantially enhanced. Hence, the effect of Fe^{+3} on MoS_2 floatability was tested over a wide range of pH values in the presence of $Ca(OH)_2$ and NaOH (Fig. 14). At 5.16×10^{-3} mole/l $FeCl_3$ concentration the data in Fig. 14 show that, at pH > 10.5 if trivalent iron is present, an abrupt decrease occurs in the floatability of molybdenite, particularly in the presence of lime.

In addition, Lenkovskaya and Stepanov[11] determined iron adsorption on MoS_2 with 'tagged' ^{59}Fe at a constant Fe^{3+} concentration (5.16×10^{-3} mole/l) over a wide pH range (these data are also shown in Fig. 14). Maximum iron adsorption is observed in the pH 10–12 range in the presence of lime and corresponds to the pH range of formation of visible precipitates. Above pH 12 the adsorption of iron decreases, and therefore the floatability of MoS_2 is restored. This pH range corresponds to the absence of visible iron precipitates. An important observation of this study is the recognition of the fact that in the pH 7–8 range the depressant effect of Fe^{+3} is minimal or almost absent. This observation has definite practical implications in the flotation of MoS_2 from primary Mo ores.

Effect of other inorganic cations and colloids

The influence of other cations—Al^{+3}, Cu^{+2}, Cu and Na^{+}—was also investigated by Lenkovskaya and Stepanov,[11] these results being presented in Figs. 12 and 13. At pH 7.5 ± 0.3 molybdenite floatability was enhanced by Cu^{+2}, whereas Al^{+3} had a depressant action. The ions of Cu^{+} and Na^{+} exhibited no effect on MoS_2 flotation. At pH 11.3 ± 0.2, except for Fe^{+3}, no ions were detrimental to MoS_2 flotation.

The depressant effect of Al^{+3} was tested over a wide range of pH values in the presence of $Ca(OH)_2$ and NaOH (Fig. 15). The aluminium salt was kept at

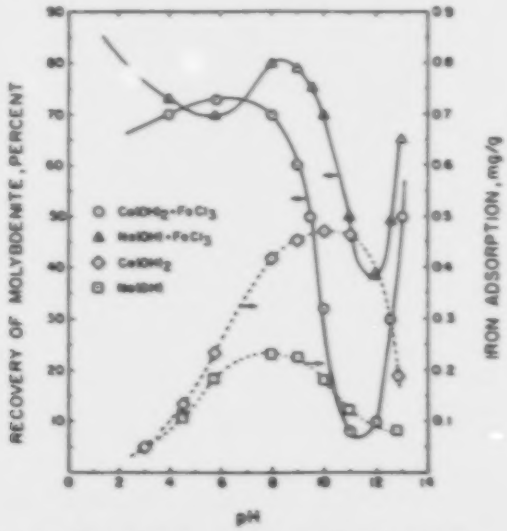

Fig. 14. Effect of Fe^{+3} salts as a function of pH on floatability of MoS_2 with xanthate (25 mg/l) (concentration of $FeCl_3$ 5.16×10^{-3} mole/l. After Lenkovskaya and Stepanov[11]

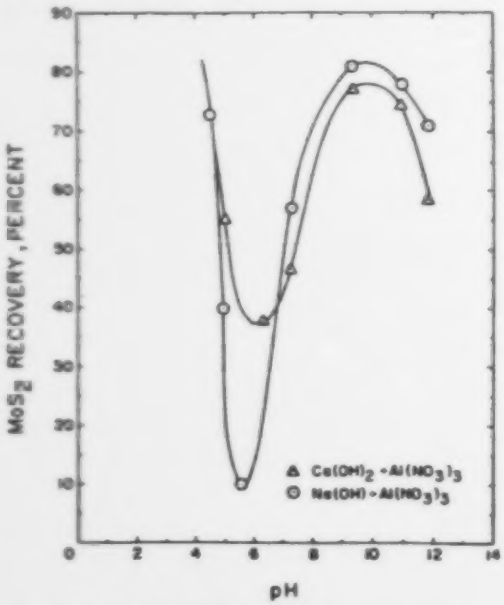

Fig. 15. Effect of Al^{+3} salts as a function of pH on floatability of molybdenite with xanthate (25 mg/l). Concentration of $Al(NO_3)_3$ 5.16×10^{-3} mole/l. After Lenkovskaya and Stepanov[11]

5.16×10^{-3} mole/l, since this concentration was (Figs. 12 and 13) the same as for the Fe^{+3} case at which maximum depression of MoS_2 occurs. The experimental results of Fig. 15 show that Al^{+++} aluminium renders the greatest depressant effect on MoS_2 in the pH 4.5–8 range and, in addition, depresses molybdenite more strongly in the presence of NaOH. Again, attention should be drawn to the fact that an intensification of the depressant action of the inorganic salts coincides with the pH range in which visible precipitates form. The experimental observation is especially marked for aluminium salts, the depressant effect of which becomes stronger in the pH range that corresponds to the formation of amphoteric aluminium hydroxides.

Effect of inorganic anions

Very little published information is available on the effect of inorganic anions on molybdenite flotation. Chander and Fuerstenau,[4,6] to obtain a better understanding of the role of molybdate ions in the MoS_2 surface processes in terms of both the zeta-potential and the flotation of molybdenite, have reported data on leached molybdenite in the presence and absence of 10^{-4} M Na_2MoO_4 (Fig. 16). In the presence of molybdate ions the zeta-potential of molybdenite becomes slightly more negative and the flotation recoveries decrease. Chander and Fuerstenau postulated that the increase in molybdate ions may also increase the adsorption of $HMoO_4^-$ or $MoO_4^{=}$ (depending on pH), and, as a result, the zeta-potential becomes more negative. The higher zeta-potential of molybdenite in the presence of molybdate ions probably increases the double-layer repulsion between the bubble and the particle, as a result of which the flotation recovery decreases. The relationship between the zeta-potential and the flotation recovery for this case is shown in Fig. 17. The depressant effect on MoS_2 flotation of molybdate ion is quite significant for molybdenite-producing operations because the concentration of Na_2MoO_4 (10^{-4} M) used by Chander and Fuerstenau[3,6] is equivalent to 9–10 ppm Mo in solution, which is well within the concentrations found, for example, in Climax recycle mill water.[33] In the absence of additional reported information on the effect of inorganic anions on molybdenite flotation we can assume that, because of the existence of numerous other inorganic anionic species in mill waters, other effects remain to be found.

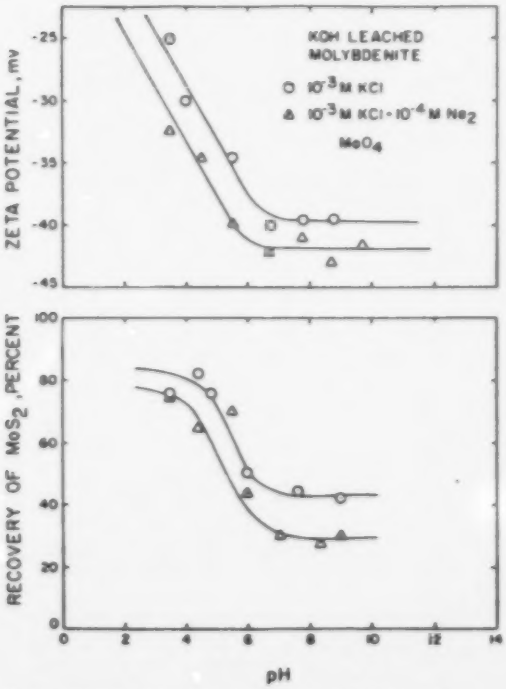

Fig. 16 Zeta-potential and flotation recovery of leached molybdenite as a function of pH with and without molybdate ions present. After Chander and Fuerstenau[3,6]

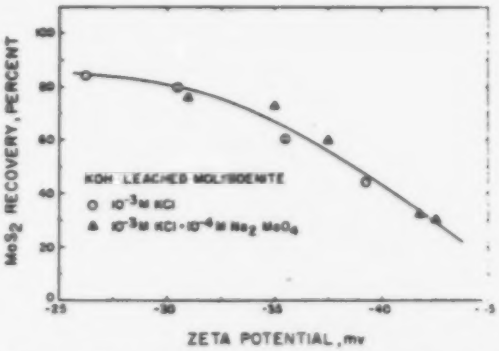

Fig. 17 Flotation recoveries of molybdenite as a function of zeta-potential. After Chander and Fuerstenau[3,6]

The picture is further complicated by the fact that in mill waters the existence of F^-, $SO_4^{=}$, Cl^- and other inorganic anions in addition to inorganic cations and organic compounds (tannin, humic acids and flotation reagents) implies the existence of cationic, anionic and organometallic complexes. For example, fluoride ions are known to form the following complexes with Al^{+3}, Fe^{+3}, Mg^{+2} and Mn^{+4}: AlF^{+2}, AlF_2^+, AlF_3, AlF_4^-, AlF_5^{-2}, AlF_6^{-3}, FeF^{+2}, FeF_2^+, FeF_3, MnF^{+2} and MgF^+. Similar behaviour is found in the SO_4^{-2} and Cl^- complexes. Tannic acid is known to reduce Fe^{+3} to Fe^{+2} and form a very stable cationic complex. A systematic investigation of water chemistry effects on molybdenite flotation and other sulphide systems will require construction of the potential–pH diagrams of all chemical species in solution to define predominant chemical species in solution. Once this has been achieved, experimental testing of the effects caused by the species to the molybdenite surface has to be carried out to describe their ultimate effect on MoS_2 flotation.

Effect of organic species

Some of the commonly used reagents for depressing molybdenite are organic hydrophilic polymers such as dextrin, starch, glue, dyes and condensation products of aldehydic substances with aromatic sulphonic acids. In addition, tannic and humic acids, known to exist in

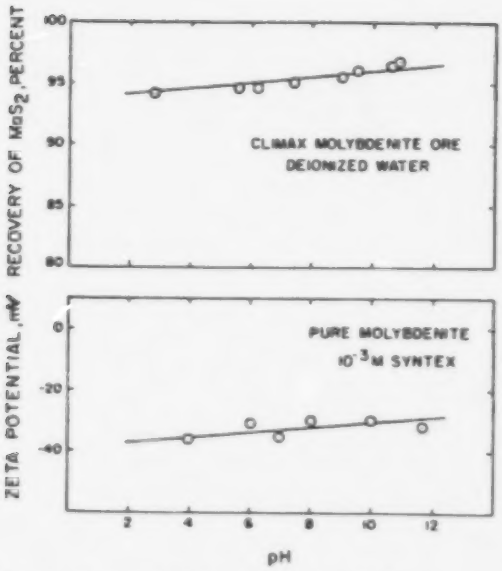

Fig. 18. Zeta-potential and flotation recovery of molybdenite as a function of pH in presence of Syntex. After Hoover and Malhotra[9]

recycle mill waters, have also been reported as molybdenite depressants. The two publications in this area have been those of Wie and Fuerstenau[29] on the effect of dextrin on the surface properties and floatability of molybdenite and by Hoover and Malhotra[9] on the effect of Syntex (sulphated coconut oil surfactant) on the flotation of MoS_2 from Climax ore. The effect of Syntex (Fig. 18) is to make the flotation and zeta-potential of molybdenite practically independent of pH. Hoover and Malhotra[9] explained this behaviour in terms of specific adsorption of Syntex on the edges of molybdenite, which, according to Chander and Fuerstenau[3,8] provide most of the negative charge of molybdenite.

Discussion

The information published to date has important practical implications for molybdenite processing operations. The experimental evidence on the effect of inorganic cations and colloids indicates that the only MoS_2 'surface-active' cation has been found to be Ca^{++}, although some preliminary experimental data show Mg^{++} and Ba^{++} as other 'surface-active' cations.[32] Ca^{++} adsorption has also been proved to be beneficial for molybdenite flotation by decreasing the zeta-potential down to the 'point of zeta reversal', higher concentrations being detrimental. All other inorganic cations studied and reported in the literature have no apparent effect on the recovery of molybdenite by flotation, with the exception of Fe^{++}, Fe^{+++} and Al^{+++}, which produce a large depressant effect on MoS_2 flotation in the pH range in which the hydroxides of these metals form.

Experimental evidence exists to show that molybdenite depression by salts of Fe^{+2}, Fe^{+3} and Al^{+3} is due to the coating of MoS_2 particles by hydrophilic hydroxides slime. As was mentioned previously, this fact is particularly clear for aluminium salts (Fig. 15), experiments having shown that they have the greatest depressant effect on molybdenite in the pH 4.5–8 range, which coincides with the pH range of precipitation of $Al(OH)_3$. The conditions that promote slime coating have been studied and reported by several investigators[16,18] and they can also be determined by use of DLVO[17,18] theory. Briefly, these conditions can be stated as follow.

(*a*) Slime coatings are promoted when the slime is charged opposite to the mineral that is being floated.[18-22] The larger the difference in magnitude of charge, the higher is the slime coating effect.

(*b*) Slime coatings are also promoted when the slime is uncharged or when the mineral being floated is uncharged.[21,22]

(*c*) The particle size of the slime has a pronounced effect on slime coating and, in general, the finer the slime particles, the greater is the depression of flotation.[22]

(*d*) Slime coating can also take place, but is less likely, when the slime and mineral that are being floated have equal charges, provided that the zeta-potential of the mineral, particle size of the slime and hydrodynamic conditions are favourable for this phenomenon to occur.[9]

(*e*) Higher concentrations of slime increase the 'slime coating' effect.[22]

As was pointed out previously, molybdenite shows a negative zeta-potential throughout the pH range with an apparent zpc at pH 2.3, whereas colloidal $Al(OH)_3$ particles were reported to have a zpc between 5 and 9.[24,25] Hence, very favourable conditions exist for heavy $Al(OH)_3$ slime coatings to take place on molybdenite at pH values below the zpc of $Al(OH)_3$, and this will eventually result in the depression of molybdenite flotation in this pH range. This can be clearly observed in Fig. 15. The stronger depression effect of aluminium salts on molybdenite when NaOH is used instead of $Ca(OH)_2$ as a pH modifier can be traced to the higher negative zeta-potential on molybdenite obtained when NaOH is used. As is shown in Fig. 5, the use of NaOH promotes a heavier 'slime coating' effect, resulting in increased depression of molybdenite.

Readers' attention should be drawn to the fact that the aforementioned explanation might be an oversimplification of the actual mechanism. It is now well established[23,26] that well below the concentration at which bulk hydroxides are formed, ions of aluminium and iron show complex behaviour. Polymeric ions, almost colloidal in size, can be formed that have high molecular weights and high positive charge and might also interact with the molybdenite surface. This area of research is a complex field that is still imperfectly understood, and much more fundamental work is required for a better understanding of this phenomenon.

Probably the most important practical effect is that of iron salts and colloids on the floatability of molybdenite, because they are continuously produced in the grinding stage when steel grinding media and steel-lined mills are used. Also, they represent one of the most abundant

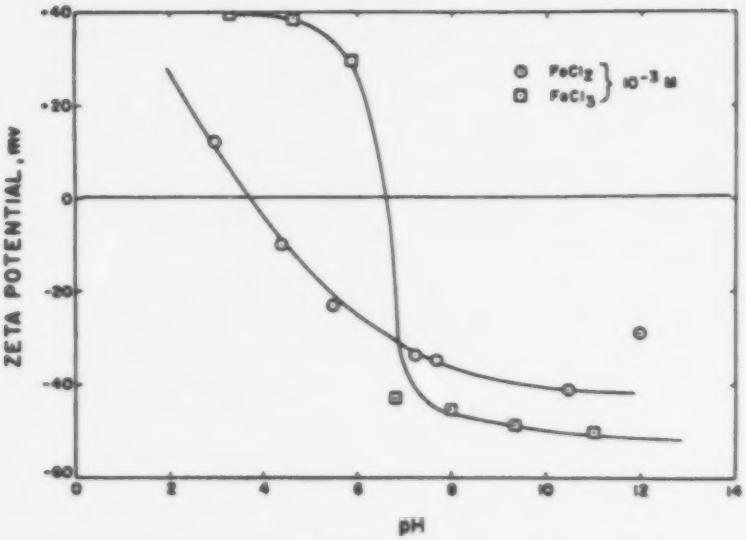

Fig. 19. Relationship between zeta-potential of MoS_2 and pH in presence of 1×10^{-3} M iron salts (HCl and NaOH used for pH adjustments)

water components found in recycle mill waters. The experimental results reported by Lenkovskaya and Stepanov[11] in Fig. 14 show the very strong depressant effect of ferric salts on molybdenite flotation, particularly in the presence of lime. To explain this phenomenon the zeta-potential of molybdenite in the presence of Fe^{+3} and Fe^{+2} was measured in the absence of Ca^{++} (Fig. 19). The potentials obtained in the presence of Fe^{+2} show that the effect of this species on the surface properties of molybdenite is minimal (non-surface active), whereas Fe^{+3} has a significant effect on the mineral surface in acid medium. Ferric hydroxide would have precipitated at these pH values, and the positively charged colloidal $Fe(OH)_3$ would have adsorbed (slime-coated) on the negatively charged MoS_2 particles under these conditions. The zpc of $Fe(OH)_3$ has been reported at pH 6.7.[28] Consequently, the slime coating of $Fe(OH)_3$ on MoS_2 is broken at about pH 7. Nevertheless, the floatability of MoS_2 still remains high in the same pH range (see Fig. 14). A possible explanation is that, in the case of molybdenite, the zeta-potential is strongly influenced by the charged hydrophilic sites (edges) whereas flotation is determined primarily by the hydrophobic part of the surface (faces). The $Fe(OH)_3$ adsorption on MoS_2 in the acid pH range should take place mainly along the strongly negatively charged MoS_2 particle edges, which does not affect the hydrophobic faces and, therefore, the floatability of MoS_2. As far as iron salts are concerned, apparently the rate of formation and range of precipitation of $Fe(OH)_3$ depends to a substantial degree on the type of alkali reagent used and the degree of dispersion and particle size.

Lenkovskaya and Stepanov[11] reported that when $Ca(OH)_2$ is used as a pH modifier a finely dispersed, slowly precipitating iron hydroxide residue is observed, whereas in NaOH the precipitate becomes gel-like and rapidly coagulates. The precipitates produced in Na(OH) and $Ca(OH)_2$ were analysed by X-ray diffraction and found to be amorphous substances; but the latter contained a substantial amount of $CaCO_3$. Clearly, the iron hydroxide precipitate vigorously adsorbs Ca^{++} from

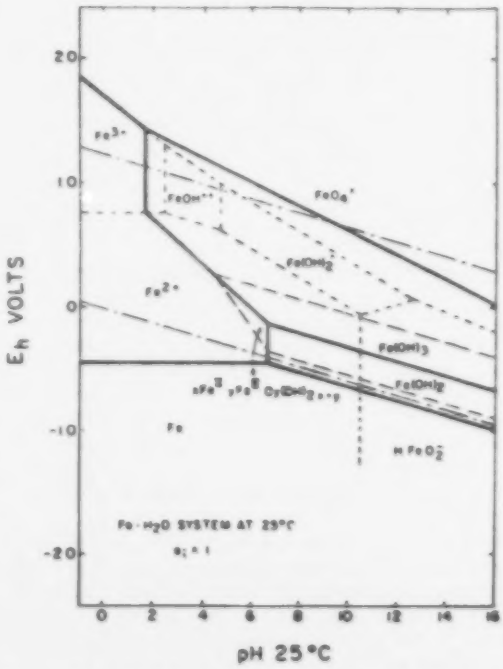

Fig. 20. Potential-pH diagram for Fe-H_2O at 25°C (solid line represents boundaries between solid-solid or solid-liquid phases, dashed lines represent boundaries between soluble species)

solution, which gives a basis to explain the differences in MoS_2 floatability noted in Fig. 14.

The stronger depressant effect of $Fe(OH)_3$ on molybdenite flotation when $Ca(OH)_2$ is used as pH modifier was observed in Fig. 14. These results can be explained in terms of the 'surface-active' character of Ca^{++} on molybdenite, which results in a decrease of the zeta-potential (Figs. 5, 6 and 7) and an enhancement of the 'slime coating' effect. In addition, the smaller particle size of the iron hydroxide precipitate obtained in the presence of lime, and the increased calcium adsorption on molybdenite in the presence of iron will also contribute to enhanced molybdenite depression. The experimental fact that at pH >12 the sorption of iron decreases, and in doing so the floatability of molybdenite is restored, can be explained by observation of the potential-pH diagram for iron shown in Fig. 20, where at pH >12 $Fe(OH)_3$ will be solubilized mainly as the ferrate ion (FeO_4^{--}).

The practical implications of the previous discussion and experimental findings for molybdenite-producing operations can be visualized by the fact that MoS_2 concentrate regrind plants at Climax[26] and Questa[32] use pebbles rather than steel balls. On the other hand, operations at Endako,[27] which started their regrind plant with pebble-mills, later switched completely to steel grinding media with no reported losses on recovery. Operations at the Endako regrind plant are reported to be carried out under conditions in which enough sodium silicate is added to adjust the pH between 9.8 and 11.0, which essentially means that the operations at the Endako regrind plant are consistent with the results presented in Fig. 14 by Lenkovskava and Stepanov[11] for the NaOH + $FeCl_3$ system, where the detrimental effect of iron is minimal in the pH range under consideration.

Experimental observations also have proved that the 'slime coating' effect on molybdenite flotation increases with increasing grade of the product that is being treated, which also explains the efforts in commercial practice to maximize the use of available fresh water in the regrind and cleaner flotation stages.

Therefore, the results reported in this review provide a practical solution for overcoming the detrimental effect of ferric hydroxide 'slime coatings' on molybdenite flotation. Also, the effect of anionic inorganic and organic species has been proved to be important—probably more than the 'slime coating' effect of inorganic colloids. Nevertheless, the state of our knowledge in this area is very limited and a systematic research effort will be required to find additional information on the effect of inorganic anionic and organic species on the floatability of molybdenite and other sulphide ores.

Conclusions

The 'state of the knowledge' of water chemistry effects on molybdenite flotation can be briefly stated.

(1) Colloidal slimes and inorganic anions have the largest detrimental effect on molybdenite flotation.

(2) At the concentrations that are usually found in mill recycle waters inorganic cations, except for Ca^{++}, and such organic materials as tannic and humic acids, with the exception of organic flotation reagents, have no apparent effect on the recovery of molybdenite by flotation.

(3) The only molybdenite 'surface-active' cation reported to date is the Ca^{++}.

(4) Low concentrations of Ca^{++} are beneficial for the flotation of molybdenite by reducing the zeta-potential up to the 'point of zeta reversal', but higher concentrations have been proved to be detrimental.

(5) Adsorption of Ca^{++} on the surface of molybdenite increases with an increase in the residual concentration of free $Ca(OH)_2$ and with an increase in the pH of the medium.

(6) When iron colloids are present adsorption of Ca^{++} on molybdenite increases, the increase seemingly being connected with the vigorous adsorption of Ca^{++} by precipitated iron hydroxide.

(7) A large depressant effect on molybdenite flotation is produced by inorganic salts of Fe^{+2}, Fe^{+3} and Al^{+3} in the pH range at which the hydroxides of these metals form.

(8) A lime medium intensifies the depressant effect of inorganic iron salts.

(9) Maximum adsorption of iron in a lime medium is observed in the pH range 10–12.

(10) Above pH 12 the depressant effect of iron disappears, and for aluminium it takes place above pH 10.

(11) The only reported inorganic anionic species that is detrimental to molybdenite flotation is the MoO_4^{--} ion. Additional work is required to identify other detrimental inorganic anionic species.

(12) Very limited fundamental research has been reported on the effect of organic ions on molybdenite flotation, and only one reference is available that is related to the effect of dextrine on the surface properties of MoS_2 in a flotation system.

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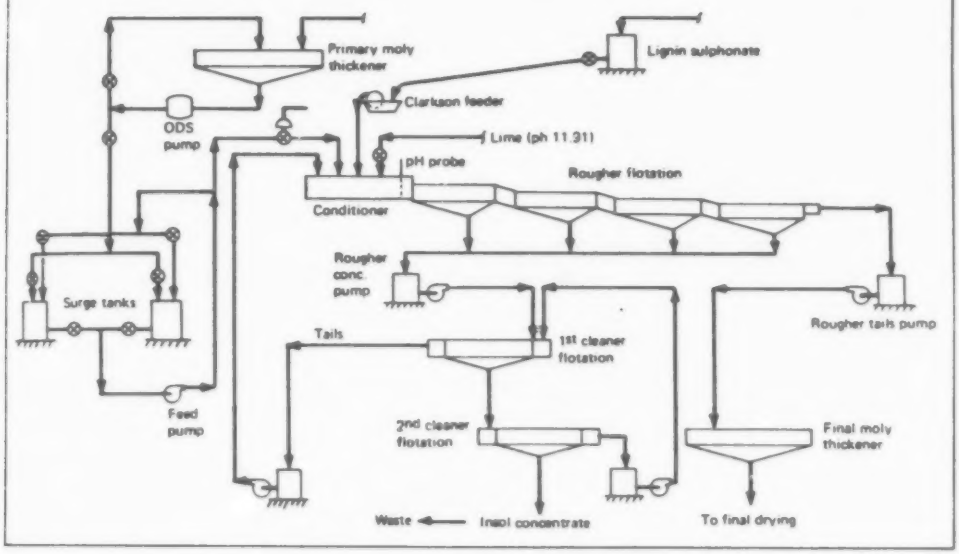
Fig. 1—Schematic of moly pilot plant



Use of lignin sulphonate as moly depressant boosts recovery at Twin Buttes

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A NEW SYSTEM USING LIGNIN SULPHONATE to depress molybdenum has allowed increased production of salable by-product molybdenum concentrates at the Twin Buttes complex in Arizona. In searching for reagents to separate insolubles—including clays and talc minerals—from molybdenum concentrates at Twin Buttes, The Anaconda Co.'s Metallurgical Research Department discovered that large quantities of lignin sulphonate, in combination with a high-pH milk-of-lime, depressed the molybdenite while allowing talcs and clays to float.

The Twin Buttes property is a typical porphyry copper operation now owned by Anamax, an Anaconda-Amax joint venture. Open-pit mining recovers ore for treatment in a 30,000-tpd flotation concentrator. As is common at most copper operations producing molybdenum, molybdenite (MoS_2) is recovered by flotation along with the copper minerals in the concentrator, resulting in a copper-moly concentrate. Molybdenum values are then separated from the copper in a concentrate by-products plant.

The use of lignin sulphonate to depress moly originated as a response to problems experienced in the operation of the Twin Buttes moly plant. After extensive laboratory testing and further testing and refinement on a pilot plant scale (Fig. 1), this process is now a part of the installation.

The Twin Buttes moly plant consists of two circuits: a primary circuit, which separates molybdenite from the copper sulphides, and an insoluble circuit, which upgrades the moly concentrate.

Copper-moly concentrate is fed after thickening to the head of the primary circuit, where it is conditioned with sodium hydrosulphide (NaHS), then processed through a rougher and seven stages of countercurrent cleaner flotation. Here copper minerals are depressed, and moly is recovered as a primary concentrate. Tailings from this circuit are sent to the final copper spray dryer, while the molybdenite concentrate is either sent to final moly spray dryers or treated in the insol circuit for further upgrading.

The insol circuit as originally installed consisted of a thickener, a spray dryer, and two stages of flotation (Fig. 2). The pulp from the thickener was spray dried to remove the collectors from the sulphide mineral surfaces. The two flotation stages then floated the gangue and discarded it, while the moly tails were sent to the final dryers.

Although the original insol circuit produced good metallurgical results (Table 1), a problem developed in the capacity of the system to treat the volume of primary con-

Fig. 2—Schematic of old Twin Buttes moly plant

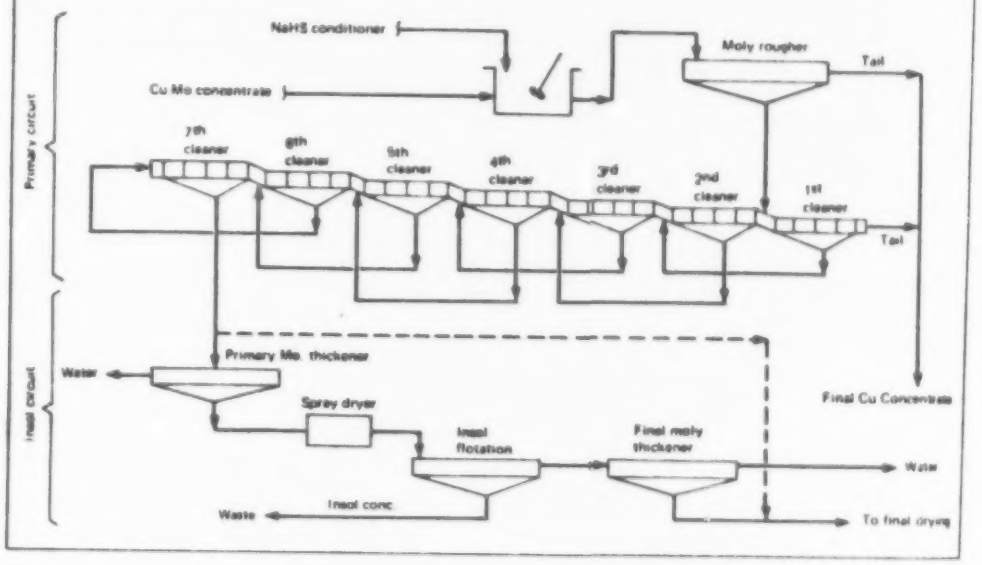


Table 1—Average results, spray dryer insol circuit

	% Assay		% Distribution	
	Mo	Insol	Mo	Insol
Insol concentrate	11.52	61.04	14.49	76.86
Moly concentrate	51.10	7.44	85.51	23.14
Feed	38.20	25.63	100.00	100.00

Table 2—Typical open-circuit flotation test results

	% Assay			% Distribution		
	Mo	Insol	Cu	Mo	Insol	Cu
Sample 1						
First cleaner conc	4.06	80.40	1.72	6.10	75.00	44.70
First cleaner tail	16.80	52.30	1.02	2.90	5.60	4.10
Rougher tail	46.20	15.90	0.84	91.00	19.40	51.20
Calculated head	27.37	44.40	1.21			
Sample 2						
Second cleaner conc	1.62	74.00	1.49	0.78	63.02	26.20
Second cleaner tail	21.40	38.90	1.14	1.66	5.34	3.24
First cleaner tail	32.40	31.20	1.06	4.81	8.17	5.74
Rougher tail	49.50	7.10	0.95	92.74	23.47	64.82
Calculated head	38.72	21.95	1.06			
Sample 3						
First cleaner conc	12.70	55.80	3.08	1.90	37.10	10.20
First cleaner tail	43.70	18.30	16.00	6.10	11.40	49.80
Rougher tail	51.30	6.30	1.00	92.00	51.50	40.00
Calculated head	48.10	10.50	2.15			

centrate produced. Due to the variable nature of the Twin Buttes ore,, the gangue at times contains amounts of talc-type layered silicates and alumina clays, such as montmorillonite, in addition to the normal carbonates and silicates. The layered silicates and clays are naturally floating and report to the primary concentrate along with the molybdenite. When present, these gangues dilute the moly concentrate, increase the volume, and may cause the grade obtained to drop as low as 15% Mo.

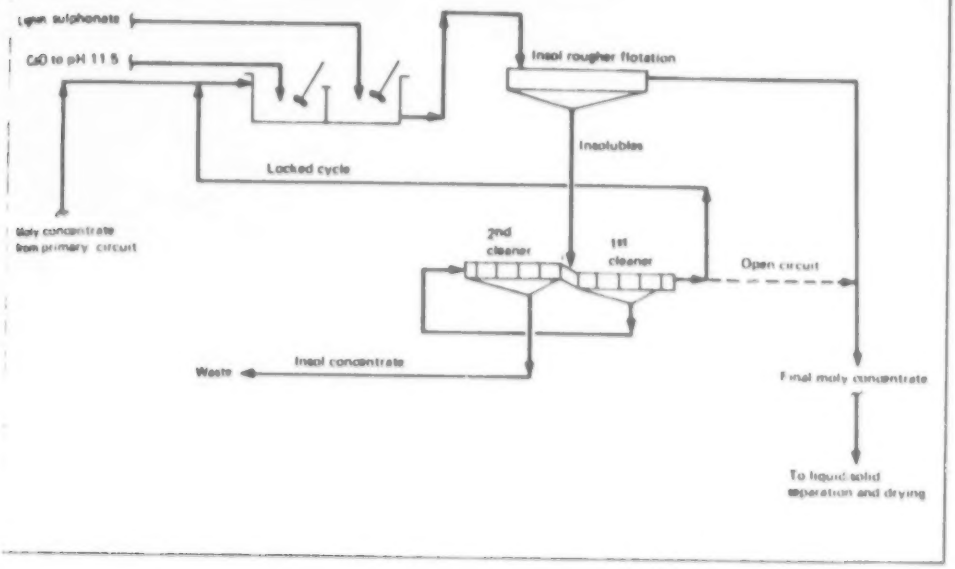
The original design specifications at Twin Buttes provided for a 1,200-tpd feed of copper-moly concentrate containing 1% Mo. The primary circuit was expected to produce approximately 24 tpd of moly concentrate, and the insol circuit spray dryer was designed to handle the load. However, depending on ore type and concentrator performance, the feed to the primary circuit may contain up to 2% Mo at feed rates over 1,400 tpd. This increased production,, along with increased bulk due to dilution of the primary concentrate, may deliver over 75 tpd to the insol circuit. At this production level, the insol circuit was overloaded,, with the spray dryer being the bottleneck.

The problem, as presented to the Anaconda laboratories, was to develop a circuit that would produce final grade molybdenum concentrates from these higher tonnage, lower grade primary concentrates.

Lab work develops basic moly-insol circuit

Phase 1 of the laboratory test work centered on finding insol depressing mechanisms that could be employed in the primary circuit to depress the talc and clay minerals. The results were generally not good. Phase 2 centered on insol depressing schemes that would operate on the primary moly concentrate in the insol circuit. For a while these efforts also met with little success.

Fig. 3—Schematic of basic laboratory setup



During this second phase, it was discovered that lignin sulphonate, normally an *insolubles* depressant, tended to have the reverse effect when present in large quantities—it depressed molybdenite, which is naturally floatable. Lignin sulphonate, a common by-product of paper pulp mills, has been used on a limited basis in mineral processing as a binder material, dispersant, and emulsifier. The reagent is inexpensive (about 8¢ per lb) and is readily available under many trade names, such as "Orzan" and "Lignosite."

Further laboratory investigation produced very encouraging results using lignin sulphonate to depress the moly while allowing gangue to float. A basic circuit was developed (Fig. 3), in which the primary moly concentrate was conditioned at reduced percent solids with lignin sulphonate and milk-of-lime (CaO). The layered silicates and clays were then floated off in a three-stage countercurrent flotation circuit, which produced a throwaway second cleaner concentrate and a final moly concentrate from the rougher tails. Retention times used in the laboratory circuit were a 20-min conditioner stage, 20-min rougher flotation, 15-min first cleaner, and 10-min second cleaner.

Extensive batch flotation tests were conducted using daily samples from the moly plant's primary circuit. Feed ranging from 27.7% to 48.1% Mo was run through the open circuit, and recovery from the rougher tails was a consistently high 91% to 92.7%. Molybdenum grades obtained were good, ranging from 46.2% to 51.3% Mo (Table 2).

In addition, locked cycle tests were conducted to determine the effects of recirculating products. Locked cycle results show high overall recoveries of 96% to 99%, with moly grades of 47% to 48% obtained (Table 3). A comparison of locked cycle and open circuit results shows that the molybdenum concentrate is slightly lower grade in the locked cycle; however, a much higher recovery (approximately 4% to 8%) is obtained.

Data generated from the laboratory tests indicated that a pilot plant study was justified, and construction of the pilot circuit began in January 1973 at the Twin Buttes moly plant. Design of the pilot circuit was based on the expected feed rate from the high volume, low grade primary concentrates. The availability of salvage equipment from the previous Twin Buttes copper concentrator pilot plant made it advantageous to build the pilot circuit for the total expected feed from the primary circuit (1 to 3 tph), rather than split the flow of primary moly concentrate and use smaller equipment.

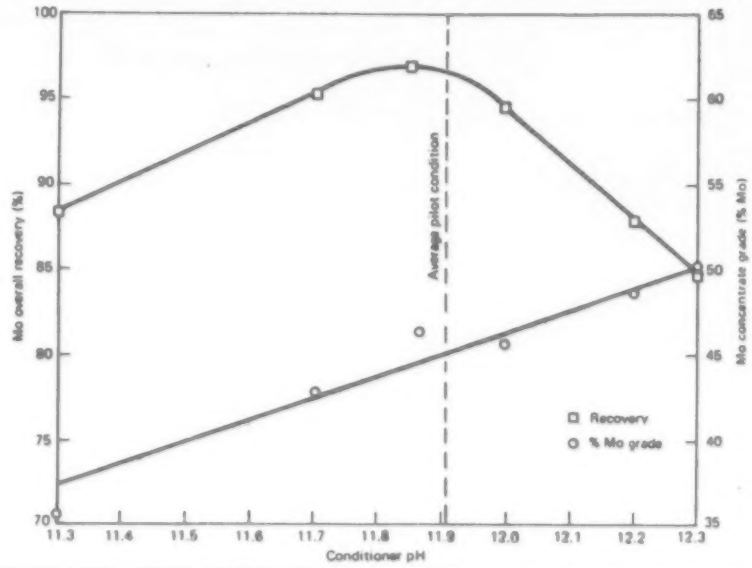
The pilot circuit, installed in place of the insol circuit, was started up in early March 1973. (See Fig. 1.) Underflow from the primary moly thickener was fed by ODS pumps to two surge tanks upstream from the conditioner. Feed to the circuit was bled off a recirculating feed loop from the surge tanks into the conditioner, which was constructed using cut-down Agitair No. 48 mechanisms in four compartments to minimize short-circuiting.

The conditioner overflow was fed by gravity to four banks of rougher cells consisting of a total of 20 Galigher No. 24 cells. The rougher tails were pumped directly to the final moly thickener, and the rougher concentrate was pumped to the first cleaner, consisting of eight Galigher No. 24 cells. First cleaner tails were pumped back to the conditioner, and the first cleaner concentrate was fed to the head of the second cleaner. The second cleaner, consisting of six No. 24 cells, produced a tail (pumped back to the first cleaner) and a throwaway concentrate.

Lignin sulphonate was metered to the conditioner by a Clarkson feeder, and milk-of-lime flow was controlled by a ball valve. Other reagents, if required, could have been added using a Clarkson feeder at any point in the circuit.

The pilot plant ran on a limited basis through the end of March, when it underwent circuit modification, including the installation of additional equipment and facilities. It was then restarted in June and ran through the end of July

Fig. 4—Molybdenum recovery and grade as a function of conditioner pH



1973. An average feed of 35.21% Mo was treated, producing a 45.87% Mo concentrate at an overall recovery volume of 91.11%. (See Tables 4 and 5.) Since the prime objective in the development of the process was the treatment of tonnages up to 3 tph, a five-shift, continuous production run was made at an average of 3.1 tph, with several shifts running over 4 tph. Metallurgical results compared favorably with the average results of the original spray dryer-insol circuit.

Key variables determined from pilot data

The relationship of key variables (retention time, lignin sulphonate dose, pH level, gangue mineralogy) in the circuit to the grade and recovery achieved was determined from the pilot plant data. In general, the retention time in the conditioner does not appear to be critical above a minimum time of 8 min. The lignin sulphonate dosage is determined primarily by the feed grade to the circuit—lower grade feed requires lesser quantities. At too low a dosage, the flotation of molybdenite is readily apparent in the roughers. At an excessive dosage, a number of problems occur, the most apparent being the formation of a persistent, voluminous foamy froth which defies control. The amount of lignin sulphonate normally used was in the range of 4 to 6 lb per ton.

Data indicate that a maximum recovery is achieved at a pH of 11.91, with higher pH values producing lower recoveries but higher grades (Fig. 4). Froth characteristics are also pH-dependent. A pH below 11.7 produces a persistent, foamy froth, while a value above 12.1 produces a brittle, watery froth that tends to carry slime molybdenite. The desired froth for good differential flotation is a tight, brown, heavy froth with the insol well flocculated.

The gangue mineralogy was determined by the difference between the *calculated* insoluble content and the insoluble content as determined by standard aqua regia digestion. This difference between the calculated and analytical assays is due to the presence of gangue minerals such as carbonates, sulphates, and chlorides, which will dissolve in the digestion and therefore not report as insol.

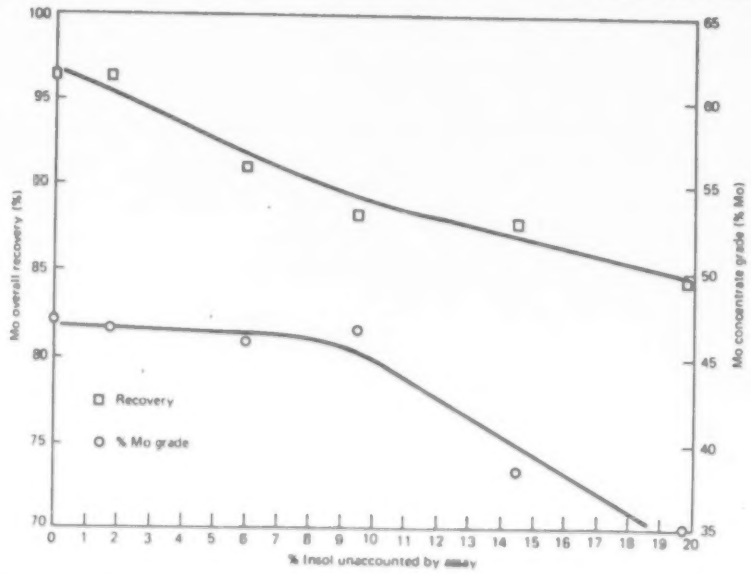
Table 3—Typical test results, locked cycle flotation of primary molybdenum concentrate

	Wt.	% Assay			% Distribution		
	(%)	Mo	Insol	Cu	Mo	Insol	Cu
Sample A							
Insol, second cleaner conc.	25.1	5.34	79.9	1.25	3.62	62.42	31.[illegible]
Moly tail	74.9	47.58	15.5	0.90	96.38	37.57	68.[illegible]
Head grade	100.0	36.77	31.1	0.98	100.00	100.00	100.[illegible]
Sample B							
Insol, second cleaner conc	29.9	1.15	79.2	0.99	0.94	62.04	31.[illegible]
Moly tail	70.1	48.45	19.4	0.88	99.06	37.96	68.[illegible]
Head grade	100.0	30.26	37.2	0.91	100.00	100.00	100.[illegible]

Table 4—Average pilot plant operating results

	Wt.	% Assay			% Distribution		
	(%)	Mo	Insol	Cu	Mo	Insol	Cu
Insol concentrate	29.95	10.41	64.52	2.08	8.89	65.75	46.[illegible]
Moly concentrate	70.05	45.87	15.22	1.12	91.11	34.25	53.[illegible]
Feed	100.00	35.21	30.58	1.42	100.00	100.00	100.[illegible]

Fig. 5—Molybdenum recovery and grade as a function of gangue mineralogy



(See Fig. 5.) The circuit performs best on silicates and slags, and as the proportion of carbonates and sulphates increases, the recovery and grade both suffer. This is as expected, since the carbonates and sulphates are not naturally floatable. Their presence in the primary moly concentrate can normally be attributed to a physical entrapment in the froth during the primary flotation separation of moly and copper.

Laboratory work done on primary concentrate samples containing higher than average amounts of copper indicated that, with the moly depressed in the lignin sulphonate system, a xanthate collector could be added to activate the copper minerals and reduce the copper content of the final concentrate. While some activation of the moly occurred, preliminary results from laboratory and pilot tests were encouraging (Table 6). Use of the collector lowered the overall molybdenum recovery value; however, there were some offsetting increases in concentrate grade. The copper content in the moly concentrate is a major price penalty, and work is continuing to further test and develop this system.

Table 5—Pilot plant average conditions

Lignin sulphonate	5.65 lb per ton
Conditioner density	14.50% solids
pH	11.91
Conditioning time	25.33 min
Rougher flotation	27.70 min

Table 6—Effect of xanthate collector, average results

Addition of 0.1 lb per ton of xanthate (approx.)	% Assay			% Distribution		
	Mo	Insol	Cu	Mo	Insol	Cu
Feed	34.89	30.89	1.30	100.00	100.00	100.00
Moly concentrate	47.47	14.80	0.79	88.60	31.64	39.13
Insol concentrate	11.40	62.13	2.23	11.40	68.36	60.87
Control—no addition of xanthate						
Feed	35.56	30.24	1.55	100.00	100.00	100.00
Moly concentrate	44.34	15.62	1.43	94.19	37.31	65.01
Insol concentrate	8.45	68.30	1.85	5.81	62.69	34.99

Evaluating the success of the new system

The new process using lignin sulphonate at Twin Buttes has indeed met the requirements that initiated its development. The aqueous moly-insol flotation system will handle primary molybdenum concentrates ranging in feed grade from 20% to 40% Mo at capacities up to *four* times the original spray dryer circuit, while maintaining equivalent metallurgical results. With this circuit on line, it is now possible to utilize both spray dryers for treating final moly concentrates, thus greatly increasing the capacity of the by-products plant. The major disadvantage of the system is its inability to effectively separate carbonate gangue from the molybdenite. If a considerable volume of carbonates is carried over into the primary concentrate, a molybdenite-carbonate separation will become necessary. □

MOLYBDENUM FLOTATION

Molybdenum recovery by flotation is carried out at AMAX's Climax Molybdenum Mine, Climax, Colorado, and at their Henderson Mine/Mill nearby, as well as at Moly Corporation's Questa, New Mexico, mine-mill.

At Henderson, all mill water is recycled, and only minewater is discharged. At Climax, 90% of the mill tailings decant water is recycled to the mill with 10% discharge to the stream. This location is in a net precipitation area, and the site, despite measures to intercept surface drainage, still serves a sizable catchment area. This single component recovery operation uses only recycled water in its mill. Discharge of the remaining 10% is necessary for water balance purposes.

Originally, the mine and mill operator camp for the Climax operation was located at Climax itself. Sewage was discharged to tailings and this according to Climax laboratory studies conducted at the time, resulted in a deterioration in molybdenum recovery. This was overcome by adding activated carbon to the tailings stream.

Several years ago, when the mining camp was moved to Leadville, Colorado, and its sewage was no longer added to the tailings dam, it was found that recoveries returned to normal without the need to add activated carbon. This occurred several years ago, and the results of these tests, which were not published, have already been transferred to the company archives.

INPACT OF STEARIC ACIDS ON MOLYBDENITE FLOTATION

An excerpt from a 1963 internal report by R. Meyertons of Climax Molybdenum Company provides clear evidence of the impact of stearic acid on molybdenite recovery by flotation. Stearic acid is generated when Na-stearate (soap) is present in water at a low pH. Sewage water is likely to contain stearates.

LEAD-ZINC FLOTATION

Mill tailings decant water is successfully recycled to the mill for Pb-Zn flotation at St. Joe Minerals' Fletcher mine and mill in Missouri to the extent that the mill and tailings achieve zero discharge.

More information on water management from this operation can be requested from:

IMPACT OF STEARIC ACID ON MOLYBDENITE FLOTATION

INTRODUCTION

The use of fatty acids to recover a mixture of tungsten, molybdenum sulfide and molybdenum oxide from by-product tailing pulp has been discussed recently. The test data here reported was obtained in 1960 and 1961 as part of other investigations involving the effect of oleic, stearic and caproic acids on molybdenum sulfide flotation. This data should not preclude investigation of mixed mineral flotation, but the investigator must be certain to check the effect of reagent combinations on rougher recovery.

TEST PROCEDURES

Standard laboratory batch tests were conducted with 6000 g ore lots, crushed to 8 mesh dry, ground wet in the laboratory ball mill with reagents specified at 50% solids. Flotation time is 12 minutes at 40-42% solids.

TEST RESULTS

The summary table discloses the essence of the results; even traces of stearic acid is detrimental to molybdenite recovery. The use of larger quantities of oleic acid and caproic acid in various combinations was not successful. Recovery with these reagents is also below normal.

These particular tests did not answer the questions:

1. Can fatty acids be used to improve flocculation of finely divided MoS_2 in present tailing pulp?

2. Are other fatty acids, such as oleic and caproic, also harmful when present in PPM quantities in the water supply?

These last two questions should be answered in any molybdenum sulfide scavenging program.

REFERENCES

"Fatty Acid Reagent Tests", R. Meyertons, December 13, 1961
"The Causes of Recovery Loss of Molybdenite", R. Meyertons, June 22, 1960.
Laboratory Notebooks, No. 27, 49, 57, 96, 99, 102.

RM:jg

SUMMARY OF EFFECT OF FATTY ACIDS ON

ROUGHER MOLYBDENITE RECOVERY

TEST	LOT	FATTY ACID OR CPD.	CONCENTRATION	PERCENT RECOVERY CHANGE
LM 493	11	Stearic Acid	2.2 PPM	-1.2
LM 493	11	Stearic Acid	0.24 PPM	-1.2
LM 493	15	Stearic Acid	2.2 PPM	-2.0
LM 493	15	Stearic Acid	0.24 PPM	-0.9
LM 495	16	Stearic Acid	3.6 PPM	-1.15
LM 495	16	Stearic Acid	0.4 PPM	0
LM 495	17A	Stearic Acid	3.6 PPM	-2.7
LM 495	17A	Stearic Acid	0.4 PPM	-0.2
LM 497	13	Stearic Acid	3.6 PPM	-4.8
LM 497	13	Stearic Acid	0.4 PPM	-1.9
LM 497	20	Stearic Acid	3.6 PPM	-3.1
LM 497	20	Stearic Acid	0.4 PPM	-0.5
LM 425	11	Sodium Oleate	0.1 lb/ton	-7.0
LM 423	14	Sodium Oleate	0.1 lb/ton	+0.5
LM 429	11	Oleic Acid	0.04 lb/ton	-11.
LM 429	11	Aluminum Oleate	0.04 lb/ton	-12.
LM 483	18	Oleic Acid	0.04-0.09 lb/ton	-6 to 8%
LM 733	39	Caproic Acid	0.1 lb/ton	-0.20
LM 733	31A	Caproic Acid	0.1 lb/ton	-0.75
LM 734	26A	Caproic Acid	0.1 lb/ton	-0.42
LM 734	41	Caproic Acid	0.1 lb/ton	-0.46

Milling Reagents Used at Fletcher Mill

Commercial Name	Chemical Name	Chemical Formula	Chemical* Dosage $\frac{kg}{\text{Metric Ton Ore}}$	Purpose
Frother 71	Long Chain Aliphatic Alcohols	C_6 to C_9	0.0345	Frother
DOW 250	Propylene Glycol Methyl Ether	$C_4H_{10}O_2$	0.0025	Frother
Z-200	Isopropyl Ethyl-thionocarbamate	$C_5H_{13}ON$	0.01	Promoter
Sodium Cyanide	Sodium Cyanide	$NaCN$	0.001	Promoter
AERO 343	Sodium Isopropyl Xanthate	$C_4H_7OS_2Na$	0.0475	Collector
Zinc Sulfate	Zinc Sulfate	$ZnSO_4$	0.384	Zinc Depressant
Copper Sulfate	Copper Sulfate	$CuSO_4$	0.068	Zinc Activant
Sodium Dichromate	Sodium Dichromate	$Na_2Cr_2O_7$	0.014	Lead Depressant
Sulfur Dioxide	Sulfur Dioxide	SO_2	0.473	Lead Depressant
Cornstarch	Starch	$C_6H_{10}O_5$	0.047	Lead Depressant
Caustic Soda	Sodium Dioxide	$NaOH$	0.0155	Lead Depressant
Aerosol GPG	Anionic Disodium sulfosuccinate	$C_{20}H_{38}O_3SNa_2$	0.07	Filter Aid

*From Casteel (55)

Milling Reagents Used at Buick Mill

Commercial Name	Chemical Name	Chemical Formula	Chemical* Dosage $\frac{kg}{\text{Metric Ton Ore}}$	Purpose
MIBC	Methyl Isobutyl Carbinol	$C_6H_{14}O$	0.09	Frother
DOW 250	Propylene Glycol Methyl Ether	$C_4H_{10}O_2$	0.005	Frother
Z-200	Isopropyl Ethyl-thionocarbamate	$C_5H_{13}ON$	0.015	Promoter
Sodium Aerofloat	Sodium Diethyl-dithiophosphate	$(H_5C_2O)_2PS_2Na$	0.045	Promoter
Z-4	Sodium Ethyl Xanthate	$H_5C_2OCS_2Na$	0.08	Collector
Zinc Sulfate	Zinc Sulfate	$ZnSO_4$	0.40	Zinc Depressant
Sodium Cyanide	Sodium Cyanide	$NaCN$	0.005	Zinc Depressant
Copper Sulfate	Copper Sulfate	$CuSO_4$	0.05	Zinc Activant
Hydrated Lime	Calcium Hydroxide	$Ca(OH)_2$	0.40	Lead Depressant
Aerosol GPG	Anionic Disodium-sulfosuccinate	$C_{20}H_{38}C_3SNa_2$	0.07	Filter Aid

*From Randall (53)

MOLY

Company	Concentrator TPD	Recycle Water	Discharge to Stream	Treatment of Discharge	Notes
Climax Molybdenum Co. Climax	43,000	90%	10%	Discharged effluent first passes through an ion exchange unit to remove Mo ions. The pH is adjusted to 12, and the water goes to electroclear flotation to remove heavy metals. Cyanide is destroyed using $NaClO_3$.	This treatment has now been modified.
Climax Molybdenum Co. Henderson	30,000	All mill water.	Mine water.	Mine water is pumped to a reservoir; flocculant is added; pH adjusted with lime. Reservoir decant is spray aerated to precipitate metal hydroxides before discharging to to environment. The recycled mill water is pumped from the tailings pond to a holding reservoir. The pH is adjusted with lime at the reservoir, and the water is pumped back to the plant.	
Moly Corp. Questa, NM	16,000	None	All	Settled in impoundments, no chemical treatment.	Temperature differential between effluent and river water, especially in winter.

ZINC

Company	Concentrator TPD	Recycle Water	Discharge to Stream	Treatment of Discharge	Notes
Asarco Tennessee Mascot, TN	11,700	All	None	Discharge tailings to thickener; overflow is recycled. Underflow to tailings pond. Decant from tailings pond is recycled. No reagents used.	-
Asarco New Market, TN	3,400	All	None	Same as Asarco - Mascot.	-
New Jersey Zinc Friedensville, PA	2,500	None	All to environment added to mine water discharge.	Mill discharge water is diluted with 20,000-30,000 gpm mine discharge water to meet EPA standards.	Mine closed 1984.
New Jersey Zinc Jefferson City, TN	2,000	All	None	No treatment of recirculated water.	Zn ion sometimes a problem
New Jersey Zinc Beaver Creek, TN	2,900	All	None	Recycle water via enviroclear thickener and filter. No chemical treatment except flocculant.	-
Jersey Miniere Zinc Co. Elmwood, TN	3,000	Small Amount	Most	Water discharged to stream is treated by percolation through a porous embankment. No treatment of return water.	-

COPPER - ZINC

Company	Concentrator TPD	Recycle Water	Discharge to Stream	Treatment of Discharge	Notes
Cities Service Copperhill, Tn	8,300	10%, no treatment.	90%	Treated with lime, aeration, and settling prior to discharge.	-

LEAD - ZINC

New Jersey Zinc Austinville, VA	2,600	Small amount. No treatment.	Almost all.	Tailings settled in a lagoon, then to river. Lead and zinc filter plant effluent water is treated with $FeCl_2$, settled, then to river.	Analysis of discharge water is sent to EPA. Zn, Pb, Fe, CN, pH, and suspended solids.
AMAX Buick, MO	6,000	None	All	Discharge tailings to a tailings pond. Water at plant discharge is pH 8.6. Water at tailings spillway is pH 8.0. Tailings dam overflow to a 3-mile meander channel for further clarification before water enters the stream.	Clear water analysis is available from Missouri Dept. of Nat. Resources at Jefferson City, MO.
St. Joe Minerals Rosa, MO		100% Millwater	Minewater	Settling pond.	

JOHN CARTER
St. Joe Minerals Corp.
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Monaca, PA 15061
(412) 774-1020

The underground Fletcher mine shaft is designed to collect underground water in a sump. Oils and greases are collected underground using skimmers.

At a lead-zinc mine, waste oil and grease after an underground repair job was discarded to an ore stream. Apparently, this interferred immediately with mill performance indicating the importance of keeping petrochemicals out of ore and water that is used in flotation operations.

COPPER-LEAD-ZINC

Numerous copper-lead-zinc massive sulfide ore deposits are mined in various parts of the world ranging from the extremely arid northern Cape Province of South Africa where Black Mountain Mineral Development Co. mines and mills a massive sulfide ore at Aggeneys, to the spectrum of complex and massive sulfide mines stretching from New Brunswick across the Canadian Shield to Manitoba; deposits in British Columbia, Alaska, Australia, Spain, Sardinia, Sweden, Finland, and many more.

Water quality is important in the flotation of concentrates from this type of ore. Several operations have experienced selectivity problems, one of which was identified as being due to soluble copper ions in the process water which activated sphalerite (ZnS) when the process calls for its suppression. This caused startup problems at Noranda's Goldstream concentrator in British Columbia. Acid mine drainage at pH 3 was used as process water in the concentrator built for the VAJASA project on the Yukon border. Soluble copper present in this water was identified as a cause of interference in the metallurgical separation of concentrates from this ore according to:

MIKE SMITH
Wittek Development, Inc.
2640 South Sheridan Way
Mississauga, Ontario L5J 2M4
(416) 823-7381

Black Mountain, Aggeneys, South Africa

At Aggeneys, water is expensive and because of the climate, the operation can achieve zero discharge. Numerous water quality effects have been noted, and several of these have been reported in the literature by TWIDLE and ENGELBRECHT (1984) and GRAHAM and HEATHCOTE (1982). This 3,000 tpd mill recycles only 0.7 m^3/t ore out of a total

use of 1.8 m^3/t water used in the mill. An additional 0.4 m^3/t ore fresh water is used for backfill of tailings,

Water management at this operation is described in Appendix I. TWIDLE and ENGELBRECHT showed the negative effects on copper recovery of using increased amounts of recycled tailings water irrespective of whether the pulp was aerated prior to flotation.

Initially, during start-up of this mine-mill complex, some oil and grease got into the ore accidentally. This was thought to have contributed to the initially poor flotation results.

700-1,200 m^3/d fresh water is used in the backfill plant. It is believed that the 500 ppm (or so) organics in recycled water would possibly result in a weakened cement.

High pyrrhotite levels in the ore have sometimes been correlated with copper recovery reductions. This effect is counteracted by installing an aeration circuit.

Higher percentage of fresh water use also improves the lead concentrate recovery.

Backfill containing cement occasionally gets into the mill feed together with ore and has been found to reduce copper recoveries assumed due to water quality effects.

When reclaimed tailings water is treated by soda ash addition, calcium is precipitated, the calcium hardness being dropped from 1,600 ppm to 100 ppm, resulting in an improved recovery in the lead circuit. Silver recovery was improved from 82.4% to 83.8% when this soda ash treatment was applied.

Elevated levels of Cu and Pb and collector in recycled water were reduced by activated carbon adsorption in laboratory tests, but this did little to improve copper recoveries.

Cu-Pb-Zn Mine-Mill G, Ontario

The following observations were pieced together from rough notes and may contain misleading errors.

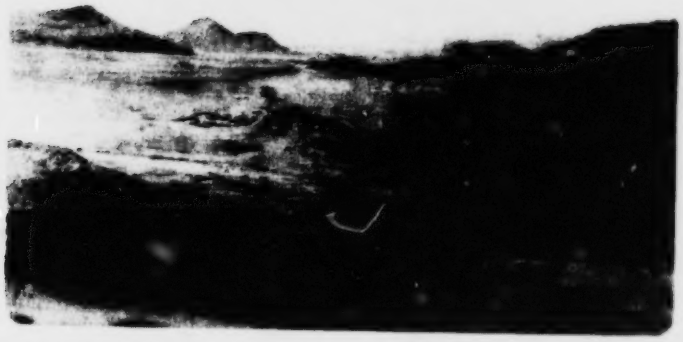
3,850 tpd ore is treated by flotation for recovery of copper, lead-silver, and zinc-silver concentrates. Tailings contain about 20% pyrite. Ammonia is used for pH adjustment in the plant because of ease of handling and because after freight-costs are included, it is found to be economical compared to lime at over C$240/t. Lime is used in the effluent treatment plant.

COPPER - LEAD-ZINC

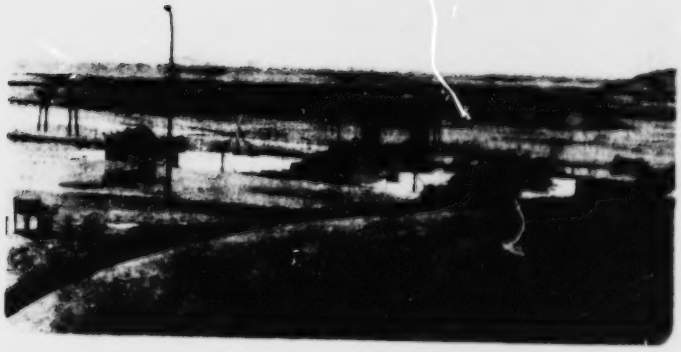
Company	Concentrator TPD	Recycle Water	Discharge to Stream	Treatment of Discharge	Notes
Black Mountain Aggeneys	3,000	0.72 m^3/t Overall Recycle 0.47 m^3/t from Tailings Pond	Zero	Evaporation	4 m^3/t Overall Used. 1.4 m^3/t Fresh Water 0.5 m^3/t Reclaimed from Tailings 2.1 m^3/t Internal Plant Recycle
Cu-Pb-Zn Mill G	3,850	1.92 m^3/t from Tailings Pond	Yes	HDS Lime	2.45 m^3/t Total Used 1.92 m^3/t Recycle from Tails 0.01 m^3/t Potable
Cu-Pb-Zn Mill M	2,750	7% of Needs	Yes	HDS Lime Settle	0.7 m^3/t Fresh Water 2.4 m^3/t Recycle Water 3.1 m^3/t Total
St. Joe Lead Brushy Creek	5,000	All	None	No treatment except the addition of flocculant to tailings thickener.	-
St. Joe Lead Fletcher	5,000	All	None	Same as Brushy Creek.	-
St. Joe Lead Viburnum	7,500	All	None	Same as Brushy Creek	-
St. Joe Lead Indian Creek	2,500	All	None	No treatment except the addition of flocculant to tailings thickener.	-

BLACK MOUNTAIN MINERAL DEVELOPMENT CO.

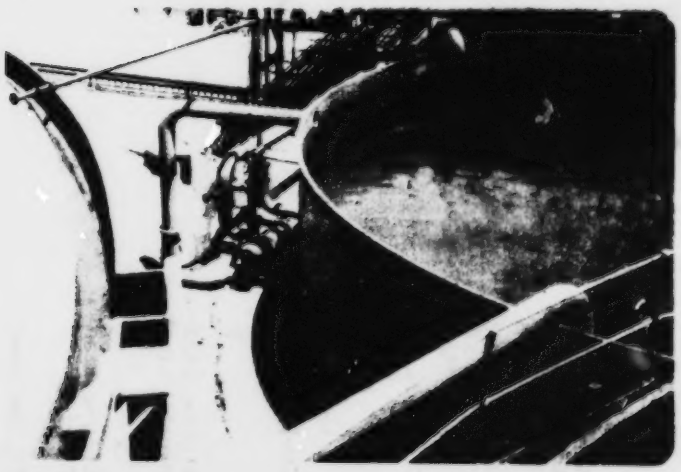
South Africa



ARID ENVIRONMENT - ZERO DISCHARGE POSSIBLE AND NO STREAMS TO POLLUTE



TAILINGS POND IN BACKGROUND



COLLOIDAL SUSPENSION IN RECYCLE WATER

80% of the water used in the mill (including firefighting and potable water) is recycled tailings water. This mill has been steadily improving its water recycle rate since 1972, and its objective is to use recycled water for 85% of its needs.

Water used in the mill-concentrator is made up as follows:

	m^3/t	%
Fresh Lake Water	0.5	10.4
Water in Ore Feed	0.02	0.8
Potable Water (Lake)	0.01	0.4
Recycled Water	1.92	78.4
	2.45	100.0

- When recycled tailings water (saturated with $SO_4^{=}$) is used for reagent mixing, it was observed that when ammonia and cyanide reagents are mixed, severe scaling occurs in the reagent system. Reagent feed control was then difficult, so fresh water is now used for reagent makeup.

- SO_2 and ammonia are premixed to form $(NH_4)_2SO_3$, which is added to the rod mill to depress zinc in the bulk Cu-Pb-Ag flotation step.

- Even though the sulfide ore is milled at an alkaline pH normally considered a cause of thiosalt generation, thiosulfate levels are only 100 mg/l in the milled pulp solution water, which is lower than in other operations. This is ascribed to lower reactivity of the sulfides in this ore.

- The mine uses cemented backfill. Lab tests indicate that cured backfill fragments in mill feed would reduce copper recovery and selectivity. Attempts to correlate calcium levels in the rod mill discharge with Cu recovery and grade were inconclusive. Could cement contain other components that interfere with flotation.

- On occasion, when selectivity problems were noted, soluble copper concentrations in process solutions were found to have increased from 6 to 12 ppm.

- Aeration ahead of flotation has three effects:

  - Improved copper flotability.
  - Enhanced galena flotation.
  - Depressed Fe sulfides.

- If aeration is too long, zinc flotation is enhanced thereby reducing primary selectivity.

° Fresh water is used in pump glands and for the Cu-Pb separation step.

Separation of Cu-Pb is impaired when recycle water is used at any point after the Cu-Pb bulk recovery. Fresh water is also used in the Cu-Pb concentrate launders.

With fresh water, a lead concentrate of 65-70% can be achieved by depressing Cu with Cyanide. With recycle water, the lead concentrate grade can get to 50% Pb with difficulty only. The actual species in recycle water that causes this drop has not been firmly identified.

Cu-Pb-Zn Mill M, Ontario

Mill M treats two massive sulfide ore types with different characteristics. One contains 40% sulfide; the other contains 25-30% pyrite. The following observations were pieced together from rough notes and may contain misleading errors.

A Cu-Pb-Ag concentrate is floated first in standard semi-bulk flotation arrangement. This concentrate is next treated by depressing lead with guar and SO_2 and floating the copper. Zinc is floated from the primary flotation tails. SO_2 helps Cu to float.

Soda ash is used for the primary Cu-Pb concentrate flotation circuit which is operated at pH 9-9.5. Sometimes SO_2 is used in the rod mill when the ore is not "clean."

Recycle water use is found to cause lower concentrate grades in the Cu-Pb separation step. Fresh water use at this point gives the best results.

Recycled water is used without difficulty for flotation of zinc from the primary flotation tailings.

Some thiosulfate is generated because sulfide ores are milled at pH 8.5.

Fresh water is added in the ball mill circuit because recycle water results in higher zinc levels in the Cu-Pb semi-bulk flotation step.

When SO_2 is not added in the rod mill, the Cu-Pb grade drops immediately.

Excess collector added at the front end of the circuit ruins selectivity of the first semi-bulk float step. Consequently, this plant runs on starvation levels of collector.

Na_2CO_3 is used for pH adjustment in the mill. Some NH_3 has been noted in this circuit which is probably a residual from underground blasting. Soda ash promotes recovery of silver sulfides--tetrahedrite, freibergite, tennantite.

Activated carbon is added to recycle water to adsorb any extraneous collectors.

Composition of reclaimed water varies with the season, e.g.:

	Winter January, 1984	Summer July, 1984
pH	6.8	3-7
Zn ppm	5.9	3.1
Fe ppm	4.70	0.9
S_2O_3 ppm	43	Tr
Pb ppm	N/A	0.06
Cu ppm	0.01-0.04	0.01
Suspended Solids	25	1.0

Goldstream Concentrator, British Columbia

MCTAVISH (1984) described initial difficulties experienced at Noranda's Goldstream operation in British Columbia which recently shut down.

The copper-lead-zinc complex ore was milled and subjected to a standard Noranda-type flowsheet in which a copper-lead concentrate is first selectively floated from the tailings in which sphalerate is depressed. Subsequently, the sphalerite is recovered as a separate concentrate, and the Pb-Cu bulk concentrate is separated into two concentrates and cleaned. In this case, when the mill was started up, the metallurgy did not respond as predicted in pilot and laboratory tests. Grade and separation of the concentrates was poor.

Eventually, the problem was identified as being due to soluble copper in the process solution. This came about because the ore contained a small layer of soluble oxidized copper ore which contributed copper to the solutions. By selective mining, thereby avoiding getting this part of the ore into the mill, the problem was solved and and design selectivity, recovery, and grade were achieved.

Cu-Pb-Zn - USE OF HEXAVALENT CHROMIUM

Hexavalent chromium is metallurgically useful in flotation circuits because it is a powerful depressant. particularly for galena. As such, it is useful in making separations of minerals or in cleaning concentrates in which, say molybdenite, is depressed but non-mineral slimes floated.

In days gone by when mill tailings were discharged without knowledge of how effluents effect the environment, the use of dichromate was of less concern as effluents were simply discharged, and water lost in this way was replaced by fresh water. Since discharge has become an environmental concern and mills are obliged to strive toward zero discharge, mill tailings solutions have to be recycled.

If there is even a low level of hexavalent chromium in reclaimed water that is used in the front end of Cu-Pb-Zn flotation mills, the dichromate will cause a reduction in lead recovery because galena recovery in the primary Pb-Cu semi-bulk float would be reduced.

Some mill designers believe that hexavalent chromium will be reduced in mill tailings ponds that contain thiosulfates generated in the milling process. However, at one such operation, namely Newmont Mining Company's Idarado Mine near Telluride, Colorado, this did not occur sufficiently to remove all traces of hexavalent chromium which was detected in groundwater downgradient from the Idarado mill tailings.

Senior Newmont metallurgical staff point out that if Cr^{VI} is to be used in a flotation step, then water used in this circuit must be kept totally isolated from the rest of the mill and the tailings to be sure that not even a trace gets into the main mill solution. Comments by Lynn Harris of Newmont Mining Corp. and by Per Broman of Boliden Metall AB, Sweden, are interesting observations.

EXXON Minerals Company, Crandon Project

EXXON Minerals Corp.'s Crandon mine and mill, now in late stages of investigation in Wisconsin, proposes to recover copper, lead, and zinc from a complex sulfide orebody.

The flowsheet proposed for this project has not yet been released, nor has the environmental impact statement, which will describe in detail the process, water recycling, water management, and effluent treatment and discharge measures to be applied.

When this environment impact statement is published, this ought to be a very valuable state of the art document because Exxon is known to have gone to great lengths to study all aspects of water recycling and treatment for reuse or discharge. Because of climatic constraints, this project will not be able to achieve zero discharge.

Individuals and consultants known to be involved in various aspects of this study for Exxon Minerals Corp. include:

EXXON MINERALS COMPANY
Post Office Box 4508
Houston, TX 77210
(713) 895-1110
Roger Kust

NEWMONT MINING CORPORATION
200 PARK AVENUE
NEW YORK, N. Y. 10166

June 15, 1984

LEONARD HARRIS
VICE PRESIDENT
METALLURGICAL OPERATIONS

Mr. Hans von Michaelis
Randol International Limited
21578 Mountsfield Drive
Golden, Colorado 80401

Dear Hans:

Many thanks for your letter of April 20, 1984 and the copy of Randol's report "CIX-RIP For Uranium Recovery".

With respect to hexavalent chromium in flotation, I note the following: You are probably right that thiosulfate ions are formed during the grinding of sulfide ores in an alkaline pulp. The problem is that sodium dicromate is not added to this circuit. It is added to the copper/lead separation circuit where little or no thiosulfate is present. Based on our experience, I think that it is dangerous to rely on the reduction of hexavalent chromium to trivalent chromium by means of thiosulfate in the tailings dam. It most certainly did not happen in our case.

When I checked into this matter about a year ago, I talked with Norman Holme, Chief Metallurgist, Cyanamid who noted that in the Missouri lead belt where dichromate is used for copper/lead separation, the water is always kept separate except at the Magmont mill where only 25 percent water is recycled. Deleterious results were experienced in the early days of operations in the Missouri lead belt.

Dichromate is a potent depressant even in very small quantities so that apart from the toxicity problem, one can expect problems in the flotation plant. In our opinion, the copper/lead separation circuit should be clearly isolated from the rest of the circuit to prevent these problems.

Best personal regards.

Sincerely

Leonard Harris

LH:emd
Enclosure

P.S. I note your reference to enhanced decomposition of thiosulfate at higher temperatures. Our problem was in the cold mountain climate of Colorado.

boliden mineral

Date
June 4, 1984

Reference

Yours dated

Your reference

Attending to this matter
Mineral Processing Development
Per G. Broman/eb

Mr Hans von Michaelis
Randol International Ltd.
21578 Mountsfield Drive
GOLDEN, Colorado 80401
USA

Dear Mr von Michaelis,

Thank you for your note on Cr (VI) reduction by thiosulphate ions. This has not been studied or even observed by us. We know however that thiosulphate could reduce Cu (II) to the monovalent or even elemental state. This is in fact what we think happens in the SO_2-promoted flotation processes.

Your idea actually made us consider this phenomenon being behind some so far unexplained Cr (VI) to $S_2O_3^{2-}$ ratios being observed in our effluent streams.

Thank you once more. We look forward to seeing your final report.

Yours sincerely,

BOLIDEN MINERAL AB
Research and Development

Per G. Broman

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Crandon Project
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Thinelander, WI 54501
(715) 369-2800
Project Manager
Carlton C. Schroeder
Surface Facilities Engineering

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Dept. of Natural Resources
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Robert P. Grefe
Environmental Engineer

CH2M HILL
Post Office Box 2090
Milwaukee, WI 53201
(414) 272-2426
Michael R. Harris

Swedish Cu-Pb-Zn Concentrators

Two interesting papers are inserted below which describe how water is recycled in European base metal operations and provide an insight into some of the testwork that is being carried out on water reuse in complex sulfide ore circuits.

Water reuse at sulphide ore concentrators in Sweden: practice, experience and current developments

Per G. Broman Dr. Eng.
Sala International AB, Sala, Sweden

Synopsis

The scarcity of fresh water resources that are available to the mining industry and the desire to reduce effluent discharge from mining and processing operations are the main reasons for the reuse of process water. The processing of complex sulphide ores by flotation is characterized by very strict demands on the chemical composition of the water phase. Usually, therefore, the introduction of reclaimed water is considerably more complicated than is the use of fresh water. First, certain reagents have been added to this water, some of which remain, and, secondly, complex ores are greatly affected by wet oxidation during the flotation process, which results in considerable release of various ions and salts in the water phase.

The fresh water source, along with the entire operational area (mine, concentrator and tailings pond) and the receiving point, should be regarded as one integrated system of water management. It is important to consider water reuse not only from the point of view of water flow but also from that of pollution. In principle, it would be possible to reduce the flow of water by reuse without actually reducing the flow of contaminants.

Reuse is accomplished by internal-circulation loops within the plants as well as by circulation from the tailings and clarification ponds (referred to here as external circulation). Practice and experience of water reuse in Swedish sulphide ore concentrators are illustrated with examples from ores of varying complexity. The examples have been selected to include cases in which reuse has increased above tolerable limits: in general, reuse-water additions to the final grinding and flotation circuits have detrimental effects on the metallurgy. The metallurgical implications of water reuse and the associated mechanisms are under investigation by mining companies and the Swedish Mineral Processing Research Foundation, and such a study is described.

The treatment of complex sulphide ores by flotation to produce clean concentrates with the highest recovery possible demands very stringent and closely controlled processing—this applies particularly to the composition and properties of the water phase.

In Sweden, with its comparative abundance of water, the *quality* of the fresh water supply seldom poses any problem; to reduce the *consumption* of fresh water the reuse of process water would be appropriate. Another, and usually more important, reason for reuse, however, is the desire to reduce effluent discharge from the mining and processing operations. The use of reclaimed water is normally much more complicated than that of fresh water: first, certain reagents have been added to the water, some of which remain in it, and, secondly, complex ores are characterized by a strong tendency to increased weathering during the wet oxidizing conditions of the flotation process, which results in the considerable release of various ions and salts in the water phase.

To determine the effects of the reuse of process water in various ways and in various types of plants on the flotation process comprehensive studies are carried out by research establishments and mining companies, and present practice in terms of water reuse and current research is summarized here.

Principles and aims of water reuse

Before details are given of the reuse of water in actual practice it may be of interest to summarize reuse in relation to the overall aim. Fig. 1 shows a broad water flowsheet. Ore treatment requires, depending on the specific process, a flow of water that is directly correlated with the flow of ore. Clearly, the reuse of water in an internal or an external loop will influence the demand for fresh water: one of the main purposes of the reuse of process water is, therefore, that of reducing the demand on the fresh water supply. Reuse might also offer the possibility of increasing ore throughput in existing plants without any increase in the consumption of fresh water above the limits that have been set by prevailing regulations.

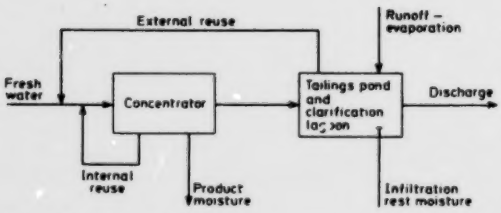

Fig. 1 General water flowsheet

Fig. 1 shows that there is a somewhat more complicated balance for the tailings pond. Effluent flow from the tailings pond to the recipient depends on the inflow of tailings suspension, direct atmospheric precipitation and surface drainage and the outflow by evaporation and recirculation. Furthermore, some of the inflowing water is retained as residual water in the dam and some water is lost throug'. infiltration into adjoining soil layers.

Internal and external reuse affect the water balance of the tailings pond in different ways: inflow to the tailings pond will be influenced by the internal recirculation only, but both will reduce effluent flow to the recipient. This is the second main purpose of reuse.

So far only the balance of the water flows has been discussed. Clean water as such seldom imposes any serious burden on the recipient. More important is consideration of the flow of pollutant material.

The principal additions of pollutants to the water take place during the concentration process. Recirculation demands the use of a process water that usually contains somewhat higher amounts of dissolved components than the fresh water. Depending on the chemical and physical conditions that prevail during the process there will be a build-up of added substances and reaction products in the water. The concentration of the added substances is usually far below the saturation level. As regards ions, which are formed by weathering of the ore, the supply of solid reactant is generally very large. Despite ample additions of oxidizing reactant by aeration a marked shortage prevails throughout the flotation process, a considerable contact period with the atmosphere being necessary before the oxygen deficiency is removed. Thus, the limited residence time will prevent saturation concentration from being reached. Recirculation of water in such a system will increase the contact time and, in principle, make it possible to attain a higher concentration of oxidation products in the water.

The inflow of surface drainage to the tailings pond will usually have a diluting effect on the water in the dam, ignoring here the extreme cases of acid precipitation and inflow of water from acid or other polluted ground.

In summary, the concentration of cumulative substances in the tailings dam water can be affected by reuse and also by dilution through precipitation. Hence, water reuse will yield a lower effluent flow to the recipient but may, in principle, give an unchanged discharge of substances that may accumulate in the water. Similarly, precipitation and surface drainage will yield a larger volumetric flow, but not necessarily a greater discharge of pollutants.

The above discussion relates to the flow of cumulative substances from the viewpoint of the *recipient* only. The question of the concentration that can be accepted from the viewpoint of the *process* is completely separate and may well be the limiting factor as to the extent to which reuse is feasible. It should be noted that dilution from atmospheric precipitation is normally beneficial to reuse, but if dilution and, hence, water quality vary considerably, the maintenance of consistent process conditions may be jeopardized over a period of time.

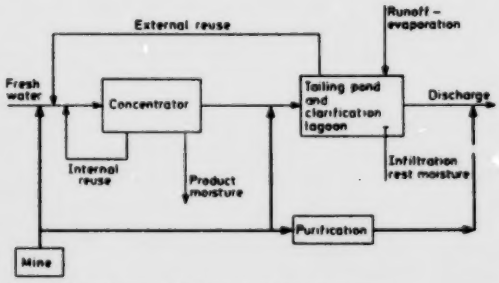

Fig. 2 General water flowsheet, including mine water

To further illustrate this complex subject a general flowsheet that includes mine water is shown in Fig. 2. In the total water balance of the mine and concentrator it is natural to include the mine, which may constitute an important water source. Mine water may go to the concentrator as a substitute for external water supply, to the tailings pond for cleaning or to separate cleaning before discharge to the recipient.

Mention was made above to the fact that reuse can be accomplished in internal and external loops.

An *internal reuse loop* comprises recirculation of water from dewatering units inside or directly connected to the concentrator, which normally necessitates dewatering of concentrate or tailings products by thickeners or filters. Dewatering of the middling products, e.g. zinc tailings prior to pyrite flotation, may also provide water for recirculation. A system of water exchange between the separate steps in a complex sulphide ore

concentration process is appealing from the process water chemistry viewpoint, but it has not been used to any great extent because of the fairly elaborate dewatering equipment necessary to obtain a water that is sufficiently clean with respect to solids.

An *external reuse loop* comprises water that is recovered from tailings and clarification ponds.

There is no basic difference between the uses to which water from the internal and the external water system is put, usage being determined by its composition.

Definitions of reuse and reuse percentage

Various definitions of the concepts of reuse and reuse percentage have been suggested. Here reuse implies deliberate action to reduce the demands on fresh water. A system at 'zero level' (no reuse) is a system with normal product flows, including recirculation of middling products within and between the flotation circuits, where any necessary dilution, in addition to the circulation of products, is made with fresh water.

Reuse indicates that the water has been used previously in the same process and that it is used in the process instead of fresh water. It was stated above that the water balance of the tailings dam in particular is very complex, the process water being diluted by precipitation and surface water. The dilution water is, in this respect, considered as part of the reuse water. Complicated boundary problems may arise in relation to circulation within grinding and flotation circuits. Diluted middlings products often contribute very significantly to dilution in the grinding and rougher flotation circuits, the need for external water for these operations thereby being reduced. Since the purpose is to return particles for regrinding, however, and water recirculation is merely a side effect, it is not considered as reuse.

Reuse percentage is defined as the percentage of the total need of process water (i.e. the demand for fresh water supply in the zero level system) that is covered by reuse.

Reuse practice and experience at Swedish sulphide ore concentrators

Current reuse practice at Swedish sulphide ore concentrators is briefly illustrated, the examples selected including cases in which reuse has been increased above tolerable limits to show the sensitivity of the process. The localities of the concentrators are shown in Fig. 3.

Fig. 3 Location map of Swedish concentrators

Kristineberg concentrator, Boliden Mineral AB

The Kristineberg concentrator is the central treatment unit for all the ores from the Kristineberg area, some 1 000 000 tons being treated per year. Five different ore types are treated in different campaigns. There are two parallel grinding and flotation sections: the simplified flowsheet (Fig. 4) is based on the *A* section; the broadly similar *B* section is normally used for ores with a low arsenic content suitable for pyrite extraction. Ores treated vary in composition and mineralogy from low-grade impregnations to massive pyrite ores, but they are as a rule highly complex. The ore that is fed to the concentrator grades 0.96% Cu, 0.52% Pb and 4.35% Zn, and the tonnage and grades of the Cu, Pb and Zn concentrates are given in Table 1.

Table 1 Kristineberg concentrate data (yearly average for all ore types)

Product	*Cu, %*	*Pb, %*	*Zn, %*	*Annual tonnage*
Cu concentrate	22.3	7.5	5.1	34 600
Pb concentrate	1.0	32.0	8.0	5 200
Zn concentrate	0.4	0.9	54.6	30 900

Concentrates are thickened, filtered and dried. The tailing, currently about 790 000 ton per year, is used in part for mine backfill. After desliming, about 60% of the tailings can be used for fill, the balance passing to the tailings pond. Fig. 5 shows a schematic water balance relating to an ore capacity of 900 000 ton per year. Reuse is performed in an internal and an external loop. The total process water demand of the concentrator is 715 m^3/h, of which 376 m^3/h, or about 53%, is covered by reuse.

Internally, water is recovered as thickener overflow and as filtrate water from the filtering of tailings sand. The water is used as dilution water for the final tailings before cyclone separation of sand for backfilling. Water from the external reuse loop is used in the rod-mills (together with mine water and fresh water), in the wet

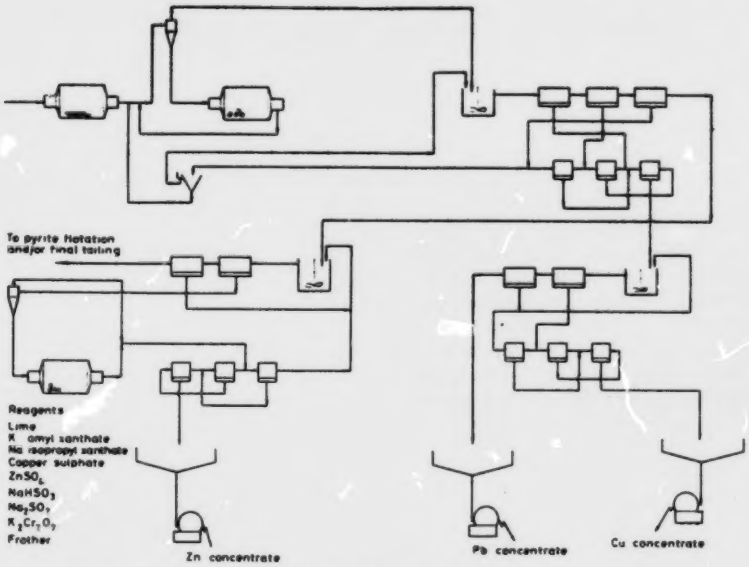

Fig. 4 Kristineberg concentrator simplified flowsheet

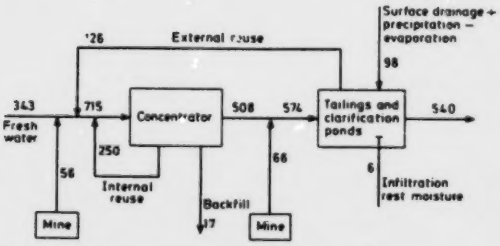

Fig. 5 Kristineberg concentrator water balance (m^3/h)

scrubbers of the concentrate dryers, as dilution water for the backfill cycloning, as dilution and spray water in the pyrite flotation and as cleansing water. Water in the external reuse loop has the average analysis (monthly average for 1978) as shown in Table 2.

froth launders in all the flotation circuits. The amount of pond water was then 15–20%. Initially, no significant changes in the process result were noted, and after a little more than half a year of the use of pond water fresh water only was used for one week. The results obtained are shown in Table 3 and compared with those of the period immediately following when reuse water was again employed.

A clearly reduced selectivity against zinc was noted in the flotation of copper when tailings pond water was used. The zinc content in the copper concentrate increased by more than 6% at the same time as the copper grade in the copper tailing increased. Whether this was due to the reduced floatability of chalcopyrite or to activation of the sphalerite is not known. Reuse in this way obviously had a very negative influence and, accordingly, limited recirculation was resumed.

Table 2 Kristineberg water quality data—tailings pond water (values in ppm)

Unfiltered sample									
pH	*Turbidity, FTU*	*Conductivity, mS/m*	*Cu*	*Fe*	*Zn*	*Pb*	*As*	*Hg, ppb*	*Cd*
8.0	7.5	171	0.030	0.23	0.32	0.013	0.011	0.66	0.008
Filtered sample									
			Cu	*Fe*	*Zn*	*Pb*	*As*	*Hg, ppb*	*Cd*	*SO_4*
			0.012	0.059	0.211	0.005	0.008	0.21	0.008	589

It has been demonstrated that it is possible to use the water in a mixture with mine water and fresh water without process disturbance in relation to primary grinding and pyrite flotation. Full-scale tests have been performed over a period of several months on the use of the water for secondary grinding and as spray water in

Stekenjokk, Boliden Mineral AB

Stekenjokk mill is the most recent Boliden plant, the concentrator processing 600 000 t per year. The ore is a complex sulphide grading 1.4% Cu, 3.6% Zn, 0.31% Pb, 19% S and 40 g/ton Ag. The main sulphides are chalcopyrite, sphalerite and pyrite.

Table 3 Kristineberg metallurgical data on Näsliden ore with and without reuse

	Mill feed			*Cu concentrate*		*Cu tailing*	*Zn concentrate*	*Zn tailing*		*Final tailing*	
No reuse											
Time	Cu	Zn	S	Cu	Zn	Cu	Zn	Zn	Cu	Zn	S
20–25 May, 1970	0.81	3.03	28.5	19.1	12.7	0.10	53.9	0.44	0.11	0.45	10.3
Reuse											
26–31 May, 1970	0.82	3.49	29.8	17.5	19.0	0.12	53.3	0.55	0.13	0.55	13.7

The ore is screened at 200 mm into fine- and coarse-ore bins and fed to the two-stage autogenous grinding circuit according to the flowsheet shown in Fig. 6. Flotation is performed stage-wise for copper and zinc. Part of the copper flotation is integrated into the grinding circuit as a unit flotation. The copper and zinc circuits are of conventional design; to the zinc circuit is added a Zn-upgrading circuit with the use of reverse flotation.

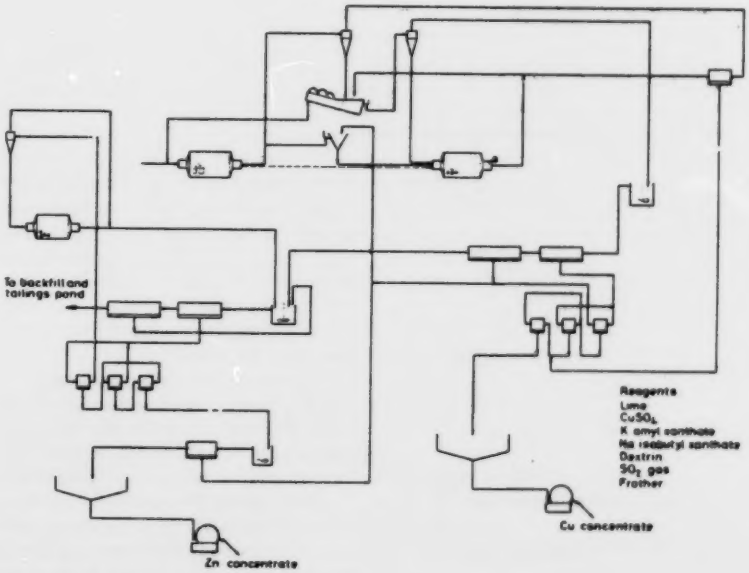

Fig. 6 Stekenjokk concentrator simplified flowsheet

The metallurgical results show a copper concentrate grading 19% Cu with 87% recovery and a zinc concentrate grading 53% Zn with 70% recovery. The concentrates are thickened, filtered and dried. The tailings are used partly for mine backfill after cyclone separation of the fines, which are pumped to the tailings pond. Of a total tailings tonnage of 538 000 per year, 78 000 ton are used for backfilling.

Fig. 7 shows a schematic water balance for the maximum permitted fresh water usage of 6 m^3/min. The total process water requirement is 8.1 m^3/min, of which 2.1 m^3 or 26% is covered by reuse. Internally, overflow water from thickeners is reused as dilution water for transport of backfill to the mine. About one-fifth of the external reuse is used as dilution water in the grinding circuit, the rest being used as water for cleansing. Unfiltered samples of the tailings pond water had the average composition during 1978 as shown in Table 4.

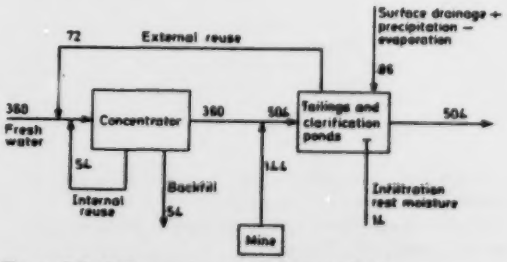

Fig. 7 Stekenjokk concentrator water balance (m^3/h)

Table 4 Stekenjokk water quality data—tailings pond water (values in ppm)

pH	Suspended solids			Conductivity, mS/m		Cu	Fe	Zn	Pb		Cd	
7.6	1			57		0.013	0.106	0.136	0.026		0.001	
Hg, ppb	Cr	Co	Ni	Mn	SO_4^{2-}	N_{tot}	NO_3-N	P_{tot}	$KMnO_4^-$ consumption		Total oil	Mineral oil
0.02	0.005	0.005	0.07	0.16	190	2.1	0.90	29	33		0.22	0.05

For distribution of reuse water to any desired point in the concentrator there is a pipe system, which is parallel to the fresh water system. By use of this pipe system a test with increased reuse was run that comprised the addition of reuse water as dilution and spray water to the zinc flotation. The arrangement was maintained for several months, but then had to be discontinued because of severe losses of zinc. Although reuse of water was not the only reason for the deterioration, it was considered to be a significant factor. No close follow-up of the water composition during the period of extended reuse was made. A slight increase in SO_4^- grade around a base level of 100 ppm was the only significant change to be observed.

The lead concentrate grades 75.4% Pb and 1.1% Zn and the zinc concentrate grades 55.2% Zn and 1.7% Pb. The annual productions are 61 600 ton of lead concentrate and 12 300 ton of zinc concentrate. The flowsheet is shown in Fig. 8. The concentrates are thickened, filtered and dried. Tailings are cycloned for generation of a backfill material for the mine. The fine product is pumped to the tailings disposal area after the addition of lime to pH 11.2. Of the total of 1 300 000 ton of tailings, approximately 66 000 ton are used as backfill. The fraction pumped to the tailings pond is cycloned at the pond to generate a coarse product for dam construction.

According to the water balance shown in Fig. 9, fresh

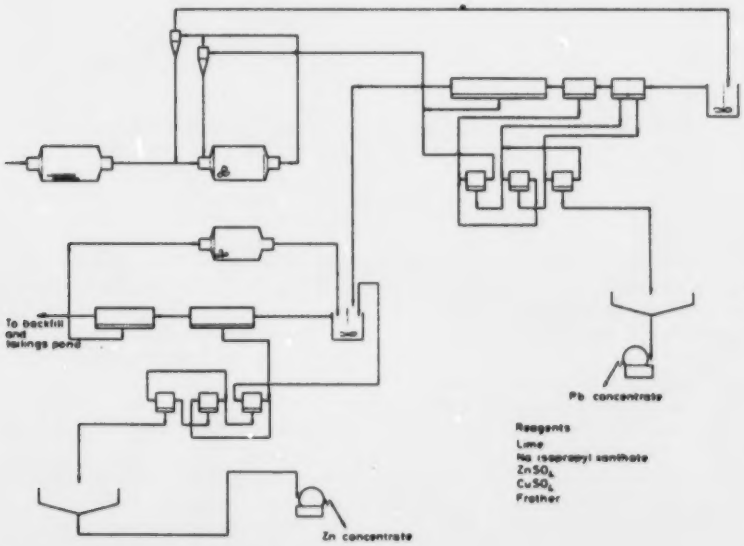

Fig. 8 Laisvall concentrator simplified flowsheet

Laisvall, Boliden Mineral AB

The concentrator at Laisvall treats a lead–zinc ore grading 3.4% Pb, 0.6% Zn and 8–10 g/t Ag. The annual output of the mine is 1 400 000–1 500 000 t. Galena and sphalerite occur as the matrix in a hard white sandstone. The content of iron sulphides is very low. The ore is ground in rod- plus pebble-mills to 36% −44 μm and floated in consecutive stages for lead and zinc, respectively.

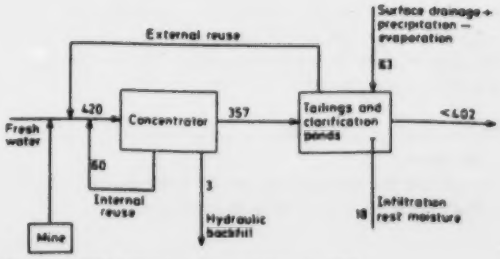

Fig. 9 Laisvall concentrator water balance (m^3/h)

water is supplied from Lake Laisan and from the mine. Internal reuse of water has been practised for several years. Reuse of water from the tailings pond was tried from February, 1979, to March, 1980 (see below).

Test period 1: mine water + tailings pond water
During the initial phase (test period 1) only mine (3 m^3/min) and tailings pond waters (4 m^3/min) were used, apart from the internal reuse of 1 m^3/min that was maintained throughout the series of tests. After a few weeks it was necessary to abandon the test because of severe problems due to precipitation in pipes and spray nozzles. The tailings pond water content of calcium (120 mg/l) and the mine water content of carbonate (60 mg/l) led to precipitation of calcium carbonate. Increased frothing indicated a build-up of frother in the system.

1.5–2 m^3/min. Mine water was fed at a rate of 4 m^3/min and the balance at up to 7 m^3/min, i.e. 1–1.5 m^3/min was supplied from Lake Laisan. Initially, the process did recover metallurgically (Fig. 10), but the target grade of the lead concentrate could not be fully attained.

Since the pH value of the process water mixture was lower than during test period 1 calcium carbonate precipitation did not occur. Fig. 10 shows that the late part of the period is characterized by a steady deterioration in lead concentrate grade. The test period was interrupted by ice blocking the return pipe from the tailings pond during a period of extreme cold.

Test period 4: mine water + tailings pond water
During the later part of February, 1980, the fourth test period was started, 4 m^3/min of tailings pond water

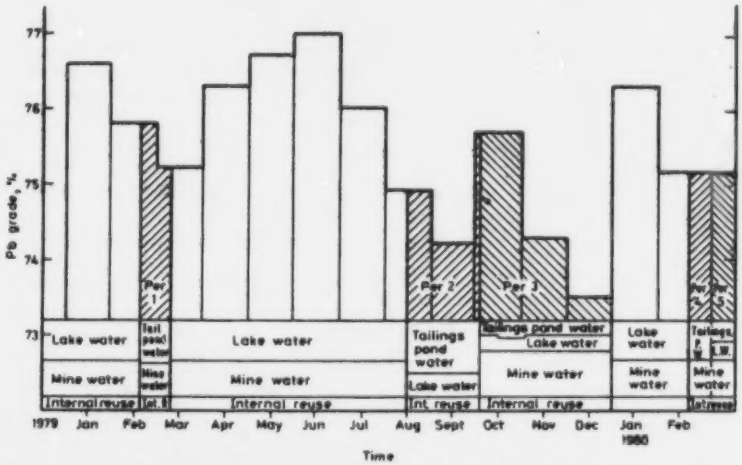

Fig. 10 Laisvall concentrator: Pb grade in Pb concentrate with and without reuse

Metallurgically, the tendency towards lower grade and recovery in the lead flotation was clear. According to Fig. 10, test period 1 yielded a deterioration in the monthly lead concentrate grade mean values.

Test period 2: lake water + tailings pond water
To allow for the continued use of tailings pond water the carbonaceous mine water was eliminated. The process water fed to the concentrator was a blend of fresh water from Lake Laisan (2 m^3/min) and tailings pond water (5 m^3/min). Slowly, but gradually, both the grades and the recoveries in the lead flotation were reduced. This was accompanied by increasing frothing problems, which resulted in frequent overflows of pump sumps. After about six weeks the grade of the lead concentrate had dropped by more than five units at an alarming increase in the tailings grade. The test period was then discontinued.

Test period 3: lake water + mine water + tailings pond water
To stabilize the process after period 2 the amount of tailings pond water was reduced from 5 to

being used. Fig. 10 shows that the lead concentrate grade was clearly affected, the impact being so marked that the mean value for February dropped by more than 1% in comparison with the January value, though the water arrangement was used for only ten days in February.

Test period 5: lake water + mine water + tailings pond water
In early March, 1980, it was decided to take steps towards the stabilization of the process. The tailings pond water addition was reduced from 3 to 1.5 m^3/min, the 1.5 m^3/min eliminated being replaced by water from Lake Laisan. As Fig. 10 shows, a further deterioration in lead grade was halted by the action to reduce tailings pond water. Whether this is a permanent stabilization or merely a temporary effect will be proved over a longer period.

Taking account of some additional observations, the following conclusions may be drawn: reuse of tailings pond water has a pronounced negative effect on the recovery and concentration of galena; the deterioration in lead flotation increases with time and possibly also

with the proportion of tailings pond water that is being reused; the process is quickly restored to its natural state after the shutdown of the reuse system; a mixture of mine water and tailings pond water could be used only if the pH of the mixture is low enough to prevent precipitates of calcium carbonate being formed that disturb the process; accumulation of frothing agents takes place in the reuse loop, which causes setbacks in the process by overfrothing; it has been possible (and necessary) to reduce the addition of frother by 25–50%, depending on the percentage of water that is being reclaimed, though without fully solving the frothing problem; and accumulation in the tailings pond water of the components calcium (from 70 to 125 mg/l) and sulphate (from 100 to 275 mg/l) has been observed.

Zinkgruvan, Vieille Montagne

Zinkgruvan, Sweden's largest zinc mine, has been owned since 1857 by the Belgian company Société des Mines et Fonderies de Zinc de la Vieille Montagne, S.A. Since 1977 the company has operated a new concentrator that treats 600 000 ton per year of an ore grading 8% Zn, 1.5% Pb and 35 g/t Ag. The main ore minerals are sphalerite and galena. Only minor amounts of pyrrhotite occur, and practically no pyrite. The gangue minerals are mainly quartz and feldspar, but up to 15% limestone and dolomite occur, making the host rock basic.

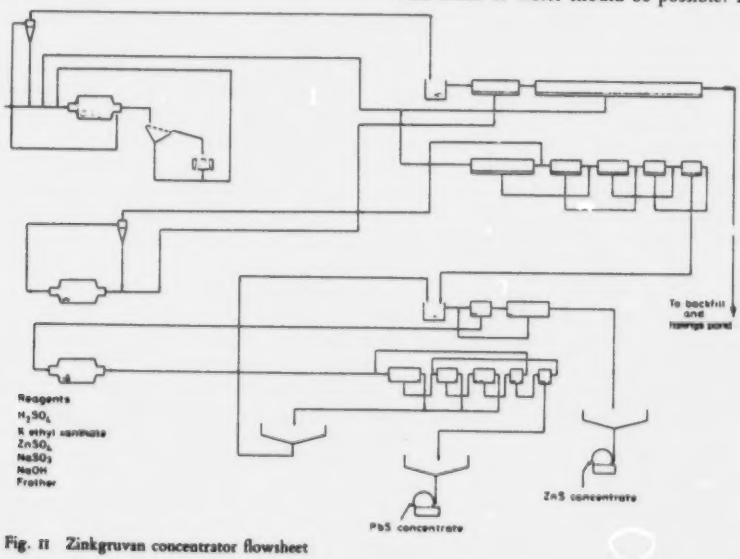

Fig. 11 Zinkgruvan concentrator flowsheet

Processing follows the flowsheet shown in Fig. 11; grinding is by primary autogenous grinding in one stage. The final grinding product has a particle size of 80% −140 μm. Galena and sphalerite are bulk-floated at pH 7–7.5. Generally, no special activation of the sphalerite is needed. Spontaneous activation is achieved by lead ions, dissolved from galena particles. After cleaning the bulk concentrate is reground in a pebble-mill and separated into a lead and a zinc concentrate by depressing the zinc. Zinc sulphate and sodium hydrosulphite are used as depressants and sodium hydroxide as pH regulator in the separation circuit. The concentrates are dewatered in thickeners, filters and driers. The final tailing is cycloned to generate a sand fraction for mine backfilling (approximately 175 000 t per year). The fines (approximately 333 000 t per year), together with the water, are pumped to the tailings pond. The tailings and clarification ponds give the water a nominal retention time of approximately three months. The lead concentrate grades 62% Pb and 12% Zn and the zinc concentrate grades 53.5% Zn and 0.6% Pb. Recoveries to the main concentrates are 87% for the Pb and 95% for the Zn.

Process control is mainly manual, an on-stream analyser being used as the basis for this control.

Fig. 12 shows the water balance. Overflows from the concentrate thickeners are combined and clarified in a middlings thickener, which is also used for thickening Pb cleaning rejects. Overflow from this middlings thickener is reused internally as dilution water for the backfilling system. Tailings pond water (after clarification in a clarification pond) is used for the same purpose and, to a minor extent, as spray water in the bulk flotation.

One reason for the bulk-selective type of flowsheet for the flotation relates to the aspects of water management. It was foreseen that the bulk flotation stage should be tolerant in regard to water quality and that the large-scale reuse of water should be possible. As soon as the

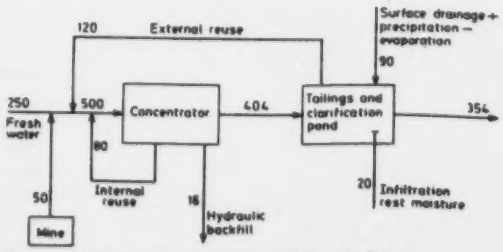

Fig. 12 Zinkgruvan concentrator water balance (m^3/h)

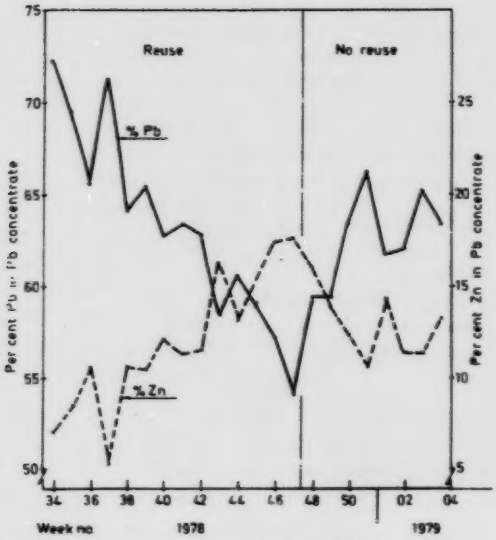

Fig. 13 Zinkgruvan concentrator: Pb and Zn grades in final Pb concentrate with and without reuse of tailings pond water

tailings and clarification ponds had stabilized after plant start-up, reuse of water was introduced on a large scale in July, 1978. The demand for process water to the grinding and bulk flotation sections was totally covered by water from the clarification pond at this stage.

Fig. 13 illustrates the development of the metallurgy during the period of reuse. The Pb grade in the final lead concentrate dropped from +70 to well below 60, a low value being recorded for week 47 (<55% Pb). The function showing the Zn grade in the lead concentrate is, not surprisingly, a mirror function of the Pb grade. The Zn grade increased from 5–7 to +17% by week 47. Since a 55% Pb and 17% Zn concentrate represents a very low commercial value it was necessary to take steps to improve the results. By cutting out the reuse loop and replacing tailings pond water by lake water, the deteriorating trend was broken. In a few weeks the concentrate grade had returned to the +60 side.

During the period of reuse the zinc concentrate remained fairly stable in composition, though the

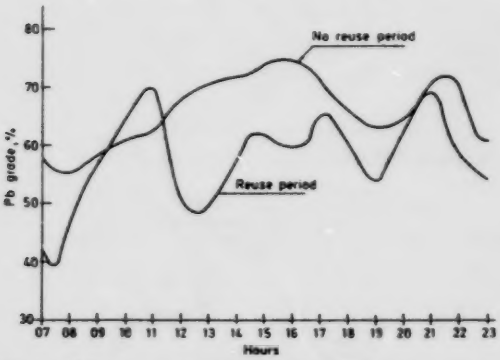

Fig. 14 Zinkgruvan concentrator: Pb grade in Pb concentrate versus time with and without reuse

amount was influenced by the zinc losses to the lead concentrate. Along with the very clear deterioration in lead flotation week by week, as shown in Fig. 13, short time disturbances in hourly and shift by shift frequencies occurred that were difficult to master.

A typical example of such short-range fluctuations in the lead flotation is given in Fig. 14. Within a 16-h period four complete cycles of ups and downs are recorded for the reuse system, whereas the no-reuse system shows only two such periods. During the reuse period the addition of flotation chemicals had to be adjusted to compensate for the successively changing chemical conditions brought about by the reuse water. The most significant change in flotation characteristics was observed in the bulk flotation, in which the sphalerite became very difficult to recover. It was frequently observed that zinc losses suddenly increased dramatically—for example, from 0.15 to 1% Zn in less than one hour. Obviously, the spontaneous activation of sphalerite by lead ions was offset by the new system. By the addition of copper sulphate it was possible to reduce the zinc losses: this, however, had a strong impact on the separation circuit. The relatively weak mode of zinc depression used was clearly inefficient, despite the increase in the amounts of depressants. A fluctuating pattern for the lead concentrate grade (Fig. 14) is typical of this period.

The reuse water gradually lost its basic character during the test period. The addition of sulphuric acid to the bulk flotation circuit could be drastically reduced. Some typical data on water quality variation during the reuse period are presented in Table 5. The clarification pond overflow, which was reused, showed, periodically, significant contents of hydrogen sulphide. The reason for this obviously strongly reducing condition in the water system is probably complex: circulation of water could be one explanation; another might be the fact that the tailings and clarification ponds were newly taken into use for this purpose and that the content of organic matter in the ponds caused strongly anaerobic conditions.

At present the concentrator is reusing clarification pond water only for the backfilling system. A future new test campaign with more extensive reuse is under consideration and it is expected that the ponds will stabilize sufficiently for reducing conditions such as those experienced during the prior test period not to occur.

Reuse at Falu concentrator—a MinFo project

From the above it is evident that extensive activity is under way at many Swedish mines with the aim of reducing fresh water consumption and effluent flow. The activities are, as a rule, fairly specific, being governed by local conditions. Since many of the problems involved in water reuse are common to several plants, a study of the subject within the central R & D foundation, MinFo—Swedish Mineral Processing Research Foundation—was initiated. Since 1978 this study has had the objective of determining the metallurgical implications of reuse of a tailings pond

Table 5 Zinkgruvan water quality data during reuse period

	Tailings water from concentrator (filtered)	*Tailings pond overflow*	*Clarification pond overflow (reuse water)*
Temperature, °C	8–22	0–15	0–15
pH	7.4–9.1	7.5–8.1	6.9–7.4
BoD 7, mg/l	11–67	2–7	0.4–6
Oxygen, mg/l O_2	2.3–6.4	0–9	0–10.5
Hydrogen sulphide, mg/l H_2S	0.06–3.4	0.04–3.5	0–32
Nitrate, mg/l NO_3-N	1.5–3.9	0.38–2.1	0.01–2.1
Sulphate, mg/l SO_4	205–390	230–330	180–330
Thiosulphate, mg/l S_2O_3	–	–	6.2–7.0
Sulphite, mg/l SO_3	–	–	0

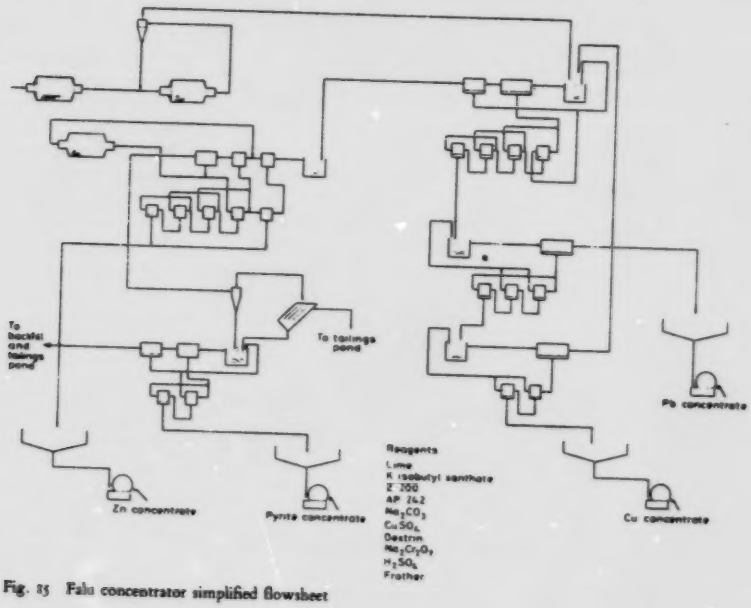

Fig. 15 Falu concentrator simplified flowsheet

water at a complex sulphide ore concentrator. The plant selected is that of Stora Kopparbergs Bergslags AB at Falun (see Fig. 3).

The concentrator treats a highly complex and mostly compact pyrite ore grading 0.3% Cu, 2.0% Pb and 6.1% Zn at a yearly rate of 200 000 ton. After grinding in rod- and ball-mills to 80% −70–80 μm—a Cu–Pb bulk concentrate is floated and separated by depression of Pb (see Fig. 15). The Cu–Pb tail is floated for zinc and then for pyrite. After desliming in hydrocyclones 50% of the tailings (120 000 t per year) is used for backfilling. The fines are pumped to a tailings dam after the addition of lime to maintain a pH in the tailings pond effluent of at least 7. Tailings pond water had not previously been reused: reuse of such water could, in principle, be made in one or more of the four separate flotation circuits. To determine to which circuit to recycle tailings pond water and what reuse/fresh water ratio to use an indicative bench-scale series of tests was run.

It was realized that the metallurgical impact due to reuse could not be forecast from simple batch experiments. It was also felt that complicated cycle tests at the bench scale, though giving more substantial data, still leave too many time- and scale-related questions unanswered. It was therefore decided to use batch tests as very rough indications only and to assess the impact on the metallurgy at the full scale. Tailings pond water

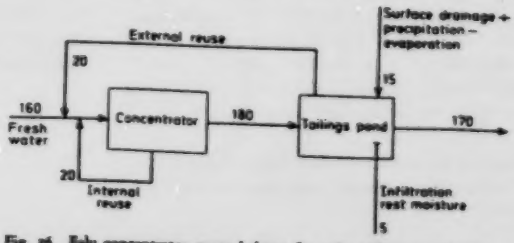

Fig. 16 Falu concentrator water balance for 75% tailings pond water in mixed water system (m^3/h)

was used in different proportions than process water in Cu–Pb flotation, Zn flotation and pyrite flotation performed as single bench test runs. Based on the test results it was decided that tailings pond water should be reused for dilution and spraying throughout the process; fresh water alone should still be used for preparation of reagent solutions, vacuum pumps, sealing water and cleansing applications; and, where used, the reused water should be added in a 25% mixture with fresh water and, if no deterioration were observed, it should be increased to 75% proportion. The water system used is illustrated in Fig. 16. The tests were started in November, 1979.

A couple of weeks after start-up it was decided to increase the reuse percentage in the mixed water system from 25 to 75%. This high proportion, however, could not be maintained for more than two months because of severe pipe-blocking problems caused by precipitation of gypsum. The tailings pond water constituted a saturated calcium sulphate solution, which was brought to precipitation at the temperature increase when piped into the concentrator building. At present (March, 1980) the proportion of reuse water is 25% in the mixed water system.

Table 6 Falu concentrator reuse water quality, December, 1979

Temperature	2.5	°C
pH	7.0	
$S_2O_3^{2-}$	72	ppm
SO_3^{2-}	5	ppm
S^{2-}	0.5	ppm
SO_4^{2-}	1580	ppm
Cu	0.1	ppm
Pb	0.35	ppm
Zn	0.52	ppm
Oxygen	6.5	ppm
Conductivity	225.3	mS/m
Suspended solids	20.8	ppm
Suspended organics	2.0	ppm
Turbidity	14	NTU
Frothing	1.2	cm*

*Froth column developed during standardized aeration.

As a routine, the composition of the reuse water is checked at regular intervals—more frequently when changes are introduced. So far, no accumulation trends have been observed. The variations recorded are mainly functions of pH variations in the pond due to variations in the additions of lime to the tailings. A representative set of water quality data from the period with high reuse percentage is shown in Table 6.

The metallurgy is followed by normal shift assaying. For various periods the selectivity in the Cu–Pb flotation for Cu and Pb against Zn and pyrite has been disturbed by reuse water. It has been possible, however, to correlate such disturbances to extreme water compositions with low pH and increased Cu ion content caused by malfunctions in the lime dosage system for tailings.

It is planned to maintain the reuse loop throughout 1980 to enable long-term changes and seasonal impacts to be followed.

Summary

The practice and experience of reuse reported here are based on a few examples only. Generalized conclusions are hard to draw because of widely differing local conditions. With this in mind the most important experiences, mainly from external reuse, can be summarized as indicated below.

Reuse is practised to some extent in all the concentrators described.

The reuse percentage is, in some cases, limited by precipitation phenomena in pipes and spray nozzles. More often, however, the reuse percentage appears to be limited by adverse effects on the floatability of the minerals.

Lead–zinc ores of minimal mineralogical complexity have shown extreme sensitivity to reuse water addition to the final grinding and the flotation circuits. The harmful influence on lead concentrate grade is dramatic. Copper–zinc–pyrite ores have shown a deterioration when reuse water has been employed in the final grinding and flotation circuits. Lower recoveries of copper and zinc have been reported. Pyrite circuits, however, seem to tolerate reuse water addition. Extensive reuse is accompanied by highly unstable process performance, specifically in the zinc circuits. Because of the harmful influence of reuse water in the final grinding and flotation circuits its use has been restricted, in the main, to primary grinding (as a mixture with fresh water), pyrite flotation, dilution of tailings before backfill cycloning and other dilution and cleansing applications where its influence on flotation is negligible.

To study the mechanisms involved, and particularly the metallurgical implications of water reuse, comprehensive work is being undertaken by the central research body and the mining companies.

Acknowledgment

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FULL SCALE TEST OF PROCESS WATER REUSE IN A COMPLEX SULPHIDE ORE CIRCUIT

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ABSTRACT

Full scale tests involving reuse of water from a tailings pond have been performed on two occasions with the same ore. The tests were made before and after the pond froze over in order to determine whether reduced oxygen supply has any effect on the sulphur anion concentration in the water, and how this and other factors affect the flotation process. Anions were analyzed by ion chromatography, which enables unstable sulphur anions to be detected quickly.

The tests showed that the greatest problem during short periods of water reuse is that the froth layer alters its nature in a way that makes it difficult to control the flotation process and creates practical problems with regard to pumping the froth. Further tests will have to include some means of analyzing suspended colloidal and organic matter, among other things, to find out what happens to the froth layer. The tests should also cover a longer period of time to enable observation of any long-term effects.

INTRODUCTION

As a result of pressure on the mining industry to start recycling its process water on a larger scale with a view to reducing water pollution from mines and concentrators, the Swedish mining industry, both under its own auspices and through the Swedish Mineral Processing Research Foundation (MinFo), has invested in an extensive program of systematic reclamation trials at a number of concentrators in Sweden. These trials involve the use of modern analytical techniques in an effort to follow pulp chemistry events as closely as possible when the source of process water changes.

Detailed pulp chemistry data from flotation circuits in Australia have been published by Woodcock & Jones (ref.1,2,3,4). The emphasis of their investigations was on metals in solution, pH, redox potential, O_2(aq), residual reagent concentrations, and concentrations of free and complexed cyanide. Other anions were not investigated, except with regard to the influence of sulphite dosage on O_2(aq) and redox potential.

Studies of the effect of sulphur anions (ref.5) on the flotation properties of sulphide mineral have been made in Norway. These studies were mainly concerned with the formation of thiosulphate as a function of pH, oxygen supply,

temperature, reaction time and particle size. Both laboratory, pilot scale and full scale tests were performed. The results indicate that the thiosulphate content of the pulp can have a disturbing effect, especially on copper activation of sphalerite.

A general description of water recycling experiments performed by a number of mining companies at concentrators in Sweden has already been published (ref. 6). It also includes preliminary results of the MinFo-supported experiments at Stora Kopparbergs Bergslags AB's concentrator in Falun. A more detailed account of the latter has since been published (ref.7).

The Division of Mineral Processing of the Luleå University of Technology has been commissioned by the MinFo to work on MinFo Project No. 15, "Circulation and Purification of Process Water". Some of the experiments have been performed at Boliden Mineral AB's concentrator in Kristineberg. In consultation with Boliden Mineral AB it was decided to run water reuse trials with Näsliden ore; this is a complex sulphide ore with high pyrite, pyrrhotite and arsenopyrite grades, so high concentrations of thiosulphate could be expected. Average assays of Näsliden ore are 1.4 g/t Au, 36 g/t Ag, 1.1% Cu, 2.9% Zn, 0.3% Pb, 1.3% As and 28% S.

The present paper reports the results of pulp chemistry measurements in experiments with water reuse in the external loop during Näsliden ore campaigns in October 1982 and April 1983. The object of the first campaign was to trace the concentration of sulphur anions with an ion chromatograph during a brief water recycling experiment. A secondary objective was to obtain background data for future measurements.

The experiments in April 1983 were a repetition of the earlier water recycling experiment. In October the tailings pond was free from ice, so availability of dissolved oxygen in the water was good. It was therefore interesting to repeat the experiment at a time when the pond had been covered with ice for 4-5 months to see if the shorter oxygen supply affected pulp chemistry conditions in any way. In theory the oxidation of sulphite, thiosulphate and polythionates should slow down when the pond is ice-covered, which would mean that the concentrations of these ions in the reused water ought to be higher during the winter than in the summer and autumn.

DESCRIPTION OF THE PLANT

The Kristineberg concentrator processes about a million tonnes of ore annually from the mines at Kristineberg, Näsliden and Rävliden. The ore is graded into five qualities, which are processed campaignwise in the two sections of the plant. Annual output comprises 35 kt copper concentrate, 65 kt zinc concentrate, 5 kt lead concentrate and 110 kt pyrite concentrate.

The water recycling experiments were performed in Section A of the plant. This is described briefly below; see also the outline flowsheet in Fig. 1.

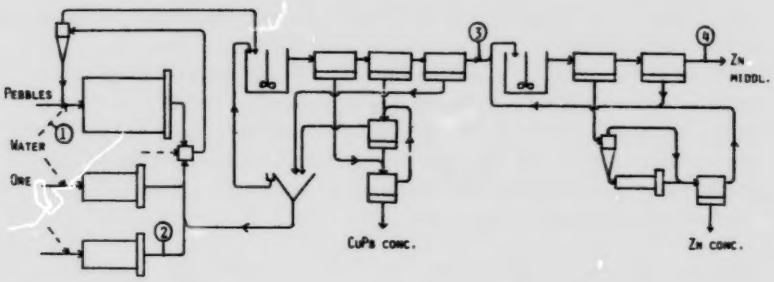


Fig. 1. Kristineberg concentrator, simplified flowsheet. Circled numbers show sampling points

Primary grinding takes place in two parallel rod mills, and secondary grinding in a pebble mill in closed circuit with a hydrocyclone. Pulp is fed back from copper flotation to the mill circuit for regrinding. Milk of lime is added to the rod mill feed to adjust the pH to 11-12. There is no actual regulation of pH; the lime dosage is a fixed proportion of the total amount of lime supplied to the section.

Copper-lead flotation is divided into two rougher stages, one scavenger stage and five cleaner stages. Flotation is performed at pH 11.3 (milk of lime) with amyl xanthate as the collector and pine oil as the frother. Zinc sulphate and sodium bisulphite are added in the cleaner circuit to depress zinc. If the lead grade in the copper-lead concentrate exceeds 10-15% by mass, the concentrate is diverted to a separation circuit where lead is depressed with bichromate and copper is floated.

Zinc flotation comprises rougher and scavenger stages and five cleaner stages. The rougher concentrate is reground in a smaller ball mill. The zinc mineral is marmatite containing about 9% Fe; it is activated with copper sulphate and then floated at pH 11.5 with isopropyl xanthate as the collector and pine oil as the frother.

Pyrite flotation is performed on two of the five qualities of ore. No further description is given here because the experiments were performed with Näsliden ore, which does not undergo pyrite flotation.

Water samples were taken at four points for chemical analysis and surface tension measurement: feed water to the pebble mill, discharge from rod mill

No. 2, Cu-Pb flotation middlings, and Zn flotation middlings. On-the-spot measurements of pulp pH, redox potential and temperature (April campaign only) were also made at these points. One set of samples was taken in the morning, and another in the afternoon. It took about four hours to collect and analyze a set of four samples.

In these experiments the section was initially run on fresh water only, reuse water from the tailings pond being subsequently piped into the water supply to the section. Fresh water was however used throughout for dilution of the hydrocyclone feed and the liquid seals of the horizontal pumps. The proportion of recycled water was therefore never more than about 75% of the total volume of process water in the section.

EQUIPMENT FOR SAMPLING AND ANALYSIS

Sampling equipment

Sampling for anion determination, especially for determination of unstable sulphide, sulphite and thiosulphate ions, makes heavy demands on equipment and technique. The equipment must allow the samples to be taken quickly, and the samples must be protected as far as possible against oxidation until they are transferred to analytical instruments. The sampling equipment was assembled from standard Millipore(R) components (see Fig. 2).

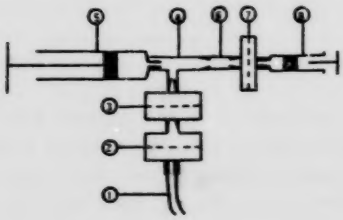


Fig. 2. Equipment for quick sampling of mineral pulp.
1. Sampling hose, 100 mm
2. Plastic filter holder, ø 25 mm, with wire gauze strainer (found by later experiments to be unnecessary)
3. Plastic filter holder, ø 25 mm, with 8 micron membrane filter
4. Plastic two-way valve
5. Plastic sampling syringe (pump), 50 ml
6. Plastic hose connector, ø 4 mm
7. Disposable plastic filter, ø 25 mm, 0.22 micron
9. Disposable syringe, 2 ml

Suitable quantities of mineral pulp samples were taken with a dipper and transferred to a 5-litre plastic pail. After brief sedimentation (<5 min), a

sample of 2-10 ml was sucked from the top layer of pulp in the pail. A separate sample was then taken from the pail and filtered for surface tension measurement and cation analysis.

The filter holder with the wire gauze strainer was removed for sampling of process water feed; the sample was sucked straight from the dipper and the quantity obtained in this way, about 50 ml, was used for ion chromatography, surface tension measurement and cation analysis.

Samples for cation, total sulphur and bicarbonate analysis and for surface tension measurement were filtered through an OOR filter and then through a 1.2 micron membrane filter.

The elapsed time from collection to injection into the ion chromatograph was 5-10 minutes for feed water samples and 10-15 minutes for pulp samples.

Surface tension measurements

Surface tension was measured with a Krüss Du Noüy ring balance. The platinum ring was rinsed in distilled water and heated in the flame of a methanol burner between measurements. The glassware was cleaned by boiling in distilled water.

Two measurements were made on each sample; tables and figures show mean readings. It may be noted that in the October campaign the second reading of a sample was consistently higher than the first. This is probably attributable to contamination with methanol (purum) from the spirit burner. Methanol (p.a.) was used in the April campaign, and this cured the problem.

After the surface tension measurements the same sample was poured into 100 ml flasks for analysis of cations, etc. This was done during the October campaign only, the reason being that filtration capacity was limited. Use of the spirit burner may therefore have contaminated the samples, but any contaminants were organic and would not have affected the analysis of inorganic substances.

pH, redox potential and temperature measurements

These measurements were made on the spot in the pulp flow, as the redox potential of the pulp rises sharply if the sample is exposed to air. It is likewise important that the measurements are made on unsedimented pulp samples. Elapsed time between sampling for anion analysis and redox measurement was 10-15 minutes. Temperatures were also measured during the April campaign.

The readings were taken with a battery-powered Radiometer PHM 80 pH meter. The GK2401C combination electrode was used for pH measurements, and the P101 platinum electrode together with the K401 calomel electrode for potential measurements.

Before each measurement the platinum electrode was carefully wiped clean with a moistened paper polishing cloth sprinkled with Al_2O_3 powder. The calomel electrode was calibrated daily against a similar electrode stored in the same

way as the one used for measurements. The difference in potential never exceeded 3 mV. Potential readings were corrected for the normal potential of the calomel electrode (+245 mV at 25°C).

Prior to pH measurements the pH electrode was checked against a suitable buffer solution. Two buffer solutions of pH 9 and 11 respectively were used, the former for process feed water measurements.

Ion chromatography

Samples were sucked into the large syringe (see Fig. 2). In the laboratory the disposable filter was attached and the sample was expelled into the disposable syringe, which was then removed and placed in the sample port of the ion chromatograph, after which the sample (approx. 0.5 ml) was injected.

The ion chromatograph, a DioneX 2010i, is equipped with a system of columns for anion analysis and two detectors, one electrochemical and one conductometric. The relative positions of the columns and detectors are shown in Fig. 3. The sensitivity of these detectors varies according to the type of ion; sulphide and thiosulphate ions are most readily detected by the electrochemical detector, while other anions were determined with the conductometric detector. The principles of ion chromatographic analysis of inorganic anions and cations are described in ref.8.

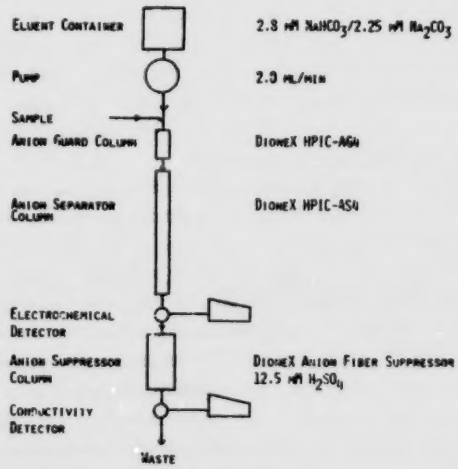


Fig. 3. Simplified representation of an ion chromatograph.

The output signals from the detectors were fed to integrators, which computed concentrations on the basis of peak areas with reference to known standard samples. During the October campaign an ordinary chart recorder and manual computation from peak heights were used for the conductometric detector. Time between samplings was governed by the time taken by the ion chromatograph (50-60 minutes) to analyze all the ions in a sample. With samples that do not contain thiosulphate this time can be shortened to 10-15 minutes.

Analysis of bicarbonate concentration

This was done during the April campaign only. The concentration of bicarbonate (HCO_3^-) was obtained by titration of a filtered (1.2 micron) sample with 0.05 M hydrochloric acid. The distance between the inflection points on the titre curve gave the HCO_3^- concentration.

Cation and total sulphur analysis

Analyses of the total concentrations of Cu, Pb, Zn, Fe, Ca and S in the samples were performed at Boliden Metall AB's Rönnskär laboratory. Filtered (1.2 micron) samples of about 100 ml were prepared for the purpose during the October campaign. One-litre samples were used in the April campaign. The samples were acidified with nitric acid to prevent precipitation of metallic hydroxides. Filtered samples in 100 ml flasks were sent for analysis of S_{tot} (as sulphate in oxidized sample).

RESULTS

Method

The October campaign lasted from 8 to 16 October inclusive; sampling began on 11 October. For an initial reference period up to and including 13 October the mill and flotation circuits were operated on fresh water only. At 0615 hours on the morning of 14 October the water supply system was reconnected to deliver reuse water from the tailings pond to the whole of Section A of the concentrator.

The April campaign began with the switch to Näsliden ore at 2155 hours on 5 April. Fresh water only was supplied to the mill and flotation circuits for a reference period lasting until 0645 hours on 8 April, when reuse water from the tailings pond was piped to the water supply system of Section A. The reuse test ended at 1230 hours on 11 April, when the fresh water supply to the system was reconnected. Sampling continued until the following day with a view to observing any transitional effects.

Pulp chemistry measurements

Detailed results of anion analysis, cation analysis, S_{tot}, and measurements of surface tension, redox potential and pH are reported elsewhere with place, time and date of sampling (ref.9,10).

The most interesting analytical results and figures derived from them are presented graphically in Figs. 4-20. These graphs have a common time axis; readings from the first round of samplings are plotted against the date, and readings from the second round against the date +0.5. (Sampling took place in the morning and afternoon.)

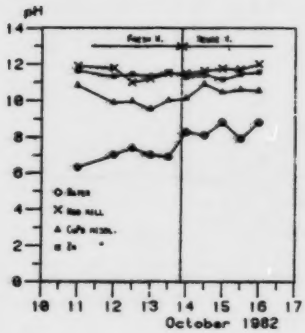


Fig. 4a. pH variations during October campaign.

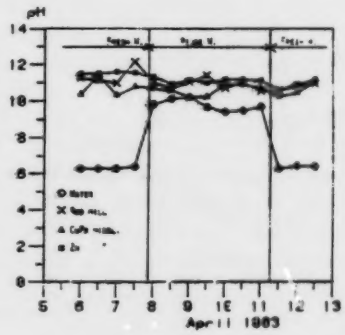


Fig. 4b. pH variations during April campaign.

The pH measurements show that changes in the pH of the feed water to the process have hardly any effect on other points (see Fig.4a&b). Indeed, no such effect is to be expected, as flotation takes place in a lime alkaline environment with pH regulation. The slight rise in pH in the Cu-Pb flotation middlings during the October campaign can be attributed to the better process monitoring that is always found in the first few days of full scale operational trials.

Redox potential readings at various points in the process show only that the redox potential of the process water has no appreciable influence (see Fig. 5a&b). There is of course a difference between measurement conditions in that the process water measurements were made in a particle-free system, whereas the other readings were taken direct from pulp. Consequently, it is not certain whether the pulp readings represent actual redox potentials (Eh) or mixed potentials, which are only comparable within the same system. For practical purposes we consider that the potential difference (Pt/S.C.E.) gives us the redox potential.

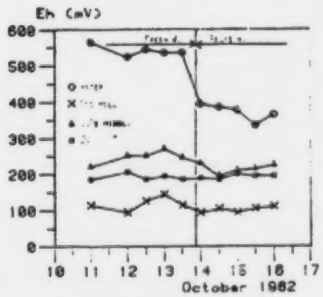


Fig. 5a. Eh variations during October campaign.

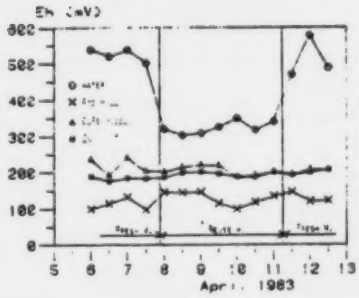


Fig. 5b. Eh variations during April campaign.

The best way to compare Eh and pH readings taken in non-uniform conditions is to plot them on Eh/pH graphs (see Fig. 6a&b). From these we can see that the various process points are well grouped and that there is no difference between readings taken during use of fresh and recycled water.

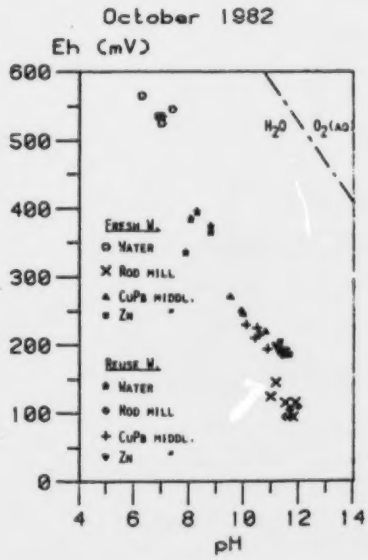


Fig. 6a. Eh/pH graph for October campaign.

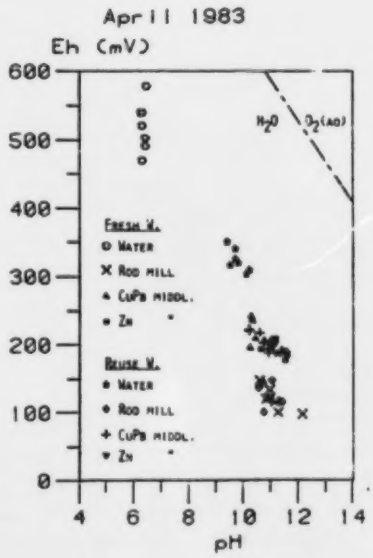


Fig. 6b. Eh/pH graph for April campaign.

Process temperatures were stable during the period of sampling (in April). Mean readings are listed in Table 1.

TABLE 1

Temperatures at process sampling points during April campaign.

Process sampling point	Temperature (°C)	
	Fresh water	Recycled water
Feed water to pebble mill	1.5	2.7
Discharge from rod mill No. 2	13.2	14.8
Cu-Pb flotation middlings	12.2	13.3
Zn flotation middlings	11.7	13.0

The chloride concentrations in the recycled water were about five times higher than in the fresh water (see Fig. 7a&b). This was partly reflected in the other sampling points, where the background level was somewhat higher.

The graphs show that the principal chloride source is the ore or substances associated with it. Concentrations in the rod mill discharge were twice as high during the April campaign as in the October campaign. This is probably because calcium chloride had been added to the ore during handling to avoid freezing problems in ore bins and chutes.

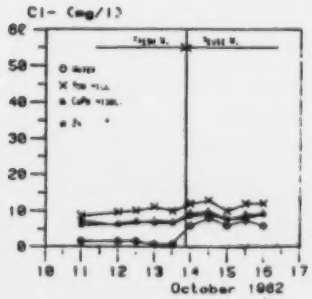


Fig. 7a. Chloride concentrations during October campaign.

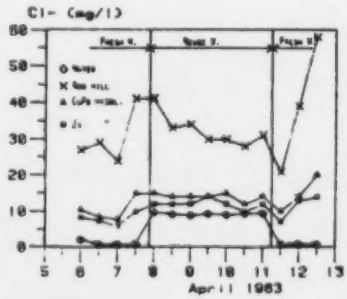


Fig. 7b. Chloride concentrations during April campaign.

Thiosulphate concentrations display a clear pattern for the October campaign, being lowest in the rod mill discharge, highest in the Cu-Pb flotation middlings, and down again somewhat in the Zn flotation middlings. The switch to recycled water produced only a marginal rise of thiosulphate concentrations in the process. During the April campaign the concentrations in the recycled water

were higher, resulting in a greater influence on the thiosulphate level in the process. No acceptable explanation has been found for the sharp rise and fall of concentration at the beginning of the April campaign.

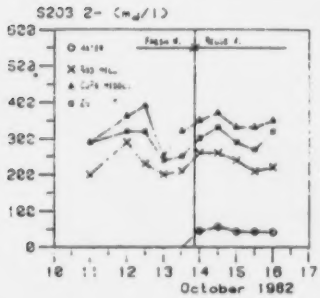


Fig. 8a. Thiosulphate concentrations during October campaign.

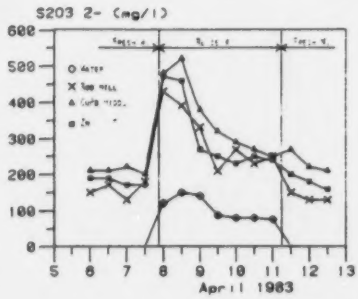


Fig. 8b. Thiosulphate concentrations during April campaign.

The sulphite concentrations show that it makes no difference in this respect whether fresh or recycled water is used (see Fig. 9a&b). The pattern of relative variations of sulphite concentration is the same as for thiosulphate - highest in the Cu-Pb flotation middlings and lowest in the rod mill discharge. Only during the recycling period of the April campaign was any sulphite detected in the process water feed.

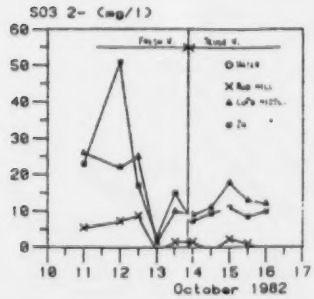


Fig. 9a. Sulphite concentrations during October campaign.

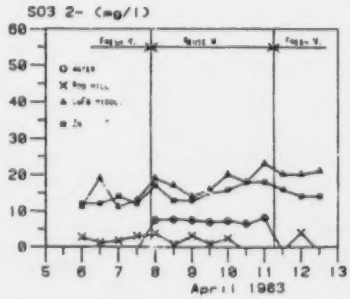


Fig. 9b. Sulphite concentrations during April campaign.

The sulphate present in the recycled feed water shows up at the other sampling points (see Fig. 10a&b). Concentrations during the October campaign were generally higher than during the April campaign; the analyses from the October campaign also show that the sulphate content of the pulp liquid can vary widely even during periods of fresh water use.

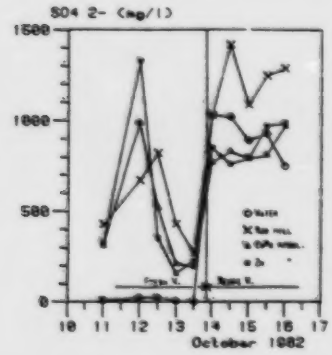


Fig. 10a. Sulphate concentrations during October campaign.

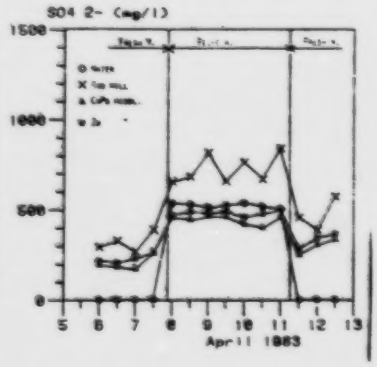


Fig. 10b. Sulphate concentrations during April campaign.

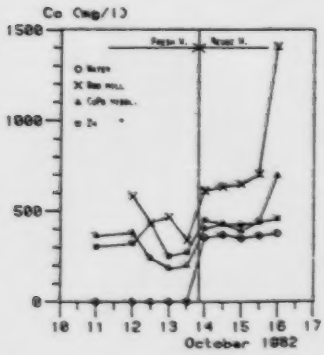


Fig. 11a. Calcium concentrations during October campaign.

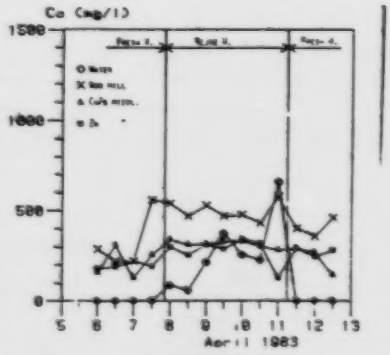


Fig. 11b. Calcium concentrations during April campaign.

The calcium concentrations in the process are highest in the rod mill discharge, and at about the same level in the middlings from both Cu-Pb and Zn

flotation (see Fig. 11a&b). The calcium concentration was very high on the last day of the October campaign. This was because the lime dosage to the rod mill was too high; at the time of sampling the pH was 12.0. It is further evident that the switch to recycled water was most clearly reflected in the rod mill discharge; the effect at other points in the process was small.

As both the calcium and sulphate concentrations show wide variations, it ought to be of interest to see whether this might be due to precipitation reactions in the pulp. To find out wheter such is the case, the ion product between calcium and sulphate was calculated (see Fig. 12a&b) and compared with the figure calculated from the known solubility of gypsum ($CaSO_4*2H_2O$), which is 2.41 g/l at 25°C (ref.11). Only at the point of discharge from the rod mill in the October campaign was there any risk that the recycled water might cause precipitation of gypsum in the pulp. Otherwise the ion product figures for the middlings are remarkably closely grouped.

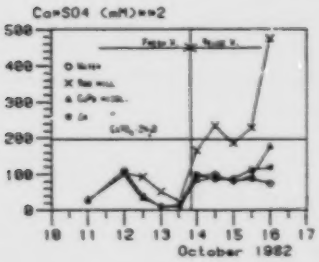


Fig. 12a. Ion product $Ca*SO_4$ during October campaign.

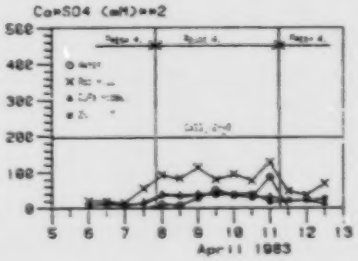


Fig. 12b. Ion product $Ca*SO_4$ during April campaign.

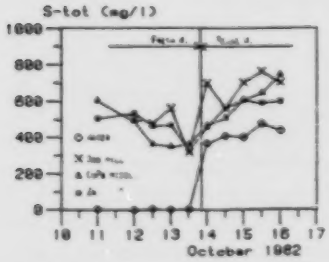


Fig. 13a. Total sulphur concentration during October campaign.

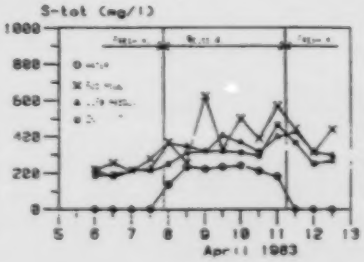


Fig. 12b. Total sulphur concentration during April campaign.

To check whether the analyses of sulphur anions were realistic, S_{tot} was also determined by a wet chemical method (see Fig. 13a&b). The analyses show that the higher concentration in the recycled water shows up at the other points in the process. Otherwise it is surprising that the S_{tot} concentrations at the various points in the process are as closely grouped as they are. A comparison with S_{tot} calculated from sulphate, sulphite and thiosulphate shows that the figures obtained by analysis are sometimes higher than the calculated figures and sometimes lower.

In the April campaign the ion chromatograph had been adjusted so that it could also analyze for nitrate (see Fig. 14). Nitrate analysis is complicated by the fact that the nitrate and sulphate peaks are eluted close to each other on the ion chromatogram, which means that high sulphate concentrations can mask smaller nitrate concentrations. The nitrate obviously originates from blasting explosive residues (ammonium nitrate) in the ore.

The bicarbonate concentration at the sampling points (see Fig. 15) was also determined during the April campaign. The concentrations vary widely, but it is evident that while the concentration is significantly higher in recycled water than in fresh water, the difference does not show up at downstream points in the process.

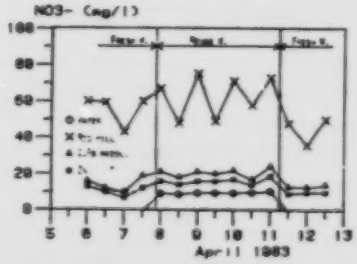


Fig. 14. Nitrate concentrations during October campaign.

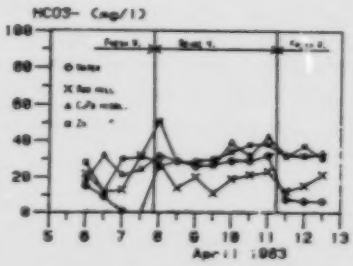


Fig. 15. Bicarbonate concentrations during April campaign.

In the course of the October campaign it was found that the sample volumes were too small to give low enough limits of detection for metals in solution. Only zinc was consistently above the limit of detection. The metal concentrations reported below (Figs. 16-19) therefore refer to the April campaign only. Metal concentrations at the sampling points were not affected by the origin of the process water. The peaks that occur are generally attributable to changes in pH.

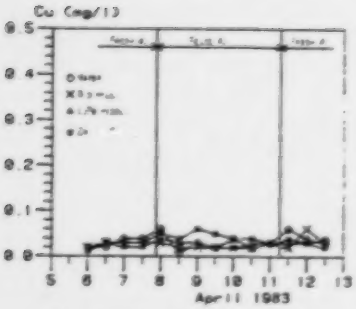


Fig. 16. Copper concentrations during April campaign.

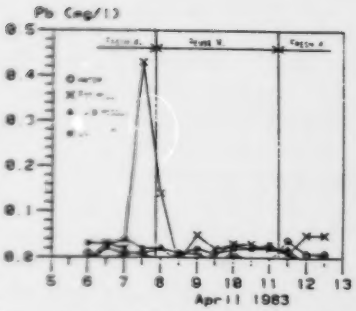


Fig. 17. Lead concentrations during April campaign.

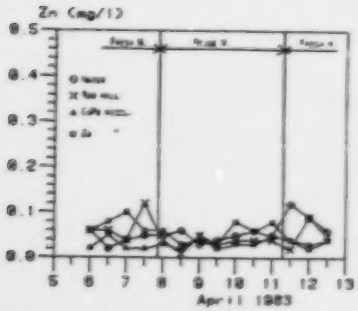


Fig. 18. Zinc concentrations during April campaign.

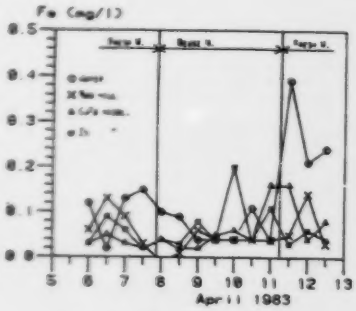


Fig. 19. Iron concentrations during April campaign.

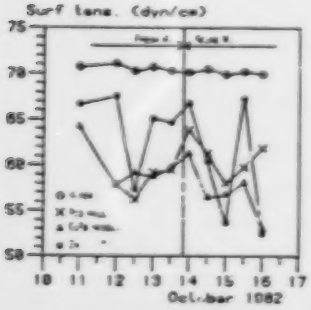


Fig. 20a. Surface tension during October campaign.

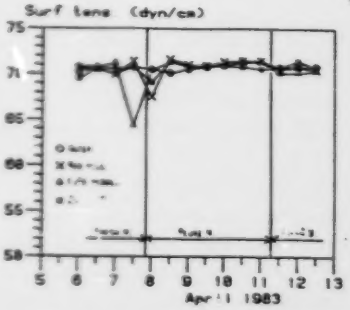


Fig. 20b. Surface tension during April campaign.

The surface tension measurements (see Fig. 20a&b) cannot account for the frothing problems that arose during use of recycled water from the tailings pond as process water. It was noted, however, that the reading were lower in the October campaign than in the April campaign. The great variations in the former can possibly be ascribed to the experimental problems mentioned earlier.

Process results

The process results are reported in detail elsewhere (ref.9,10). No dramatic effects of the differences in process water quality can be traced in the daily beneficiation statistics. The greatest problem was that the froth tended to "run" in the cleaner stages, though this is not directly reflected in the analyses of the concentrates. Consequently only the Cu-Pb concentrate grades (Fig. 21a&b) and the grade/recovery ratios for the Zn concentrate (Fig. 22a&b) are given here.

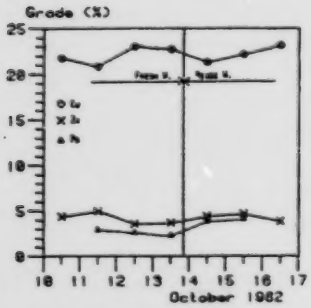


Fig. 21a. Grades of Cu-Pb concentrates during October campaign.

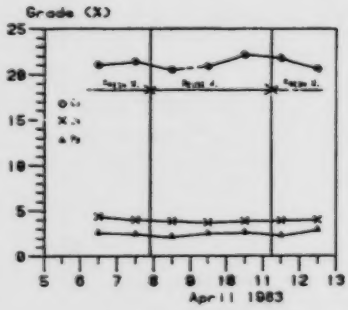
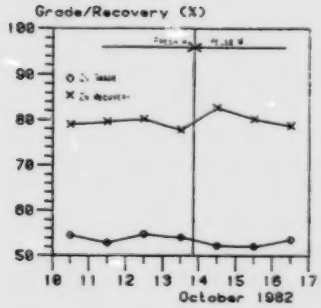


Fig. 21b. Grades of Cu-Pb concentrates during April campaign.

A certain switching effect can be detected from the daily analyses in Fig. 21 . The copper grade in the concentrate is slightly lower the day after the switch to reuse water, but this is compensated by an increase in copper recovery. To compensate for the runny froth layer and its adverse effect on selectivity, the frother dosage was reduced to about half the normal amount. The most noticeable effect of the switch is the rise in the Pb grade of the Cu-Pb concentrate during the October campaign.

The switching effect is also noticeable in the zinc concentrate (see Fig. 22a&b). The process disturbance was greater here than in the Cu-Pb flotation, and so were the problems with runny froth in the cleaner stages.



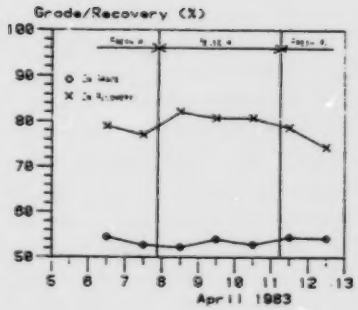


Fig. 22a. Grade/recovery ratios of Zn concentrate during October campaign.

Fig. 22b. Grade/recovery ratios of Zn concentrate during April campaign.

DISCUSSION

Sampling, October 1982

Pulp chemistry measurements detected thiosulphate concentrations ranging from 200 to 400 mg/l, so the comparatively low concentration in the recycled water did not show up in measurements at points downstream.

It should be noted that the reference samples of Kristineberg ore pulp taken in Section B during the October campaign show lower concentrations of thiosulphate than the corresponding samples of Näsliden ore pulp (see Table 2). This means that the concentration of unstable sulphur anions depends on the nature of the ore, which suggests that different ores have different levels of tolerance for such parameters as the thiosulphate content of the process water.

TABLE 2

Pulp chemistry data on Kristineberg ore in Section B.

Sampling point	pH	Sulphur anions (mg/l)		
		Thiosulphate	Sulphite	Sulphate
Discharge from rod mill	11.0	160	6	1200
Cu-Pb flotation middlings	11.6	230	52	810

There is a clear correlation between the sulphate concentration in the process feed water and the sulphate levels in the concentration process. Only at the discharge from the rod mill do conditions for precipitation of gypsum exist. At the other analysis points the value of the ion product is governed by some other complexing or precipitating reaction. The reaction in question is probably between calcium and carbonate, the latter originating from dissolved atmospheric carbon dioxide.

The sulphite concentration was consistently lowest at the discharge from the rod mill, with the exception of process water in which sulphite could not be detected. The limit of detection was about 1 mg/l.

Despite repeated attempts it was not possible to detect sulphide, S^{2-}, in any of the samples. Here again the limit of detection was about 1 mg/l. It is possible that the metallic copper gauze used in the prefilter may have precipitated any sulphide ions that were originally present, but this seems unlikely, as no sulphide ions were detected either when the prefilter was not used.

The process was relatively little affected from the metallurgical point of view by the used of recycled pond water. The effect that was noticed first was increased frothing in the cleaner stages with a consequent drop in selectivity. This was however corrected by a reduction in the frother dosage.

The results for the Cu-Pb flotation indicate that recoveries of copper, gold and silver were the same during the reuse period as when fresh water was supplied to the process. The most apparent effect was a rise of about one percentage unit in the Pb grade of the Cu-Pb concentrate.

Another noticeable effect of the use of recycled water was the formation of a hard-to-pump froth in connection with pulp X-ray analysis. The return pumps had to be restarted several times to prevent the sumps from overflowing.

Sampling, April 1983

The pulp chemistry measurements show that both sulphite and thiosulphate concentrations in the recycled water were higher during the campaign in April 1983 than in the one in October 1982. The probable reason for this is that at the time of the April campaign the tailings pond had been frozen over for five months, and the oxygen content of the water was therefore low. It is unlikely that the temperature of the recycled water, i.e. of the tailings pond, had any significant effect on the concentration of thiosulphate, as the October measurements were made just before the pond froze over.

The stable level of the thiosulphate concentration in the recycled water was about 80 mg/l compared to 50 mg/l in October. The effects of the switch to recycled water were therefore more noticeable in April.

The sulphate concentration in the recycled water was lower than in October. This was likewise due to the shorter oxygen supply in the tailings pond. There

was no risk of gypsum precipitation at any of the sampling points, even though the sulphate concentration rose considerably in the process when the reuse water was connected.

The bicarbonate concentrations indicate that there is also some carbonate activity in the pulp - probably a reaction between calcium and carbonate to form calcium carbonate. This compound will act as a calcium trap in the process, an assumption supported by the fact that only exceptionally does the ion product $Ca*SO_4$ reach the gypsum precipitation level.

Once again, the metallurgical effect of recycled water on the process was relatively small. There was however a tendency to a lower Cu grade in the Cu-Pb concentrate, though Cu recovery was unaffected. In addition, the recovery of zinc was somewhat higher, but the concentrate grade somewhat lower, during the recycling period. These observations are probably connected with the frothing problems that arose when reuse water was supplied to the process. Traditional surface tension measurements failed once again to detect any difference between periods of fresh and recycled water supply.

No immediate difference could be detected when the process switched to using recycled water, but heavy frothing occurred in the cleaner stages after 6-8 hours, while the Cu-Pb rougher flotation remained unaffected. The dosage of frothing agent (pine oil) was then reduced to less than half, and this alleviated the frothing problem. Attempts to run the process without any frother at all were unsuccessful, as the Cu and Pb grades of the Cu-Pb flotation middlings rose immediately.

The large volumes of froth made it necessary to run both the regular and standby pumps in some of the pumping stages to prevent overflowing. The froth was finely divided and contained very little mineral. Similar problems were experienced in Zn cleaner flotation, especially in the final stages. The froth from the last Zn cleaner stage was also so hard that there was some difficulty in obtaining samples of Zn concentrate for X-ray analysis of the pulp. In the Zn circuit, too, some of the pumping stages had to be doubled up.

These difficulties with froth represent the major problem connected with short-term recycling experiments: one the one hand we get a runny, poorly mineralized froth, and on the other an over-stabilized froth. This indicates that the problems are caused by one or more surfactants which are not degraded in the tailings pond; alternatively, they may be degradation products of process reagents. It also appears that the oxygen supply in the tailings pond is significant, as the problems were much greater during the April campaign.

CONCLUSIONS

The following conclusions can be drawn from these trials:

1. The concentration of sulphur anions in the recycled water is at present so low compared to the normal level in the pulp that the additional amounts are unlikely to interfere with the flotation process.
2. The use of recycled pond water gives rise to great frothing problems in the cleaner stages, probably as a result of insufficient degradation of frothers and collectors in the tailings pond.
3. The frothing characteristics of the recycled water ought to be investigated by registration of the height of the froth layer when air is blown through a column. This is only a relative method, but preliminary results indicate that it is much more sensitive than surface tension measurement.
4. As the immediate problems concerned the behaviour of the froth layer, future studies must be widened to include other methods of analysis. In particular, the content of suspended colloidal matter, the biological oxygen demand and the content of organic matter ought to be measured.
5. The studies should also include other types of ore.
6. Above all, the trials must be conducted over longer periods of time to enable detection of any cumulative effects in tailings ponds.

ACKNOWLEDGEMENTS

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The authors further wish to thank Boliden Mineral AB for allowing them to take measurements at the company's Kristineberg concentrator. Cordial thanks are also due to the personnel at Kristineberg for their unstinting help with the collection of measurement data.

Bertil Pålsson wishes to thank the staff of the CSIRO Mineral Engineering and Mineral Chemistry Divisions for thought-provoking and valuable discussions.

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NICKEL-COPPER FLOTATION

Water management for Ni-Cu operations at Falconbridge at Sudbury and at Onaping mine-mill complexes and at INCO Metals, Copper Cliff Works is discussed in trip reports in Appendix I.

Although these trip reports primarily discuss effluents and tailings and macro site water management, one interesting observation was made at the Onaping operation. Here, the seepage from old tailings drains into the Fecunis Lake adjacent to an operating mill. Previously, the Fecunis Lake water containing nickel at levels above 10 mg/l used to drain into Moose Lake which forms part of the macro recycle and treatment system applied at Onaping. Through reversing the flow of Fecunis Lake water, it is now used as feedwater to the mill which operates at pH 10. At the high pH, Ni precipitates from solution. Consequently, by rearranging water flows, the need for a lime precipitation plant to treat Fecunis Lake water was avoided. In this case, the mill acts as a treatment plant, discharging the water ultimately with mill tailings from which it decants to Upper Moose Lake and ultimately to Lower Moose Lake with well below 1 ppm Ni^{2+}.

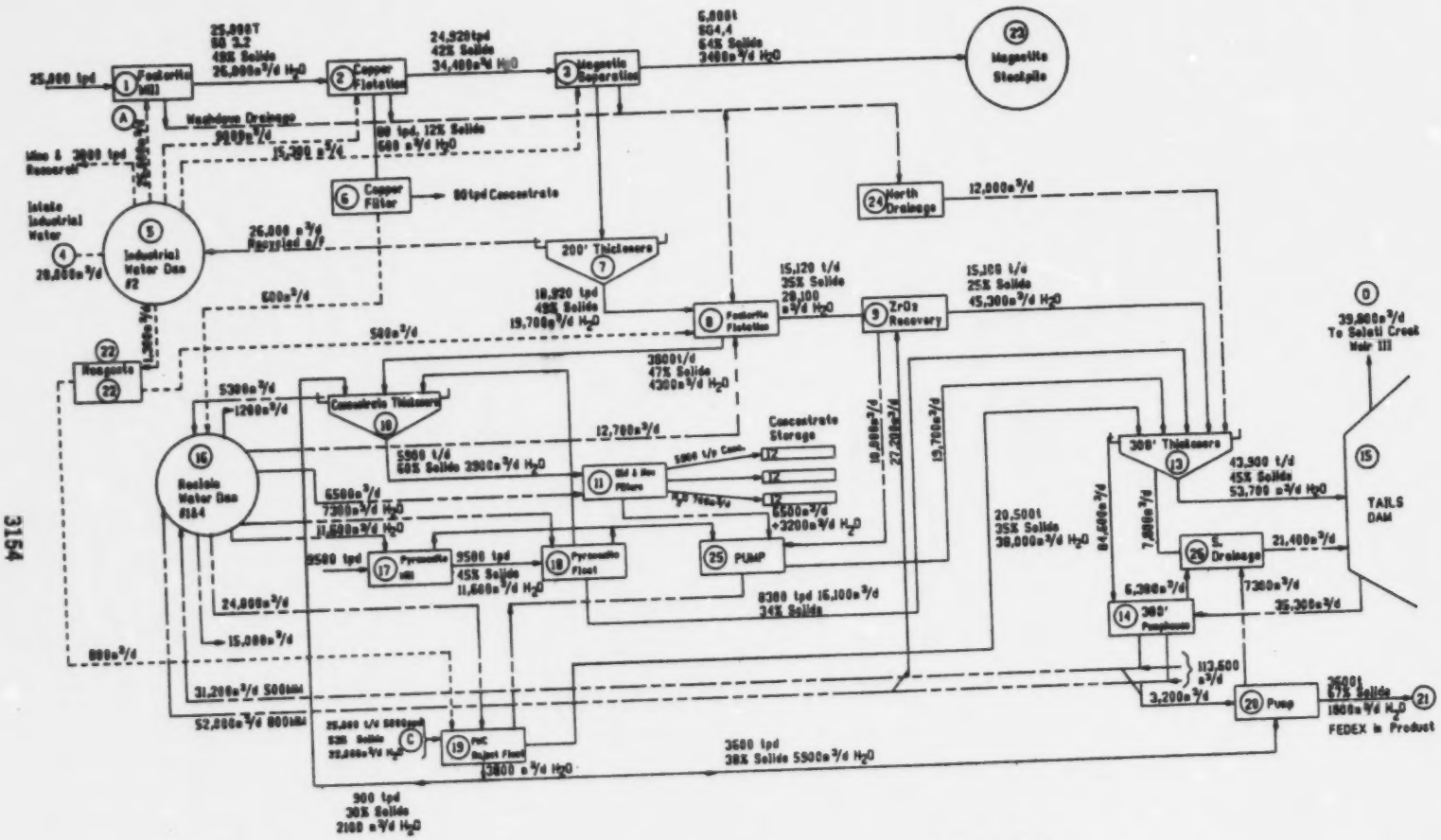
At Rustenburg there are several mines that produce a norite ore containing copper-nickel sulfide minerals associated with platinum group metals.

A former chemical treatment plant not belonging to any of the present mining companies operating in the area today used to discharge a sodium sulfate effluent to an unlined impoundment in this area. Apparently, this Na_2SO_4 solution seeped into the mineworkings and, on the way, leached magnesium from the pyroxonite rocks. When this minewater was used in the flotation concentrators, apparently problems resulted, e.g., higher reagent consumptions, etc.

During the 1983-1984 drought, great emphasis was placed on the need to save water, and more mill tailings water had to be recycled with the result that TDS levels built up. Concentrator metallurgists were making enquiries about how to overcome recovery deterioration effects which they ascribed to water quality, but not one of the operations would provide any information on these aspects for this report. Platinum recovery metallurgy details are considered company confidential in South Africa.

Trip reports on Falconbridge at Sudbury and at Onaping describe the intriguing integrated systems approach adopted by this company in their water management program. These are older mine-mill complexes, which started operations under a different set of environmental rules, but have innovatively adapted to meet the needs of the 1980's.

FOSKOR WATER FLOW DIAGRAM



LEGEND

- INDUSTRIAL WATER
- SLURRY
- RECYCLED WATER
- WASHDOWN DRAINAGE

1. FOSKORITE MILL
2. COPPER FLOTATION
3. MAGNETIC SEPARATION
4. INDUSTRIAL WATER
5. INDUSTRIAL WATER DAM #2
6. COPPER FILTER
7. 200' THICKENERS
8. FOSKORITE FLOTATION
9. ZrO2 RECOVERY
10. CONCENTRATE THICKENERS
11. OLD & NEW FIBERS
12. CONCENTRATE STORAGE
13. 300' THICKENERS
14. 300' PUMPHOUSE
15. TAILS DAM
16. RECLAIM WATER DAM # 1 & 4
17. PYROXENITE MILL
18. PYROXENITE FLOAT
19. PMC REJECT FLOAT
20. PUMP
21. FEDEX PRODUCT
22. REAGENTS
23. MAGNETIC STOCKPILE
24. NORTH DRAINAGE
25. "GAT" PUMPS (IN A HOLE)
26. S. DRAINAGE

PHOSPHATE-COPPER

Phalaborwa-Foskor

Phosphate and copper minerals are recovered by flotation from a carbonatite ore at Phalaborwa, Transvaal, where two operators mine a huge deposit. Palaborwa Mining Company (Rio Tinto) recovers a copper sulfide concentrate and pumps their tailings across the fence to Foskor (Phosphate Development Corp.) which then recovers foskorite minerals. Foskor also teats 25,000 tps ore mined and stockpiled by PMC by crushing and grinding, followed by a sequential flotation of a copper sulfide concentrate and phosphate minerals followed by heavy mineral recovery of baddeleyite.

To operate these two flotation plants treating a combined total of 50,000 tpd ore, Foskor uses 28,000 m^3/d of "industrial water" to augment 22,000 m^3/d water received with the 25,000 tpd PMC tail stream. 50,000 m^3/d water enters the plantsite , and 39,800 is discharged to the creek as an effluent while 4,300 m^3/d is lost through evaporation. The "industrial water" is drawn primarily from the Olifants River seven km away.

A detailed water flow diagram and water balance is shown in the trip report on Phosphate Development Corp. in Appendix I.

In other words, Foskor uses about 28,000 m^3/d fresh water, and recycled water ammounts to about 22,000 m^3/d or 44% of total needs. Net water consumption works out to 1 m^3/t ore treated. Considerable quantities of water are internally recycled in the plant.

From a water management point of view, the most interesting aspect is the effect of high TDS on the flotation process and how it has been overcome through reagent addition. Foskor faces a water quality problem in that the 22,000 m^3/d water delivered with PMC tailings contains 5,100 ppm TDS of which 3,408 ppm is hardness. This water contains 1,260 mg/l Ca and 2,148 mg/l Mg as well as high concentrations of F^- (5.4 mg/l) and alkali metals. Concentration of SO_4 is 3,000 mg/l.

The trip report shows how water is recycled to various sections of the plant so that new water is used for milling and flotation of the ore crushed by Foskor, whereas reclaim water is used for treatment of the PMC flotation tailings from which, in turn, water is pumped to the tailings pond via a thickener to recover water which is recycled to a reclaim water dam.

Foskor has developed a flotation process which allows the poor quality water delivered with PMC tailings to be used.

However, testwork has shown that if 80% of the PMC water is replaced by fresh water, then a significant savings in reagents results.

Water quality effects are due primarily to interaction between the ore and water. Main gangue minerals in the PMC tails feed to Foskor are calcite, dolomite, phogopite, and olivine/serpentinites.

The hardness of the water interfers with the froth and reacts with the fatty acid collector used to float apatite to form Ca and Mg oleates. These are insoluble soaps and have a detrimental effect on the float system.

To overcome the effect on flotation, increased amounts of gangue depressant have to be used. In the primary flotation circuit, poly glycol ether is used as a gangue depressant. In the flotation plant treating PMC tails, poly glycol ether plus a modified polysaccharide is used.

Several types of poly glycol ethers have been tested. The one found to be most suitable is a nonyl-phenol tetra glycol ether. Polyglycol ether helps to emulsify the fatty acid and may adsorb on the calcite surfaces to help depress the gangue.

Chemically modified polysaccharide is supplied to Foskor by Trochem SA (Pty) Ltd. The modified polysaccharide is manufactured from guar beans and is known as Acrol LG 21 and Acrol LG 31. Typical doses are 120g per ton solids. Foskor's annual consumption of flotation reagents is confidential, but it is known to be "substantial," amounting to several million rands.

If clean water is used for flotation, a carboxylic acid derivative collector such as Hoechst 3309 has been indicated to work well and economically. However, with over 5,000 ppm TDS and such high hardness, the consumption of this experimental collector has been found to be excessive as it appears to be precipitated before it can get to the mineral.

Addition of waterglass Na_2SiO_3 has been found to act as a modifier/dispersant and also as a slight depressant for mica. Foskor uses about 600g waterglass per ton solids in their flotation reagent mix. Waterglass addition has also been found to remove some calcium and magnesium from solution.

Considerable testwork of flotation reagents and effects on and of ion populations in flotation pulps on flotation reagent consumption and recovery have been carried out by Foskor. The Council of Mineral Technology MINTEK carried out some considerable work on the same aspect of Foskor's flotation in the early 1970's as described by LOVELL, et al. (1971). Their work showed, amongst other things, that Foskorite recovery and selectivity of the flotation improved markedly with waterglass addition reaching a maximum at between 50 and 120 ppm Si in solution.

In the past, flotation difficulties in the main plant could sometimes be ascribed to a change in the raw water quality. The hardness of the industrial water fluctuated with

the seasons, reaching a peak before the first summer rains, and was shown to have an effect on apatite recovery from Foskorite.

The amount of suspended solids in industrial water, when the Olifants River was in flood, also was found to have an influence on apatite flotation, both in lab tests and in the plant.

Foskor investigated the roles of additional ions present in flotation plant water, and their interaction with ions from flotation reagents and from the mineral constituents of pyroxenite and foskorite ore, with particular emphasis on calcium and magnesium.

Several interesting observations were made:

1. Foskorite constituents, e.g., phlogopite, olivine, magnetite, calcite, and apatite all contributed ions to the water phase of the flotation pulp, and an alkaline pulp was obtained in each case.

2. Reagent additions to the ore pulp in dosages giving optimum apatite recovery constantly caused a removal of ions from the aqueous phase.

3. A significant removal of silicate ions was consistantly found. Soluble silicate was removed from solutions by gangue minerals calcite, and iron-bearing olivine, magnetite, and phlogopite, but not by apatite. Sodium silicate acts as a depressant of magnetite and olivine and lowers the iron content of apatite concentrates.

4. Very little flotation depression of calcite was observed in the absence of apatite although, in the presence of apatite, the same reagent combination gave excellent apatite-calcite separation and selective depression of calcite.

5. Once the mineral mixtures had been milled and conditioned with all essential flotation reagents, the flotation water could be filtered off and be replaced by demineralized water and the mineral subjected to flotation without any subsequent change in flotation recovery of apatite.

This latter discovery is a very significant observation, and it would be important to find out whether the same principles apply in any other cases--i.e., water quality in the mill has an important effect on the coatings on the mineral grains which determine flotation characteristics in this case.

EFFECTS OF REAGENTS AND ORE ON PULP WATER QUALITY

- Foskorite in different stages of weathering contributes calcium and magnesium to the system, and an alkaline pulp is always obtained.
- The reagents sodium hydroxide and sodium silicate soften the flotation liquid.
- Less reagents are necessary for successful flotation of apatite when demineralized water is used compared to industrial water.
- The order of addition of sodium silicate and sodium hydroxide affects the flotation recovery of apatite--soluble silicate reagent is removed from solution by the ore.
- Addition of sodium silicate and sodium hydroxide, either separately or together, caused a reduction in calcium and magnesium in solution in the pulps.
- Phlogopite contributes potassium, calcium, magnesium, and sodium to pulp solutions.
- Addition of NaOH to several mineral slurries resulted in a reduction in Ca and Mg that went into solution.
- Addition of calcium to a phogopite slurry resulted in an increase in potassium ions in solution.

ENVIRONMENTAL AND EFFLUENTS

Although flotation is a physical process, reactions between gangue and ore minerals and water or reagents can and does change the chemistry of the tailings effluent. In the case of Foskor, a high TDS and high F^- ion concentration at 3.9 ppm in tailings pond decant solution must be taken into account environmentally. A special dispensation from the Dept. of the Environment allows Foskor to discharge effluents to 4 ppm F^-.

PMC tailings water contains around 140 ppm K^+ which has been suspected of being a possible cause of a fishkill, but this has not been confirmed. Surprisingly, even though phosphate minerals are the principal value recovered, the level of PO_4^{3-} in recycled and effluent waters remains well below 1 ppm.

SCALE AND CORROSION

Despite very high TDS levels (3,500-5,500 ppm) with high Ca^{2+} (400-1,200 ppm) and SO_4^{2-} (1,500-3,000 ppm), which are well in excess of saturation, scale is not a problem

at Foskor. One possible reason for this is the very high Mg^{2+} (900-2,000 ppm) which seems to modify the solubility of $CaSO_4$, but no doubt other factors also play a role.

RECYCLING

The Foskor operation recycles large quantities of water, and the recycling flow pattern is relatively complicated as is shown in water balance diagram. Solution flows in two main recycling loops designed to keep the PMC tailings water out of the main Foskor flotation circuits while reclaim water is used to dilute the PMC tailings.

FLUORSPAR FLOTATION

Martin Wilson of U.S. Borax and Chemical Corp. was awarded U.S. Patent 4248708 dated February 3, 1981, which describes an improved process for treating water in fluorspar flotation circuits which substantially reduces slimes and interferring soluble materials, allowing the water to be recycled in the process and also improving its quality to make it suitable for discharge to the environment.

The process refers to a specific combination of coagulants and flocculants to obtain a clear recycle without adverse effects on fluorspar recovery allowing of in excess of 90% treated water.

The reagents used are a combination of a cationic polygalactomannan derivative as primary flocculant and a high molecular weight polyethylene oxide as a secondary flocculant. The polygalactomannans are polysaccharides composed of galacton and mannose units usually found in the endosperm of leguminous seeds such as locust beans, honey locust, flame tree, etc. Cationic derivatives of these are used for the water treatment process described by WILSON.

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United States Patent [19]
Wilson

[11] 4,248,708
[45] Feb. 3, 1981

[54] PURIFICATION OF FLOTATION TAILINGS WATER

[75] Inventor: Martin Wilson, Irvine, Calif.

[73] Assignee: United States Borax & Chemical Corporation, Los Angeles, Calif.

[21] Appl. No.: 69,415

[22] Filed: Aug. 24, 1979

[51] Int. Cl.[3] C02F 1/56
[52] U.S. Cl. 210/727; 210/728
[58] Field of Search 210/53, 54, 51, 52

[56] References Cited

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3,278,277	10/1966	Goren	210/54 X
3,498,912	3/1970	Kieper et al.	210/54 X
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Primary Examiner—Thomas G. Wyse
Attorney, Agent, or Firm—James R. Thornton

[57] ABSTRACT

Tailings slurry from fluorspar flotation is clarified and purified by sequential addition of a cationic polygalactomannan derivative and a poly(ethylene oxide).

10 Claims, No Drawings

PURIFICATION OF FLOTATION TAILINGS WATER

This invention relates to the clarification and purification of water from fluorspar flotation processes.

BACKGROUND OF THE INVENTION

Acid grade fluorspar (calcium fluoride) is generally obtained by means of a froth flotation procedure in which the fluorspar ore is ground and slurried with water, treated with flotation reagents and then submitted to a froth flotation procedure. The floated concentrate containing the calcium fluoride is recovered and may be submitted to further cleaner flotation steps. The tailings from the flotation procedure consist of silicates and carbonates which may be discarded or processed further for recovery of desirable products. A large volume of water is required in the process and, in the past, most fluorspar flotation operations did not recycle the water.

Fluorspar flotation is very sensitive to water quality since soluble salts may interfere with the flotation and reduce the grade and recovery of the product. Accordingly, only fresh and in many cases softened water is used in most fluorspar flotation operations. However, with increased concern for environmental contamination, it is desirable to recycle a large portion or possibly all of the process water used in such operations. In order to recycle the water, the tailings from the flotation procedure must be treated and clarified to minimize the build-up of slimes and interfering soluble compounds.

Various flocculating agents or coagulants such as aluminum sulfate and ferric chloride have been proposed for settling slimes in the tailings water from fluorspar flotation operations. However, since soluble salts build up in such water, they are usually unsuitable, either for recycle or discharge into the environment. Various organic polymers have been proposed as coagulants or flocculants for use in mineral processing and waste water treatment. For example, the use of polyacrylamides, polysaccharides, and flocculating glues is proposed in U.S. Pat. No. 3,138,550. High molecular weight ethylene oxide polymers were proposed by Manley, U.S. Pat. No. 3,141,816 as flocculants for removing fibers and other solid materials from waste water from paper making processes. Technical Service bulletins for POLYOX ethylene oxide polymers and JAGUAR C-13, a cationic guar derivative, recommend their use as flocculants in mineral processing.

SUMMARY OF THE INVENTION

There is provided by this invention an improved process for treating water obtained from a fluorspar flotation procedure in order to substantially reduce slimes and interfering soluble materials so that the water may be recycled in the process and further to improve the overall quality of the water so that, if necessary, some or most may be discarded without adverse effect on the environment.

The present invention provides a process utilizing a specific combination of coagulants or flocculants in order to obtain a significant improvement in tailings waters from a fluorspar flotation operation. By use of the combination of reagents of the present invention, one can obtain clear water which can be recycled in the flotation process with no adverse effect on the fluorspar metallurgy. Recovery and grade of fluorspar in subsequent flotation procedures, using an excess of 90% of the treated process water in recycle, is not significantly affected.

DESCRIPTION OF THE INVENTION

The present process employs a cationic polygalactomannan derivative as the primary flocculant and a high molecular weight poly(ethylene oxide) as a secondary flocculant. Polygalactomannans are polysaccharides composed principally of galactose and mannose units and are usually found in the endosperm of leguminous seeds such as guar, locust bean, honey locust, flame tree, and the like. The polygalactomannan derivatives employed in the present invention are cationic; that is, they have cationic substituent groups on the molecule. Such cationic groups may be formed by reaction of the polygalactomannan with a haloalkyl-substituted quaternary ammonium compound under alkaline conditions such as described by DeMartino in U.S. Pat. No. 4,031,307. The resultant quaternary ammonium ethers of polygalactomannan gum generally have a degree of substitution between about 0.01 and 3. Typical examples of such quaternary ammonium ethers are the trialkylammonium halide-alkenyl or alkyl-ethers such as the 4-(trimethylammonium chloride)-2-butenyl ethers of guar and locust bean gum. Other examples of cationic derivatives of polygalactomannan are disclosed in U.S. Pat. No. 3,467,647.

The high molecular weight polymers of ethylene oxide employed in the present process are non-ionic and generally have a molecular weight in excess of 200,000, preferably at least about 5 million. Such polymers are sold commercially by Union Carbide Corporation under the trademark POLYOX.

The flocculants are added sequentially to the tailings water with the cationic polygalactomannan composition being added first and then the poly(ethylene oxide) added second. The flocculants are conveniently added by means of dilute solutions in water, slowly with vigorous stirring. The solids are then allowed to settle and the clear supernatant liquid separated, such as by decantation.

The amount of cationic polygalactomannan composition added to the water to be treated is in the range of about 0.05 to 0.5 lb. per ton of ore (corresponding to about 0.1 to 1.0 lb. per ton of tailings solids) and the amount of polyethylene oxide is in the range of from about 0.005 to 0.1 lb. per ton of ore (corresponding to about 0.01 to 0.2 lb. per ton of tailings solids). A preferred ratio of polygalactomannan derivative to poly(ethylene oxide) is about 10:1.

The following examples are presented to illustrate the invention.

EXAMPLES 1-3

An aqueous slurry comprising the tails of a combined rougher and cleaner froth flotation of fluorspar was treated with reagents as described in Table I. The slurry to be treated (1600 ml.) had a specific gravity of about 1.25 and a pH of about 9.5. The slurries were first treated with the polygalactomannan derivative (JAGUAR C-13 0.1% solution) in three stages with about 1.5 minutes between each stage. The poly(ethylene oxide) (POLYOX 0.1% solution) was then added at the end of the third stage. The treated slurry was allowed to settle and the settling rate was recorded. The clarity of the cleared liquor was also determined by a turbidity meter after 5 and 10 minutes, as well as the amount of solids remaining in 50 ml. of the cleared liquor after 10 minutes. The following results were obtained.

TABLE I

Ex.	1	2	3
JAGUAR (lb/ton ore)	0.12	0.12	0.12
POLYOX (lb/ton ore)	0	0.012	0.012
Settling rate (ft./hr.)	93.7	120.5	105.5
Clarity - 5 min. (NTU)	63	18	32.5
Clarity - 10 min. (NTU)	51	12	32
Solids (clear liquor) (ppm)	100	16	18

EXAMPLES 4-8

The procedure of Examples 1-3 was repeated except 100 ml. of slurry was used in the test. The following results were obtained.

TABLE II

Ex.	4	5	6	7	8
JAGUAR (lb/ton ore)	0.24	0.24	0.16	0.20	0.32
POLYOX (lb/ton ore)	0	0.024	0.016	0.02	0.032
Clarity - 10 min. (NTU)	64	29	56	44	23
Solids (clear liquor) (ppm)	63	4	15	5	2

Various changes and modifications of the invention can be made, and, to the extent that such variations incorporate the spirit of this invention, they are intended to be included within the scope of the appended claims.

What is claimed is:

1. The method of purifying and clarifying a basic aqueous flotation tailings slurry which comprises sequentially adding first a cationic polygalactomannan flocculant and then a non-ionic poly(ethylene oxide) flocculant to said slurry, allowing the solids to settle and separating the purified and clarified liquor from said settled solids.

2. The method in accordance with claim 1 in which said poly(ethylene oxide) has a molecular weight in excess of 200,000.

3. The method according to claim 2 in which said poly(ethylene oxide) has a molecular weight of at least about 5 million.

4. The method in accordance with claim 1 in which said cationic polygalactomannan is a quaternary ammonium ether of polygalactomannan.

5. The method in accordance with claim 1 in which said tailings slurry is from a fluorspar froth flotation.

6. The method according to claim 5 in which said cationic polygalactomannan is a quaternary ammonium ether of polygalactomannan.

7. The method according to claim 5 in which the weight ratio of said cationic polygalactomannan to said poly(ethylene oxide) is about 10:1.

8. The method in accordance with claim 1 in which about 0.1 to 1 pound of said cationic polygalactomannan and about 0.01 to 0.2 pound of said poly(ethylene oxide) is added per ton of solids in said tailings slurry.

9. The method in accordance with claim 8 in which the weight ratio of said cationic polygalactomannan to said poly(ethylene oxide) is about 10:1.

10. The method in accordance with claim 9 in which said flotation tailings slurry is a basic aqueous slurry from a fluorspar froth flotation, said cationic polygalactomannan is a quaternary ammonium ether of polygalactomannan and said poly(ethylene oxide) has a molecular weight of at least about 5 million.

• • • • •

SEAWATER IN FLOTATION

In locations where an adequate supply of fresh water is not available, it has at several locations become necessary to use seawater in flotation mills. Examples of these locations are:

- An operation in Ireland, possibly Tynagh (?).
- Copper precipitate flotation on the Peruvian coastline
- Texada Mines, Texada Island, British Columbia
- Pennarroya-Mediterranean Operations:
  - -- Carthagene (Spain), Pb-Zn
  - -- Argentiera (Sardinia), Pb-Zn (Closed in 1963)
  - -- Laurium (Greece), Pb-Zn
  - -- Ain Barbar, Cu-Pb-Zn
- Cominco-Greenland
  - -- Greenex, Cu-Pb-Zn

COMPOSITION OF SEAWATER

Typical seawater contains 35,000-45,000 mg/l TDS made up of:

Constituent	mg/l
Cl^-	19,000
Na^+	10,500
$SO_4^=$	2,700
Mg	1,350
Ca	400
K	380
HCO_3^-	142
Br	65
Sr	8
SiO_2	6
B	5
F^-	1.3

There are considerable differences in the inorganic composition of seawater, depending on geographic location. For example, the Red Sea has a higher TDS content than the Atlantic Ocean.

There are also significant differences in the organics content of inshore seawater from site to site. For exsmple, efforts to desalinate seawater from the South West African

coastline failed due to a suspension of homogenized organic constituents in the water, possibly the remnants of plankton biomass or surf homogenized seaweeds, etc. Such species could well also be expected to interfere with flotation processes if they were present, even if only in dissolved oxygen denudation.

SPECIAL CONDITIONS FOR SEAWATER FLOTATION

When seawater is used in flotation, the corrosiveness of the highly saline water must be taken into account. Special materials must be used for pumps, pipes, and tanks, etc.

According to COMINCO technical staff, sulfide minerals float well in seawater as long as the minerals are treated as rapidly as possible. That is, contact of a short duration with seawater has a minimal effect on the floatability of mineral grains but after an extended period of time, an effect is noted as the surfaces of the mineral grains start reacting. Cominco Ltd. staff had no further details to offer about the Greenex project, but Randol is grateful to them for providing the two papers inserted below. Mike Smith, who worked on this project startup for BECHTEL CORP., recalls that the key to successful operation was found once a good froth could be generated. He can be reached as follows:

WITTEK DEVELOPMENT, Inc.
2640 South Sheridan Way
Mississauga, Ontario L5J 2M4
(416) 823-7381
Mile Smith

BECHTEL CIVIL AND MINERALS
Fifty Beale Street
San Francisco, CA 94119
(415) 768-6427
Lawrence D. Hartzog
Principal Engineer

Apparently, ENAMI was involved in Cu precipitate flotation plants in Chile. A Dow collector Z-200 was preferred in this case because the conventional crysilic acid frother, although less expensive, did not give a good froth in seawater.

Interesting details are included in the following reports by REY, et al. (1966) and HAIG (1974) inserted below.

THE UNIVERSITY OF BRITISH COLUMBIA
DEPT. OF MINING AND MINERAL PROCESS ENGINEERING
6350 STORES ROAD
VANCOUVER, B.C., CANADA
V6T 1W5

December 20, 1984

Dr. Hans von Michaelis
Randol International Ltd.
21578 Mountsfield Drive
Golden, Colorado 80401
U. S. A.

Dear Dr. Michaelis:

My review of "the use of salt water in flotation circuits" was presented orally only and was not completed in a form suitable for publication. I believe that a good review of the theory and operating experiences of salt water flotation would still be a meaningful contribution but it is currently on the "back-burner" for me to complete.

Sincerely,

George W. Poling
Professor and Head

GWP:bj

Mr. M. Rey, Director and
Mr. P. Raffinot, Principal Engineer
Societe Miniere et Metallurgique
de Penarroya
Paris, France

FLOTATION OF ORES IN SEA-WATER

February - 1966

Milling plants bordering the sea sometimes use sea-water when fresh water is not available in sufficient quantity.

Our purpose is to describe the characteristics of this type of flotation and to indicate the measures which must be taken in the construction of these mills to avoid excessive corrosion.

Application of Sea-Water

Sea-water, like strongly saline solutions, has a high frothing power. On the other hand, it increases the water repellency of minerals, such as sulphur, graphite, coal, and talc, which show natural floatability (1). It has even been proposed to clean coal by floating it in sea-water without any reagent addition (2).

Sulfides and native metals are easily floated in sea-water by soluble collectors such as xanthates. This is how, around 1930, Tocopilla Mining Company in the north of Chile floated a chalcopyrite ore (3).

Differential flotation is also practised, but it is, as a rule, a little more delicate than in fresh water. Several examples are mentioned in publications (4) (5). Société Minière et Métallurgique de Peñarroya and its subsidiary, Société de Pertusola, use or have used sea-water alone or with fresh water in mills around the Mediterranean.

These mills are the following :

Carthagene (Spain)	Pb-Zn ore
Argentiera (Sardinia)	Pb-Zn ore (until 1963)
Laurium (Greece)	Pb-Zn ore
Ain Barbar (Algeria)	Cu-Pb-Zn ore
(see annexed map)	

Flotation of oxidized ores is more difficult than flotation of sulphides. Oxidized lead ores can be sulphidized with sodium sulphide, but conditions are apparently more delicate than in soft water. This operation has been practised occasionally in the mills of Société de Peñarroya, but the study has not been pushed far enough to draw conclusions of general interest.

Little information is available regarding operations which use colloidal reagents, such as soaps and amines. They should not be impossible as it is well known that soluble salts can be floated with amines in saturated solutions There are, on the other hand, patents regarding flotation of cryolite in sea-water using fatty acids or soaps (6). One of the difficulties, of such operations, however, is that sodium silicate, which is regularly used in this type of flotation, precipitates in sea-water and to a large extent loses its efficiency. Slimes should be neutralized with an organic colloid.

In summary, it is believed that sea-water flotation could be used extensively, but its application is not known in all details because the number of mines where the problem arises is small.

Control of Frothing Power and Selectivity

As mentioned above, sea-water has frothing power, and the use of frothing agents is usually unnecessary. Certain authors even state that some frothing agents develop anti-frothing properties in sea-water.

This question is complex and not well elucidated. It has been noted, in a synthetic sea-water, that certain frothing agents increased the volume of the froth and others decreased it. The order of decreasing frothing power was :

Dowfroth Aerofloat 31 Methylisobutylcarbinol	increase froth volume
Pine oil Cresylic acid Kerosene	practically without effect
Flotol	decreases froth volume

The froth produced in sea-water easily carries gangue slimes. Special precautions are necessary to obtain clean and selective froths, and much attention must be paid to cleaning operations.

The reagent which is often the most important for control of froth is lime. This reagent which is standard for the treatment of copper ores is little used on lead and zinc ores, except when it is necessary to depress pyrite. In sea-water it is nearly always necessary.

It depresses gangue and it gives cleaner froths, but, chiefly, it controls the volume of the froth. With a deficit of lime, the froth is bulky and poorly mineralized. With an excess of lime, on the contrary, the froth is too heavily loaded and of insufficient volume. It overflows with difficulty from the cells. This effect is not apparent on sea-water alone, so that lime appears to act by increasing the mineralization with galena. It is the weight of galena which decreases the volume of the froth. Lime also depresses pyrite and enhances the depressing effect of cyanide on sphalerite and pyrite.

Of course, lime increases the pH but only slightly because sea-water acts as a strong buffer. Natural pH of sea-water is 8.2 On the Carthagene ore an addition of lime of 1 kilogramme per ton, which is normal, gives a pH of 8.7, whereas the same addition made in fresh water would give a pH of 10 or 11.

Cyanide, used in small amount as a depressant, also has an influence on the froth, and, like lime, it gives a cleaner and less abundant froth.

Gieser (4) indicates the use of sodium carbonate and mentions that kerosene gives a more brittle and more selective froth which entrains less pyrite. He advocates the use of kerosene in the cleaning steps. Kerosene is a well-known anti-froth reagent so that this is not surprising.

Differential Flotation

Differential flotation functions in a similar manner using either sea or fresh water. The various reagents, collectors, depressants, and activators retain their normal properties. The same is not true of frothing agents, as stated above.

However, in lead-zinc ores a certain tendency in activation of sphalerite or a certain difficulty in sphalerite depression is sometimes noticed. When

this is the case, and if fresh water is available, it is possible to make a bulk float of galena and sphalerite and to separate the sulphides in a cleaning operation. It is also possible, if the concentrates are contamined by sea-water, to purify them by cleaning in fresh water.

These difficulties are, however, not universal and, frequently, differential flotation is quite normal.

Reagent consumption is, however, usually higher than in soft water. In laboratory tests on ores and dump material from the Carthagene area, cyanide and copper sulphate consumptions were increased by 50 percent in sea-water.

It must be noted, regarding laboratory tests, that these can be effected in synthetic sea-water, such as is used in corrosion laboratories under the condition of properly adjusting the pH. The results are identical. The United States Navy uses a very simple formula for synthetic sea-water (7).

Flotation rate can be affected by sea-water and must be checked when a flotation investigation is made. It has been noticed by Peñarroya that flotation of galena was slow in the absence of lime and that one of the functions of this reagent was to increase the flotation rate. Marmatite or ferruginous sphalerite flotation is accelerated in sea-water. We lack experience regarding non-ferruginous sphalerite.

Metallurgical Results

It is not possible to give comparative industrial results of flotation in sea and in fresh water, as in general the mills have only one type of water available.

Laboratory and pilot-plant tests were made in 1952 and 1953 by the Peñarroya company on ores from Carthagene and, usually, the results were very similar.

We can cite the following results obtained on a low-grade galena sphalerite ore (known as Carthagene silicates) :

		Soft water	Sea water
Feed	Pb (%)	2.20	2.10
"	Zn (%)	0.87	0.82
Cleaned lead concentrate	Pb (%)	56.78	59.40
" " "	Zn (%)	2.32	1.92
Cleaned zinc concentrate	Pb (%)	1.10	3.25
" " "	Zn (%)	41.60	40.51
Tailing	Pb (%)	0.37	0.36
"	Zn (%)	0.40	0.32

The ore is partially oxidized, a fact which explains the relatively high grade of the tailing.

It will be noted that the zinc concentrate is low-grade. This is due to an insufficient liberation of the values and to insufficient cleaning. Another reason is that zinc is in the form of marmatite, a high-iron zinc sulphide.

The commercial mill (Roberto mill) has been in operation since 1957 and uses sea-water exclusively. The tonnage treated is 3,000 metric tons per day. Since 1960, the regrinding and retreatment of lead-zinc concentrates to purify them has been worked out, and a high selectivity is now obtained in spite of the use of sea-water.

The results of August 1965, for example, were as follows :

	Pb (%)	Zn (%)
Feed	1.46	0.56
Lead concentrate	77.70	1.72
Zinc concentrate	0.31	53.13
Tailing	0.15	0.17

The ore is very low-grade but is cheaply mined in an open pit. The marmatite, or ferruginous sphalerite, cannot be raised to a higher grade.

Intermediate Formulas : Sea-water - Fresh Water

We have noted that in certain cases it was of interest to clean in soft water concentrates obtained in sea-water. The froth which overflows from flotation cells has a high pulp density so that it must be diluted for cleaning. Fresh or brackish water is used for dilution and washing through the launders instead of sea-water. This water is largely recycled to the head of the circuit with cleaner tails, and dilutes the original sea-water to a useful effect. In certain cases, one can use in this way 30 percent of fresh water and 70 percent of sea-water.

Another interesting scheme is to feed the mill with water from filtering wells dug on the beach. The filtering action of the sand clears the water. On the other hand, it is often much less loaded with salt than sea-water, this is because, in addition to the sea-water obtained by infiltration, the wells often drain soft water which flows towards the sea from underground water-levels. The composition of the water, however, is variable.

This method was used between 1952 and 1963 at the Argentiera mine in the North of Sardinia and is used at the Laurium mine in Greece.

Chlorine Content of Concentrates

The chlorine content of concentrates should preferably be under 0.05 percent : 0.10 percent (1000 grammes per ton) is often the maximum for the smelter. Filtered concentrates contain about 10 per cent water, and since the chlorine content of sea-water is 19 grammes per litre (21.6 grammes per litre in the Mediterranean), the chlorine content of concentrates amounts to 1,900 grammes per ton, that is, two or three times too high.

Sometimes fresh water is used as wash water on the filter. Filter cakes could also be repulped with fresh water and filtered a second time, but this is usually not necessary.

Mill Construction

Mills using sea-water are situated on the coast-line, and humidity is much higher than in mills which are located at higher elevations.

Moreover, ore pulps made up with sea-water are very corrosive. Chemical corrosion is added to the usual abrasion. It is therefore necessary to use materials resistant to these two types of attack.

Wood, which was formerly widely used (flotation cells, launders, etc.), has now been replaced by plastics and rubber. In the mills of Société de Peñarroya, vinylic plastics are used on a large scale as linings and pipes. In spite of their low hardness, these plastics, being smooth, resist abrasion well, as long as the flow is laminar. But, when the flow is turbulent, it is necessary to use rubber (pipe-bends, moving parts of pumps or flotation machines, etc.). Plastics can also be used to protect concrete. If their costs can be lowered, fluorine compounds and silicones will very likely be of interest.

Alloy steels can, of course, be used but with precaution. Many have only a mediocre resistance in marine environment. When steel is used, it must be painted and the paint must be frequently renewed.

In summary, the most important points to consider are as follows :

Power

Electric motors must be of a type specially constructed for marine service. In some of our mills, infrared heating has been adapted to old motors. Without this precaution, after a fifteen-minute interruption, they cannot be started again. Electric lines must also be protected by plastic tubing.

Piping

Water piping is exclusively in polyvinyl plastics. For ore pulp, the straight portions are in polyvinyl and the bends in reinforced rubber.

These should be in non-putrescible wood or better, in rubber-lined sheet-metal. The agitators should be rubber-lined.

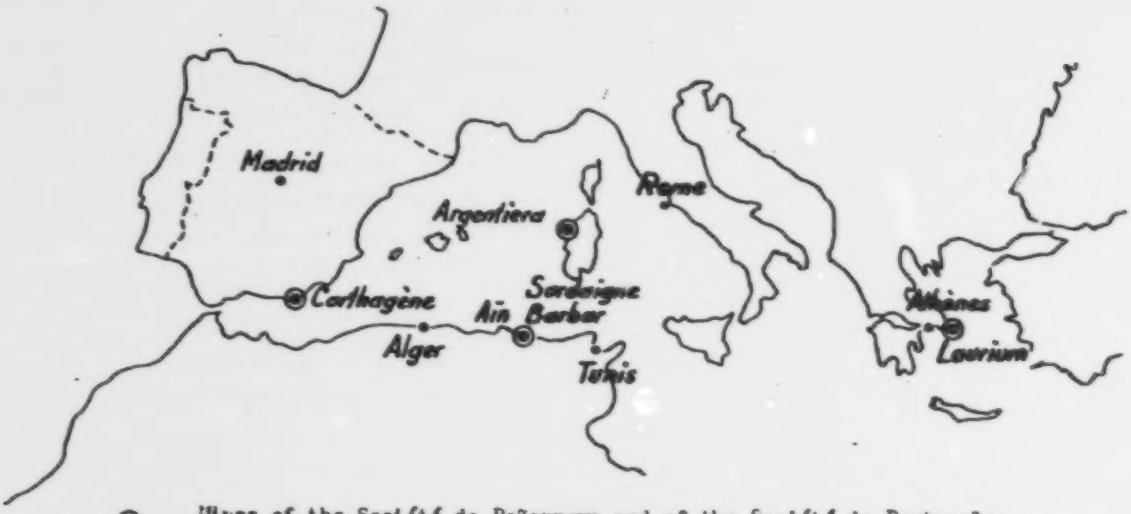
Pumps

Rubber-lined.

Launders

These should be protected by rubber or better, plastic linings.

It should be noted that rubber linings are of interest for use in grinding mills but they are not indispensable.



◉ Mines of the Société de Peñarroya and of the Société de Pertusola
Using flotation in sea-water

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that the Ni-Cu sulphide ore (-10 mesh) used in the grinding tests was in a partly oxidized state. The dissolved sulphate content of the ore slurry increased with grinding time.

The increase in sulphate content was rapid during the first minute of grinding and it increased gradually over the remainder of the grinding time. The rapid increase in sulphate during the first minute of grinding was concomitant with a rapid decrease in pH. A gradual increase in pH occurred after the first minute of grinding.

The initial rapid increase of sulphate and decrease of pH may be assumed as due to the dissolution of partially oxidized sulphur compounds contained in the ore.

Because of the presence of partially oxidized sulphides and the tendency of these compounds to dissolve in the aqueous slurries, the ball wear vs. grinding time curves were more complex than those found during the iron ore grinding tests.

The use of pH control and corrosion inhibitors reduced corrosive wear of steel balls during the wet grinding of sulphide ore. The pH was controlled by adding NaOH to the slurries. Ball wear decreased above pH 11 until at pH 13.7 there was a 50% reduction in wear.

With 1% $NaNO_2$ in the slurry, a 50% reduction in ball wear was observed at pH 10 whereas a similar reduction in ball wear occurred at pH 13.7 in slurries without $NaNO_2$. Sodium nitrite did not inhibit corrosive wear of grinding balls at initial pH values lower than pH9.

Addition of NaOH and $NaNO_2$ to the ore slurries did not have a significant effect on the work done on the ore during the 20-minute grinding tests as determined by wet-sieve analysis of the ore at the end of each run (%-200 mesh).

Conclusions

- Abrasive wear of carbon-steel grinding balls is accompanied by a significant amount of corrosive wear when certain iron ores and sulphide ores are ground in laboratory ball mills.
- Corrosive wear is reduced by the use of corrosion inhibitors and pH control without affecting the work done on the ore during grinding.
- Addition of sodium borate and sodium nitrite to the ball mill reduced ball wear in iron oxide and sulphide ore slurries by 50%. Sodium silicate reduces ball wear in iron ore slurries by 37%.
- Addition of sodium hydroxide to the ball mill reduces ball wear in sulphide ore slurries. At pH 14.7 wear is reduced by 50%.
- Corrosive wear occurs, in part, by the following overall reaction

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe_2 + 4OH^-$$ □

TABLE 2 – CORRELATION OF CORROSIVE WEAR WITH OXYGEN CONSUMPTION IN IRON ORE SLURRIES

D.H. Dobrowolsky

GRINDING TIME (min)	CORROSIVE WEAR (mole Fe x 10^3)	O_2 CONSUMPTION (mole O_2 x 10^3)	RATIO* (mole Fe/mole O_2)
10	5.8	2.3	2.5
15	7.8	3.6	2.2
20	10.6	4.7	2.3
25	10.6	5.7	1.9
30	13.4	7.0	1.9
35	17.7	7.8	2.3
40	18.4	9.2	2.0
45	15.7	10.1	1.6
50	22.0	11.0	2.0
55	24.7	12.5	2.0
60	27.5	13.6	2.0
80	37.4	15.6	2.4

* $2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$

R.F. Steck

Sea water flotation

L.D. HAIG – SMILLIE

Texada Mines, located at tide water on the west side of Texada Island 100 miles northwest of Vancouver, B.C., runs a mill that operates five days a week producing 1900 long tons of premium sinter iron concentrate per day, assaying 65% iron, 0.055% copper, 0.40% sulphur, and 42% -100 mesh. This is made by blending two iron concentrates:

- A coarse iron concentrate made from ball mill circulating load assaying 64.5% iron, 0.09% copper, 0.50% sulphur, 16% -100 mesh.
- A fine iron concentrate made from rougher flotation tailing, 66% iron, 0.03% copper, 0.25% sulphur, 70% -100 mesh. The proportions depend on the ore being treated. To yield the highest net cash return it is necessary to produce the maximum amount of coarse iron that can be blended with the fine iron concentrates.

Over grinding is costly and undesirable. The primary grind is kept as coarse as possible. Tailing is collected, dewatered, reground and floated for additional copoper recovery.

A by-product copper concentrate, containing gold and silver, high in pyrite, makes the operation economic.

To meet contract specifications processing is done in three distinct circuits, identifiable on Fig. 1.

Coarse Iron Concentrate

A portion of the cyclone underflow in each primary ball mill is cut out and sent to six stage magnetic separation. The concentrate is dewatered in a vibrating dewaterizer and the concentrates go to the drying kiln collecting conveyor.

Fine Iron Concentrate

Primary cyclone overflow goes to a conditioner then to an 8 cell DR=30 followed by an 8 cell =48 Agitair flotation machine. The tailings go to 4 stage magnetic separation. Magnetic concentrate goes to a thickener which also acts as a hydro separator. The underflow is filtered and is conveyed to the 9 ft x 60 ft drying kiln where the moisture is reduced from 10.5 to 5%. The concentrate is weighed and stacked in an open stock pile.

Regrinding and Flotation

All the iron circuit tailings are collected, dewatered and ground in two parallel regrind circuits.

The coarse iron tailing is divided between two 36 in. classifiers. Sands from the first classifier go to an 8 ft x 10 ft Allis-Chalmers ball mill then an 8 cell =48 Agitair flotation machine, followed by single stage magnetic separation. Separator tailing goes to the fine iron tailing sump.

First coppper cleaner tailings are retreated in this circuit.

Sands from the second classifier go to an 8 ft x 12 ft Marcy regrind ball mill, then to an 8 cell =48 Agitair machine. Tailings go to a double drum magnetic separator and then to waste. The fine iron tailings are cyclomed to remove the sands for regrinding in the 8 ft x 12 ft Marcy mill.

The magnetic separator tailing is very dilute. Cycloning then is essentially a dewatering operation. This overflow water plus excess classifier weir overflow and the recleaner tailing is floated in a 6 cell DR#30 flotation machine. Tailings from the DR go to a double drum separator then to waste.

Flotation History

Fresh and reclaimed water supplies were not adequate. In order to maintain the operation it was necessary to supplement the water supply with sea water.

It was recognized from the start that Texada ore pulps were subject to a buffering action. Lime additions from two to five pounds per ton were required to change the alkalinity from the normal pH8. Increasing the lime increased the grade of concentrate but very substantially reduced the recovery.

Microscopic examination revealed a slime and a carbonate coating on the sulphide mineral. Frequently numerous clean chalcopyrite grains could be found in the tailing.

In 1966 tailings disposal problems made it necessary to add an additional 500 g.p.m. of sea water to the tail race. Copper froth began to appear on the lower reaches of the tailings launder.

Some of the problems in the flotation circuit were:

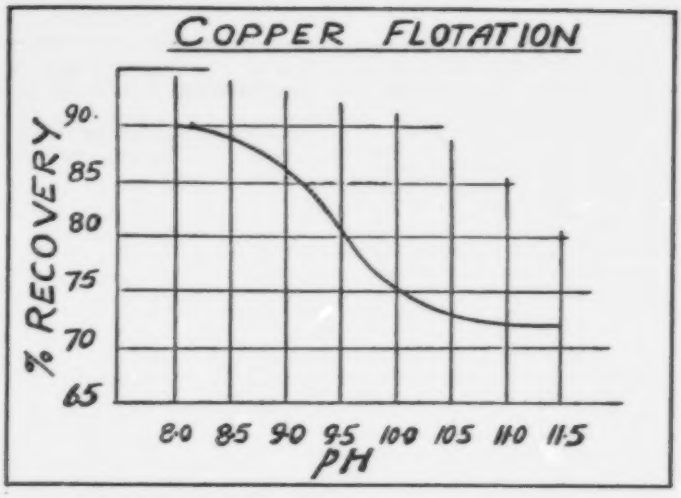
- Lime, being a flocculand, was favoring slime coatings on the mineral surface.
- The calcium ion and or the OH ion was excluding or displacing the xanthate from absorbing onto the mineral surface.
- The calcium coating deposited could be dissolved with excess dilution.
- Sea water had no detrimental effect on flotation.

All the lime was removed from the circuit and just enough soda ash added to ensure an active pyrite float. Recoveries increased enormously.

In 1966 the mine went to trackless mining and underground water supplies were unusable due to colloidal slimes and oil. The unusually dry season created a critical water shortage so the mill went to 100% sea water.

Solubility

The 8 ft x 12 ft regrind ball mill was designed to operate in sea water. Plant scale tests were run to determine the solubility of Texada copper in sea water. The maximum copper detected was 0.25 ppm – the average 0.004 ppm. Copper values while milling in fresh water were so similar that the operators concluded that there was no appreciable solution of copper during processing. This is not true for several mines in B.C. Corrosion is severe because there is no stifling by corrosion products. But it is less severe in sea water than in fresh or fresh-sea mixtures.



REAGENT CONSUMPTION PER LONG TON ON A YEARLY BASIS FOR THREE TYPICAL PERIODS

Reagent	1973	1967	1965
Sodium Isopropyl Xanthate	0.024	0.115	0.058
Reagent 238	0.010	0.007	0.013
Reagent 242	0.001	0.001	
Aerofloat 33	0.005	0.0016	0.001
Aerofroth 65	0.016	0.023	0.025
Z-200	0.005	0.004	–
Soda Ash	0.048	–	–
Sodium Cyanide	0.002	0.0002	0.0002
Lime	0.066	0.45	0.71

Reagent consumption has been reduced in full use of sea water.

Corrosion grinding media

A sharp increase in the grinding media and liner steel consumption was anticipated with sea water in contact with fresh abraded iron and steel.

Steel consumption did not increase until the fall of 1970 when a fourth ball mill was started. Consumption rose from 0.626 to 0.787 pounds per long ton – entirely due to finer grinding.

No sea water entered the grinding circuit until 1960. During the first years of operation grate and pan liner wear was excessive. It was obvious from the worn parts that electrolytic corrosion and not abrasion was the cause of the failure. The nickel content of the liners was increased and 3/8 in. stainless steel shims were placed under the grates. The problem disappeared. Liner steel consumption is down in primary grinding with the full use of sea water.

Regrind ball mill

Corrosion is most severe with large amounts of pyrite in aerated sea water. Mixtures of sea and fresh water are the most corrosive of all.

The regrind mill was designed to be operated in sea water, grinding the highly pyritic tailing and the platey cupriferous pyrite from the rougher concentrate.

Two sets of half worn Manganese feed end liners lasted 11 months each. Two sets of new Ni-Hard discharge liners lasted 10 months each. Manganese lifters and chrome molly shell plates gave normal life. Liner bolts required very heavy maintenance as they dissolved very rapidly. The mill was converted to rubber in 1966 using standard profile Skega. Shell Plates are still in place.

Regrind mill

The regrind mill was installed with a half worn set of Ni-Hard liners. These liners lasted 20 months and were changed only because it was not practical to change single worn liners. The service life was far in excess of what was anticipated. The mill was rubber lined.

Corrosion – filters

With the use of sea water corrosion problems were greatly reduced. Boot parts originally lasting 1-1/3 yrs. now last over seven years. Valve life is more than doubled.

Marine life

Marine life is always a problem when using sea water. The foot valves, intake, delivery lines, and the holding tanks rapidly build up with barnacles, mussels, oysters, clams, starfish, sea urchins, and sea worms up to 18 in. long and 1/2 in. or more in thickness.

This marine life can easily be destroyed but most of it remains fastened to the place of growth for long periods of time making an excellent site for new growth. When these shell fish do come loose they drift into pipe lines and cut off the flow of water. They are particularly troublesome in magnetic separator spiggots.

Several quick hard air blows are made into the water filled pipe then the bottom drain is quickly opened. If there is any plug up, the process is repeated. Shell removal is excellent and complete.

Summing up the 17 years of operation, it was found that the full use of sea water gives a very stable, easily controlled float. Reagent consumption is greatly reduced and reagent feeding has been simplified. The natural pH of the sea water is the most satisfactory level for Texada ores. It is extremely important to float certain types of pyrite and this is best done at low pH after making allowance for final grinding. Steel and liner consumption is less in full sea water than it was in fresh and mixtures of sea and fresh water.

Atmospheric corrosion is severe and causes more problems than the sea water in the processing. This is a location problem and not a function of the use of sea water. □

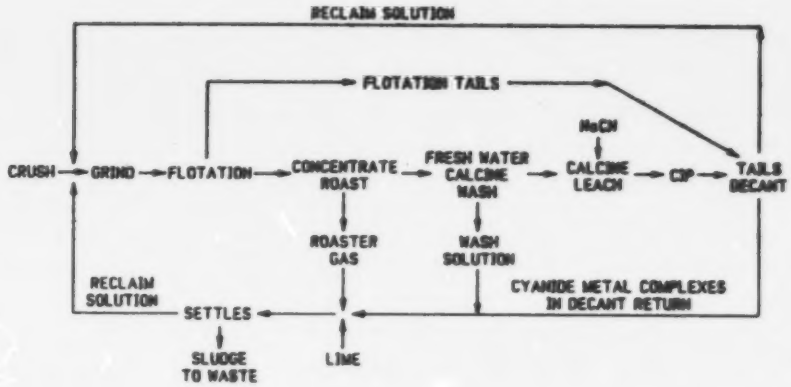
FLOTATION OF PYRITE AND GOLD

Gold and silver often occur in "refractory" sulfide ores, and they can sometimes best be recovered by flotation to a concentrate for roasting and leaching or for shipment to a smelter. The flotation tailings may also contain enough cyanide-soluble gold to justify leaching. Alternatively, gold and pyrite can be floated in order to make a smaller, more concentrated tonnage of material which can be subjected to very much more aggressive fine-grinding and concentrated cyanide leaching, while the flotation tailings receive a standard leaching treatment.

When a flotation concentrator is located near a cyanide leach plant, great care must be exercised if water is to be reclaimed for reuse in the mill from the tailings pond. It has been common practice, especially in Canada and Australia, to recombine the leached calcine tailings with the flotation tailings and to dispose of them to the same tailings pond as described in the trip report on GIANT YELLOWKNIFE MINES. In the case of GIANT, no water is recycled. Decant water is treated by alkaline chlorination and discharged to the lake via a creek. If such tailings water is to be recycled to the flotation mill, a very real danger exists that there could be a deterioration in flotation recovery as cyanide is an effective depressant of pyrite.

Where tailings are backfilled to underground mines, it is possible that minewater may find a measurable cyanide level as has been the case at Homestake Mining Company, Lead, South Dakota. Although the Lead minewater is not used in a flotation circuit, it serves as an example of how cyanide can get into water. Another example of minewater that contained a low cyanide level is the GIANT mine referred to above and described in Appendix I. In the case of Giant, backfill is not practised, but cyanide reached the underground minewater through seepage from their final decanting pond until the new cyanide treatment plant was installed upstream of it.

What this leads to is that when gold-pyrite concentrates are to be recovered by flotation in the vicinity of a cyanide-leach plant, very careful consideration must be given to how water from the two circuits will be kept isolated to avoid getting cyanide into the flotation circuit, or how it is to be treated to remove cyanide to levels that will not cause a problem.



GOLD-PYRITE FLOTATION-WITWATERSRAND

Hartebeestfontein Gold Mining Company Limited

At 'HARTIES,' a pyrite gold-uranium concentrate is floated at a high pH from run of mine ore. After ultra-fine grinding, the concentrate is leached first in sulfuric acid to recover uranium and then in cyanide to leach gold. The flotation tailings are also leached for uranium and gold recovery in that sequence. The reason for floating a concentrate is that the smaller volume of high grade concentrate (250 g/t gold) allows more aggressive treatment at an affordable cost VIZ fine-grinding (99% minus 44 u), and leaching at higher reagent concentrations (0.8% NaCN) and for longer times than would be economically advantageous for bulk ore. The 'HARTIES' flowsheet achieves a higher overall recovery than other Witwatersrand mills.

'HARTIES' was described in RANDOL (1983). The cyanided pyrite concentrate is roasted to produce sulfuric acid which is used to leach uranium and in that way, no cyanide in the leached concentrate gets into the water system. After leaching the flotation tailings, these are disposed of to a tailings pond and, undoubtably, decant solutions are recycled. It is not known how cyanide in the recycled solution is prevented from returning to the flotation plants. One possibility is that residence time in the tailings pond and reclaimed water reservoir is long enough for cyanide to be lost by natural degradation. Alternatively, water used in the flotation plants may be recovered for reuse in the primary milling and flotation circuit by solid liquid separation not shown on the general arrangement flowsheet below.

Final cyanide-leached tails are filtered to recover a pregnant solution. Soluble gold is recovered by washing with only 0.5% soluble loss on one state of filtration which indicates that very little cyanide is left in the filter cake when the tailings are repulped. By

repulping with tailings return solution rather than barrens which contain cyanide, cyanide levels are kept very low in the tailings pond solution to start with. Cyanide in slimes dam runoff water from Loraine is shown in one of the documents inserted below to be unsuitable for use in flotation plants, even if it contains only 1 ppm cyanide. The effect of cyanide on high pH pyrite flotation is discussed below.

ERGO

The East Rand Gold and Uranium Recovery Ltd. (ERGO) operation recovers a gold-pyrite-uranium concentrate by flotation from 1.5 million tons per month of reclaimed tailings.

Water management at this operation is described in Appendix I. In this case, flotation is operated at an acid pH. Water used in the process is made up of underground minewater and reclaimed tailings solution. There are two main challenges:

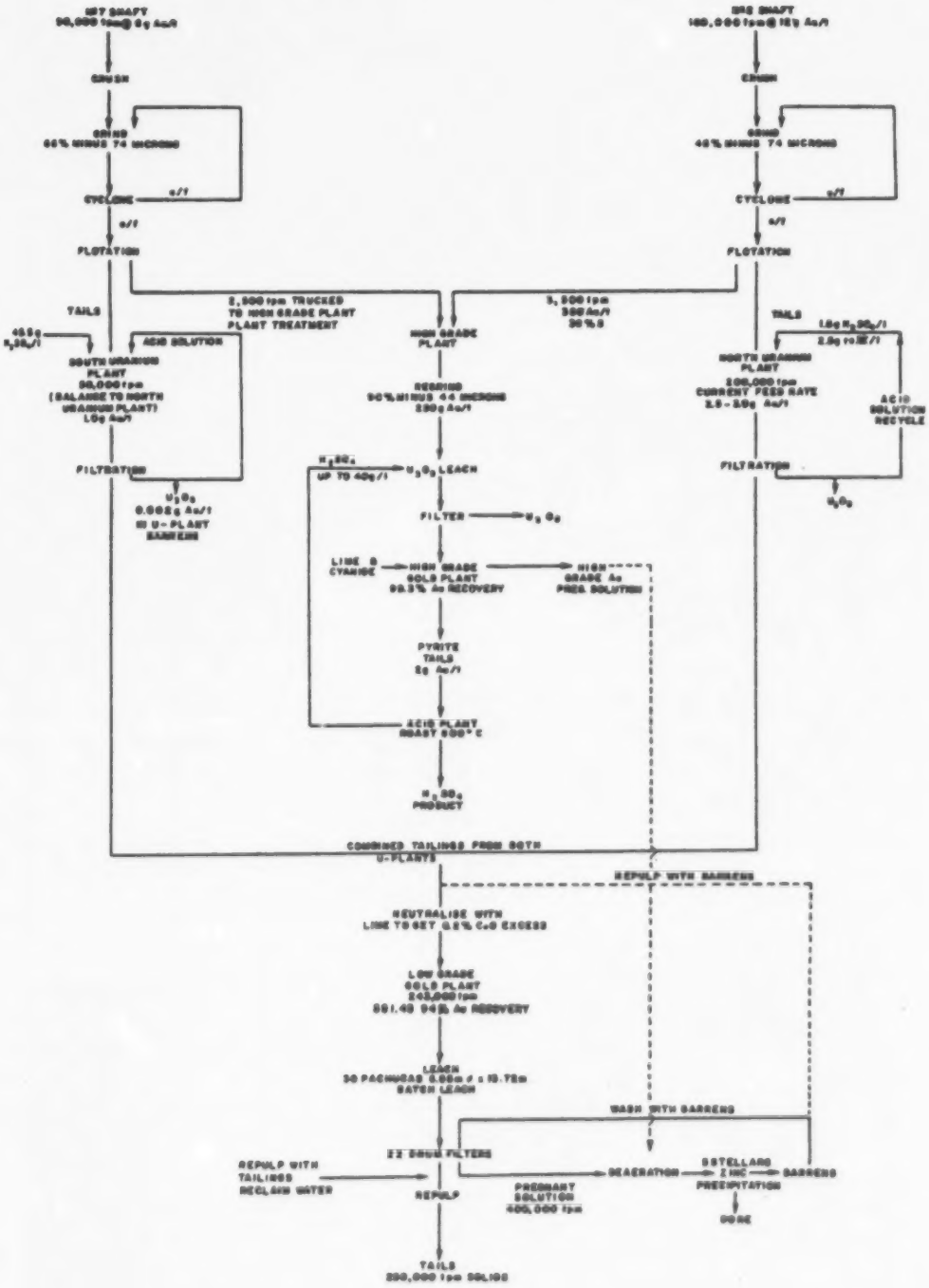
1) Scaling due to high concentrations of gypsum.

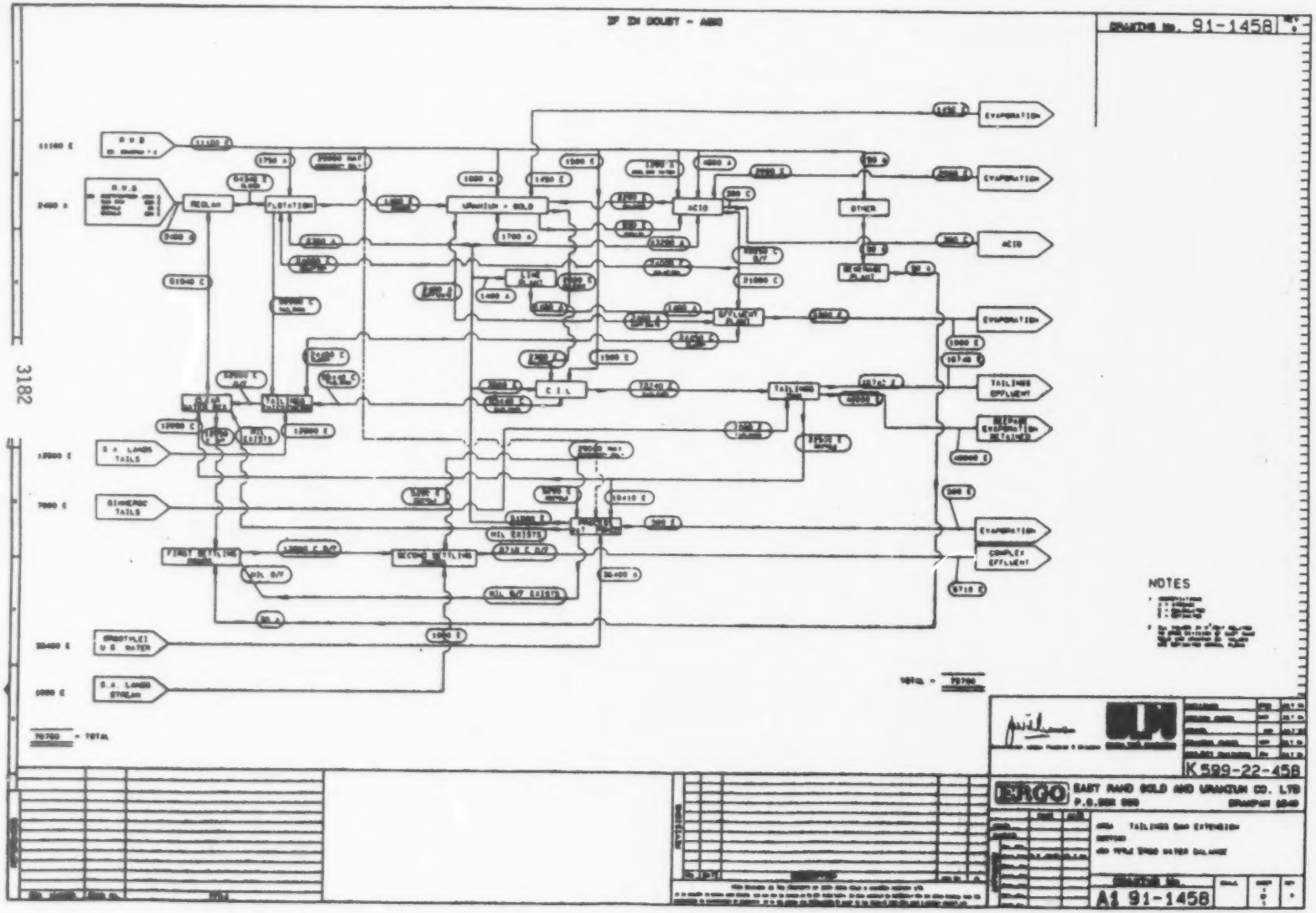
2) Ultimately TDS of effluents discharged may have to be reduced to meet new effluent regulations.

In 1985, ERGO started up a massive new leach and CIP gold recovery operation to recover gold that otherwise would not have been recovered in the flotation step. Here it is interesting to see how cyanide in the CIL tails effluent is kept separate from the flotation plant solution. Cyanide in the calcine leach tailings is reduced to below 0.5 ppm by treatment with lime and uranium plant raffinate containing a very high iron content. In the new CIL plant, the last 7 of 11 stages of carbon contactors were installed to remove cyanide from the pulp solution prior to being pumped to a huge new tailings dam from which water is recovered for reuse. Tailings from the SIMMERGO CIP plant also go to this tailings dam. The recovered decanted water is used in part in the flotation circuit as can be seen in their water balance diagram shown below.

HARTEBEESTFONTEIN GOLD MINING COMPANY LIMITED

GENERAL ARRANGEMENT

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ERGO
EAST RAND GOLD AND URANIUM CO. LTD
A1 91-1458

3182

Rand Mines Milling and Mining Co. Ltd. - RM3

This operation, known as RM3, on the Witwatersrand also combines flotation of a pyrite-gold-uranium concentrate with cyanidation and CIP gold recovery and recycles large volumes of water as shown in the flowsheet overleaf..

In this case, water quality has presented some problems, although not in the flotation circuit, even though quite large volumes of CIP tailings decant water are returned to the sand dump repulper ahead of clarification and flotation. Either the residual cyanide is lost by natural degradation, or it is taken out of solution by large amounts of iron in the recycled solution and, most likely, any residual cyanide is lost when the tailings are repulped at pH 2.5 which would volatilize any cyanide.

RM3 uses as much recycled water as possible as well as surface water from a local stream. Some initial metallurgical recovery problems were attributed to the quality of this streamwater which was affected by upstream industry and was thought to be one possible cause of carbon fouling in the CIP circuit.

Buffelsfontein Gold Mining Co. Ltd.

'BUFFELS' has applied an interesting wrinkle to gold-pyrite flotation from current gold leach tails. In this case, after leaching gold, the tailings are acidified to pH 3.5 and powdered activated carbon added to the pulp. In the ensuing flotation step, this gains two advantages:

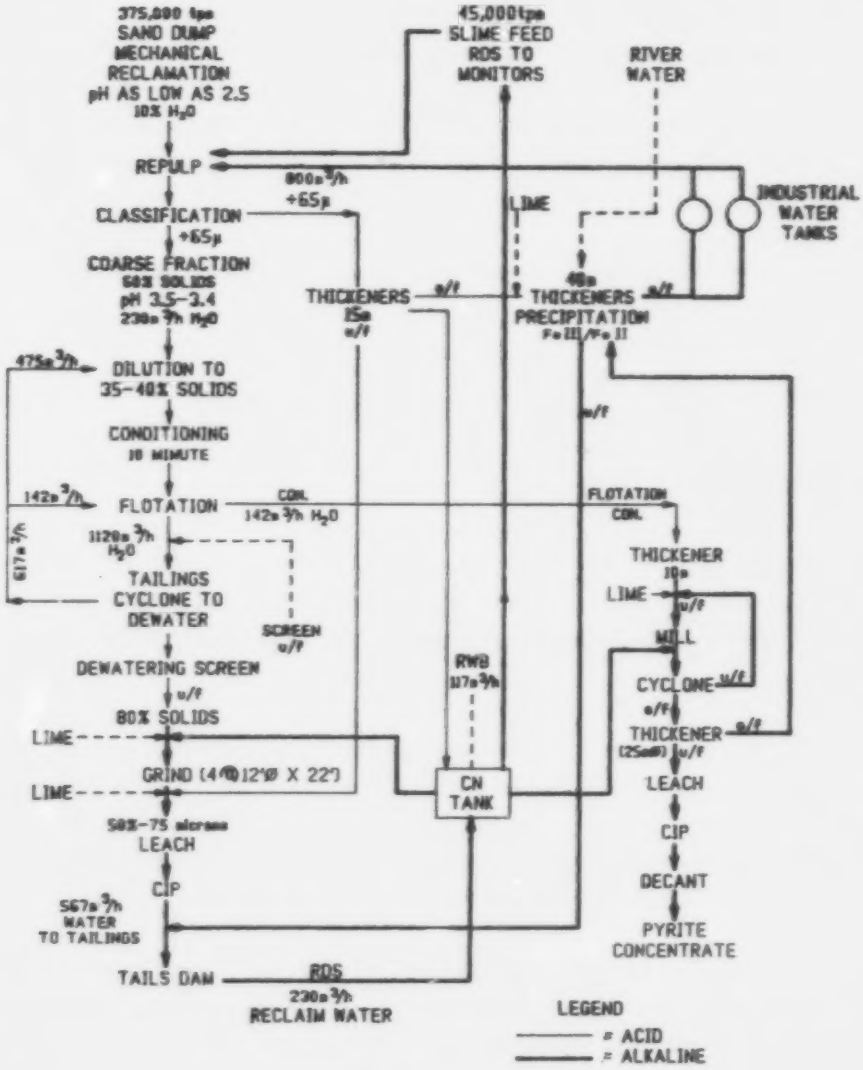
1) The activated carbon at low pH helps to decompose any cyanide that may be left in the tailings pulp, thereby avoiding the possibility of pyrite being depressed.

2) The powdered carbon adsorbs residual gold which is recovered with the pyrite concentrate and recovered by cyanidation of a calcine after roasting.

More will be learned about the effectiveness of this step at the XVe IMPC Congress in Cannes, France, when VAN ASWEGEN (1985) describes the process and results achieved. Meanwhile, enquiries may be directed to:

GENCOR LTD.
Post Office Box 1820
Marshalltown 2107
South Africa
(011) 836-1121
P. Van Aswegen

RM3 FLOWSHEET



LIME TREATMENT OF FLOTATION PLANT DILUTION WATER

The Anglo American Research Laboratories undertook detailed flotation tests to determine whether or not a tailings thickener should be operated in the alkaline pH range and, if so, at what pH to recover water of optimum quality for recycle to a flotation plant recovering pyrite and gold.

Their results were inconclusive. Using water from one tailings dam and two sets of plant waters, lime treatment of the flotation plant dilution water from pH 7.5 to 9.5 produced no significant improvement in flotation response. However, when a sample from a second dam and another set of plant waters were used for a similar test, there was a dramatic improvement in the pyrite flotation response after lime treatment of the water. This had the effect of allowing significantly more gold to be recovered direct to final product from the rougher flotation circuit compared to when untreated water was used. Generally, however, lime treatment to pH 7.5 produced as good results as to pH 9.

In a second set of tests using the standard OFS mill flotation technique on a sample of tailings from a tailings dam near Welkom, Orange Free State, it was found that if the flotation plant dilution water was treated by adding lime to pH 10.5 and then settled prior to its use for density control measures, then the initial pyrite grade could be increased from 24-25% sulfide sulfur to 30-37% S. This means that of the gold recovered in the rougher flotation circuit, 60% could be routed direct to final product and 40% to the cleaner circuit when treated water is used. When untreated water is used, all the rougher concentrate must be routed to the cleaner circuit. Treatment of the flotation plant dilution water had a less significant effect when the standard flotation method was used.

When another dam sample was tested using fresh plant water samples, only marginal benefits were found from the treating of the water with lime, and no optimum pH could be defined.

Clearly, water chemistry involved here is complex, and more may be learned through further testwork. This topic might be discussed with:

ANGLO AMERICAN RESEARCH LABORATORIES
Post Office Box 106
Crown Mines 2025
Brian K. Loveday
Manager
Peter J. Cabasi

Loraine Gold Mining Company - Flotation of Au, Pyrite, and U_3O_8

The Anglovaal Research Laboratories undertook a systematic evaluation of various alternative water sources. These tests show a remarkable difference in flotation results

FIGURE 19 PLANT WATERS K 654 AND K 652 STORED FOR ONE WEEK

DOR SAMPLE K 648. BULK TESTS.

RANGE OF OVERALL GOLD RECOVERIES USING FOUR

METHODS OF CALCULATION.

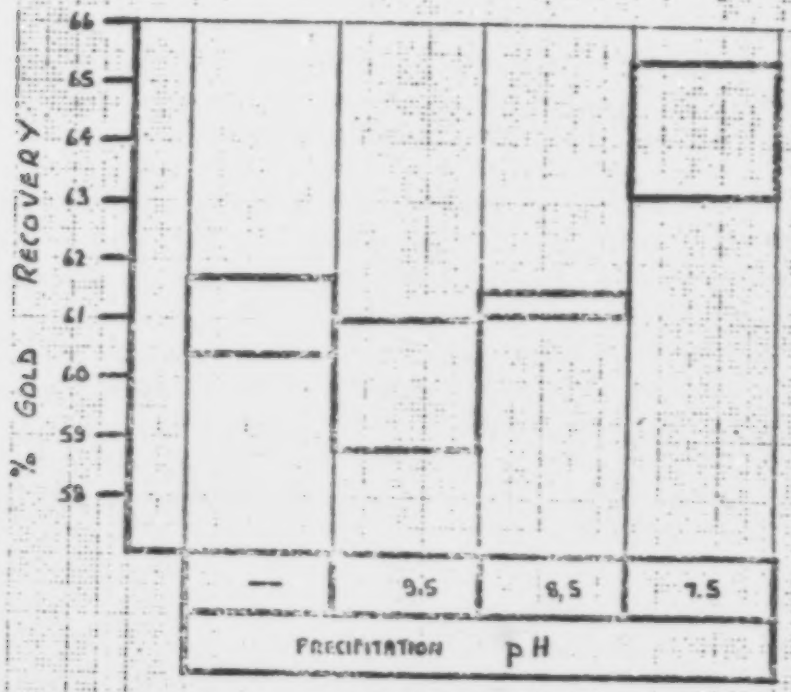
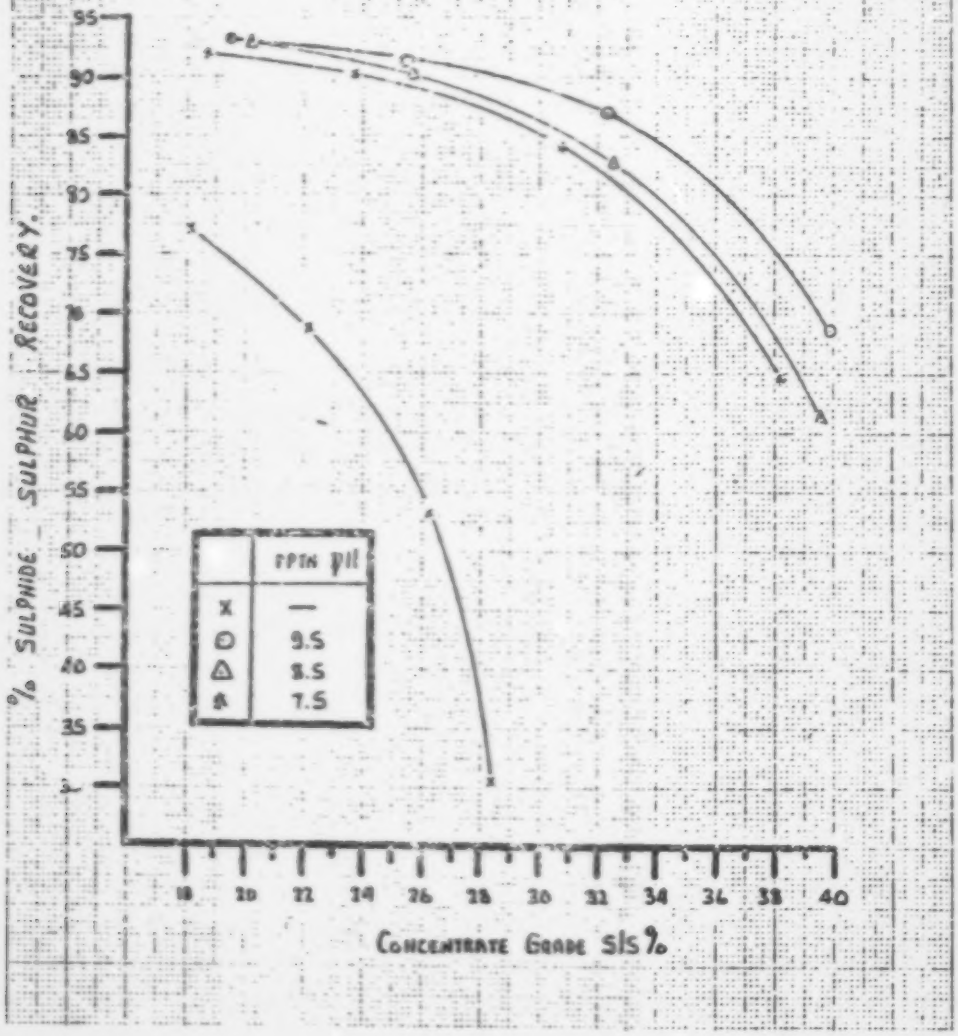


FIGURE 20 PILOT WATERS K654 & K653 STORED FOR ONE WEEK.

DAM SITE K648 BULK TESTS.

SULPHIDE SULPHUR GRADE - RECOVERY CURVES.



from one to the other and also quantify the degree to which recoveries are reduced by the presence of cyanide in recovered water when used for flotation of gold, uranium, and pyrite.

It is also interesting that some water samples tested gave better recoveries than Rand Water Board water which is the regional water supply usually used.

More information on water quality effects on flotation recovery of gold, pyrite, and uranium can be obtained from the metallurgists that undertook this excellent piece of research:

ANGLOVAAL RESEARCH
LABORATORIES
Post Office Box 1
Florida 1710
South Africa
(011) 672-0460
Gerhard Overbeek
Manager
C. R. Heathcote

USE OF RECLAIMED SEWAGE WATER IN FLOTATION

In several parts of the world, water is in short supply, and the mineral processing industry has sought to use reclaimed sewage water in flotation recovery operations. This has often led to poor results, and the industry has sought to find out why and a treatment method which would make the water amenable to mineral processing, especially flotation.

In talking to industry, one does come across cases where reclaimed or even raw sewage is added to tailings ponds and where water containing various amounts of blended wastewater of this kind is used in mineral processing. There are many more people involved with mineral processing, it seems, who say that it cannot and should not be done.

Above, the example of CLIMAX MOLYBDENUM DIV. was mentioned where sewage from a mining camp, when it was formerly located at Climax, was discharged to their tailings pond, and the negative effects on flotation were counteracted by adding activated carbon to the pulp. In that case, the purpose of disposing of sewage to the tailings pond was to avoid the need for a sewage treatment plant. In any case, the volume of wastewate added to the system in this way would have been miniscual in relation to the volume of tailings and the volume of water recycled to the plant. CLIMAX testwork dated 1963 by Ralph Meyertons showed that even traces of stearic acid is detrimental to molybdenite recovery. Stearates are constituents of soaps that can occur in sewage effluents which

provides a lead to one possible cause of flotation problems when sewage reclaim water is used in Cu-Mo mills.

The following is an excerpt from an ANGLOVAAL report describing testwork aimed at exploring the use of alternate sources of water.

2. INTRODUCTION

Current drought conditions have restricted the off-take of potable water for metallurgical purposes.

The aim of this investigation is to evaluate the various unused Loraine local waters for possible future use in the flotation application, by a series of comparative flotation tests.

2.1 Inference

2.1.1 Slimes dam run-off water

2.1.1.1 The presence of trace quantities of residual cyanide make this water unsuitable for use in the flotation plant.

Tests revealed that cyanide concentrations as low as 1 ppm have a detrimental effect on flotation performance.

Table 1 Cyanide Concentrations versus Gold, Sulphur and Uranium Rougher Recoveries

Cyanide level	Actual Recovery % (t = 12 min)		
ppm NaCN	Gold	Uranium	Sulphur
8,5 ppm	75,05	10,37	16,99
6,2 ppm	77,52	15,72	36,39
3,5 ppm	80,53	14,78	41,02
2,5 ppm	82,13	21,55	62,18
1,3 ppm	77,40	19,85	68,16
Nil	79,20	25,35	86,12

2.1.1.2 At the extremely high cyanide levels (180 ppm), encountered when using undiluted slimes run-off water, even gold, which appears less sensitive to cyanide depression, was completely depressed and only 3,0% could be recovered by flotation.

2.1.2 Swartpan water

Treating the Swartpan water by increasing the pH to >11,0 and removing the precipitated solids prior to use, increased the recoveries of gold, uranium and sulphur to levels higher than the standard water.

Table 2 Swartpan Water - Gold, Uranium and Sulphur Recoveries

Water	Actual Recovery - % (t = 12 min)		
	Gold	Uranium	Sulphur
Swartpan (Untreated)	69,57	14,56	92,20
Swartpan (Treated)	87,20	32,83	92,30
Rand Water	82,95	27,17	86,50

2.1.3 Mill return water

As expected, excellent recoveries of gold, uranium and sulphur were obtained with this water.

Table 3 Mill Return Water - Gold, Uranium and Sulphur Recoveries

Water	Actual Recovery - % (t = 12 min)		
	Gold	Uranium	Sulphur
Mill return water	89,13	36,95	95,60
Rand Water	82,95	27,17	86,50

Residual flotation reagents in the mill return water enhanced the collectors added during the test to produce these excellent results.

2.1.4 Stinkpan water

2.1.4.1 Stinkpan water, both aged and fresh, had a very detrimental effect on gold, uranium and sulphur recovery.

2.1.4.2 Even at the 10% replacement level, gold recoveries were considerably lower than the Rand Water standard (see Table 4).

Sulphur and uranium recoveries appear to be little affected at this replacement level.

Table 4 Stinkpan Water - Gold, Uranium and Sulphur Recoveries

Water and % Replacement	Actual Recovery - % (t = 12 min)		
	Gold	Uranium	Sulphur
Aged			
100 %	13,59	7,65	22,02
50 %	39,47	15,24	49,29
10 %	71,40	27,04	90,35
Fresh			
100 %	52,99	27,81	85,22
50 %	67,16	30,16	91,16
10 %	74,72	29,89	91,11
Rand Water	82,95	27,27	86,50

2.1.5 Sewage water

The flotation behaviour of sewage water appeared very similar to aged Stinkpan water, recoveries of gold, uranium and sulphur decreasing as the water replacement percentage increased (see Table 5).

Table 5 Loraine Sewage Water - Gold, Uranium and Sulphur Recoveries

Water and % Replacement	Actual Recovery - % (t = 12 min)		
	Gold	Uranium	Sulphur
Sewage Water			
100 %	13,58	6,35	15,83
50 %	46,17	14,59	69,23
10 %	76,52	27,80	92,46
Rand Water	82,95	27,17	86,50

3. RECOMMENDATIONS

3.1 Slimes dam run-off water, Stinkpan water and sewage water should not be used in the flotation plant in their present untreated form, as their use will result in lower gold, uranium and sulphur recoveries.

3.1.1 Further testwork sould be conducted on the slimes dam run-off water to investigage free and complex cyanide removal by such methods as activated carbon, ion exchange or sulphur dioxide treatment to render this water suitable for flotation usage.

3.1.2 Sewage effluent from the new sewage treatment plant to be erected at Loraine should be evaluated when this water becomes available, especially if the plant has been designed to remove phosphates from the sewage effluent. Water quality would then be similar to the Stilfontein new plant sewage water, which was suitable for flotation.

3.2 Test work should be conducted to optimise flotation circuits to make them less sensitive to waters of poorer quality.

Areas which could be investigated include flotation reagents suites, pH and conditioning time.

3.3 The development of other metallurgical routes which would be more water efficient and less sensitive to water quality.

3.4 Although no flotation evaluation was conducted on the sample of underground (dated 12 May 1983) submitted for analysis, analytical results indicate that it is highly unlikely to be harmful when used for flotation purposes.

4. SAMPLES

4.1 Loraine Mill Feed

Laboratory Reference Number RS 54082

Chemical Analysis

Gold	=	5,19 g/ton
Uranium	=	57 g U_3O_8/ton
Sulphur	=	1,21 % S

Table 6 Chemical Analyses

Element		Slimes Dam Run-off Water			Stinkpan Water	
		6.4.83	18.4.83	5.5.83	Aged 6.4.83	Fresh 5.5.83
Conductivity µS/cm		7 000	3 600	5 000	26 000	1 500
T.D.S. mg/ℓ		4 088	3 786	5 055	20 359	1 305
Susp. solids mg/ℓ		95,5	58,7	146,6	712	98,1
Total Hardness (as $CaCO_3$)	ppm	6 366	1 544	2 108	3 337	376,5
Zn	ppm	-	-	11,51	-	-
Pb	ppm	0,1	0,2	0,1	0,4	0,1
Cu	ppm	16,7	20,2	17,8	< 0,1	< 0,1
Fe	ppm	1,6	7,6	2,03	0,3	0,1
Ca	ppm	668	688	824	814	126,2
Mg	ppm	23,8	13,8	12,2	376	149
Na	ppm	609	574,7	625,4	5 223	332
K	ppm	34,8	36,0	40,3	86,2	24,4
P	ppm	-	16,1	6,8	4,1	9,8
CO_3''	ppm	18	18	-	12	-
HCO_3'	ppm	396,5	189,1	116	549	305
OH'	ppm	-	-	-	-	-
CN'	ppm	93	97,0	14,3	1,3	7,0
CN (Total)	ppm	138	-	55	-	-
SO_4''	ppm	1 382	1 101	1 850	5 263	496
Cl'	ppm	1 193	911,3	1 106	7 226	200,4
pH		8,22	8,40	7,30	7,05	6,63

Contd.

Table 6 Chemical Analyses (continued)

Element		Sewage water Aged	Swartpan water		Mill return water
		6.4.83	6.4.83	18.4.83	18.4.83
Conductivity µS/cm		2 000	17 000	11 000	4 500
T.D.S. mg/ℓ		1 188	15 216	9 732	3 002
Susp. solids mg/ℓ		201,5	7,5	13,1	23,2
Total hardnes ppm		609	4 600	3 485	1 544
Zn	ppm	-	-	-	-
Pb	ppm	0,1	0,2	0,2	0,1
Cu	ppm	< 0,1	25,8	25,6	0,1
Fe	ppm	0,1	109,8	188,2	0,2
Ca	ppm	105	454	945,7	617,6
Mg	ppm	100	1 093	273	0,4
Na	ppm	140	2 530	1 188	433
K	ppm	30,2	95	4,1	33,6
P	ppm	13,8	-	-	1,4
CO_3''	ppm	33	-	-	36
HCO_3	ppm	1 055	610	-	-
OH^1		-	-	-	23,8
CN^1	ppm	2,1	0,14	< 0,1	1,3
CN (total)	ppm	-	-	-	-
SO_4''	ppm	216,0	5 944	5 032	1 020
Cl^1	ppm	394,1	4 198	1 952	750
pH		7,00	2,97	2,69	11,16

Element		Underground Shaft Water 12.5.83
Conductivity µS/cm		4 500
T.D.S. mg/ℓ		2 799
Susp. solids mg/ℓ		25,8
Total Hardness ppm		1 129
Zn	ppm	0,071
Pb	ppm	0,041
Cu	ppm	0,053
Fe	ppm	0,078
Ca	ppm	408,5
Mg	ppm	26,4
Na	ppm	466,9
K	ppm	11,1
P	ppm	0,8
CO_3''	ppm	-
HCO_3	ppm	97,6
OH^1	ppm	-
CN^1	ppm	< 0,1
CN Total	ppm	-
SO_4''	ppm	843,2
Cl^1	ppm	745,1
pH		8,77

FALCONBRIDGE, at both their Falconbridge and Onaping, Ontario operations, disposes of sewage into their tailings and minewater system but again, the volumes are miniscual in relation to the tailings, and no adverse effects on flotation results have been found nor would be expected.

The type of sewage water use of interest here is where it is added as a supplementary water supply and constitutes a significant percentage of the water used in the plant. To date, no operation was found which relies heavily on reclaimed sewage water as a source of process water. It was rumored (unconfirmed) that Chuqinquamata, Division of CODELCO, reuses their treated sewage water in the mill.

FISHER and RUDY (1976) described an investigation into sewage wastewater use in copper-molybdenum recovery operations. Their paper was inserted above. They showed a distinctly improved copper and, particularly, molybdenum recovery when demineralized water is used compared with sewage effluent. They showed how recovery differences were greater near neutral pH than at high pH values and that when the wastewater is treated with activated carbon, recoveries improve but not to the levels achieved with demineralized water. Sewage water caused a reduction in recovery of 2.4% and 16.2% for copper and molybdenum respectively. There were other effects such as uncontrolable frothing.

They found that tertiary treatment of sewage effluent by activated carbon results in a significant improvement in terms of flotation recoveries. Ion exchange removal of anions from sewage effluent results in a significant improvement in copper and Mo recovery and also reduced the foaming effects. They concluded that it was the anion content that is mainly responsible for deterioration in the moly and copper recovery.

Foam fractionation improved the frothing problem but not the metal recovery deterioration.

In flotation of pyrite and gold from Witwatersrand tailings, the persistant drought of 1982-1984 created an urgent need to conserve water, and mining houses explored the possibility of using reclaimed sewage water in their operations. A few observations and opinions are of interest:

- <u>President Brand Gold Mining Co. Ltd., Welkom, O.F.S.</u>
  There are several large mines and mills around the city of Welkom, Orange Free State. These include gold cyanidation mills and uranium leaching plants, flotation plants, and roasting operations followed by calcine leaching to recover gold. The large municipal area as well as the huge mineworker hostels accommodating tens of thousands of people generate large volumes of sewage water. Cases have occurred where treated sewage effluent got mixed in with tailings reclaim water used in the flotation plants. It was found that when sewage water gets into the pulp, then sporadically the recovery of gold and pyrite are adversely affected. This operator

observation was not supported by hard data since there are so many contributing factors to flotation plant performance that none could say for certain what caused the sporadic reductions in flotation efficiency.

- When various individuals involved were questioned about the reduced recovery of gold/pyrite in flotation plants when sewage water is mixed into the system, several speculations as to the cause surfaced:

  -- Polyacrylate coagulants/flocculants used in the sewage plant may interfere with flotation.

  -- Organic compounds in sewage similar to humic acids interfere with flotation.

  -- Residual detergents and soaps interfere with flotation.

  None of these was backed up by data. The problem of analyzing for low levels of organic polymer surfactants in sewage water was mentioned.

- A consulting metallurgist at a mining house head office in Johannesburg pointed out that it had been found that when reclaimed sewage effluent is used in the Peabody scrubbers, that clean pyrite roaster gas (prior to conversion of SO_2 to SO_3), then the resulting water can be used in flotation circuits without reduced flotation recoveries. Again, no hard data was presented to support this claim.

- The Anglo American Research Laboratories undertook several intensive flotation tests on a large laboratory scale both with and without sewage plant effluent addition. These tests were inconclusive.

Anglovaal Research Laboratory Tests

Anglovaal Research Laboratories tested treated sewage water from two adjacent sewage plants located at Stilfontein Municipality in the Transvaal at their laboratories to determine relative performance in flotation of pyrite and gold. Their tests were for high pH flotation similar to that employed at Hartebeestfontein Gold Mining Company (HARTIES). The purpose of their tests was to determine whether Stilfontein sewage water could be used as an alternate water supply in the Hartebeestfontein two-shaft flotation plant.

The two sewage treatment plants sampled include an 'old plant' which uses a standard trickle filter for secondary treatment. The 'new plant' employs activated sludge technology for reduction of ammonia and phosphate.

The Anglovaal Research Labs' results are summarized as below. Additional discussion on this extremely useful quantitative research could be directed to:

ANGLOVAAL RESEARCH LABORATORIES
Post Office Box 1
Florida 1710
South Africa
(011) 672-0460
Gerhard Overbeek
Manager
C. R. Heathcote

These are some aspects of how the tests were performed that Anglovaal asked to be kept confidential.

2. INTRODUCTION

The water optimisation programme has revealed that Stilfontein sewage effluent may be a valuable additional source of water for metallurgical purposes at Hartebeestfontein.

This test work investigates only its effect on gold, sulphur and uranium recovery by flotation.

2.1 Inference

2.1.1 Summary

2.1.1.1 Stilfontein 'Old Plant' sewage water

Wide variations in flotation behaviour were obtained using Stilfontein old plant water. These ranged from totally unacceptable results to results which were better than the standard Rand water tests.

Flotation behaviour appears to be linked to the quality of this effluent water. When high phosphate levels occur together with very low Redox potentials, poor flotation conditions result, producing high mass low grade concentrate from stable voluminuous froths.

When the Redox potential of the water is higher, even though phosphates are present, acceptable metallurgy is obtained (as in water sample received 2 May 1983).

Table 1 Stilfontein Old Plant Water

Poor Flotation (25. 4.83)			Good Flotation (2. 5.83)		
pH	EH *	P ppm	pH	EH *	P ppm
7,76	-256	13,5	7,34	125	10.4

* millivolts versus standard calomel electrode

2.1.1.2 Stilfontein 'New Plant' sewage water

Stilfontein new plant sewage water produced very similar results to the standard Rand water. Froth texture and stability were of such a nature as not to produce problems on the concentrator, and, if this water was phased in progressively over a period of time, no flotation problem should be encountered.

Table 2 Stilfontein New Plant Water

Good Flotation (25. 4.83)			Good Flotation (2. 5.83)		
pH	EH *	P ppm	pH	EH *	P ppm
7,73	- 25	5,7	7,65	134	2,7

* millivolts - versus standard calomel electrode

Complete chemical analyses of all water types are included in Table 3.

2.1.2 Gold Recovery/Sulphur Grade Curves (Roughers)

Figures I and II appended, compare the flotation behaviour of the various water types and blends with respect to gold recovery versus rougher concentrate sulphur grades.

From the figures, the following conclusions can be drawn :

2.1.2.1 Stilfontein new plant sewage water behaved very similarly to Rand water.

2.1.2.2 Stilfontein old plant sewage water (Rec. 25.4.83) was unsuitable for use in the flotation plant, except at addition levels lower than 10%, however.

2.1.2.3 Old plant water (rec. 2. 5. 83) performed slightly better than the standard water.

2.1.2.4 Figure I clearly shows that longer conditioning, i.e. 20 minutes, improved the flotation behaviour of the sewage water (composite of equal parts old, new and worst case), producing a recovery/grade curve which was higher than the standard Rand water test (unconditioned).

2.1.2.5 When poor quality waters, having excessive frothing properties caused by polyphosphates, are used in flotation, the addition of frother plays an important part in the recovery/grade relationship. As the frother addition is reduced to gold recovery drops and sulphur grade increases at constant flotation time (compare 'worst case' 50% 10 and 14 g/ton frother and 'old plant' 100% 10 and 4 g/ton frother). In effect, the rougher float is cleaner (less gangue floats) but the kinetics are a bit slower.

3. RECOMMENDATIONS

3.1 Old plant sewage water should not be used in Hartebeestfontein 2 Shaft flotation plant because of the wide variations of water quality emanating from this plant.

Poor quality sewage water could have disastrous effects on flotation performance.

3.2 From the samples of Stilfontein new plant water evaluated, it appears that this water type could be used in the Hartebeestfontein 2 Shaft flotation plant.

Progressive introduction of the water over a given time period, together with careful frother control, will ensure the least disruption to the circuit.

4. SAMPLES

4.1 Ore Samples

4.1.1 Hartebeestfontein 2 Shaft Rod Mill Feed (Tests 1 to 21)

Laboratory Reference Number RS 49083

Chemical Analysis

Gold	=	12,665 g/ton
Uranium	=	120,75 g/ton
Sulphur	=	1,258 %

4.1.2 Hartebeestfontein 2 Shaft Rod Mill Feed (Tests 22 to 35)

Laboratory Reference Number RS 47044

Chemical Analysis

Gold	=	12,379 g/ton
Uranium	=	127,90 g/ton
Sulphur	=	1,271 %

4.2 Water Samples

4.2.1 Stilfontein sewage water - new plant (Rec. 25 April 1983)

4.2.2 Stilfontein sewage water - old plant (Rec. 24 May 1983)

4.2.3 Stilfontein sewage water - worst case (Rec. 24 May 1983)

4.2.4 Stilfontein sewage water - new plant (Rec. 2 May 1983)

4.2.5 Stilfontein sewage water - old plant (Rec. 2 May 1983)

Table 3 Chemical Analysis

Element	Stilfontein Sewage Water				
	New plant (25.4.83)	Old plant (25.4.83)	Worst case (25.4.83)	New plant (2.5.83)	Old plant (2.5.83)
Conductivity µS/cm	1 700	1 400	1 600	1 500	1 600
Total Dis. solids ppm	1 069	1 010	1 070	1 084	1 050
Sus. solids ppm	9,81	60,28	13,14	2,0	13,7
Total Hardness (as $CaCO_3$)	757,6	803,0	756,3	523	434
Ca ppm	177,2	183,8	169,2	107,9	100,1
Mg ppm	76,6	83,6	81,1	73	73
Na ppm	138,6	138,1	134,3	152	163
K ppm	27,3	31,2	30,0	26,8	30,0
Fe ppm	0,13	0,13	0,26	0,09	0,09
Cn ppm	0,015	0,015	0,016	<0,1	<0,1
Pb ppm	<0,1	<0,1	<0,1	0,1	0,1
SO_4'' ppm	387,7	276,1	384,4	383	358
Cl' ppm	150,9	143,2	140,5	142,2	260,5
CN' ppm	<0,1	<0,1	<0,1	0,17	0,16
CO_3'' ppm	-	-	-	3	-
HCO_3' ppm	347,7	536,8	311,1	253	214
P ppm	5,7	13,5	11,4	2,7	10,4
pH	7,73	7,72	7,75	7,65	7,34
EH millivolts vs S.C.E.	-25	-256	-78	134	125

5. EXPERIMENTAL

5.1 Preparation of Flotation Feed

Representative 2 000 gm portions of Hartebeestfontein 2 Shaft rod mill feed were milled for various times, in a stainless steel laboratory rod mill to produce a milling curve.

The water under test was then used for milling to produce flotation feeds of 65% - 75 µm.

After milling the pulp was diluted to a relative density of 1,242 prior to flotation.

Test water was used for all washing and dilution purposes.

5.2 Flotation Technique

5.2.1 Flotation conditions are outlined below :

Table 4 Flotation Conditions

Stage	Reagent Addition - g/ton				Time - minutes			pH
	$CuSO_4.5H_2O$	AP 3477	SNPX	S 5004	Grind	Condition	Froth	
Rod mill	-	-	-	-	22	-	-	
Pyrite Ro. 0	80	-	-	-	-	2	-	11,0
1	-	15	40	4-10	-	1	1	
2							1	
4							2	
8				4		-	4	
12							4	

Note: (i) AP 3477 = Aero Promoter 3477
S 5004 = Senfroth 5004

(ii) pH was adjusted to pH 11,0 by lime addition prior to conditioning

5.2.2 All tests were conducted in a Denver D 12 laboratory flotation cell, using the following conditions :

	Cell size litres	Impeller speed	R.D	Solids %
Conditioning and flotation	5,2	1 800	1,242	31

5.2.3 In all tests, five separate rougher concentrate were collected over a 12 minute period and cumulatively represent recoveries at 1, 2, 4, 8 and 12 minutes, respectively.

6. RESULTS

6.1 Stilfontein Sewage Water (Rec. 25 April 1983)

6.1.1 Mineral Separation

Gold recovery/sulphur rougher concentrate grade curves were used to evaluate mineral/gangue separation (Figure I).

Curves in the upper right hand section indicate gold separation - the higher the curve in that direction the better the separation, while curves in the lower left hand quadrant represent poorer separation.

6.1.1.1 Stilfontein Sewage Water - New Plant

Mineral/gangue separation produced by this water type was very similar to the Rand water standard (See Figure I).

The rates of flotation for gold, uranium, sulphur and gangue for the sewage water were higher than the standard water.

Sulphur rougher concentrate grade is governed by the sulphur and gangue kinetics and as the increase in sulphur flotation rate was higher than the increase in gangue flotation rate, no marked change in sulphur rougher concentrate grade occurred.

K values for the various sewage water blends relative to the standard Rand water are presented below in Table 5. Actual rate constants are tabulated in Table 6.

Table 5 *Relative Au, U_3O_8 and S Rate Constants

Percent Test water	Frother g/ton	Relative Rate Constants			
		Gold	Uranium	Sulphur	Gangue
Rand Water					
100 %	14	1,000	1,000	1,000	1,000
Stilfontein 'New Plant' Sewage Water					
10 %	14	1,3785	1,5167	1,6731	1,2414
50 %	14	1,3134	1,5599	2,1699	1,4385
100 %	10	1,4076	1,3568	2,7126	1,4578
Stilfontein 'Old Plant' Sewage Water					
10 %	14	1,5225	2,0001	2,2868	1,9441
100 %	10	0,5002	0,6709	1,0985	4,3298
100 %	4	0,3013	0,2884	0,6656	2,6255
Stilfontein 'Worst Case' Sewage Water					
10 %	14	1,0626	1,1242	1,2129	1,0158
50 %	14	1,6812	2,0865	2,5588	3,6138
50 %	10	1,0485	0,9824	1,3613	1,0229
100 %	10	1,3408	1,1893	1,7518	1,5193

$$* \quad \text{Relative rate constant} = \frac{\text{Test water rate constant}}{\text{Standard water rate constant}}$$

6.1.1.2 Stilfontein Sewage Water - Old Plant

Stilfontein old plant sewage water at the 10% replacement level produced mineral/gangue separations which were just acceptable (See Figure I).

At the 100% replacement level extremely poor mineral/gangue separation occurred. This condition was caused by a voluminuous non-selective uncontrollable froth which persisted despite reduced frother addition (See Figure I).

The rate of flotation of gold, uranium and sulphur dropped drastically, while the gangue flotation rate increased so producing low grade concentrates and poor recoveries.

Relative and actual K values are presented in Tables 5 and 6.

6.1.1.3 Stilfontein Sewage Water - Worst Case

Mineral/gangue separation at the 10% replacement level was the lowest curve in the family of acceptable results (See Figure I). However, as the replacement level rose to the 50% level, a marked drop in mineral separation occurred (See Figure I).

On reducing the frother addition level from 14 to 10 gram/ton for the subsequent 50 and 100% replacement tests, acceptable mineral separations were obtained (See Figure I).

The rate of flotation of gold, uranium, sulphur and gangue were higher than the standard.

Uranium and sulphur recoveries for the sewage blends were generally equal to or better than the Rand water standard.

Table 7 Gold, U_3O_8 and Sulphur Actual Recoveries for Various Sewage Water Blends (Rec. 25.4.83)

Percent Test Water	Frother addition g/t	Actual Recovery - Percent					
		Gold		Uranium		Sulphur	
		Cumulative Flotation Time - minutes					
		1	12	1	12	1	12
Rand Water							
100 %	14	72,04	92,78	18,74	40,35	51,21	94,97
Stilfontein 'New Plant' Sewage Water							
10 %	14	76,08	90,86	23,64	41,99	64,63	95,66
50 %	14	76,38	92,25	23,46	41,65	70,92	96,41
100 %	10	76,13	90,28	22,09	41,16	77,49	98,20
Stilfontein 'Old Plant' Sewage Water							
10 %	14	78,28	91,99	26,87	42,58	72,34	96,00
100 %	10	49,82	84,02	15,53	47,22	45,60	97,26
100 %	4	40,98	79,29	7,83	31,35	35,63	95,98
Stilfontein 'Worst Case' Sewage Water							
10 %	14	70,90	89,50	20,40	41,64	56,33	94,64
50 %	14	78,76	90,79	28,57	44,36	74,97	96,56
50 %	10	71,32	90,22	17,54	37,62	60,30	96,05
100 %	10	75,11	90,07	18,60	37,03	66,56	96,41

Table 8 Gold, Uranium and Sulphur Equilibrium Recoveries for Various Sewage Water Blends (Rec. 25.4.83)

Percent Test Water	Frother addition g/ton	Equilibrium Recovery - R - Percent		
		Gold	Uranium	Sulphur
Rand Water				
100 %	14	94,12	42,44	99,88
Stilfontein 'New Plant' Sewage Water				
10 %	14	92,20	43,04	98,52
50 %	14	93,25	42,62	98,68
100 %	10	90,70	42,49	100,00
Stilfontein 'Old Plant' Sewage Water				
10 %	14	92,89	42,88	97,70
100 %	10	88,63	53,22	100,00
100 %	4	83,03	42,91	100,00
Stilfontein 'Worst Case' Sewage Water				
10 %	14	90,72	43,36	98,14
50 %	14	91,34	44,43	98,07
50 %	10	91,03	40,00	99,61
100 %	10	90,11	38,29	98,87

6.2 Stilfontein Sewage Water (Received 2 May 1983)

6.2.1 Mineral Separation

Gold recovery/sulphur rougher concentrate grade curves were used to evaluate mineral/gangue separation (See Figure II).

6.2.1.1 Stilfontein Sewage Water - New Plant

Similar mineral/gangue separations to Rand water were obtained at all percentage replacements using this sample of Stilfontein new plant sewage water (See Figure II).

5.3.2 Results clearly show the vast improvement brought about in the flotation behaviour of these waters when conditioned.

Tables 13 to 17 below compare results for the various water types and conditions.

Table 13 Concentrate Grade

Test Water and Conditions	Frother addition g/ton	Rougher Concentrate - Grade					
		Gold g/ton		Uranium g/ton		Sulphur g/ton	
		Cumulative Flotation Time - minutes					
		1	12	1	12	1	12
Unconditioned							
Rand water	14	524,7	216,2	1 282	883	37,23	22,09
New Plant	10	394,7	219,4	1 016	887	38,40	22,81
Old Plant	10	112,8	73,98	333	394	10,57	8,77
Worst Case	10	409,1	217,9	966	854	38,09	24,51
Conditioned							
Rand Water	14	423,9	233,7	1 034	973	45,60	26,28
Sewage * Composite	10	300,9	200,6	890	765	31,64	21,12

* Composite - Equal parts 'old, new and worst case'

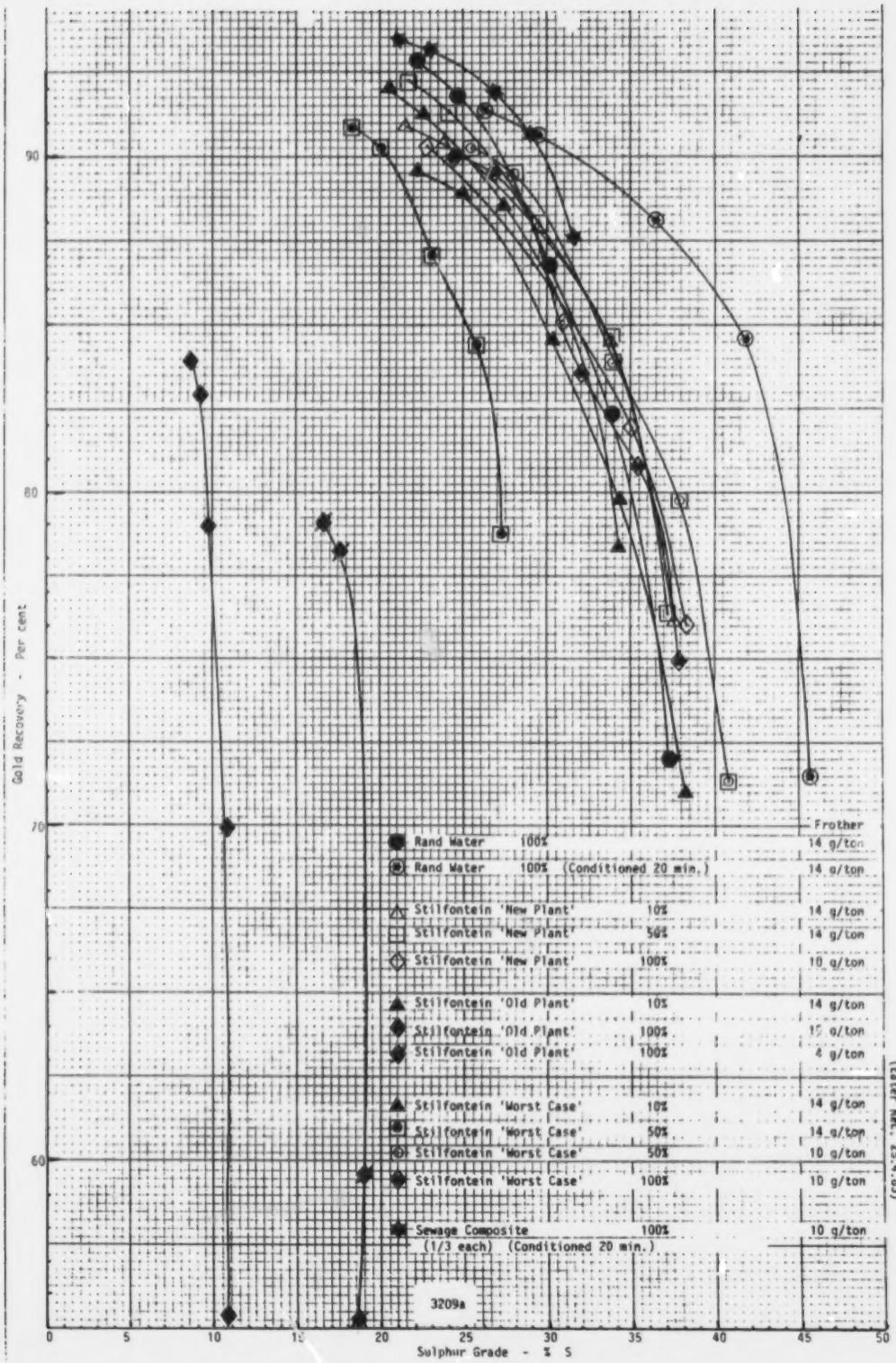


Figure 1 Gold Recovery/Sulphur Grade Curves (Eater Rec. 25.4.83)

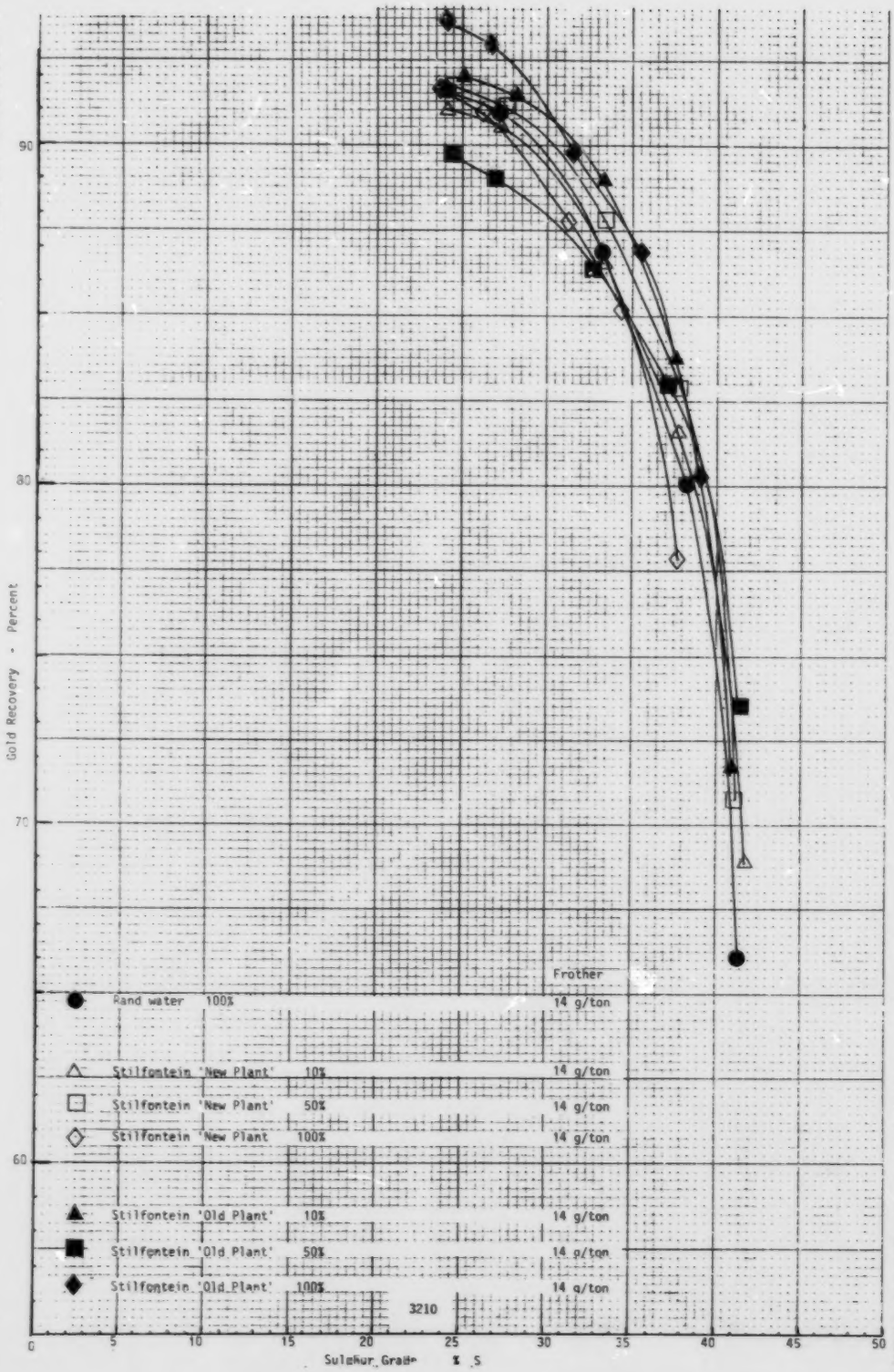


Figure 11 Gold Recovery/Sulphur Curves (Water Rec. 2.5.83)

mountain states

8. SPECIFIC ENVIRONMENTAL PROBLEMS ASSOCIATED WITH THE PROCESSING OF MINERALS

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ABSTRACT

This paper considers specific environmental problems associated with the processing of minerals. The topics covered include the development of special attributes of mineral processing engineers as pollution experts; a discussion on the environmental problems associated with the use of common and specific flotation reagents; an examination of the effect of hazardous metallic ions in plant effluents; and a plea for the incorporation of environmental awareness and training as integral parts of mineral engineering curricula.

INTRODUCTION

In his persistent efforts to satisfy his insatiable demand for mineral resources, man has often exploited them without regard to consequence. It would be fruitless to deny that the mineral industry by its very nature contributes to certain pollution problems. Open pit mining, underground operations,

hydraulic mining, oil and gas production, metal smelting, fuel refining and all other extractive efforts disturb our environment to some degree. Some damage to the environment is inevitable even with the best extraction procedure and land restoration methods. The mined ores are moved and handled several times before they are processed, thus creating dust, noise, and other forms of air pollution. Mining wastes and drainage usually contribute to stream pollution and create a solid waste disposal problem.

It is for these reasons that the mineral industry is identified by a large segment of the uninformed public as a major contributor to the overall pollution problem. This is far from the truth. In the first place, only a small percentage (about 0.14 per cent) of the total land in the United States has been adversely affected by mining. Moreover, practically no public attention has been drawn to the extensive as well as expensive efforts made by the mineral industry to minimize the environmental impact of its operations. Many extractive companies take great pride in the responsible manner in which they have conducted their business. Their efforts in the environmental control field have gained national recognition and praise from government agencies as well as the public.

As members of a progressive engineering society it is our responsibility to achieve maximum conservation of a finite supply of minerals with minimum contamination of the environment. We must continue to develop and implement operational practices, processes and techniques to achieve the above goal and to assure full consideration of health, safety and welfare of the public as well as the people working in our industry.

As mineral processing engineers we must do our part in creating a safe and pollution-free environment in and around our mills and processing plants. Moreover, because of our special expertise in understanding pollution situations and in prescribing economic solutions to such problems, it is imperative that we provide the needed lead not only in our own industry but also in other fields of endeavor.

It is not the intention of the authors to cover in detail the environmental problems associated with mineral processing.[1-4] Rather, the primary objectives are to develop the special attributes of mineral processing engineers as pollution experts, to pinpoint some specific problems encountered in different phases of processing, to discuss in some

detail the environmental problems associated with the use of common and specific flotation reagents, to examine the effect of hazardous metallic ions in plant effluents and to plead for the incorporation of environmental awareness and training as integral parts of mineral engineering curricula.

MINERAL PROCESS ENGINEERING AND POLLUTION CONTROL

Since the art and science of metallurgy deals in the separation of valuable material from waste products either in the solid, liquid or gaseous form, it is easy to appreciate that mineral processing engineers have a special competence for understanding and remedying pollution situations. The same basic principles that govern metallurgical processes also control pollution abatement technology, and most of the common processing machinery can be applicable to pollution problems. Classifiers, cyclones, electrostatic precipitators, thickeners, flotation cells or aerators, digesters, filters, extractors, and the like are all mineral processing units that have found specific applications in pollution control schemes.

According to Aplan[5] the essence of mineral process engineering consists of particle technology, applied surface chemistry, and chemical dissolution which are also basic elements of a pollution control program. Furthermore, the technology of solid waste disposal, recovery of secondary metals and recycling all depend on the unit operations and processes that are the basis of separation of metals and minerals from their ores. A typical flowsheet proposed by Sullivan *et al.*[6] for waste disposal as illustrated in Figure 10 clearly reveals that it is comparable to the flowsheet for recovery of minerals from their ores.

For these reasons, it is up to the metallurgists and mineral processing engineers to pave the way for improvements and innovations in the pollution abatement technology and to share their knowledge with environmental engineers in providing the badly needed mineral resources and metals with a minimum degradation of the environment. Also for these reasons, there is no excuse for the absence of abatement systems in mill design and the existence of pollution and environmental problems in processing plant operations.

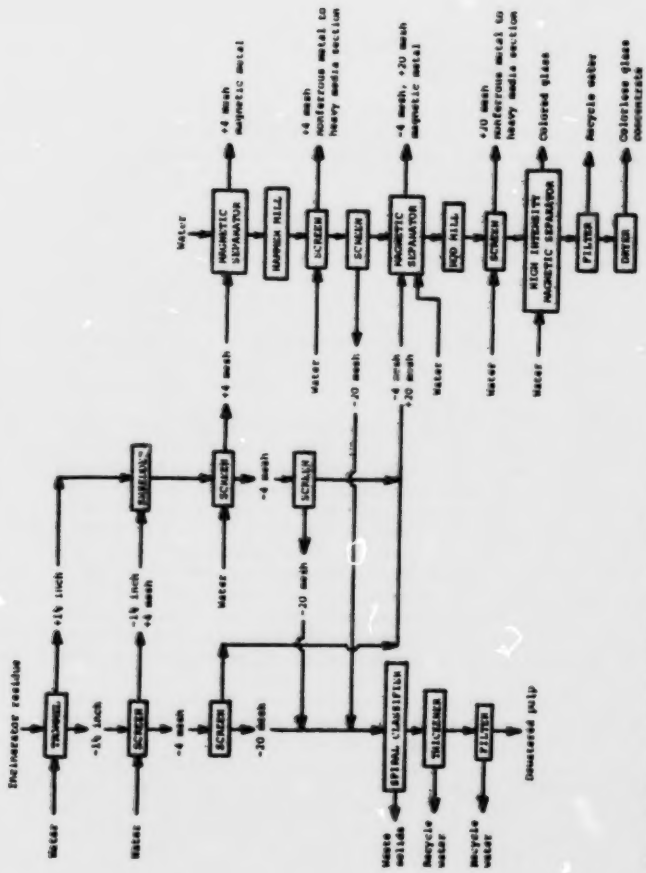

Figure 10. Physical beneficiation flowsheet for concentrating valuable materials contained in incinerator residues (according to USBM).

ENVIRONMENTAL EFFECTS OF FLOTATION PROCESSING

Froth flotation is the most widely used technique for the recovery of valuable minerals from ores. In this process, the disposal of the solids in the tailings and the residual reagents and soluble metal ions and complexes contained in the liquid portion of the tailings constitute the major pollution problems.

The task of controlling and abating the extent of pollution problems from a flotation circuit should be critically evaluated during laboratory-pilot plant testing. The mineral processing engineer designing or evaluating a given flotation operation should consider critically not only the per cent recovery, concentrate grade and overall reagent costs, but also the environmental problems associated with each flotation scheme.

In the future, it is anticipated that most of the water control boards and environmental protection and improvement agencies will demand environmental position or feasibility reports not only from newly proposed flotation plants but also from operating plants.

The major contributors to the pollution problems in the flotation plant are the rather noxious reagents used in the process. These include a wide variety of collectors, frothers, depressants, activators, and modifiers. Such organic and inorganic reagents constitute hazardous pollutants in ground or surface waters due to flotation effluents in the soil, breakage of tailings dam or pipelines, and accidental spills.

The pollutants contained in the aqueous portion of the tailings may be grouped into two major classes: first, the residual organic and inorganic reagents added deliberately to the flotation circuit to recover the valuable minerals, and second the light and heavy metal ions and complexes contributed to the aqueous phase by the ore itself due to partial solubilities of various minerals in water and/or to their dissolution by some of the flotation reagents.

EFFECT OF FLOTATION REAGENTS

A critical examination of Table XII reveals the following observations concerning the residual reagents contained in the aqueous portion of the tailings:

Table XII

Environmental Considerations for Common Flotation Reagents

Reagent Type & Name	Chemical Composition	Amount Added	Reagents Distribution: Solids	Reagents Distribution: Solution	Toxic Species
Collectors					
Xanthate	$ROCSSH$	<0.1	Mostly complexed	Minor	CS_2
Thiophosphates	$(RO)_2PSSH$	<0.1	Mostly complexed	Minor	$H_2PO_4^-$, HS^-, H_2S
Fatty acids	$RCOOH$	0.5 to 2.0	Complexed with minerals and ions	Minor	Biodegradable
Sulfonates and Sulfates	RSO_3H RSO_4	0.5 to 2.0	Complexed with minerals and ions	Minor	Biodegradable (except Cyclic)
Amines	RNH_2Ac	0.2 to 2.0	Adsorbed on silicates	Minor	Free amine*
Fuel oils	Saturated	0.1	Selectively adsorbed	Minor	Volatile hydrocarbons
Frothers					
Pine oil	Aromatic alcohols	< 0.1	Carried over in froth	Appreciable	Volatile, carcinogenic
Dow froth	Higher alcohols	< 0.1	Carried over in froth	Appreciable	Volatile, biodegradable
MIBC	Methyl isobutyl-carbinol	< 0.1	Carried over in froth	Appreciable	Volatile, biodegradable
Conditioners					
Sodium sulfides	Na_2S, $NaHS$	1 to 15	Selectively complexed	Major	HS^-, H_2S, $SO_4^=$
Phosphorus Pentasulfide	P_2S_5	1 to 4	Selectively complexed	Major	HS^-, H_2S
Sodium Cyanide	$NaCN$	0.005 to 0.1	Mostly complexed	Minor	CN^-
Sodium Silicate	Na_2SiO_3	0.2 to 1.0	Mostly complexed	Appreciable	H_4SiO_4
Milk of Lime	$Ca(OH)_2$	1 to 4	Mostly complexed	Appreciable	OH^-
Separan	Polyacrylamid	<0.01	Mostly adsorbed	Minor	Biodegradable

*Unknown toxicity.

1. The amounts of flotation reagents used in the process are very small and kept at a minimum (starvation levels) not only because of economics but also to avoid the detrimental effects of excess reagents on the flotation results and water quality of the plant effluents.
2. Most of the added reagents are more or less completely consumed during the flotation process due to adsorption onto the mineral surfaces or complexing with appropriate ions in solution.
3. The trace amounts of some organic reagents, such as hydrocarbons, alcohols, and esters, remaining in the tailings water evaporate, decompose or biodegrade.
4. In general, inorganic reagents contribute either active cations or anions that react at the mineral surfaces or in the aqueous phase, leaving one or the other in the tailings liquid. Since most of these cations or anions are always present in streams and natural ground waters, they do not act as pollutants in the small amounts added to the flotation systems.

From these observations it is evident that the limited amounts of several reagents added to the flotation circuits are almost completely consumed or complexed in the process or are eliminated or decomposed during the impounding of the tailings. Therefore, in general, they do not contaminate the decant water discharged into the stream, river or lake, nor do they pollute the ground water due to seepage.

However, some toxic reagents if used indiscriminately or carelessly in the flotation systems can constitute a major water pollution hazard and even a fatal pollutant under plant operating conditions. Cyanide and hydrogen sulfide are two such reagents that need a more detailed scrutiny. These reagents are widely used in sulfide flotation systems, especially in the selective flotation of molybdenite from copper concentrates. Because of their extremely toxic nature to man, animals and aquatic life, they have been under investigation by the state and federal environmental protection agencies.

Davis[7] has thoroughly covered the topic of control of water pollutants from flotation plants.

The common methods proposed for the treatment of flotation plant effluents prior to their discharge in streams, rivers, lakes or ground water are chemical alteration and precipitation, coagulation and sedimentation, activated charcoal adsorption, biological treatment, filtration, and foaming. In addition to these, the processing engineers should consider some of the newly developed methods such as ion exchange, reverse osmosis and electrodialysis.

The Cyanide Problem

Wright and Bhappu[8] have discussed the environmental problem associated with the use of cyanide in flotation circuits. The primary reason for adding sodium cyanide to the molybdenite flotation circuit is to depress pyrite and other gangue sulfide minerals in the ore so that they will not float along with the molybdenite. This depressing action of cyanide is due primarily to the formation of extremely stable water-wettable complexes with heavy-metal cations in two stages: first, precipitates of relatively insoluble cyanide salts form, and second they dissolve in excess cyanide to form cyanide complexes.

For example, the cyanide ion reacts with the ferrous ion in aqueous solution to form the complex ferrocyanide ion $[Fe(CN)_6]^{-4}$. A similar complex forms with ferrous ions present on the pyrite surface, thus depressing pyrite in the selective flotation of molybdenite. Corresponding cyanide complexes also form on the copper and zinc sulfides if present in the ore.

In flotation systems, the effect of alkali cyanide additions to depress gangue sulfides depends to a large extent on the pH of the system. Sodium cyanide hydrolyzes in aqueous solutions to form free alkali and hydrogen cyanide, relatively insoluble in water:

$$NaCN + H_2O \rightleftarrows HCN + NaOH \qquad (1)$$

According to this equation, the presence of free alkali in solution shifts the hydrolysis to the left. Since the concentration of CN^- determines its availability for depression of gangue sulfides, a higher pH favors its depression effect (see Table XIII).

Besides complexing with heavy-metal cations on the surfaces of the minerals as well as in the

Table XIII

Influence of pH on Relative Abundance of CN^- Ions and Dissolved HCN[9]

pH	Millimole/millimole Total Alkali Cyanide As CN^-	As HCN
6.0	0.0005*	0.9995
6.5	0.0015	0.998
7.0	0.0047	0.995
7.5	0.0146	0.985
8.0	0.045	0.955
8.5	0.129	0.871
9.0	0.320	0.680
9.5	0.597	0.403
10.0	0.825	0.175
11.0	0.979	0.021
12.0	0.999	0.001
13.0	1.000	0.000

*To obtain the CN^- in milligrams per milligram of sodium cyanide, it is sufficient to multiply the numbers in this column by 0.531.

solution, cyanide also has a tendency to dissolve sulfide minerals of copper, zinc, and iron. The end products of these reactions are the corresponding metal cyanides, thiocyanate, and sulfate. For example, pyrite reacts with cyanide thus:

$$FeS_2 + 7NaCN + 2O_2 = Na_4Fe(CN)_6 + Na_2SO_4 + NaCNS \qquad (2)$$

From this discussion, one can see that the cyanide added to the flotation system should be used up in complexing with metal cations on the mineral surfaces and in solution or in forming thiocyanate. Also, because of the presence of appreciable amounts of gangue sulfides as well as heavy-metal cations in the flotation plant feed and tailings, no free CN^- should remain in tailings water. The only cyanide products that could be present in the tailings water would be complexed heavy-metal cyanides and thiocyanate.

Table XIV gives average analyses for free cyanide, thiocyanate, ferrocyanide, sulfide, phosphorus, and metal ions present in the plant effluents from several flotation plants in which molybdenite is selectively floated from copper concentrates with the use of sulfides and cyanides. The results clearly indicate that no free cyanide remains in any of the plant effluents, except a very small amount of free cyanide in the reclaimed water that is recirculated in the plant.

Table XIV

Average Analyses of Effluents from Selective Sulfide Flotation Plants

	Plant Tailing	*Reclaimed Water*	*Tailing Discharge*
	(all values in ppm)		
Cu	0.01	0.01	< 0.01
Zn	0.02	0.05	0.03
Pb	0.07	0.10	< 0.01
Fe	0.05	0.20	< 0.05
Mn	0.50	0.90	0.10
Ca	71.0	65.0	31.0
Mg	17.5	16.0	6.0
Mo	3.0	3.8	0.0
Cn	< 0.005	< 0.005	N.D.
SCN	0.10	0.12	N.D.
Fe(CN)	N.D.	N.D.	N.D.
$S^{=}$	N.D.	N.D.	N.D.
P	N.D.	< 0.01	< 0.01

N.D. - none detected

Therefore, the limited amount of cyanide added to the flotation systems does not constitute a hazardous condition either at the mill or in the plant effluent. The only way in which free cyanide can remain in the tailings effluent is if it is added in excess, a condition that should never be

allowed to exist in an efficient and safe flotation plant.

In recent years, the removal of residual cyanide from waste effluents has received much attention. Most of the published literature is concerned with the treatment of spent solutions from electroplating plants.[10] Methods for cyanide removal include oxidation processes (with Cl_2, NaOCl, O_3, H_2O_2, and electrolysis), ion exchange formation of insoluble cyanide complexes acidification-aeration process, and biological decomposition.

Hydrogen Sulfide Problem

Alkali sulfides have been used extensively in flotation systems both as activators (for oxide or tarnished sulfide minerals) and depressants (for depressing gangue sulfides in selective flotation of particular sulfide minerals). These systems have been critically examined by Cox *et al.*,[11] Gaudin[9] and Dudenkov *et al.*[12] Theoretical work suggests that the actual depressant is the hydrosulfide ion, HS^-, rather than sodium sulfide or hydrogen sulfide.

An examination of Table XV reveals that the availability of HS^- ions increases with increasing pH up to 9.0 after which the concentration of the ions remains more or less constant. Therefore in order to obtain maximum benefit of the reagent, the flotation should be carried out at higher pH values.

From environmental and safety considerations, the major factor to watch for is the liberation of H_2S in the flotation system. Although the solubility of H_2S in water is relatively high (0.12 m/l at one atmosphere), under the existing flotation conditions there are good possibilities for evolution of H_2S, thus causing a hazardous operating condition. It is fortunate that sufficient dilution of H_2S with fresh air takes place in most of the operating plant to keep its concentration below the threshold level. Nevertheless, the problem does exist and efforts should be made to keep down the H_2S concentration through suitable operating controls and proper ventilation.

The toxicity of H_2S is greatly underrated. In sewage disposal, 1 ppm of sulfide under certain conditions (mostly acidic) causes a most lethal atmosphere.[13] Lethal concentrations for H_2S are similar to those for hydrocyanic acid. However, the latter is more soluble in water and thus somewhat less hazardous.

Table XV

Relative Abundance of H_2S, HS^- and $S^{=}$ as a Function of pH[9]

For every millimole $Na_2S \cdot 9H_2O$ added per liter, there is

pH	*Dissolved H_2S (millimole/liter)*	*Dissolved HS^- (millimole/liter)*	*Dissolved $S^{=}$ (millimole/liter)*
4.0	1.0	0.0010	2×10^{-14}
4.5	1.0	0.0030	2×10^{-13}
5.0	0.99	0.010	2×10^{-12}
5.5	0.97	0.030	2×10^{-11}
6.0	0.91	0.09	2×10^{-10}
6.5	0.75	0.25	1.6×10^{-9}
7.0	0.50	0.50	0.5×10^{-8}
7.5	0.25	0.75	6.5×10^{-8}
8.0	0.09	0.91	2×10^{-7}
8.5	0.030	0.97	7×10^{-7}
9.0	0.010	1.00	0.000002
10.0	0.0010	1.00	0.00002
11.0	0.00010	1.00	0.0002
12.0	0.000010	1.00	0.002
13.0	0.000001	0.98	0.02
14.0	0.0000001	0.80	0.20

Since the concentration of H_2S is dependent on the pH, the safest as well as the most effective method in the plant is to try to maintain a high pH in the flotation circuit with the use of caustic. This is especially true for those circuits using Nokes' reagent containing phosphorus pentasulfide (P_2S_5). The most critical phase of the use of this reagent is in the preparation of Nokes' solution for plant use. It is imperative that ultimate precautions be taken in the mixing step to make sure that all the P_2S_5 has reacted with caustic and that the solution is stabilized. If equilibrium is not reached, decomposition of the reaction product can occur, giving off H_2S.

The optimum conditions can be met by digesting P_2S_5 slowly in at least a 10% excess caustic over the stoichiometric requirement. Since the reaction is exothermic and since the decomposition of the reaction product is enhanced at higher temperatures, precautions must be taken to keep the temperature down, preferably below 120° F. Provisions should also be made to have available at the mixing tank a source of caustic so that, if needed, it can be added to the mixture to prevent its decomposition. Additional safety devices such as alarm systems based on H_2S detection should also be installed at strategic locations and operators should be trained to avert a possible disaster.

Hazardous Metallic Ions in Plant Effluents

As pointed out earlier the mill tailing water contains several light and heavy metal ions and complexes that are normally contributed to the system due to natural solubility of valuable and gangue minerals contained in the ore. Some of these dissolved metals such As, Cr, Hg, Pb and Se constitute serious pollution problems and are considered "hazardous substances" by the environmental protection agencies.

In order to prevent the degradation of the environment and injury to man, animals, and aquatic life, the government agencies have adopted "regulations" concerning the discharge of hazardous substances. Typical regulations adopted by the New Mexico Water Quality Control Commission on August 27, 1971, are as follows:

Regulation Number 6 - Discharge of Hazardous Substances

A. No person shall cause or allow effluent from a new process or plant to discharge directly or indirectly into water as defined by the Water Quality Act unless the effluent, as indicated by any single sample, conforms to the following:

Arsenic	0.05 mg/l or less
Barium	1.0 mg/l or less
Boron	0.75 mg/l or less
Cadmium	0.01 mg/l or less
Chromium (Total)	0.01 mg/l or less
Copper*	0.05 mg/l or less
Lead	0.05 mg/l or less

Manganese	0.1 mg/l or less
Mercury	0.001 mg/l or less
Molybdenum	0.01 mg/l or less
Nickel	0.1 mg/l or less
Selenium	0.01 mg/l or less
Silver	0.05 mg/l or less
Zinc*	0.1 mg/l or less

*Provided that effluents from a community sewerage system may contain 0.1 mg/l copper and 0.5 mg/l zinc.

B. Subsection A does not apply to constituents in the water diverted. Samples shall be examined in accordance with the latest editions of Standard Methods for the Examination of Water and Wastewater published by the American Public Health Association, or Methods for Chemical Analysis of Water and Wastes published by the Environmental Protection Agency, where applicable.

Regulation Number 4 - Effluent Quality

A. Except as otherwise provided in this regulation, no person shall cause or allow effluent to discharge directly or indirectly into water as defined by the Water Quality Act unless the effluent:

1. as indicated by any daily composite sample, conforms to the following:

Biochemical Oxygen Demand (BOD)	less than 30 mg/l
Chemical Oxygen Demand (COD)	less than 125 mg/l
Settleable Solids	less than 0.5 ml/l

2. as indicated by single sample, conforms to the following:

Biochemical Oxygen Demand (BOD)	less than 160 mg/l
Chemical Oxygen Demand (COD)	less than 250 mg/l
Settleable solids	less than 1.0 ml/l
Fecal coliforms	less than 500 organisms/ 100 ml
pH	between 6.7 and 8.6

Upon application, the Director of the Environmental Improvement Agency may eliminate the pH requirement for any effluent source that the Director determines does not unreasonably degrade the water into which the effluent is discharged.

As mineral process engineers we can appreciate the primary reasons for the very low concentration of metallic ions in tailing effluents. First, the solubility of many naturally occurring minerals (sulfides, oxides and silicates) is limited. Second, most of the dissolved metallic ions tend to hydrolyze at higher pH values normally used in the flotation systems and since the solubilities of most of the metal hydroxides are limited (see Table XVI), the ionic concentrations are correspondingly low (well below the specified regulations). Moreover, some of the metal ions such as Mo, W and V complex with calcium (available through lime addition to the flotation circuit) to form very insoluble compounds such as $CaMoO_4$ and $CaWO_4$. Finally, many light and heavy metallic ions are complexed with flotation reagents (collectors, depressants and modifiers) to form insoluble complexes. The end result of all these chemical reactions in the flotation system is the depletion of hazardous ions in the tailing effluents.

In the event that concentrations of hazardous ions in the plant effluent are above specified limits, then water must be treated to comply with the regulations. Methods commonly used in the tertiary treatment of municipal waters and abatement of pollutants in industrial effluents can be readily applicable to the treatment of mill effluents. These include neutralization, chemical alteration and precipitation, charcoal adsorption, ion exchange, biological treatment and foam flotation.

The above discussion clearly indicates that with proper understanding of the mineral-chemistry, surface-chemistry, ionic equilibria and the flotation mechanisms coupled with the abatement technology, it should be possible to economically remove hazardous substances from plant effluents. Certainly, the technology and the proper incentives are available to the mineral process engineers to operate economically without polluting the environment.

Table XVI

Solubility of Selected Minerals, Precipitates and Organo-Metallic Complexes

Minerals or Compounds	*Solubility in Water (ppm)*	
	Cations	*Anions*
Cu_2S	2.2×10^{-14}	5.4×10^{-12}
CuS	1.9×10^{-7}	9.6×10^{-9}
PbS	5.8×10^{-4}	9.0×10^{-10}
HgS	1.26×10^{-21}	2.0×10^{-23}
NiS	3.2×10^{-5}	1.7×10^{-5}
ZnS	2.0×10^{-6}	1.0×10^{-6}
$PbWO_4$	12	5.7
$PbSO_4$	0.8×10^{3}	0.38×10^{3}
$CaCO_3$	3.7×10^{3}	5.6×10^{3}
CaF_2	8.6×10^{-3}	8.2×10^{-3}
$Ca_3(PO_4)_2$	8.4×10^{-4}	1.26×10^{-3}
$CaSO_4$	0.52×10^{3}	1.26×10^{3}

	Hydrolysis Product (Ksp)	*pH of Precipitation*
$Fe(OH)_2$	1×10^{-15}	7.0
$Fe(OH)_3$	1×10^{-38}	3.0
$Al(OH)_3$	1×10^{-32}	4.2
$Cu(OH)_2$	1×10^{-20}	5.5
$Mg(OH)_2$	6×10^{-12}	10.5
$Ca(OH)_2$	8×10^{-6}	11.5

	Solubility Products (Ksp)
Zn - ethyl xanthate	5.3×10^{-9}
Pb - ethyl xanthate	6.7×10^{-16}
$Ca(Ol)_2$	3.9×10^{-13}
$Mg(Ol)_2$	1.6×10^{-11}
$Ba(Ol)_3$	1.3×10^{-12}
$Fe(Ol)_2$	3.9×10^{-13}
$Mg(RSO_3)_2$	10^{-8} to 10^{-11}
$Ca(RSO_3)_2$	10^{-8} to 10^{-14}
$Fe(RSO_3)_2$	10^{-18} to 10^{-21}
$Al(RSO_3)_2$	10^{-16} to 10^{-18}

NEED FOR ENVIRONMENTAL AWARENESS AND TRAINING

It is obvious that the mineral process engineer of today and the future has to play a dual role, that of a metallurgist as well as environmentalist. Traditionally, he is trained in the basic sciences and engineering common to both fields. What is needed is a keen awareness and concern to fulfill the dual responsibility that our mineral-based society has imposed on him.

This awareness and technical competence can only be developed through a realistic and well-balanced engineering curriculum. It is not necessary that the undergraduate engineer be required to take a specific course or courses in environmental science and engineering. However, it is essential that the student be made aware of the similarities in the two fields throughout all the engineering courses. With proper orientation and a minimum of deviation an instructor can do an adequate job of training the mineral process engineer so that he will be in a position to solve the environmental problems facing him in his professional career.

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CHAPTER 55

WATER MANAGEMENT IN GOLD AND SILVER RECOVERY

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INTRODUCTION

Only recently have mining companies begun to see water management as a critical issue for gold and silver recovery, that is except for the mechanical engineering aspects of pumps, pipes, valves and storage tanks. Water needs for mining gold and silver have even in bygone eras resulted in ingenious means of supplying water to gold and silver recovery facilities. This brings to mind the ingenious U-tube transportation of water from Lake Tahoe on the southern side of the Reno Valley to Virginia City on the northeastern side of the valley which required no pumping. The 27 mile long 4 inch diameter pipeline built in 1882 to furnish water from the White Mountains for the mills and town of Candelaria was hand riveted in Scotland and shipped across the Atlantic and around Cape Horn by sailing vessel. Another mammoth project supplying water to gold and silver operations is the pipeline built from Mundering Weir near Perth in Western Australia to Kalgoorlie and the goldfields that are the basis for the town's existence, a distance of 600 kilometers away.

A questionaire was sent to about 200 gold and silver mines and mills enquiring about water use and management practices in the main gold mining districts of the world. The responses to this questionaire have been summarized in a table at the end of Chapter 3 and in a summary extract inserted below.

MOTIVATION

Motivation for today's water management practices include:

- Shortage of water.
- Excess of water both underground and precipitation.
- Meeting permit requirements.
- Cost of water.
- Quality of water.
- High cost of reagents and the need to recycle them.
- Contaminants in ores, concentrates and calcines.
- Environmental constraints.

CLIMATIC INFLUENCE

The approach to water management for gold and silver recovery operations varies markedly to meet site specific needs. Climatic influences are one of the most important.

Desert Climate = Shortage of water or poor quality of groundwater. Net evaporation allows zero discharge operaions.

Extreme Cold Winters = Need to contain tailings and effluents without decant recycling through the frozen months. Need for an unfrozen water supply. No natural cyanide degradation in winter.

Tropical Climate = Excess precipitation for outdoor heap leaching. Wet or very wet seasons.

Regulatory Climate = Varies from highly supportive encouragement to downright discouragement and obstructionism.

Modern water management in gold and silver mining operations has come a long way but remains at a low point on the learning curve. Water management will be the mother of technical invention. For example, in the People's Republic of China a thiourea leaching circuit employing an iron in pulp recovery process was developed because of feared toxicity effects if cyanide were to be used so close to the capital Beijing (Peking). Other examples are the new biological water treatment process for removal of cyanide, metals, thiocyanate and ammonia developed by Homestake Mining Company; water effluent equipment and circuits etc. Anticipated higher costs of fresh water in South Africa, Western Australia and elsewhere will undoubtedly stimulate further innovations.

Some observations concerning water management for gold and silver recovery at the main gold and silver producing countries of the "free" world are commented on below.

Summary of available data on net water consumption by gold and silver recovery operations gathered in an industry-wide survey is provided in the table overleaf. From this it appears that:

1) Water consumption in gold and silver recovery operations expands to need the amount available.

2) Heap leaching requires 0.15 - 0.50 m^3 net new water per ton ore which is much less than needed for conventional milling. Further refinements could lead to still greater water efficiency.

A critical aspect of water management in estimating the water needs of an operation where water is in short supply is to be sure to take seasonal fluctuations in both the water consumption needs and the source of supply into account.

If the average needs of a heap leaching operation of say 1000 tons per day are 0.20 m^3 water per ton ore, this means that a source of 37 USgpm will be required. However, at the height of the summer the actual daily needs may increase to 0.5 - 0.6 m^3 water per

ton solids requiring a supply of 100 US gpm. The time when the maximum water supply is needed, also coincides with when the water supply may be at its lowest.

Likewise, it is possible to select different types of sprinklers for solution application as a means of conserving water when necessary, e.g., direct application of solution without sprays or by using a solution mist sprayer to enhance evaporation when the water inventory is too high. In this way water consumption for one operation can be manipulated between 470 US gpm to 800 US gpm as a water balance managing tool.

WATER CONSUMPTION FOR GOLD AND SILVER RECOVERY

	Tons Milled	Net Water Consumption	m^3 Water/ Ton Ore
1. Witwatersrand Typical Total Use Mine - Mill Au and U_3O_8 (Note augmentation by domestic effluent not included.)		1.03 m^3/t	2.5
2. Kiena Gold Mine, Quebec	400,000 tpa	254,040 m^3/a	0.64
3. Noranda, Hemlo (Design)			
Overall - Case I	2,500 t/d	219 m^3/h	2.07
Overall - Case II	4,000 t/d	330 m^3/h	1.98
Mill Only - Case I	2,500 t/a	185 m^3/h	1.8
Mill Only = Case II	4,000 t/a	296 m^3/h	1.8
4. S. E. Asian Conventional Mill CIP (Design)	100,000 t/a	100,000 m^3/a	1.0
5. Campbell Red Lake	1,100 t/d	3,272 m^3/d	2.97
6. Mercur Gold Mine Total	3,000 t/d	3,323 m^3/d	1.11
Mill Only	3,000 t/d	2,215 m^3/d	0.74
7. Hecla Mining	250 st/d	86,000 US gpd	
Republic, WA	227 t/d	330 m^3/d	1.45
8. Cortez Gold Mines			
Mill	2,000 st/d		
HL	1,095 st/d		
Total	3,095 st/d	120 US gpm	
	2,814 t/d	660 m^3/d	0.23

WATER CONSUMPTION FOR GOLD AND SILVER RECOVERY (Continued)

	Tons Milled	Net Water Consumption	m^3 Water/ Ton Ore
9. Freeport Gold Company	1,300,000 st/a	550 mm g/a	
	1,181,800 t/a	2.11 mm m^3/a	1.79
10. Giant Yellowknife Mines Total (No Recycle)	325,000 t/a	1,727,703 m^3/a	5.31
11. Con Mine, Mill	273,750 t/a	600,000 m^3/d *	2.19
Yellowknife NWT, Total	273,750 t/d	1,095,000 m^3/d *	4.0
12. Pamour #1 Mine	2,700 st/d	1,000,000 lgpd	
Flotation & Cyanidation of cons.	2,454 mt/d	4,545 m^3/d	1.85
13. ASARCO Troy Mine Flotation	8,500 st/d	8,727 m^3/d	1.03
Heap Leaching			
14. Candalaria Mine Hawthorne, NV	2,750,000 tpa	404,307 m^3/a	0.15
15. Draco Mines - Peter Kiewit	350,000 stpa	68,000 m^3/yr	0.2
Monte Vista Co. (est.)	320,000 tpa		
16. Amoco Minerals	880,000 stpa	200 gpm summer	0.50
Northumberland Project		50 gpm winter	0.13
		100 gpm Ave.	0.25
	800,000 t/a *	200,000 m^3/a	

* Subject to confirmation.

South Africa

The Witwatersrand has supplied forty percent of the gold ever mined in the world and currently accounts for 67% of free world gold production, concentrated around the edge of an underground basin perhaps 300 X 200 km in extent.

In South Africa the overall shortage of water and associated medium term water quality projections in the industrial heartland of the country centered around Johannesburg

have become a matter of national urgency. A recent study of demographic, socio-economic and industrial growth projections revealed that the availability of suitable water will be a serious limiting factor. A second study by HEYNIKE (1983) investigated the cost to the economy resulting from further buildup in total dissolved solids in the main water supply and concluded that the steady buildup of TDS must be arrested and if possible reversed.

Many of the gold mines and mills have associated byproduct uranium recovery plants. To generate sulfuric acid for uranium leaching, pyrite is floated from gold-uranium ore and tailings and roasted. Gold is also recovered by leaching the calcine. The industry is characterized by very large hot and deep, labor intensive mines and multiple integrated mine-mill complexes. Typical mill capacities are 100,000-300,000 tons per month although some are larger. The ERGO tailings retreatment facility treats 1,500,000 tons per month of reclaimed tailings. The VAAL REEFS complex treats 9 million tons per year of underground ore. KEMPE (1981) estimated that from 1884 to 1980 a total of 37 billion tons of ore had been treated on the Witwatersrand.

Macro Problem

The gold industry of the Witwatersrand is located east, west and south of Johannesburg, which is also the industrial hub of South Africa with major metropolitan concentrations totaling over 1.6 million.

The climate is characterised by dry winters and convection rainfall in summer. The whole area draws its water from the Vaal River and Vaal Dam and there is a macro recycling loop in effect. Very little water actually leaves the Vaal River along the natural drainage into the Orange River and in fact serious consideration is being given to reversing the flow of the Vaal River to draw water into the system instead of the present drainage from it. This water is settled and treated before distribution by State owned regional water authorities such as the RAND WATER BOARD, OFS WATER BOARD, and the WEST RAND WATER BOARD.

Summer precipitation over much of the area comes in torrential downpours associated with thunderstorms and drains into the Vaal Dam and the Vaal River via a host of tributaries. It has been found that dissolved salts that cannot be removed economically by conventional water treatment e.g., precipitation, are building up in the Vaal Dam water. A number of industries have been identified as point source contributors of dissolved solids in effluents that eventually drain to the Vaal River. One of the major point source contributors is the gold and uranium mining and milling industry. The most obvious of the point sources is underground mine drainage water which is pumped to the surface from some of the deeper mines such as East Rand Proprietory Mines Ltd. (ERPM) and S. A. Land & Exploration Co. Ltd. (SALLIES) which are points from which underground mine water draining from large areas of mineworkings in the east rand (east of

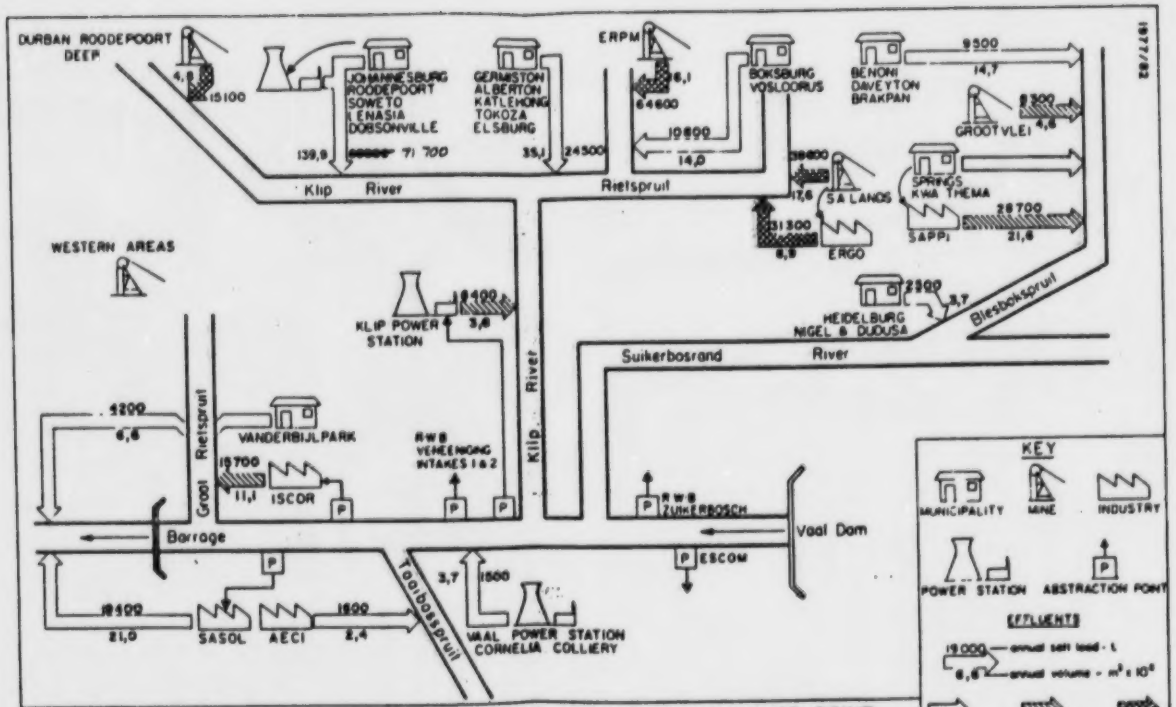

FIGURE 15 SCHEMATIC DIAGRAM OF STUDY AREA SHOWING MAJOR POINT DISCHARGES: OCT 1977 - SEPT 1982 FLOWS ($m^3 \times 10^6$) AND LOADS (t)

Johannesburg) are pumped. In Witwatersrand stopes, mine water comes in contact with sulfide minerals in the presence of air at relatively high temperatures and becomes acid on account of the oxidation of pyrites to sulfuric acid. There may also be some seepage of high TDS solutions into the mineworkings. On neutralization this underground water has relatively high levels of $SO_4^{=}$, Ca^{++}, Cl^{-}, Fe^{++}, ec. and a tds level approaching 3,000 mg/l.

A major study has been carried out by a firm of consulting engineers in South Africa for the Dept. of Environment Affairs which quantitatively shows the relationship of mining industry point source effluents in relation to that from other industries. A summary of this so-called GREEN REPORT has also been prepared. Further information could be requested from the authors or possibly from the Dept. of Environment Affairs.

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This report does not discuss the impact of the West and Far West Rand gold and uranium operations on the water of the Vaal River, nor the Orange Free State Goldfields impact on their local water supply. For the southern PWVS region the mean annual intakes, and discharges in the Vaal Dam catchment area from 1977 to 1982 were as follows:

	Municipalities	Industries	Mining and Milling	Total
Water Supplied (10^6 m^3/yr)	329	136	68	533
Effluent Discharged (10^6 m^3/yr)	244	63	43	350
Percentage Returned	74	46	63	65
TDS Load Discharged (tpa)	160,200	97,100	129,400	386,700
Mean Effluent Concentration (mg/l)	660	1,550	3,000	1,100

Emergency measures to conserve water and the quality of the public water supply to the PWVS area are being called for on account of the drought. These will be very expensive and represent an economic burden on the mining industry and ultimately the country.

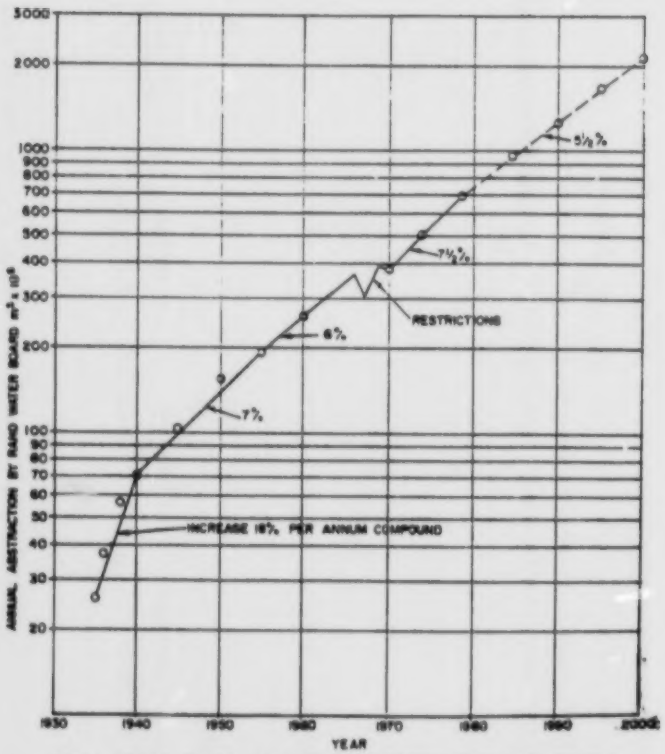


FIG. 2. ANNUAL RAND WATER BOARD ABSTRACTION FROM VAAL SYSTEM 1935 TO 1979 AND PROJECTED ABSTRACTION 1980 TO 2000.

PAST AND PROJECTED AVERAGE ANNUAL TDS CONCENTRATION AT THE RAND WATER BOARDS VEREENIGING INTAKE

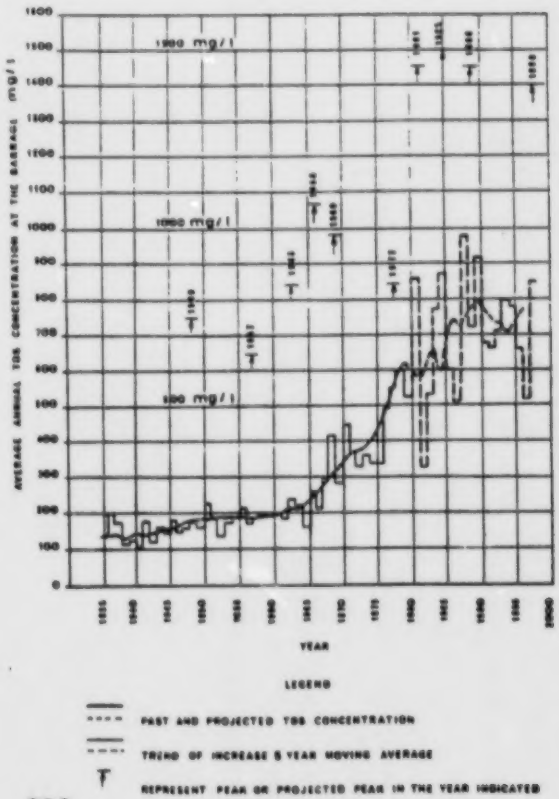


FIG. 3.

Industrial use and impact on water quality has become so great that it has now become unrealistic to hope that when the present climatic cycle shifts to a high rainfall phase, the volume of drainage will increase and the Vaal Dam will overflow releasing large quantities of high TDS water ultimately to the Atlantic Ocean to the extent that Vaal Dam salt load will be adequately reduced.

Unfortunately, the statistical evidence of TDS in the Vaal reported by HEYNIKE & McCULLOCH (1983) are quite conclusive in showing that climatic cycles over the last fifty years have not been able to arrest the marked increasing trend in this salt load, as industrial and municipal demand and impact on this water reservoir steadily grew.

It was observed that the quantity of water received by the gold mines included water pumped from the mines and a comparatively small volume of water obtained from the Rand Water Board or other above ground sources. These mines however discharged about 34% of the point source TDS load in only about 12% of the effluent volume. This last estimate has caused the mining industry to become one of the primary targets of the Dept. of Environment Affairs in their primary objective of reducing TDS buildup in Vaal water.

The gold and uranium ore treatment process (and there are several variations in the way uranium and gold processes are integrated) require several sequential pH changes. For example, consider a mill using acid mine water in a "forward leach" configuration:

1) Neutralization of acid mine water (pH 3.5).
   Precipitation of gypsum, $Fe(OH)_3$, etc.

2) Addition of lime to pH 10 in gold extraction plant.

3) Chemicals in eluate from CIP plant after gold recovery.

4) Reduction of pH - Acid addition in uranium leach.

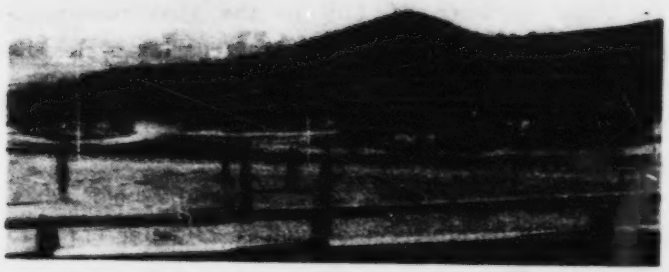
5) Use of acid in the SX strip plant.

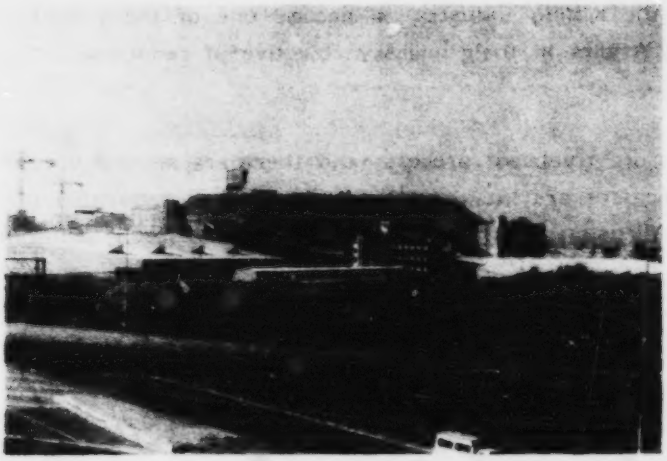
6) Addition of lime to neutralize tailings and raffinates before pumping to tailings.

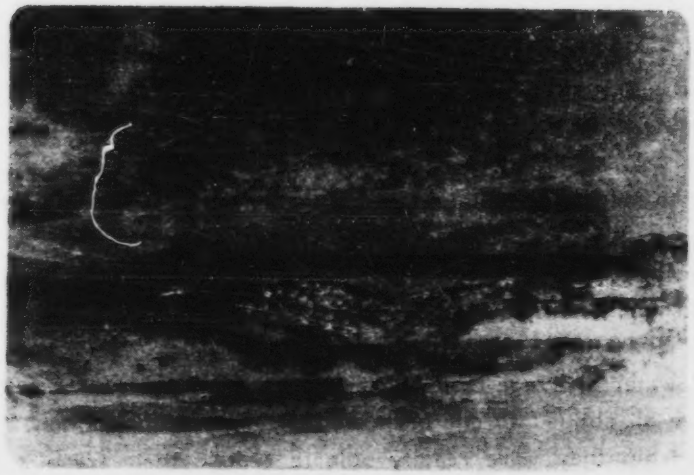
Numerous processing steps each add to the salt load. However, considerable quantities of precipitate are settled and left in the tailings impoundments.

Because of the acute water shortage over the last three summers (1981, 1982 & 1983) the mining companies were all obliged to cut back on their water consumption. The fact that without any real hardship they were readily able to reduce their fresh water intake by about 30-40% indicates that hitherto not very much effort had been needed in this

MILL TAILINGS IN JOHANNESBURG







SINKHOLES AT A MINE TOWNSHIP WEST OF JOHANNESBURG

direction. Some of these mining and milling complexes in 1984 still do not know the precise details of their internal water balance. One complex consists of several gold and uranium mills and associated mines and its 1984 budget, just to quantify internal and external water balances, was around R500,000.

To the west of Johannesburg gold ore is overlain by dolomitic sedimentary rocks divided into separate virtually water tight compartments by dikes. Natural groundwater stored in these dolomitic aquifers is of excellent quality and it is established that they could potentially be used to store excess water during times of plenty and then serve as a supplementary supply during dry years.

Several mines are located to the west of Johannesburg with milling operations located at surface over the dolomites. These include mines such as Randfontein Estates Gold Mining Co.; Venterspost G. M. Co. Ltd.; Elandsrand; Deelkraal; West Rand Consolidated G. M. Co. Ltd.; Westernareas G. M. Co. Ltd.; West and East Driefontein; Kloof G. M. Co. Ltd.; etc. The mines have three potential effects on the dolomitic aquifers:

1) Many of the mines pump huge amounts of water to the surface to dewater their underground workings. This has resulted in a lowering of the water table and a severe sinkhole problem in the farming areas around some of the mines.

2) Tailings dams, wasterock piles, tailings solution reclaim ponds and evaporation ponds are seldom lined and seepage from these into groundwater may add significantly to dissolved solids in groundwater, some of which may migrate back to the surface or into underground workings. It is fair to note here, however, that many tailings dams are constructed on a naturally occurring black clayey silt of limited permeability. Modern slimes dams are designed to catch surface runoff for evaporation in ponds which are also usually not lined and may contribute.

3) Recirculation of minewater which is often reinjected into the dolomites at some distance from the mine and partly finds its way back to the underground workings results in an uptake of further TDS due to oxidation of stopes underground.

All around the Witwatersrand even in the outskirts of Johannesburg there are huge tailings heaps. Runoff and seepage, especially from the older sand tailings and wasterock piles that contain pyrite and significant quantities of $CaSO_4$ and leachable iron undoubtedly contribute significantly to the dissolved solids that enter both the surface waters draining to the Vaal and also the groundwater that drains into the dolomitic aquifers 20 miles west of the city. The effect of water draining from and seeping through mine tailings dumps and wasterock piles is currently under study and the results will not be known until 1986.

However, visual inspection of the area from the air gives a pretty good qualitative idea of how the results of these investigations may turn out.

The investigation of seepage and runoff contamination from several tailings dams of different ages and wasterock piles is being undertaken by:

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Brian Middleton

SUMMARY OF MACRO PROBLEMS - SOUTH AFRICAN GOLD AND URANIUM INDUSTRY

The mining industry on the Witwatersrand is being pressed to achieve the following:

1) Reduce fresh water intakes.
2) Minimize dissolved solids in point source effluents.
3) Reduce dissolved solids loss to groundwater to preserve the quality of potentially usable aquifers.

If, on account of restricted use of fresh Rand Water Board Water, some of the mine-mill complexes located over dolomitic aquifers are obliged to use more underground minewater and to recycle more tailings reclaim solution, then it is conceivable that the dolomitic water (currently already at 1,000-1,500 ppm TDS in places) may locally deteriorate further even to above the SABS allowable drinking water standard of 2,000 ppm tds. In such an event there could be a potential conflict with the law, especially the Water Act as recently ammended as discussed in Chapter 7 on regulations.

The WATER ACT, No. 54 of 1956 paragraph 23 is clear in its intent:

"Prevention of pollution of water.

23. (1) Any person who wilfully or negligently, and, where any provision of section twenty-one or twenty-two applies, contrary to that provision, does any act whereby any public or private water, including underground water, is polluted in such a way as to render it less fit for the purposes for which it is ordinarily used by other persons (including the Government, the South African Railways and Harbours Administration and any provincial administration) entitled to the use thereof, or for the propagation of fish or other aquatic life, or for recreational or other legitimate purposes, shall be guilty of an offence.

(2) (a) The Minister may out of moneys appropriated by Parliament for the purpose, take any steps which he may consider necessary to prevent the pollution, as a result

of seepage or drainage from any area on which mining or other industrial operations have been carried on, of public or private water, including underground water, after such operations have been abandoned, and may in his discretion recover the cost of any part of the cost incurred in taking such steps from any person who carried on or is entitled to carry on such operations.

(b) The Minister or a person acting under his authority may at any time enter upon any land for the purpose of taking any steps referred to in paragraph (a), and may take with him on to such land any men, animals, vehicles, equipment, appliances, instruments, stores or materials, and may erect such camps and construct such works as may be necessary for that purpose.

(c) No compensation shall be payable to any person for any loss which may be sustained by him in consequence of any action taken under this sub-section, except by order of a competent court."

Since the regulatory enforcement climate is currently in a state of flux in South Africa with respect to water conservation and effluent discharge and since the mining and milling water management practices at current operations were brought into production during times when water quality had not yet been recognized as an issue, mitigating measures may have to be adopted retrospectively in some cases.

South Africa - that is, the government, the people and industry are of course conscious of the important - actually vital - role of mining as the backbone of their economy. Mining was the main reason for the development of Johannesburg and neighboring cities in the first place. Current difficult economic conditions and high inflation may temper the regulatory ideals of the Dept. of the Environment for awhile. - However, since the need to conserve water and preserve its quality are also perceived as vital for the economy, it is clear that over the next 5 years there will be major changes in water management and water treatment practices on Witwatersrand gold and uranium mines and mills.

Historically mine-mill complexes could discharge effluent to surface water courses provided these effluents met a set of relatively easy standards. If they did not, then greater quantities of low cost fresh water were injected into the system. With RWB treated water available at R0.17 - R0.20/m^3 ($0.09 - $0.10/$m^3$) and untreated Vaal River water for those with access at R0.04/m^3, it was and still would be more cost effective to apply the well known idiom "The solution to pollution is dilution." This does not mean that the freshwater tap had to be opened directly at the effluent discharge point; the same effect can be achieved simply by using more fresh water in the milling operation. This measure could be supplemented by segregation of the worst quality effluents which could be pumped to the tailing dam or to ponds to be evaporated.

The Witwatersrand climate is one of net evaporation, and zero discharge is possible for most mine-mill complexes. Water balances of others are complicated by the need to dewater mines and discharge large amounts of water.

ALTERNATIVE WAYS TO REDUCE WATER CONSUMPTION AND CONTROL TDS RELEASE

In order to meet the three macro problems, the following list of alternatives is under consideration. Several additional ideas are mentioned. Since in the new regulatory climate and details of enforcement focus is still to be determined, much of the discussion is still speculative at this stage.

1) Reduction of Fresh Water Intake - Increased Recycling

This requires that greater internal recycle must be used. Through using more recycle water, the volume of effluent has been reduced in several operations. However, on account of recycling, TDS and contaminant levels could increase, except where large amounts of lime are used in conjunction with U-plant raffinates containing iron and aluminum which leaves at least some of the TDS in the tailings pond as a precipitate. See the trip report on Vaal Reefs in Appendix I.

Incentive to use less Rand Water Board water is expected to come in the form of a significant increase in the price of water from R0.17/m^3 to perhaps R0.75 - R1.00/m^3. Other restriction have been invoked such as stricter water use permits.

2) Use of Underground Minewater

The Chamber of is Mines developing a system whereby minewater pumped from underground is reused for the combined purposes of generating hydroelectric power underground and providing hydraulic power to operate underground drills etc.

Water used in the hydraulic powered tools must have a very low level of suspended solids which would otherwise result in severe abrasion costs. Research into the most effective means of removing suspended solids to the low levels required is receiving priority attention at the Chamber of Mines Research Laboratories.

On another front, it has been found that underground sludges are best settled underground and brought to the surface separately as clarified water and as thickener underflow sludge. Several improved underground settlers have been in use on the Witwatersrand. One, a cylindro-conical underground settler was developed by the CSIR under sponsorship by Anglo American Corp. and General Mining and subsequently improved by AARL. Platepack lamella settler clarifiers have also been introduced.

Earlier underground settlers were of horizontal design whereas the CSIR Cylindro conical units are vertical. Some discussion of the design of these units, flocculant selection and dosage is included in the chapter on solid liquid separation. In general it was found that some flocculants can achieve much lower turbidities at significantly lower cost than others ranging down to 0.5-1.0 cents per 1000 gallons.

CHAMBER OF MINES OF SOUTH AFRICA STATEMENT TO PRESS, JUNE, 1983

Water Restrictions

Members of the Chamber of Mines of South Africa and which fall in the areas served by the Rand Water Board, the Orange Free State Goldfields Water Board, and the Western Transvaal Regional Water Company reduced their use of water from the Vaal Dam by 18.3 percent during April in comparison with that month's consumption in the previous year.

In doing so, these mines which include practically all the large gold and platinum mines of South Africa almost met the appeal by the Minister of Environment Affairs and Fisheries on 8th March, that industries dependant on the Vaal Dam save 20 percent of the water obtained from that source.

The reduction has not affected production in any way--it being a condition of the mines' concerted water saving effort that production would be regarded as sacroscant.

The Chamber of Mines members have achieved a reduction of 106.3 megalitres a day in the water they obtain from Water Boards, mainly by cutting down on the use of water for domestic uses and by making greater use of water from sources other than the Vaal Dam.

For example, sewerage effluent from the Welkom municipality, which would otherwise have gone to waste, is now being used in the reduction process of gold mines in the vicinity in place of Vaal Dam water.

In other instances, hostel showers have had 30-second time switches installed, and water has been collected from every possible source, including slimes dams runoff.

The mines' options to save water have been considerably reduced over the years by repeated appeals. During the late 1960's, and on several subsequent occasions during similar water emergencies, all possible avenues to save Vaal Dam water were explored and implemented. At considerable cost, many mines duplicated reticulation systems so that their own underground water could be used in mineral process plants and for watering gardens and sports fields instead of water supplied from the Vaal Dam.

Resultant cuts in the use of Vaal Dam water have been as high as 28 percent and currently, most water used on mines is underground water occurring naturally in subterranean crevices or cavities. This water drains into the mines and is pumped to the surface but most often be treated at considerable expense before it can be used.

Other factors which make it difficult for the mining industry to reduce its dependance on Vaal Dam water include the big expansion in mining activity since the rise in the gold price in the early 1970's and particularly since 1980. To extend the lives of the gold mines, grade has been steadily reduced which means that more rock must be mined and milled to get the same output.

Water is the lifeblood of mining, and up to 2½ tons of water are required to mine a ton of ore. The quantity of ore treated by gold mines by members of the Chamber has increased from 73 million tons a year in 1972 to 95 million tons in 1982.

The past decade has also seen great progress in improving the environment underground which, in effect, means the use of more water to keep down harmful dust and to cool the underground workings. As mines go deeper, more and more refrigeration is necessary. This places a heavy demand on the use of high-quality water provided by sources served by the Vaal Dam. Another problem is that some of the new mines opening up are either relatively dry or in a transitionary stage and unable to capitalize on the water "make" underground.

In these circumstances, the savings achieved by the mines are most commendable, but the industry is far from satisfied, and many schemes to save Vaal Dam water are in the pipeline.

One of the most expensive is a scheme to pump underground minewater from one Orange Free State mine to another in the area, which can use this water. This pipeline scheme is to cost about R4 million. There are a number of other schemes costing anything between a quarter of a million rands and several millions of rands.

The Chamber's member mines were able to react quickly to the Minister's pleas because they had seen the water shortage writing on the wall already towards the end of last year and had started planning through Group Head Offices and through Chamber committees.

At the beginning of this year, Vaal Dam water consumption by mines, which had been rising steadily for some years, started to drop steeply and has done so ever since.

The savings achieved varies from mine to mine, with one large gold mine having cut its consumption of Rand Water Board water by 73% compared to the same period last year.

Some mines, often due to circumstances beyond their control such as rapidly expanding mining activity, are now using more Rand Water Board water than they were a year ago, but overall, the use of purified water from the Vaal Dam is down on mines in the area served by the O.F.S. Goldfields Water Board. For instance, in the four weeks ended 4th May, mines in this area reduced their Board water consumption by 24.3%.

The Chamber of Mines accepts that there is still room for improvement and thanks to the highly organized nature of the South African mining industry, further savings of purified water from the Water Boards can be expected in the future."

3) Use of Alternative Secondary Sources of Water

Use of tailings dam reclaim water and collected runoff in the mill or reclaimed treated sewage water from mine hostels or local municipalities. These may not be suitable for all process applications or may require special pretreatment as discussed in the previous chapter. At Vaal Reefs, there are five sewage treatment plants, all of which employ biofilters. After treatment, this water has been found satisfactory for use in gold and uranium recovery plants. Furthermore, with sophisticated further treatment, this type of water may even be used in flotation.

4) Lining of Tailings Dams, Wasterock Piles, Reclaim Water Ponds, and Evaporation Ponds

If and when tailings dams, evaporation ponds (sometimes located on top of tailings dams) and reclaim water storage ponds are established to be a cause of contamination of groundwater or useful aquifers, through seepage, then corrective measures may be required. Only those mines in sensitive locations would be affected from a contamination point of view. However, this measure would undoubtably save significant quantities of water that today go to waste.

Tailings dams

Old dumps consist of "sand" stamp mill tails which are porous and since many of these contain residual values, these are being reworked. Some do not have adequate values in them and represent a continuing source of acid mine drainage. Since the 1950's, all tailings disposed of have been "slimes" which are constructed in a form that has low permeability. However, some earlier slimes dams were poorly designed and were not maintained, resulting in erosion and distribution of AMD-generating material to the environment. The task of lining existing tailings impoundments may not be economically feasible.

The modern Witwatersrand approach to tailings disposal is to use a layered "dry" tailings disposal approach in which water is decanted from the surface and the lower

reaches of the dams drained through a system of underdrains. This approach avoids the hazards of a hydrostatic head against the dam walls and the enhanced seepage effects from dams with such a head. In this way most solution is segregated from the tailings which are essentially "dry." Decanted and underdrain collection water is stored in ponds for reuse or evaporation, and modern slimes dams are maintained on an ongoing basis. Better ways are constantly being researched. This technique results in a considerable evaporation loss.

Many of the older tailings dams are being reclaimed for secondary recovery and are then disposed of in more modern tailings dams equipped with underdrains. Pyrite is recovered by flotation from most tailings retreatment projects. This greatly reduces the AMD generating capacity of the residual materials as well.

The extent of seepage beneath tailings dams and of runoff water from tailings dams is still under evaluation. If serious enough it is possible that more extensive collection sytems will be required beneath the "dry" tailings dams, but the requirement to line tailings disposal sites is not anticipated.

Reclaim Water Ponds

Reclaim water storage ponds located over sensitive aquifers may require lining. Already some ponds perched on the banks of the Vaal River have been lined. These are mentioned below. Based on preliminary information the treated Bentonite linings are less expensive than plastic membranes. However, because bentonite is believed to fail in low pH conditions, the solutions must be neutralized first.

Evaporation Ponds

Evaporation ponds may become the least expensive way to dispose of excess contaminated solutions. When reclaim water ponds are lined, and if surface water runoff from wasterock piles, tailings etc. has to be impounded, the water balance of mine-mill complexes may require a bleed.

Evaporation ponds result in high TDS concentrations which would be particularly damaging to aquifers if lost through seepage. In sensitive locations, such ponds will likely need to be protected from leaks and seepage losses.

Wasterock Piles

Wasterock piles expose a large surface area of sulfidic materials to rain and air and undoubtedly generate substantial quantities of diffuse source TDS which drains currently to the river system and/or seeps into the aquifers below. These may in future have to be located on impermeable clay base materials (Some fortuitously

already are). Alternatively a system of underdrains may in future be required to collect seepage below the wasterock piles.

It can be anticipated that seepage and runoff diversion drains will be required around wasterock piles and the collected water will need to be stored. This water is already recognized as a potentially useful source of additional process water after treatment.

A firm of geotechnical consultants in South Africa that are particularly familiar with the problems and realities of the situation is:

STEFFEN ROBERTSON AND KIRSTEN
Post Office Box 8856
Johannesburg 2000
(011) 834-6061
Dr. Oscar Steffen

The overriding characteristic of the Witwatersrand situation as it affects the water supply is its hugeness. The hugeness of the impact potential and the hugeness of the cost of fixing old or existing waste disposal sites should this be found necessary. To be successful on a long-term basis, the tailings and wasterock must be disposed of in a way that does not require "perpetual" maintenance of each site.

All the measures discussed above would reduce the loss of dissolved salts through seepage. Especially as more water is recycled, TDS and contaminant levels are likely to build up in the solutions, and contaminant will become even more important.

AFFECT OF ABOVE MEASURES

Several results of increased recycle, reduced seepage and salt load buildup in plant solutions can be anticipated.

- Much greater use of lime can be expected to treat effluents and tailings, allowing more water to be recycled. For example, the major Vaal Reefs complex on the far West Rand has achieved zero discharge and consumes 10-12 kg lime per ton tailings slime treated which amounts to a cost of $7.8 million per year or R0.86/t ore treated.

- Galvanic corrosion effects especially in the acid uranium sections of the plant would be enhanced. The high pH in the gold circuit would inhibit corrosion there.

In the uranium plant, corrosion would become a problem everywhere that acid resistant materials have not been used - e.g., service water piping, filters, etc. Increased use of corrosion resistant stainless steels can be anticipated.

- Lining of return water dams and some tailings dams would change the water balance and provide additional quantities of return water available for recycle.

- Effluent streams would have higher concentrations of some dissolved solids and would be unlikely to meet the effluent discharge limits. In this sense the threatened stricter effluent salt content regulations could result in more water being evaporated because it does not meet effluent limits and consequently less water for discharge. The Vaal Reefs trip report in Appendix I shows how this huge mining and milling complex recovers as much water as possible from their tailings for reuse and has achieved zero discharge apparently with an equilibrium salt balance in their recycled water, since salts are precipitated in the tailings material and left in the tailings impoundments.

- It is significant that TDS levels in the Vaal River which flows through the huge Vaal Reefs Exploration and Mining Company Ltd. operating area does not increase from the point of entry to exit from the property. This is an excellent illustration that the effect of a major mining and milling operations on TDS of water in the area can be controlled.

ALTERNATIVE APPROACHES AVAILABLE

The above discussion deals with anticipated effects that would be likely to occur if possible future new interpretations of existing regulations as well as new effluent limits are enforced at the same time as further restrictions on water use. Obviously the mining companies are examining all alternatives on a site specific basis. The following is a discussion of a few of the aspects involved.

Greater use of recycled solutions is likely to result in a build-up of TDS not only in the recycled process water but also in aquifers accessible by seepage.

1) Segregation and Evaporation - Ponds and Linings

One means of reducing overall TDS is by segregating the effluent solutions with highest TDS and other undesirable contaminants for separate disposal or treatment. These could be the excess U-plant raffinate containing 30,000 mg/l TDS. Also possibly the regeneration solutions from boiler feedwater pretreatment plants and boiler blowdown might be segregated. Lined evaporation ponds may be required to dispose of these solutions and others. However, raffinate with its high iron content

seems to be useful at both ERGO and VAAL REEFS for reducing arsenic and cyanide levels in reclaimed water.

One company was found that specializes in lining evaporation ponds with activated bentonite which they claim is more effective, safer and less expensive than plastic linings. To date they have lined over 2 million m^2 of dams including one pond of 160,000 m^3, believed to have been installed to prevent seepage of raffinate from a pond perched alongside the Vaal River in the Klerksdorp area for Vaal Reefs Mining & Exploration Company. The cost of installing an activated bentonite liner at 10Kg/m^2 with a 150 mm (6") thick compacted till cover is around R5.00/m^2 (US$0.30/$ft^2$). More details on the application are available from the vendor:

AQUASAVE (PTY) LTD.
Box 68288
Bryanston 2017
(011) 789-1206/7
Chris Lee
Managing Dirctor

It is believed that similar activated bentonite lining materials are offered in the USA by:

VOLCLAY, INC.
Division of American Colloid Company
Environmental Products Division
5100 Suffield Court
Skokie, IL 60077
(312) 966-5720

Evaporation of minewater from a new mine in the OFS Goldfields was discussed by BENTEL and JAMES (1983) of Steffen, Robertson and Kirsten. This case must refer either to BEISA or BEATRIX mine of GENCOR LTD. In that part of the country aquifers are very high in chloride levels which would require desalination to make the water usable - an expensive alternative. BENTEL and JAMES (1983) discuss design aspects of evaporation dams which conform to the requirements of the South African Water Act of 1956. The act also requires trenches to collect seepage and prevent its migration to adjacent farmland.

The cost of desalination was found in this instance to be about three times that of evaporation in the unlined ponds which, according to their paper cost only R5000-R10,000 per hectare. If the ponds had to be lined the approximate cost in the USA would be $150,000 per acre for the complete pond. Lining using the Aquasave method is estimated to cost about R50,000/hectare in addition to the basic pond construction cost, i.e., a total of around R60,000/hectare ($13,000/acre).

Based on BENTEL and JAMES (1983) statement that desalination would cost three times evaporation, it would appear then that if the ponds had to be lined in

sensitive locations to protect usable aquifers, then partial desalination at least may become economically attractive especially if the price of water were raised to say R0.50-R1.00/m^3. The point is that desalination in such a scenario is no longer so far out of line cost-wise as to be ruled out.

2) Corrosion and Abrasion Control

One of the most important revelations concerning the impact of water quality on mining costs was made by Alec Mokken, a former consulting metallurgist from Union Corporation Ltd. before it merged into Gencor Ltd. MOKKEN (1964) points out that the cost of pipe, pump and valve replacement in Witwatersrand gold mines is significantly greater per ton of ore mined than the total cost of milling the ore. Much of the replacement costs are the result of corrosion which is directly attributable to water quality effects and abrasion.

His paper was inserted in Chapter 23 on acid mine drainage.

ALEC MOKKEN
Consulting Metallurgist
35 Lakefield Avenue
Lakefield, Benoni
South Africa 1500
(911) 54-2038

Various types of abrasion and corrosion control measures may be considered. Measures adopted by Rössing Uranium Ltd. in Namibia, South West Africa could be emulated in the uranium plants - e.g.:

- Use of recycle solution for pump gland service. This requires installation of stainless steel pump shafts and seal housings. Possibly this would be an area where the innovative plastics component designer in Virginia OFS could play a role:

  MR. ALAIN LEGER
  Post Office Box 47
  Virginia OFS
  South Africa 9430
  (017) 3-3075/3-2194
  Telex: 8-4770

- Corrosion protection of thickener parts made of stainless steel. Some success has been achieved using polyurethane coatings. Two sources could be evaluated:

ATLAS FOAM (PTY) Ltd.
Post Office Box 2268
Trekker 1547
South Africa
(011) 558-504
Graham Pole

- This two component polyurethane product is also offered by BAYER, LEVERKUSEN, West Germany, and a similar product is offered by Uniroyal in the U.S.A.

- A proprietory polyurethane coating with similar properties is made and installed by:

WEAR RESISTANT MATERIALS (PTY) LTD.
2 Kelsey Place
Asquith NSW 2078
Australia
(02) 476-5655
Telex: Chatswood Public Telex Office,
WRM POL AA 70410

3) Scale Control

Since scale and corrosion are frequently associated with bacteria these may possibly be inhibited through use of appropriate bactericides.

Enhanced scale due to gypsum buildup may be countered through the regular use of scale inhibitors and particularly devices such as Calgon Corporation's dynamic scale monitor for use in selecting the correct reagent and dose.

There are several companies that offer such water treatment products but in South Africa so far only Calgon Corporation offers the dynamic deposit monitor as well as access to the CALGARD computer program for predicting scale and corrosion properties of various solutions.

FLOCCOTAN (PTY) LTD.
Post Office Box 39
Pietermaritzburg 3200
(011) 429-001
(0331) 33265
Telex: 6-43195

CALGON CORPORATION
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Leo Weaver
Vice President
Ron Losasso

It is interesting to note that RAND WATER BOARD water cannot be used directly to wash filtercake on drum filters in gold circuits. This is because the bicarbonate in the water results in $CaCO_3$ scale formation in the webbing of the filters and will eventually restrict the hydraulic capacity.

$$HCO_3^- + OH^- + Ca^{++} = H_2O + \underline{CaCO_3}$$

Every so often it is necessary to acid wash the filters to remove scale. An acid corrosion inhibitor is used to prevent attack by the acid of the steel. The corrosion inhibitor is an organic compound which adsorbs onto the steel surface. It was described in the SAIMM Journal, February 1958, pp. 307-342. It is marketed by

REEF CHEMICAL (PTY) LTD.
Boksburg North
South Africa

This is one case where use of barrens or tailings return solution is more suitable for filtercake washing than fresh water, from a scale point of view.

Polypropylene peg scouring of solution lines may be required more frequently as a means of removing scale accretions.

Fungus Control

Another water quality effect that has been found to affect filtration, this time in the acid uranium circuits, is due to fungus growth in the warm solution. It is not known to what extent increased recycling of solutions would affect this phenomenon which can blind the filter media and the wooden webbing behind it. By treating the filter cloth with hot water at 90°C for one hour per week, filter duty of media has been extended from 20 days to over 55 days. Another means of controlling the fungus that could be considered would be through dosing with a fungicide.

4) Water Treatment

Control of dissolved metals build up in recycled solutions may be achieved by treating a slip stream.

One operation observed that when iron and manganese build up in their process solutions, recovery of gold tends to drop.

In order to control levels of dissolved metals including Fe and Mn, an effective process employing lime, air, raffinate, and a mixture of tailings and recycled water is employed very effectively at Vaal Reefs (see Appendix I). The following additional processes might be tested.

- Lime to pH 10.5 and aeration followed by precipitate settling and clarification of solution.

- Lime-soda-alumina desalination can reduce even SO_4 levels as described in Chapters 13 and 51.

- Alkaline chlorination to decompose metal cyanide complexes prior to aeration, flocculation and settling. Alkaline chlorination does not remove iron cyanide complexes however and results in chloride ion buildup.

- SO_2 or roaster gas conditioning of tailings or recycle solution at pH maintained near 9 to decompose metal cyanide complexes including iron cyanides and precipitating metals.

- Greensand filtration may aid in polishing Fe and Mn from effluents after precipitation of bulk metals. Generally greensand filtration is not economic for removal of more than about 10 ppm Fe and Mn, however.

Further solution treatments that may be considered include:

- IX removal of Fe and Mn.

- Lime soda softening to remove calcium.

- Aeration at pH below 7 to remove HCO_3^- which otherwise results in scaling on activated carbon when pH is raised.

- A new improved variation of the theme of High Density Sludge precipitation of metals from Witwatersrand effluents is under development which may remove CN^- as well as metals.

5) Desalination Alternative

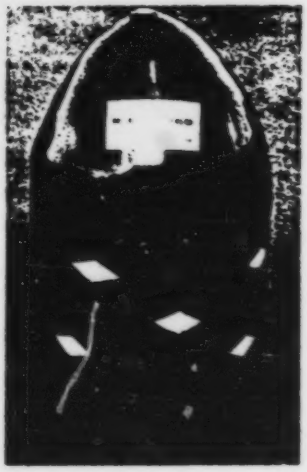
The new slurry seeded R. O. and Evaporation processes offer particular promise for scaling solutions containing Ca^{2+} and $SO_4^=$.

Advantage of Desalination: Reduces TDS including species which lime - settling and clarification cannot remove, for example, chloride and sodium. Several alternatives are available. A major advantage of desalination is that it recovers good quality water.

Disadvantage of Desalination: High capital and operating costs. Desalination processes are discussed in Chapters 15-19. However, operating cost estimates of

PIPE CLEANERS

The PIPE CLEANING SYSTEM



Step 1: To determine smallest diameter of scale build up within the pipe.

Take a foam swab and pump it through the line. The foam swab will wear down to the smallest diameter inside the pipe. By measuring this diameter the size of the 1st studded Polly-Pig can be determined.

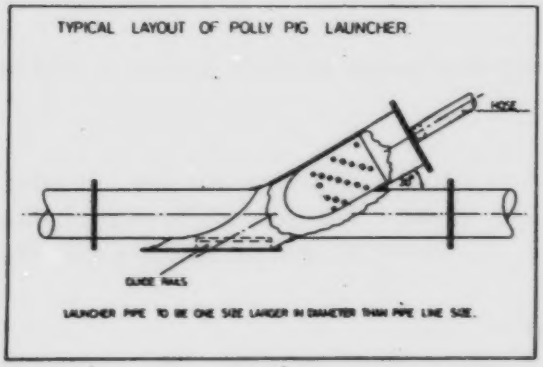
Step 2: Removal of Scale Build-up

Having determined the smallest diameter of the scale build-up within the pipe insert the studded Polly-Pig of same diameter and pump through the line. The operation is repeated using studded Polly-Pigs 12 mm larger in size, until the original diameter of the pipe is reached. The pipe should now be free of scale.

Step 3: Brush and polish for final cleaning

Once all the hard scale has been removed a Javelina Polly-Pig is pumped through the pipe line. This removes final traces of scale and cleans pipe to a smooth finish.

Sizes available from 50mm to 1500mm (in 12mm increases per size)



R. J. SPARGO Ltd.
228 Fuchs Street, Alrode, Tvl.
P.O. Box 3793, Alrode 1451
Tel. (011) 864-2744 Telex 4-20365

$0.50-R0.60/m^3, including capital amortization, is not that much out of line with lime treatment of effluents in parts of Canada (C$0.60-C$1.80), or Vaal Reefs bulk neutralization process requiring R0.80/t ore in lime for water treatment.

6) In most cases with Witwatersrand-type climates, if alternate sources of water can be found, it will be cheaper to dispose of high TDS effluents by evaporation than by trying to treat the solutions, especially if desalination is involved.

Use of mine drainage water pumped from underground causes a cone of depression around the tapping point and should cause migration to the tapping point of contaminants in the aquifer. This offers a possible way to clean up contaminated aquifers.

7) Significant quantities of treated sewage water are available from sewage plants at the mine hostels and local municipalities.

- Treated sewage effluent water can be used without problems in gold recovery operations when the Merrill-Crowe process is used. Its effect on CIP performance needs to be studied.

- It is believed, without firm plant scale data, that reclaimed sewage water used in acid pH flotation of pyrite-gold from tailings results in a drop in recovery of gold, pyrite, and uranium. These observations have been indicated at President Brand Gold Mining Company where from time to time some reclaimed sewage water is said to have got into the process solution.

- Anglovaal Research Laboratories tested reclaimed sewage water from two types of sewage plants for high pH flotation of gold and pyrite. In one case the results were as good or better than when fresh water is used; in the second case there was a definite interference.

- The first flotation test case (where no interference was found) used reclaimed sewage water from the new Stilfontein sewage treatment plant which uses an activated sludge process. The second case (where there was interference) used water from the older sewage treatment plant which uses biofiltration. These tests indicate the possible merits of activated sludge sewage treatment where the product water is to used for flotation.

- Anglo American Corporation has observed, again only quantitatively, that if reclaimed sewage water is used in the Peabody scrubbers to clean and cool SO_2 gas after roasting, then after this step it becomes usable in flotation without interference in the flotation process.

- President Brand Gold Mining Co. used a reclaimed sewage water component in CIP gold recovery from leached calcines. It was found that CIP recovery was adversely affected, although there were other contributory factors.

- Rohm and Haas has developed an experimental resin for removal of humic acids from solutions and pulp. This product is not commercially available.

- The discussion on water quality effects on flotation in Chapter 54 mentions several potentially useful observations on the use and impact of sewage water on flotation recoveries.

It was mentioned that either the R & H experimental polymeric coagulant XE-392 or their range of Ambersorb carbonaceous adsorbents might be useful for this application. The price of these products is however relatively high at $11-14/lb. More information can be obtained from:

ROHM AND HAAS COMPANY
Independence Mall West
Philadelphia, PA 19105
(215) 292-2376
Carl A. Panza

8) The possibility of polyelectrolyte or polyacrylate flocculants and other long chain organic compounds present in treated sewage water having an adverse effect on carbon adsorption of gold requires further investigation. One way to consider would be biological degradation - another would be through the use of clays to scavenge these materials and settle them. More information about new applications of this sort for activated bentonite can be obtained from:

MR. JOHN DENT
Drillchem (Pty) Ltd.
Post Office Box 78642
Sandton 2146
(011) 783-4456

9) Stearic acid, even in trace amounts, have an adverse effect on molybdenite flotation. Possibly, stearates (soap) in sewage effluents are one possible cause of interference in flotation efficiency.

10) Witwatersrand gold mines are very deep and hot. All water pumped underground is first disinfected by chlorination to breakpoint. Mineworkers are accustomed to drinking whatever water they can find in the stopes and since undoubtedly a considerable amount of coliform bacteria is generated underground, thorough disinfection is considered essential.

One mining house, Gold Fields of South Africa Ltd., has been seeking ways to use reclaimed sewage water as cooling water underground. However, since the water contains relatively high ammonia levels the problem of excessive chlorine consumption to achieve breakpoint each 1 lb NH_3 consumes 10-15 ppm Cl_2. If less chlorine is used, chloramines are formed. These chloramines may be toxic or may themselves be adequate as a means of disinfecting minewater. This is a topic for ongoing research. At some Gold Fields operations (e.g., Kloff), a sewage treatment process yielding an effluent with max. 0.5 ppm NH_3 has been installed.

Calgon Corporation proposes that the use of chlorine dioxide would be more economical for disinfection of reclaimed sewage water and also for minewater containing coliform bacteria. More information can be obtained form FLOCCOTAN (PTY) LTD. or CALGON CORP., whose addresses were listed above.

11) Use of reclaim sewage water containing ammonia and chlorides in underground refrigeration and also in the above ground compressor cooling stations introduced a problem in that copper-nickel heat exchanger coils were corroded. After investigating the problem with the help of the CSIR, the problem was solved by appropriate materials selection.

More information of this aspect could be obtained from:

GOLD FIELDS OF SOUTH AFRICA LTD.
Post Office Box 1167
Johannesburg 2000
South Africa
Bill Pullen

COUNCIL FOR SCIENTIFIC AND
INDUSTRIAL RESEARCH
Post Office Box 395
Pretoria 0001
(012) 86-9211
Dr. Bird

CALGON pointed out that copper corrosion by ammonia attack of refrigeration tubes could be inhibited by use of a calgon product called TOLYTRIAZOL. This reagent is also not destroyed by chlorination.

12) Ongoing research in South Africa at the National Institute for Water Research, Pretoria is investigating the use of a clay known as Clinoptilolite to remove ammonia from solution. Tests to date indicate that NH_3 can be reduced from 20 ppm to below 1 ppm without much difficulty. Clinoptilolite is used for this purpose in some U.S.A. municipal water treatment plants. See Chapter 22 on ammonia removal.

Requests for information may be directed to:

NATIONAL INSTITUTE FOR WATER
RESEARCH
Council for Scientific and
Industrial Research
Post Office Box 395
Praetoria 0001
(012) 86-9211
Telex: 3-630 SA

Progress and details on this project may still be confidential.

13) The Chamber of Mines Research Laboratories in conjunction with the Water Research Commission (S. A. Government), Rand Mines Ltd. and various desalination technology companies is testing several approaches to acid mine drainage treatment and desalination at the East Rand Propriatory Mining Co. (ERPM) near Springs. The innovative slurry seeded Reverse Osmosis process and EDR testwork are discussed further in Chapter 15 on desalination and Chapter 24 on acid mine drainage treatment. Also see the trip report on ERPM in Appendix I.

At the time of the Randol visit some aspects of the project were confidential but more information may now possibly be available about the desalination program from:

THE CHAMBER OF MINES RESEARCH
LABORATORIES
Post Office Box 91230
Emmerentia,
Auckland Park 2006
(011) 736-3020
Dr. Brian Protheroe
Mr. Don Hebden

Information on Slurry Seeded Reverse Osmosis in general may be obtained from the inventors:

RESOURCES CONSERVATION CO.
INTERNATIONAL
Post Office Box 784561
Sandton 2146
(011) 783-7121
Pat di Benedetto

RESOURCES CONSERVATION CO.
INTERNATIONAL
Post Office Box 3766
Seattle, WA 98126
(206) 828-2400
Mr. Tom Wolf

Information on EDR is available from:

PROCESS SYSTEMS (PTY) LTD.
Post Office Box 10142
Johannesburg 2000
(011) 802-4230
Ralph A. Jones, Managing Director

IONICS INCORPORATED
65 Grove Street
Watertown, MA 82172
(617) 962-2500
Telex: 922473
Bill Katz, Vice President

ERPM acid minewater is currently neutralized with lime and settled to remove the "easier" metals using the HDS process.

Several publications have described the Bethlehem Steel Company High Density Sludge (HDS) Process. Although installed and in use in a variety of forms at several companies, the best source of information is probably still Bethlehem Steel Co. who offer the technology and knowhow for sale together with an innovative way to make the sludge disposable under the new Hazardous Waste Regulations in the USA.

BETHLEHEM INTERNATIONAL ENGINEERING CO.
Bethlehem, PA 18016
(215) 694-7763
Telex: 847417 Mesbeth
Jim Forand, Vice President
Stewart Hermann

The process has also been described by among others VAN STADEN (1979); KOSTENBADER & HAINES (1970); HERMAN (?); HERMAN & KORB (?); BIEC Technology, Issue 4, July 1982; and TEMMEL (1971).

14) Examining the water quality parameters listed below for a typical Witwatersrand mine-mill complex it is clear that when manganese is used as an oxidant for uranium leaching, then manganese levels can be high in the tailings and in U-plant raffinate. It may be necessary to remove manganese from effluent streams. Manganese has been a problem in the past in the municipal water supply of at least two metropolitan areas downstream from gold and uranium extraction plants.

In order to precipitate manganese by aeration a very high pH is generally required. Surface effects and bacteria also play a role in precipitating manganese according to HEM (1970). Sulfide addition will quantitatively remove manganese even in alkaline solutions as described by LARSEN & ROSS (1976).

The CSIR in South Africa developed a process whereby divalent manganese is precipitated by adsorption into MnO_2 coated sand. Details of this process were considered confidential early in 1984, but now more information may be available. The process is very pH dependent with faster and more complete removal above pH 9. Addition of chlorine up to 50 mg Cl_2/l has a marked improvement on manganese removal which can be almost quantitative even at pH 7.0 after ten minutes. The combination of pH increase and Cl_2 addition makes it possible to accelerate

removal of Mn^{+2} to below 1 ppm. However addition of minute quantities of MnO_4^- has a dramatic effect on Mn^{+2} removal to extremely low levels.

AMAX Inc. is believed to have experience with innovative practical applications of some manganese/chlorine reactions, but these are company confidential.

Manganese removal has been extensively examined by numerous authors and is discussed in Chapter 43 of this report. However, the tailings/raffinate treatment with lime described for Vaal Reefs (Appendix I) shows that manganese can be kept below 1 ppm in tailings return water. However, lime costs are high to achieve this.

CHOICE OF PROCESS CIRCUITS

South African gold and uranium recovery plants have historically used a highly efficient drum filtration for solid-liquid separation ahead of gold and uranium recovery. In the late 1970's belt filtration was introduced at some South African uranium plants, notably Vaal Reefs East, Harmony, Randfontein Estates and the Chemwest Ltd. operation at Stilfontein. Belt filtration was also used at Randfontein Estates for gold recovery but it has not become widely accepted for this application. The South African industry preferred to use filtration as a means of solid-liquid separation because the Witwatersrand ore filters quite well despite its fine grind, especially at the high pH levels used in gold plants. At Vaal Reefs South and other locations, large CCD thickeners were installed for uranium recovery with some success although more dilute solutions result.

There are several process sequence arrangements to choose from in recovering gold and uranium from Witwatersrand ores and tailings. These will be reexamined from the point of view of water consumption requirements and subsequent effluent treatment costs. The variations on this theme are too many to be evaluated here. Some general ideas are mentioned as to where future innovations may be found - from a water management point of view.

1) Belt filtration provides a means of applying multiple counter-current washing steps of a leached ore, as well as the potential for dry tailings disposal. The use of belt filtration on the Witwatersrand has to date been limited to uranium circuits, except for the Cooke Plant of Randfontein Estates where it is used for gold recovery. Washing performance in the uranium plants has proven not nearly as good as originally expected with reports of 2-4% soluble losses apparently being typical. Randfontein Estates claims 0.5% soluble gold loss at Cooke Plant. It must be pointed out, however, that the uranium plant belt filter installations do not apply the filters as designed either - they are not using multiple counter-current washes because of operating difficulties in doing so.

New innovative approaches to solution distribution in filter cakes may, if combined with appropriate operator training and revised maintenance approaches, make belt filtration attractive even to the extent of being appropriate for gold filtration. One such idea with merit involves the addition of wood pulp fiber as a filter aid to the pulp ahead of filtration. This has not yet been proven, and probably would be a bad idea if the tailings were to be repulped and leached as feed to a CIP plant.

The main attraction of belt filtration is that it can theoretically wash a pulp to yield less than 1.0 tons of pregnant solution per ton solids. Belt filtration has been selected for its water efficiency both inside and outside South Africa, but even in France, where the most sophisticated use of belt filtration has been made, typical installations yield 2-2.2 m^3 pregnant solution per ton ore. Pioneer Nuclear Corp. in the late 1970s designed and tested a two-stage counter current leach and washing circuit for uranium leach pulp to be installed in Colorado where water in very limited supply. CCD circuits require typically 3.0-3.5 tons water per ton solids and expose large areas for evaporation losses.

At this point, however, conventional drum filtration is still a safer bet than belt filtration as far as soluble loss is concerned, yet requires much less water than CCD and yields solutions with lower suspended solids than either CCD or belt filters. Drum filters are, however, more expensive to install.

2) Carbon-in-pulp has become accepted in South Africa as a "conventional" process. The advantage of the process is that better gold recoveries are achieved and capital costs are lower. These factors are even more noticeable in calcine leaching. One major disadvantage is that the CIP process does not offer the opportunity to recycle cyanide-bearing barren solution back to leaching and filter wash, except after decantation in the tailings pond. Even then, cyanide value recovery would be poor.

Overall water requirements for CIP and drum filtration are about equal assuming 45% solids is used in the CIP circuits. However, CIP tailings go to the dam before solution can be decanted for recycle by which time much of the cyanide values will be lost to natural degradation, especially if the tailings are commingled with other effluents in the neutralization plant.

It may be possible to modify tailings disposal concepts to reclaim more cyanide values from CIP tailings. There are options that can be considered on a site specific basis.

3) In recycling solutions, TDS and metal ions are likely to build up unless removed by treatment. CIP adsorption of gold is generally more tolerant in this respect than zinc precipitation, and offers some advantages. FLEMING (1982) of MINTEK claims that resin in pulp offers additional advantages and these are being evaluated in South Africa.

4) For efficient carbon elution, water quality is critical and fresh water, possibly even demineralized water should be used for this step.

5) There is an increased interest in pressure oxidation of some Witwatersrand ores as a means of liberating locked up gold and improving both gold and uranium recovery. This would replace flotation, roasting, and calcine leaching for gold and leaching the flotation tailings separately for gold and uranium. It is too soon to tell what the impact will be on overall water consumption or water treatment needs. Tailings from this process being already oxidized will be inert and less likely to generate acid and TDS.

6) Several wasterock piles on the Witwatersrand are subject to study as potential heap leaching targets. In order to leach wasterock it is possible that the older piles will be re-sorted using ore sorters and the discard from these may be further crushed and stacked for leaching. This would present an opportunity to place the material on impermeable pads which could serve as a means of collecting solutions draining through the heaps long after heap leaching ceases. This concept is still in its infancy and is experimental. It will not replace the need for crushing and grinding of ore however but represents possible incremental recovery.

7) Experimental work on in-situ leaching of sand tailing dumps has not yet been published, and it is too early to evaluate water management needs and techniques for this process approach.

8) Heap leaching of reclaimed sand tailings is practiced at one site on the Witwatersrand but is unlikely, despite its apparent success, find general application. At Sevcorp's operation, tailings are disposed of by selling the sand to contractors.

9) There is a major expansion in re-processing of gold mill tailings on the Witwatersrand. Such projects include:

ERGO	1,500,000 tpm	U, Au, and S
Sallies-Daggafontein	1,000,000 tpm	U, Au, and S
RM3	420,000 tpm	
Chemwes Ltd.	270,000 tpm	U
Severin Resources	Small	Au and Sand

Various processing arrangements are in use. One major impact these will have on water impact is that the tailings can be disposed of in a more modern fashion which can reduce the impact of the tailings on ground and surface water. Pyrite values are recovered by flotation in several cases which reduces the acid generating capacity of these tailings when disposed of in their final impoundments.

TYPICAL WITWATERSRAND GOLD-URANIUM MINE-MILL WATER REQUIREMENTS

The water chemistry and balance of a hypothetical Witwatersrand gold and uranium mine situated over a dolomitic aquifer is shown below.

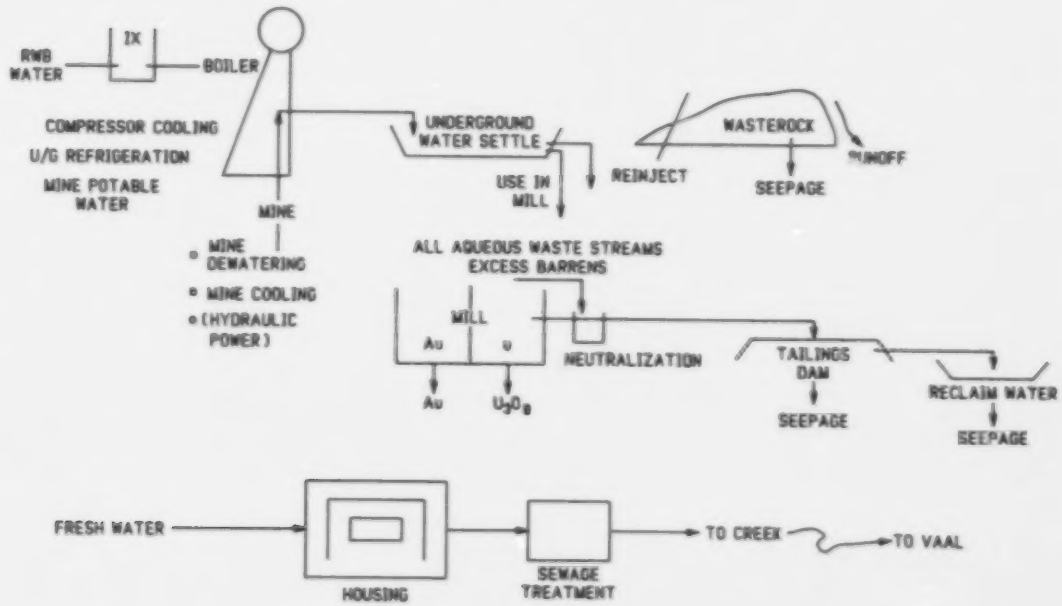
If tailings reclaim solution is to be recycled to the plant, then it is logical to expect TDS in the solution to increase. TDS in dolomitic water drawn from underground aquifers may increase due to seepage from the surface.

It is noted that a bulk neutralization tank receives water and tailings from all over the plant. After neutralization it is pumped to the tailings pond, and then reclaimed for judicious use in the metallurgical plants.

1) Repulped tailings from U-Plant filters.
2) Excess raffinate from barrens storage tank.
3) U-Plant spillage.
4) Precipitate hosedown water.
5) Boiler blowdown via lined ponds.
6) Boiler feedwater softening waste via lined ponds.

This represents a typical present case based on blended fragments of information for several operations. Many of the Witwatersrand mine-mill complexes are net users of water and do not discharge any point source effluents. What the situation would be if seepage from tailings dams and reclaim water ponds etc. were to be eliminated is not yet quantified.

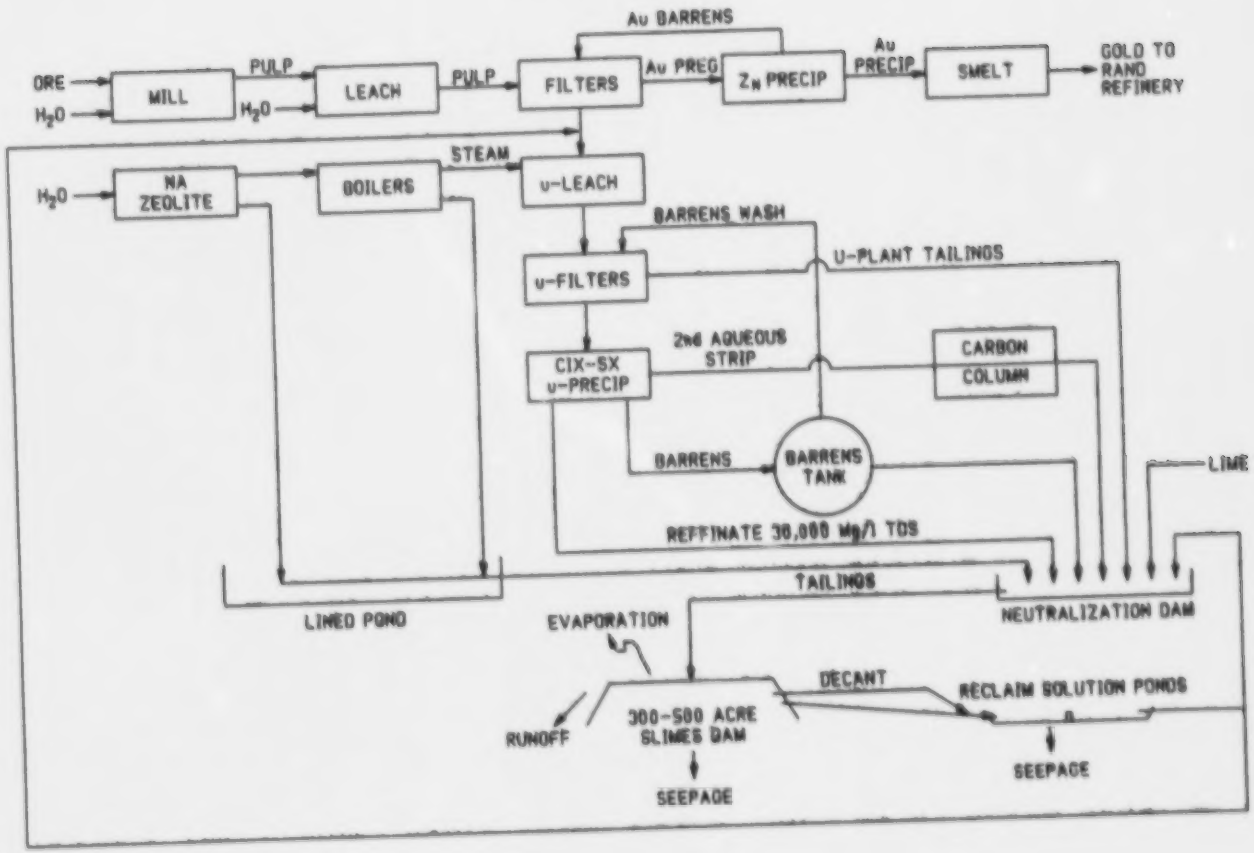
WITWATERSRAND MINE-MILL COMPLEX



ADDED COMPLICATIONS: FLOTATION PLANTS FOR PYRITE RECOVERY
FORWARD/REVERSE LEACH
ROASTERS AND H_2SO_4 PLANTS
CALCINE LEACH FOR GOLD

TYPICAL WITWATERSRAND GOLD-URANIUM COMPLEX

(FORWARD LEACH ARRANGEMENT)



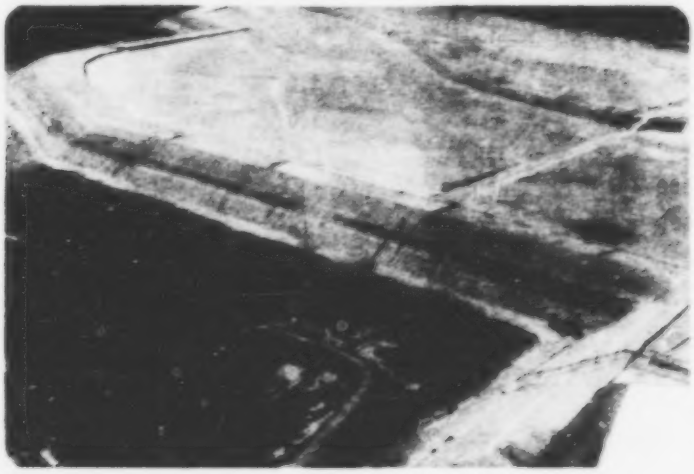
TYPICAL WATER FLOWRATES FOR 10,000 tpd MINE-MILL COMPLEX

Stream	Flow m/d
Mill circuit filter sprays	3000
Mill circuit makeup	1600
Mill circuit gland service	2000
Gold filter repulp water	1100
Guar makeup	300
Gold circuit gland service	180
Precipitate makeup water	600
U-plant hosedown and spray	2400
Boiler steam	720
U-plant belt filter seal water	1000
Flocculant makeup	300
U-plant hose and spray	240
U-plant vac. pump gland service	3000
Demineralized water	120
Excess raffinate (barrens)	3200
U-plant aqueous regen and column effluent	60
Neutralization of slurry	1100
Neutralization gland service	720
Potable water use	500
Sewage effluent	500
U-plant spillage	500

PROCESS WATER CHEMISTRY AROUND WITWATERSRAND Au-U PLANT

	U-Plant Raffinate	U-Plant Tailings	Boiler Water	Au Plant Return Solution
Na mg/l	300	300	90	300
K	70	60	15	15
Ca	600	700	250	400
Mg	130	90	7	0.2
Cl^-	250	300	200	60
HCO_3^-	0	0	0	0
$CO_3^=$	0	0	30	260
$SO_4^=$	17,500	14,000	700	700
SiO_2	400	300	20	20
CN^-	33	47	3.0	150
CNS^-	0	5	3.0	70
Fe^{II}	730	350	1	0.25
Fe^{III}	500	600	2	0.5
NO_3^-	160	140	120	250
NH_3	0.1	0.1	16	30
F^-	0.1	0.1	0.4	0.7
Mn	1700	1300	0.5	0.5
Heavy Metals (Ni + Co)	110	100	1	70
TDS	24,480	5,570	1540	3000
S/S	750	90	200	80
pH	1.5	1.6	11	11

WITWATERSRAND GOLD MINE - NOTE DRAINAGE TO FOREGROUND



SEMI-DRY TAILINGS AND DECANTED WATER EVAPORATION

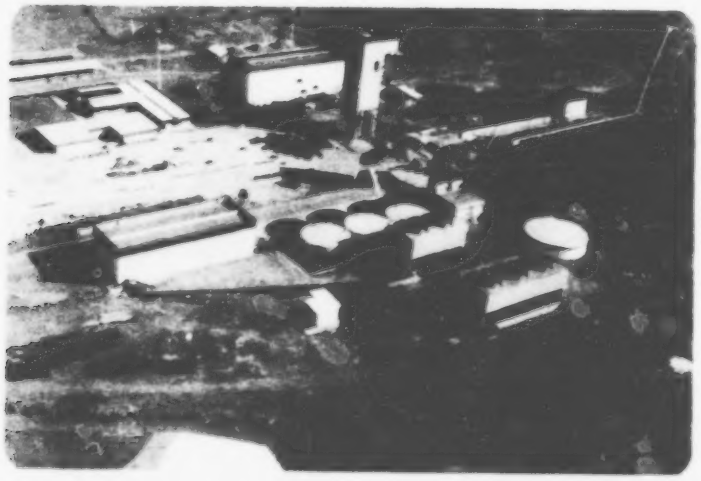
WASTEROCK DISPOSAL AT WITWATERSRAND MINE

MAKEUP WATER CHEMISTRIES

	RWB	Operating Shaft	Dolomitic	Potable	Shaft
U_3O_8	N/A	N/A	N/A	N/A	N/A
Na	30	230	130	30	80
K	10	10	5	5	5
Ca	40	160	230	30	400
Mg	15	25	50	10	120
Cl^-	30	30	90	10	30
HCO_3^-	122	0	65	130	40
$SO_4^=$	80	850	800	60	1560
SiO_2	10	30	30	15	30
CN^-	0	0.3	0	0	0.1
CNS^-	0	0	0	0	1.3
Fe^{+2}	0.02	4.0	0.5	1.0	1.0
Fe^{+3}	0.04	5.0	0.0	0.2	6.0
NO_3	0	270	12	0	1.0
NH_3	0	45	0	0	2.0
F	0.3	0.5	0	0.6	0.6
Mn	0.2	1.2	1.0	0.2	12
Heavy Metals	0.5	5	2	0.1	1.5
TDS	330	1660	1427	300	2500
S/S	-	364	0	0	50
pH	7.5	4.7	6.0	8.0	7.5

SEWAGE PLANT FOR TRANSVAAL GOLD-URANIUM MINE

MODERN MINE SEWAGE PLANT CLOSEUP: YIELDS 0.5 mg NH_3-N/l EFFLUENT



COOLING PLANT AND WATER TREATMENT FOR u/g GOLD MINE

SOUTH AFRICAN EFFLUENT STANDARDS
(PARTIAL LIST mg/l)

	Special Standard	General Standard	1983 Proposed General Limit	SABS Maximum Allowable Drinking Water Std.
	Section 21 of Water Act 1956 R553		R553 Table 2	
pH	5.5-7.5	5.5-9.5		5.5-9.0
S/S	10 mg/l max	25 mg/l	25 mg/l	
Na	50 mg Na/l over intake	50 mg over intake	50 mg/l over intake	
Cl_2 Residual	Nil	0.1	0.1	-
NH_3 as N	1.0	10.0	10.0	-
NO_3 as N	1.5	-	-	-
As	0.1	0.5	0.5	-
Boron as B	0.5	1.0	1.0	-
Hexavalent Cr	-	0.05	0.05	-
Total Cr	0.05	0.50	0.50	-
Copper	0.02	1.0	1.0	1.5
Selenium as Se	-	-	0.05	-
Phenolics as phenol	0.01	0.10	0.1	0.002
Mercury as Hg	-	-	0.02	-
Lead as Pb	0.1	1.0	0.1	-
Phosphorus Total as P	-	-	3.0	-
Phosphates as P *	2.0	-	1.0	-
Iron as Fe	0.3			0.7
Manganese as Mn	0.1		0.4	0.4
Cyanide & Related Compounds as CN	0.5	0.5	0.5	-
Sulfides as S	0.05	1.0	1.0	-
Fluorine as F	1.0	1.0	1.0	-
Zinc as Zn	0.3	5.0	5.0	15.0
Cadmium as Cd	-	-	0.05	-
Chloride as Cl^-	-	-	-	600
Magnesium as Mg	-	-	-	150
Sulphate as SO_4	-	-	-	400
TDS	-	-	2000	2000
Max Ca CO_3 hardness	-	-	-	1000

* Note: Regional standards subsequently limit phosphate levels of discharge in certain area including Pretoria - Witwatersrand - Sasolburg to 1 ppm max.

RAND MINES MILLING AND MINING CO. LTD.

Rand Mines Milling and Mining Company Ltd. (RM3) recovers gold and uranium from large gold mine tailings on the outskirts of the city of Johannesburg. RM3 is the subject of a trip report, but it is of interest here because of possible water quality effects on metallurgical recovery in this type of metallurgical plant. Comments made in this respect are hypothetical to illustrate some of the factors that need to be considered in designing such plants.

The basic flowsheet employs repulping of the tailings feed and a sand-slime split, with slimes going directly to cyanidation and CIP recovery. Sand is floated to yield a concentrate containing enriched gold and pyrite values. The concentrate is ground to 95% minus 200 mesh, cyanided, gold recovered in a separate CIP circuit and then floated again to make a 40% sulfide concentrate for shipment to roasting plants to make sulfuric acid.

The sand flotation tails are milled to 50% minus 200 mesh, and added to the slimes fraction for cyanidation and gold recovery by CIP. Capacity of the operation is 375,000 t/mo sand and 45,000 t/mo slimes.

Recycled water, runoff, and water from a local creek meet almost the entire needs of the operation. 45,000 m^3/mo recycled tailings dam water is used for the repulping of slimes dam material using monitor jets. 656,000 m^3/mo recycle and surface water with some Rand Water Board water are used to repulp the sand tailings.

The CIP plant performance has not been quite as expected on the basis of pilot plant tests. RM3 believe that this was due to two main factors:

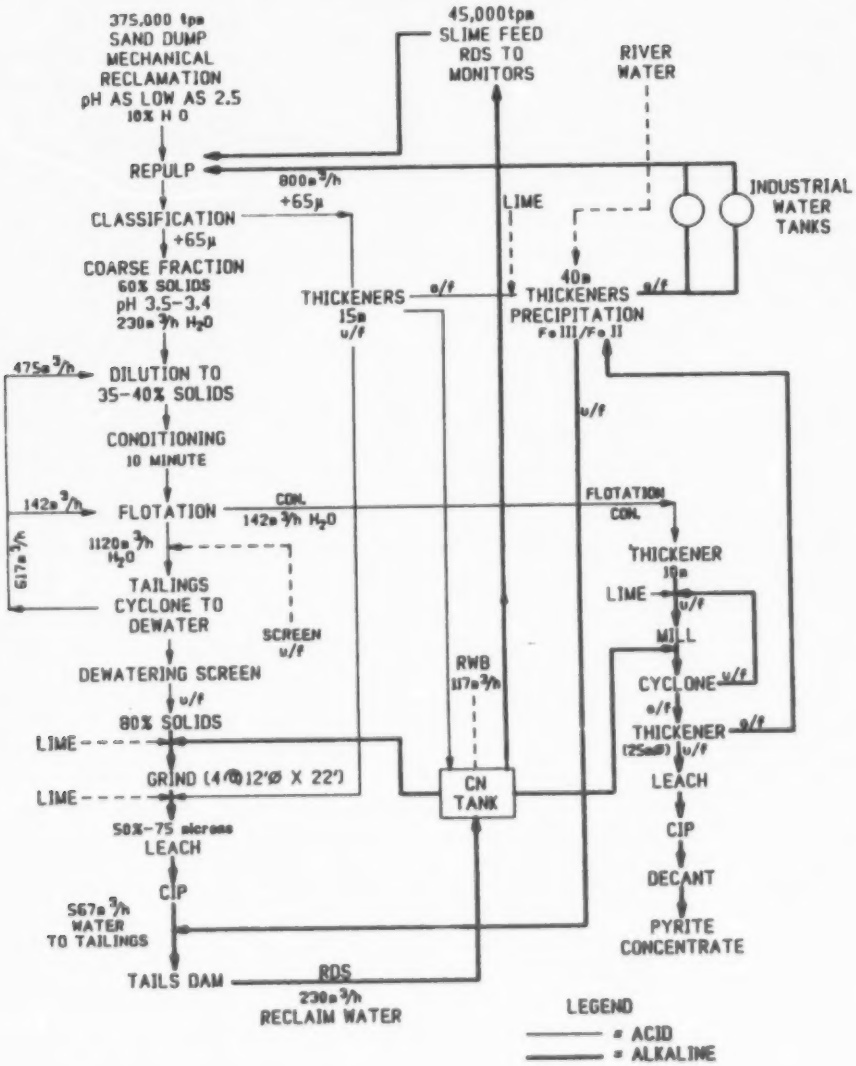
1) Flotation reagents caused initial interferences with carbon adsorption of gold. This was overcome by using a different frother known as TEB supplied by NCP.

2) Water from the local creek that was used proved to be contaminated with organics believed to have originated from upstream industry.

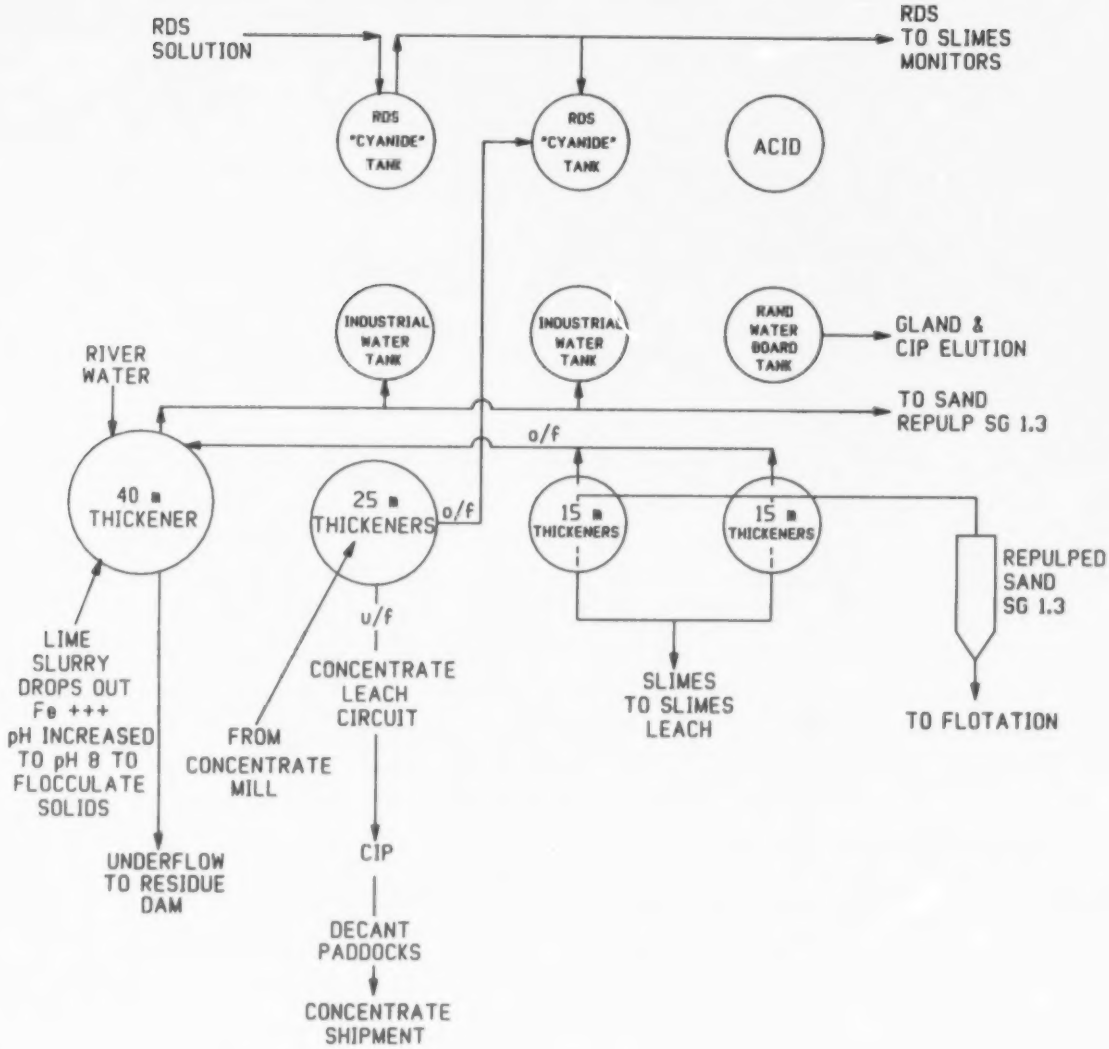
If the operation is examined from a water management point of view, it is found that water is recycled in two main loops. In the first, sulfide-bearing tailings in varying degrees of oxidation are repulped with recycle water primarily from the tailings dam, and from so called industrial water tanks which contain recycle and stream water which has been lime precipitated and settled.

It is believed that this recirculation of water that has been in contact with oxidizing tailings as well as the flotation concentrate may build up levels of thiocyanate, soluble

RM3 FLOWSHEET



RM3 WATER RETICULATION



sulfide, sulfate, ferrous and ferric ions and cyano complexes and possibly some humic acids and degradation products from the flotation reagents. One might speculate that thorough aeration of this recycled water at a high pH to oxidize and precipitate ferrous iron, or additional water treatment steps--e.g., biological--could have a positive influence on metallurgical recoveries.

West Australia

West Australia is arid but no more so than much of Nevada as far as climate is concerned. What sets it apart is that good quality groundwater does not appear to be available in areas such as Kalgoorlie - Norseman, which has been Australia's major gold mining center since before the turn of the century.

Significant development of the gold deposits in this area had to wait until the Goldfields Water Scheme was installed to bring water from Mundaring Weir near Perth, a distance of over 300 miles.

Present day mining and metallurgical operations rely on water from the following sources in addition to that piped in by the Goldfields Water Scheme:

Saline Groundwater (up to 15% TDS)
Recovered Process Water
Harvested Storm Water
Recovered Community Effluent

The Western Australian gold deposits are relatively small compared with South African operations - generally 500-2000 tpd on the Golden Mile, 1600 tpd at Western Mining's operation at Kambalda, 1000 tpd at Whim Creek's operation Meekatharra, and numerous small operations scattered throughout Western Australia.

Many of the ores are associated with sulfides and base metals and ore types are by no means uniform from one deposit to another - on the contrary, mineralogy of the ores is highly variable. Several of the ores require roasting to make them amenable to cyanidation. Calcines are washed before leaching.

Water at around A$1.00/m^3 is expensive and not always of the best quality. Water is recovered for recycle to the greatest extent practicable. However with further growth in the mining industry in this region available water supplies may become hard pressed to meet demand and further conservation and recycle may be needed.

Western Australian gold mines were visited during 1982, but it was not possible to visit them again to determine operating parameters with respect to water. Questionnaires have

been sent to each operator enquiring as to their water management practices, and responses have been summarized in Chapter 3.

During September and October 1984 Broken Hill Proprietory Ltd. was retained to undertake a survey of the Western Australian water needs and at what price water pumped from the Mundaring Weir near Perth would be economically substituted by alternative sources of lesser quality. Some additional information might be available from:

BROKEN HILL PROPRIETORY CO. LTD..
GPO Box 86A
Victoria 3001
Australia
60-0701
Hilton Duke

Although the study is probably client confidential BHP would undoubtably be able to provide some general insight into the Western Australian approaches to water management.

Some of the water conservation measures observed in Western Australia are as follows:

1. Placer Mining Without Water

Australia is known for very large gold nuggets in some of its desert placer country. One innovative way of recovering these has been by mounting multiple metal detectors on a wheel mounted frame that is driven across the desert. Any signals are investigated to find nuggets. It is questionable whether this innovative technique will account for more than a very limited gold production in extremely site specific instances. It, however, consumes no water - only gasoline and beer.

2. Evaluation of Placer Gold Deposits where Water is not Available

When a major gold deposit is found then water of some or other quality may be found at some distance and piped in. During the exploration and evaluation phase however, large bulk samples must be tested and the options are to truck ore to the nearest water or to truck water to a test site adjacent to the deposit. In Western Australia this could mean hauling ore or water thirty miles or more. Even though these units achieve a lower recovery of say 70% compared to jigs for which 90% recovery is claimed by some, results from these test units can be calibrated accordingly. If a deposit is proven to be economically viable, then part of the capital investment may be allocated to bringing in good quality water

Information on the cone concentrators is available from:

RCR ENGINEERING (PTY) LTD..
Wilson Road
Bunbring, WA
Australia
(097) 211-355
Charlie Birmingham
VICKERS XTAL
Lucca Road
Post Office Box 137
Wyong NSW
Australia
(043) 53-1233
Telex: AA 25271
Ron Goodman

McSWEENEY AND PARTNERS
91 Kensington Street
East Perth WA 6001
(09) 325-4744
Telex: 92896
David Bales

ROGEX INDUSTRIES (PTY) LTD.
10 Alue Street
Bayswater WA
(09) 279-8611
Frank Rogers

3. Flotation and Roasting

Several Western Australian gold ores require flotation and roasting before the gold is amenable to cyanidation. Examples of such plants are:

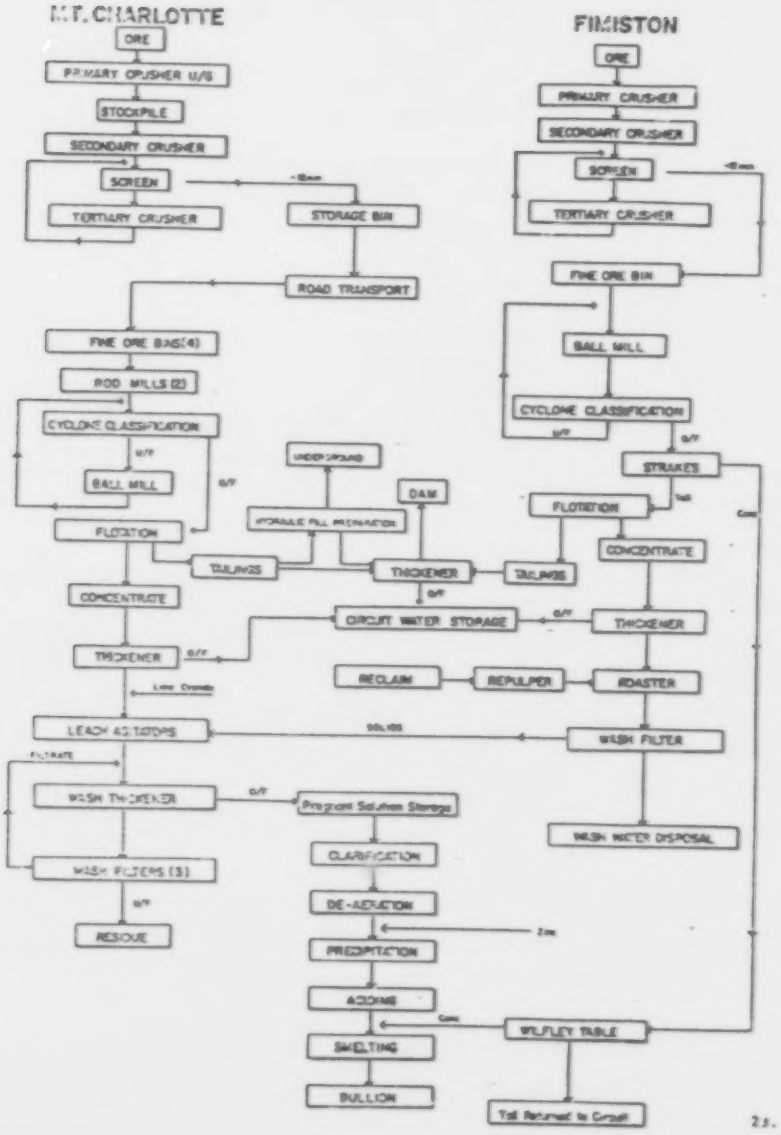
1) Kalgoorlie Mining Associates, Fimiston
2) North Kalgoorlie Mines Ltd., Fimiston
3) CSR Paringa Mining Co. (Pty) Ltd., Kalgoorlie
4) Lancefield Gold Project, Windarra
5) Several additional deposits under evaluation in Western Australia

Cyanide depresses pyrite flotation and must therefore not be present in flotation plant water. This must be taken into account when recycling water in such operations which employ flotation, roasting and leaching.

Fortunately Western Australia has a very hot climate especially in summmer and solutions need not be aged very long for natural degradation to decompose cyanide. However, evaporative losses are also likely to be very high. Also the extent to which ferro and ferricyanides are removed in the tailings pond is not known, nor is the degree to which these stable cyanide complexes interfere with flotation of pyrite and gold.

After roasting, calcines are washed in water to remove soluble metal salts e.g., Fe, Cu, Ni, which otherwise would consume cyanide and interfere with subsequent

METALLURGICAL FLOW DIAGRAM



processing steps. It is not known how the wash solutions are disposed of or recycled at the existing operations. The KMA flowsheet does however show the washwater as being disposed of rather than recycled.

Alternative 1: Reclaim Usable Water Using HDS from Barren Bleed and Calcine Washwater

Calcine washwater contains metals in acidic solution as hydrated cations in the absence of cyanide. Barren bleed contains base metals and iron in the form of cyanide complexes.

Randol International Ltd. suggests four possible ways in which usable water can be reclaimed from these wash solutions.

- Precipitation of metals from the calcine wash solution with lime using HDS, settling and clarification.

- Blended of wash solution with barren bleed containing cyanide complexed metals for HDS cyanide removal, metal precipitation, HDS, settling, and recovery of water.

- Use of the Prussian Blue precipitation with cross-flow filtration to remove metals as cyanide and hydroxide precipitates, allowing decant solutions to be recycled.

- FeS addition should probably be avoided because of undesirable affects of sulfide ions on subsequent cyanidation steps. HDS is recommended for the following reasons:

  1. HDS results in efficient lime use;
  2. HDS results in a high density sludge for easy disposal; and
  3. HDS will remove iron, heavy metals and cyanide from the combined flow with less reagent addition than required to treat both solutions separately.

  Note: The above is a purely conceptual application of HDS and requires proving on laboratory, pilot and commercial scale.

Calcine tailings after cyanidation should be stockpiled in a separate disposal site for possible future treatment. This would also keep cyanide out of the flotation tailings from which decant water is recycled back to the front of the process.

More information on the HDS process particularly on details as to how it can be applied for cyanide removal (patent applied for) can be obtained from the developers of the process. Bethlehem Steel application of HDS for cyanide removal should be regarded as confidential until their patent is issued.

BETHLEHEM INTERNATIONAL ENGINEERING CORPORATION
A SUBSIDIARY OF BETHLEHEM STEEL CORPORATION

BIEC TECHNOLOG
ISSUE 4 • JULY 1982

High-density sludge process– an improved technology for treating acidic metal-bearing wastewaters

Many wastewaters from steel plant and mining operations have traditionally been difficult to treat effectively prior to approved discharge into public waters. The reason: conventional neutralization processes that treat acidic metal-bearing wastewaters produce very dilute sludges and are not efficient in precipitating mixtures of dissolved heavy metals. Bethlehem International Engineering Corporation is authorized to license a high-density sludge process that does this job better and more economically than conventional processes.

Also applicable to the treatment of acid mine drainage, the process may reduce costs to build and operate a treatment facility. This economy results from: (1) a substantially higher-density sludge, (2) improved slurry filterability; (3) improved reduction of metal concentrations, and (4), in some cases, the smaller size of the clarifier/thickener required.

The process is in operation at three Bethlehem Steel Corporation plants, five Bethlehem Mines Corporation bituminous coal mines, and a South African gold mine. A new facility for a Bethlehem Mines Corporation anthracite coal mine is under construction. (See Table, Figure 3, on reverse side of this sheet.)

This technology is now available for licensing from Bethlehem International Engineering Corporation.

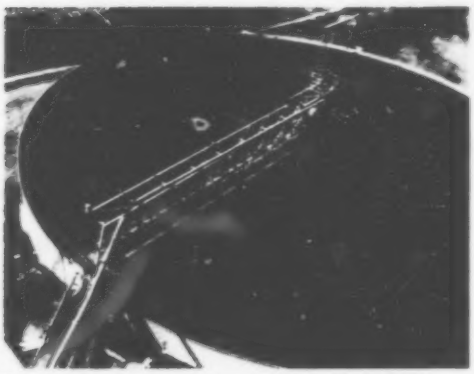


Figure 1: Full-scale plant in operation at Bethlehem Mine's Mine 38, Cambria, Pa.

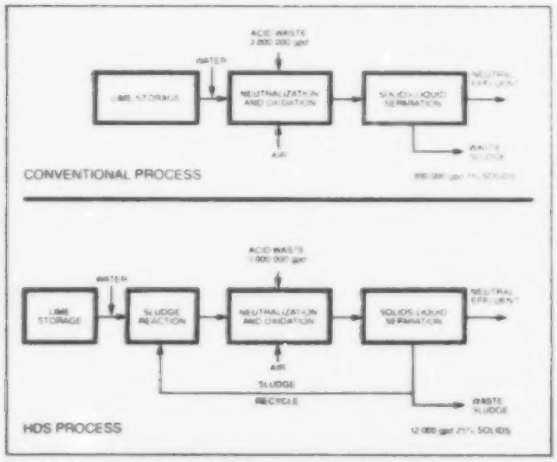


Figure 2: Lime neutralization of pickling wastewaters, two methods.

BETHLEHEM INTERNATIONAL
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Bethlehem, PA 18016
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Telex: 817417 MESBETH
Jim Forand
Vice President

Alternative Water Sources

1. High TDS Saline Water

If saline water is used in flotation, we have no experience in the extra costs involved or metallurgical effects in this environment.

Note: Chuquiquamata Div. of Codelco is believed to use high TDS water for copper flotation with success.

2. Reclaimed Sewage Water

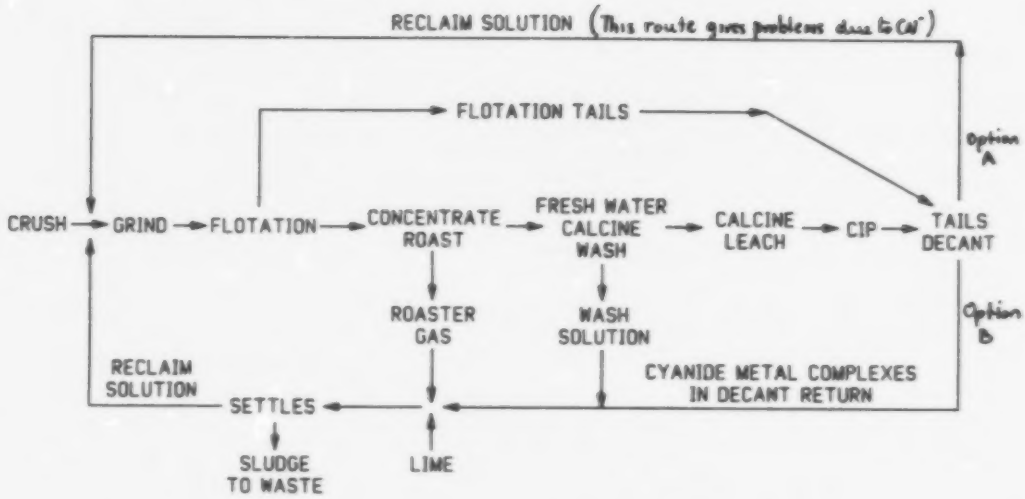
Has been tested in South Africa and found to have resulted in varying gold and pyrite recovery losses depending on the quality of the treated sewage effluent. Qualitative observations found that if this water is used as a coolant inside the Peabody scrubbers in the roaster gas stream, it becomes usable. Tests have also shown that activated sludge sewage effluent treatment may render it usable with no detrimental effects on flotation recoveries.

3. Harvested Storm Water

No problems anticipated as long as there is enough of it and suspended solids are removed.

Alternative 2: Use of Roaster Gas

This alternative uses calcine washwater and barren bleed from cyanidation to supplement process water in the grinding of the incoming ore. Cyanide and metal values interfere with flotation and must be removed. SO_2-Air and lime can be used to pretreat the mixed solution to destroy cyanide and precipitate dissolved metals. Alternatively the pulp flotation feed can potentially be conditioned with SO_2 at pH 8-9 prior to flotation as a means of destroying cyanide and precipitating base metals and soluble iron before the flotation step.



Note 1) After multiple recycling of flotation tailings reclaim solution, these may develop characteristics that are deleterious to flotation and require additional treatment steps.

Note 2) Calcine leach and CIP tails should be stockpiled separately from flotation tailings to keep CN out of the flotation tailings reclaim water.

Note 3) Additional water could be recovered by dewatering flotation tailings which would then be disposed of as "dry" tailings. Economics of this step depends on the price of water.

Note 4) INCO Ltd. market the patented SO_2 process for cyanide removal.

Information on the use of SO_2 for cyanide destruction and metal removal from recycle solutions can be obtained from the world experts in this field:

INCO TECH LTD.
Division of INCO LTD.
J. Roy Gordon Research Labroatories
Sheridan Research Park
Mississauga, Ontario
Canada L5K 179
(416) 822-3322
Dr. Bruce R. Conard
Mr. Eric Devuyst

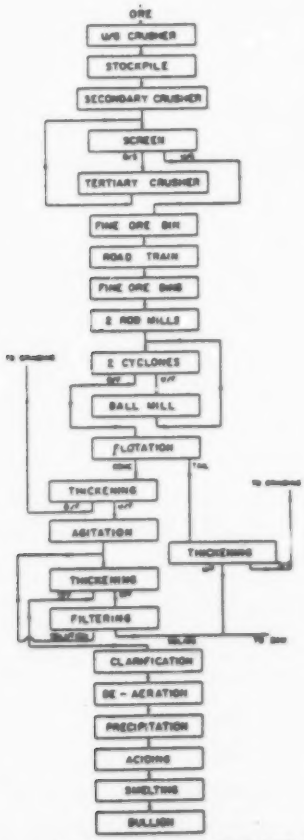
3. Alternative Metallurgical Processes

An alternative patented process has been described by DUNN (1983) which requires no grinding and virtually no water. Roasting of finely crushed ore in a shaft furnace would require very little energy. It is noted that this process is still in the

developmental stage and has yet to be proven on pilot and commercial scale. High water prices or lack of water availability may give this process some added appeal. It is certainly a simple concept with potential overall cost and recovery improvements.

4. Flotation and Leaching of Concentrate

Certain sulfide ores in Western Australia do not leach well directly. However, a flotation concentrate from these ores can be reground and leached under more aggressive conditions with adequate recoveries avoiding the need for roasting. One such ore was the Mt. Charlotte ore of the Kalgoorlie area company now known as Kalgoorlie Mining Associates in which Homestake Mining Company of the USA has an interest. A flowsheet of the process used for this ore is provided below. It shows flotation concentrate and tailings thickener overflow solutions were both returned to the grinding circuit.



Flowsheet of Croys treatment plant of Kalgoorlie Mining Associates.

This flowsheet allows a regrind of the concentrate, aeration and cyanidation using more concentrated reagents than could be economically justified for the whole ore.

The flowsheet of the Oroya treatment plant shown above is based on water availability at a reasonable cost. In it there is a significant bleed of water to the tailings dam with leached concentrate and thickened flotation tailings. No reclaim recovery of this water beyond the thickener o/f is shown. After aging in the tailings pond, decant solution from the tailings pond may be used directly in the front end of the process if all free cyanide has been lost by natural degradation or alternatively some or other cyanide removal process may be necessary:

- Alkaline chlorination.
- Bethlehem Steel HDS process with added iron.
- SO_2 cyanide destruction in presence of copper.
- Bacterial cyanide removal.
- H_2O_2/Cu cyanide decomposition.
- $FeS/FeSO_4$ addition followed by aeration.

Alternative Sources of Water

High TDS water may be used possibly without detriment depending on its composition.

Sewage reclaim water may possibly be used, but only after appropriate activated sludge treatment or by treating it with roaster gas, subject to confirmatory testwork.

If the price of water is high enough, the flotation tailings water could be partially recovered by installing a dewatering step e.g., filtration to dewater the tailings for dry tailings disposal using a belt press.

Consolidated Gold Fields Ltd. in considering a spectrum of metallurgical processes for the Mahd adh Dhahab ore deposit in Saudi Arabia in a hot desert climate have elected to recycle solutions as follows from a combined flotation-leach-CIP circuit, albeit leaching the flotation tailings rather than the concentrate:

1) Dewatering Flotation tailings, recycling water to grind and flotation.

2) Dewatering CIP tailings by filtration and recycling cyanide-bearing barren solution to repulp flotation tailing prior to leaching.

3) Discard "dry" tailings as a filtercake.

Such an arrangement has been calculated to save adequate cyanide in the recycle to justify the capital and operating costs of the barren solution recycle.

Water consumption in the circuit is found to be reduced to one third of that for a plant in which water would not be recycled according to LEWIS (1984).

FLOTATION AND CYANIDATION OF TAILINGS

An example of this flow sheet is that proposed for the Lancefield Gold Project of Western Mining Corporation, and Shell Company of Australia at Laverton, WA. In this case flotation removes most of the gold plus cyanicides, pyrrhotite, pyrite and arsenopyrite which must be roasted before leaching, and a flotation tailing with some gold that justifies leaching.

The cyanide consumers and oxygen consuming species in the flotation tailings are high enough to require high cyanide and lime levels during leaching ahead of CIP. Unless such ores are thoroughly aerated difficulty can be experienced with carbon adsorption and elution.

Calcine from the roaster will be quenched in water which will be recycled via a thickener. About 80% of the washwater will be recycled and 20% bled to keep dissolved metal levels within manageable limits ahead of cyanidation. Temperature in the quench tank is found to be critical - optimum is 60°C. Should temperatures rise to 80°C, gypsum scale formation is serious.

The 20% calcine wash solution bleed could, if economics dictated, be recovered and treated as described in earlier cases.

CIP tails could be dewatered for recovery of cyanide values and water depending on the prevailing cost of water and cyanide and levels of other interfering metal complexes.

A description of the development testwork by LEWIS (1984) on the Mahd adh Dhahab deposit in Saudi Arabia offers interesting insight into cost effective measures for this type of processing arrangement at a location that is both hot and dependent on expensive water.

EFFECT OF CYANIDE SOLUBLE METALS IN ORE

Other factors that can prove important in water management for such flowsheets are the presence of cyanide-soluble copper, nickel and also iron in the flotation tails that leach during cyanidation.

Due to solution recycle, copper levels may build up eventually to levels at which problems are experienced with zinc precipitation by Merrill-Crowe, or copper and nickel can reach

levels that depress gold adsorption on carbon if CIP is used. In some cases these metals may be present at levels that cause problems even when solutions are not recycled.

SCERESINI (1982) showed that 60 ppm Ni in the leach solution from Western Mining Corporation's Kambalda gold ore which contains 0.15-0.25% nickel of which 10% leaches in cyanide, resulting in about 6000 ppm nickel adsorption onto carbon. To reduce the depressing effect of nickel on gold loading additional cyanide is added to the circuit which also reduced the level of copper that adsorbs onto the carbon in the CIP step. LAXEN (1982) however showed that additions of nickel to over 100 ppm did not have a serious effect on carbon adsorption of gold during experiments performed at Gencor Ltd.'s Grootvlei Gold Mine in South Africa.

Nevertheless, careful recycling of solutions could result in nickel level buildup which would have to be treated every so often if they became a problem. More information may be available from:

DR. PETER A. LAXEN
Council for Mineral Technology
Post Office Box X 3015
Randburg 2125
Johannesburg
(011) 793-3511

BRUNO SCERESINI
Western Mining Corporation
Kambalda WA 6442
Telephone: Kambalda 27-1211

EFFECT OF PHRRHOTITE

Work at Homestake Mining Company at Lead, SD showed that pyrrhotite must be completely oxidized by preaeration of the pulp before leaching to avoid excessive cyanide consumption and problems in the CIP adsorption/desorption circuit. SALISBURY (1982) point out that when the CIP circuit was started up at Lead, South Dakota, before adequate aeration capacity was installed, gold adsorbed on the carbon partly in the metallic form and was very difficult to elute.

EFFECT OF TEMPERATURE ON CYANIDE CONSUMPTION

HALBE et al. (1979) showed that cyanide consumption at Homestake goes up in summmer which they found was due to the formation of thiocyanate by reaction with soluble sulfides such as pyrrhotite. The rate of this reaction was found to increase sharply above 10° C. Since tailings pond water at 20° C in summer is recycled to the process a greatly increased cyanide consumption was observed compared with an earlier system in which

fresh process water at 4° C was added to the system. Spray cooling was practiced in 1978 with some success and the spray cooling was to be expanded in 1979.

Clearly, one way to reduce cyanide consumption and thiocyanate levels in tails is to leach pulps that generate CNS at a reduced temperature where possible.

If water is to be conserved due to its cost then spray cooling is unlikely to be an adequate answer in the searing Western Australian summers.

EFFECT OF TEMPERATURE ON CARBON ADSORPTION

Gold and silver adsorption on activated carbon is improved at lower temperatures. Consequently recycling of solution to tailings and/or the use of black painted steel pipes to transfer pulps and/or solutions in the plant should be avoided where these are exposed to the summer sun.

VAT LEACHING

Three vat leaching companies were visited in Western Australia. These were:

Grants' Patch Partners, Kalgoorlie
Horseshoe Lights Project, Contech (Pty) Ltd., Perth
Elaura Enterprises (Pty) Ltd., outside Perth

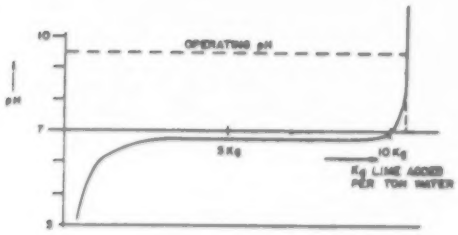
Grants' Patch Partners operates numerous small vat leaching operations treating old dumps scattered around the Kalgoorlie district and employing portable carbon canisters to adsorb gold. These are then transported to Kalgoorlie where the carbon is eluted at a central elution plant.

Water for their operations is usually accessible around or in the old mine workings where the tailings are located, frequently in the flooded shafts of old mines.

Water quality is often a problem. Grants' Patch Partners have used water with up to 1.3% TDS but this was considered close to their upper limit.

There are tailings piles where the only available water contains 20,000 ppm tds which is not usable. In such cases water treatment processes might make the water usable depending on the overall economics of the situation. To date no such water treatment systems have been installed either because the economics of the situation do not justify such installations or because Grants' Patch Partners experience in water treatment is limited.

pH VERSUS CaO ADDITION
BUFFERED MINEWATER



Alunite and gibbsite frequently occur in West Australian gold ores and are found in the tailings. In one case 15% of the ore was gibbsite, which is a hydrated aluminium oxide. The gibbsite buffers the minewater available from the area at pH 6-7 and this water may require up to 10 Kg lime per ton to bring the pH up to the working level of pH 9 or 10.

Based on other evidence in similar instances for water drawn from flooded mine workings, at least a part of the extra lime consumption may be due to high H_2CO_3 in the water. This phenomenon is believed to contribute toward severe carbon scaling in carbon columns and CIP when the pH is increased in the presence of calcium.

One possible way to reduce lime consumption in such cases was demonstrated at the Panther Valley Division of Bethlehem Steel Company where air is blown through the mine drainage water to remove excess CO_2 before lime is added. More information on the phenomenon is available from:

RESEARCH LABORATORIES
Bethlehem Steel Corporation
Bethlehem, PA 18016
(215) 694-7763
Telex: 847-417 MESBETH
Stewart T. Herman

More information concerning water quality phenomena in Western Australian vat leaching may be obtained from:

GRANTS' PATCH PARTNERS
McKenzie Buildings
Hannan Street
Kalgoorlie WA 6430
(090) 215-777
Patrick Harford
Managing Director
Nick Giorgetta
Chief Metallurgist

The importance of removing bicarbonate ions and H_2CO_3 from solutions before addition of lime is grossly underrated in operations. Not only will scale effects be reduced and lime consumption be more economical, but the amount of precipitate that is generated will be reduced too. This factor is particularly significant when a thickener or clarifier is installed as the extra solids generated may even impair the thickener performance due to overloading.

HEAP LEACHING

The only heap leaching visited by Randol International Ltd. in Western Australia was that of Whim Creek Consolidated NL at Meekatharra.

This 300,000 tpa operation combines heap leaching of coarse material with agitation leaching of fines after grinding, followed by CIP.

Whim Creek gets its water from flooded underground mine workings. No information was available on water quality.

It was stated that despite relative costs of \$280/t for Na_2CO_3 compared with \$80/t for lime, soda ash is used for pH control in the leach circuit. The reasons given for this were:

1) A lower cyanide consumption when soda ash is used.

2) Less scaling effects when soda ash is used.

3) Although more expensive than lime, less pounds of soda ash are required for the same rise in pH.

It is not possible to comment on water management based on the information available. Certainly the reasons for Na_2CO_3 preference over $CaCO_3$ invite further investigation. It would be of interest to know what the HCO_3^- level in the raw water is and whether aeration of this water would help reduce scaling when lime is used for pH control.

Although solutions are recycled many times at Whim Creek, no serious scaling problems on the carbon are recalled, but this should be confirmed.

AUSTRALIS MINING N.L.

Use of High Salinity Water in CIP Operations

WEBB (1982) described the Australis Mining Cip Plant at Norseman, Western Australia which was operated at 400 tpd ore throughput containing 1.5 g Au/t.

Saline water was drawn from nearby Lake Cowan, normally a "surface-dry" salt lake overlying a water reservoir contained within sediments and precipitated solids, notably gypsum. Extra channels and holding ponds were excavated to overcome both the shortfall in seepage replenishment rates and the low water reclamation rate from the plant tails, at times verging on negligible recovery. Low precipitation and hence runoff of surface water into the lake immediately prior to the commissioning period aggravated the water supply problems. The high dissolved solids content of the water, typically 100,000 ppm have not presented insurmountable problems within the processing circuit.

One minor problem encountered during commissioning included premature failure of pumps supplying process water from Lake Cowan. Severe corrosion within the pumps limited unit life to approximately six weeks.

More robust pumps now in use offer improved reliability and service. Areas of high abrasion within the plants were identified and corrective action taken. Pump impellors and discharge lines required upgrading.

Process water from Lake Cowan is rather acidic and pH values of 3.5 are not uncommon. The pH varies with the rainfall and the fraction of recycled tailings water in the process water. Lime consumption attributable to the ore accounts for the balance of lime used, 0.010% of free lime (as $Ca(OH)_2$) in the tailings solution allows for upward fluctuations in lime consumption during unmonitored periods, while maintaining a protective buffered pH for cyanidation. Lime consumption of up to 2 tons per day is not unusual during dry periods (4.5 Kg lime per ton ore).

As with lime consumption, cyanide consumption depends to some extent on the process water used. Typical consumption of cyanide is 0.3 Kg/ton ore processed.

A carbon-in-leach arrangement is employed in four tanks in series with a six hour retention itme, although cyanidation is generally complete after the first two hours.

Since carbon is not reactivated after each desorption, losses in carbon activity are compensated for by increasing carbon concentration in the pulp. Fresh carbon addition is made when soluble gold in the tailings rise above 0.05 mg/l. Initial gold loading averages 1500 g Au/ton however severe fouling of the carbon after several cycles reduces its activity to a point where only 1000 g Au/ton carbon is achieved. This was also affected

by the fact that acid washing was not carried out at the custom elution plant used to desorb the gold from the carbon. It was believed by Australis Mining personnel that the highly saline process water is responsible for some of the observed reduction in carbon activity, but this was not confirmed.

Periodic reactivation (about every 5 cycles) and acid washing with 5% HCl with every desorption cycle appears to allow consistent and reasonable gold loadings and soluble gold control in the tailings is also easier to manage.

It is not known whether this Australis Mining NL operation is still in production since at 1.5 Au/t the headgrade was low for a 400 tpd CIP operation, however if it is, more information can be requested from:

ANTHONY P. WEBB
Chemist, Plant Operations
Australis Mining NL
Norseman WA

Western Australia - Summary

1) Western Australian goldfields in general are short of water of good quality. Water pumped 350 miles from Perth is expensive and there is a limit to its availability. Locally available water is often extremely high in TDS.

2) Depending on the price of water and its availability, various measures to enhance water recovery from tailings and effluents become economically attractive in relation to purchasing fresh water. So far however there are no known sophisticated water treatment installations to reclaim water from tailings and to make it and contaminated effluents usable.

3) Numerous possible measures are available to improve recycled water quality which could be installed at a not too exorbitant cost. Some are simple such as segregation of cyanided and non-cyanided effluents. Others are more costly and may involve new technology with which these operations are not familiar.

4) Incentive to recycle more water and treat it will increase if it becomes available on a tighter allocation or if the cost of available fresh water goes up, but there is a limit to how much Western Australian operations can afford to pay for water.

5) Each site specific case must be evaluated on its own merits depending on ore characteristics, metallurgical process performance, availability of alternate water supply etc. Cases are reported e.g., Australis Mining at Norseman, where high TDS can be used for CIP with satisfactory results.

CANADA

Canada is a huge country mostly with cold to extremely cold winters. Some parts of Canada have a significant net precipitation while other parts are arid. Gold and silver operations are located in each of these climatic regions, although the main gold producing areas are faced with too much rather than too little water.

Gold Production in Canada

Northwest Quebec:	e.g., Around Val d'Or
Eastern Ontario:	e.g., Around Kirkland Lake, Timmins, Detour Lake, etc.
Central Ontario:	Hemlo District, Campbell Red Lake
British Columbia:	Several Small Gold Mines
Northwest Territories:	Giant Yellowknife Mines Con Mine at Yellowknife Lupin Project of Echo Bay Mines
Yukon Territory:	Several Placer Deposits

Silver Production in Canada

Most of Canada's silver production is believed to come as a coproduct with flotation concentrates of copper and lead recovered from complex sulfide ore deposits. These are located in the main mining districts and are spread out from New Brunswick, (Heath Steele, Brunswick Mining and Smelting Corp.) through Quebec (to include Noranda and Mattagami operations of Noranda) then through Ontario north of Lake Superior (including such Noranda operations as Geco and Mattabi). The largest of all is Kidd Creek Mines at Timmins.

Silver is also produced in sulfide base metal concentrates at several mines in British Columbia including Equity Silver.

Based on general observations made during a 1984 tour through the Canadian Mining districts the main characteristic of water management practices associated with Canadian gold operations is catering to the cold climate and concern about toxic effluent discharges to lakes and streams. Canada's Federal environmental regulations are promulgated under the Fisheries Act and are unquestionably fish-oriented. Canada has 37% of the world's surface fresh water resources. Although there are currently no Federal regulations regarding cyanide in effluents, these are under review. Any major cyanide damage to

the environment, especially fish, at this time would be likely to result in pressure on regulators and stricter ultimate rules. Two or three cyanide leach plants have been shut down at different times in the recent past due to concern about cyanide leaks to surface waters.

The Canadian federal Environment Protection Service has gone to great lengths to finance and support plant-scale trials of cyanide destruction or removal processes including alkaline chlorination, SO_2-Air cyanide removal and electrolytic removal of cyanide. These are described in Chapter 40 on cyanide removal.

Unfortunately Canadian winters are so cold that natural degradation of cyanide is unlikely to work for much of the year; six months of the year at Yellowknife.

During springtime when the ice and snow melt, large quantities of excess water runoff must be dealth with, although it also acts as a diluent.

Canada is not short of land space nor water. Some mining companies build very large tailings ponds to contain their tailings and effluents through winter as well as spring runoff. In summer natural degradation gets a chance to work and may be helped along by effluent treatment facilities to remove or destroy cyanide, base metals and arsenic as well as for pH adjustment. The natural degradation process was modelled by SIMOVIC, et al. (1984).

With so much water available, it seems that Canadian operations use more of it resulting in more effluent to treat and discharge.

Some of the older Canadian gold mines have no treatment plant for their effluent and rely on natural degradation. All new gold mining operations have, however, installed cyanide treatment plants with the exception of Echo Bay Mines' Lupin project in the Northwest Territories which employs a hugh shallow impoundment for natural degradation in summer.

Whereas Western Australian gold operations are likely to treat effluents and tailings so as to recover more water for recycle; and whereas South African operations may have to focus on limiting TDS in discharged minewater, the Canadian gold industry is concerned about disposing of tailings and effluent in a way that protects their fish. Regulatory limits are accordingly particularly strictly enforced at the headwaters of the more important salmon streams.

Of all the gold mining countries of the world, Canada is more concerned about cyanide excursions and heavy metal contamination of surface waters. Although a relatively small producer of gold by world standards, more cyanide destruction facilities have been installed at Canadian gold mines than in any other country. At last count there were eight plants, if Western Mines facility is included (which destroys cyanide in base metal

flotation effluent), but of these, two no longer operate. One has shut down and the other no longer uses cyanide.

Canadian regulations recognize that zero discharge is impossible for most Canadian mines. Canadian regulations seem also to recognize that mining is an essential part of their economy. The impression gained from regulators in Canada is that they are seeking to find out what can be done and the best economic way of achieving it.

PROCESS FOR DEGRADATION OF CYANIDE

Canadian experience particularly as orchestrated by Environment Canada has been largely responsible for stimulating improved insight into cyanide toxicity effects, cyanide determination techniques and cyanide decomposition or removal methods.

Since cyanide is the subject of a whole separate chapter, it is not discussed here again, except to refer to the plants that use cyanide destruction processes and to list a few Canadian experts in this field.

CANADIAN CYANIDE REMOVAL PROCESSES

Company	Location	TPD	m^3/d Treated	Process
Mosquito Creek	BC			Alkaline Cl_2
Scottie Gold Mine	BC			INCO SO_2-Air
DuPont Exploration	Baker Lake, BC	Now Closed		INCO SO_2-Air
Carolin Mines		No Longer Uses CN^-		INCO SO_2-Air
INCO	McBean, Quebec			INCO SO_2-Air
Western Mines	Campbell River, BC			Alkaline Cl_2
Giant Yellowknife	Yellowknife, NWT	1,250		Alkaline Cl_2
Cominco Con Mine	Yellowknife NWT			FeS
Projected				
Noranda	Hemlo	1,500/4,000	341/545	SO_2-Air
Kiena Gold Mines Ltd.	Ontario		Pulp	Emperor SO_2
Equity Silver Mines	British Columbia			Alkaline Cl_2

Canadian ores are not all free milling. Those at Giant Yellowknife Mines Ltd. require flotation and roasting as they do at Campbell Red Lake Mines. Formerly the Con Mine in Yellowknife also had a roaster, but now treats non-refractory ores. Pamour Schumacher

mill in Timmins also adopts a non-roasting hydrometallurgical approach to relatively refractory ores.

There was a time when companies did not need to worry too much about the effect they had on the environment. Cominco's Con mine recently invested $13 million to install a processing facility to treat 30,000 tons of arsenical flue dust collected from the baghouse on their roaster - neither of which are in operation today. Although it is hoped to profit from the sale of arsenic and an incremental gold production, the alternative need to prevent arsenic excursions from the sludge ponds on the site was an additional incentive.

There are several very interesting water management concepts that are put into practice at Canadian gold recovery operations as needed to meet site specific requirements. A reasonable cross section of water management practices in Canadian gold recovery operations is gained through a summary of the following:

1) Noranda Mines at Hemlo
2) Scottie Gold Mines
3) Carolin Mines
4) Dome Mines, Timmins Ontario
5) Giant Yellowknife Mines, NWT
6) Con Mine Yellowknife NWT
7) Echo Bay Mines Lupin Project, NWT
8) Lac Minerals, La Mine Doyon, Quebec

HEAP LEACHING

Heap leaching of gold ores is attracting a lot of attention in Canada at this time. Water management is a major consideration for heap leaching in the Canadian climate with its frozen winters and net precipitation in many areas.

It is believed that heap leaching may be carried out indoors at far northern locations but to date no such project is in operation in Canada.

Anaconda minerals did bring one heap leaching project into operation on the eastern seaboard of Canada; this was their Caribou project in Nova Scotia. This operation was designed to be installed and completed within one summer season to avoid problems with freezing and thawing. It is believed that much useful data was gathered, but it will have to wait for a future evaluation.

Water management for Canadian heap leaching projects are not discussed here. Sponsors are referred to the following consultants known to have worked on this aspect.

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Post Office Box 1368F
Reno, NV 89507
(702) 356-7107
Daniel W. Kappes
Michael Cassidy

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2640 South Sheridan Way
Mississauga, Ontario
Canada L5J 2M4
(416) 823-7381
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Mrs. Peggy Witte

STEFFEN ROBERTSON AND KIRSTEN
1030 West Georgia, #801
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Roy Fletcher
Vice President

NORANDA HEMLO PROJECT

The mines and mills under development in the Hemlo district by NORANDA, LAC MINERALS and TECK Corp. will collectively about double the Canadian gold production and the tonnage of ore mined and milled for the purpose.

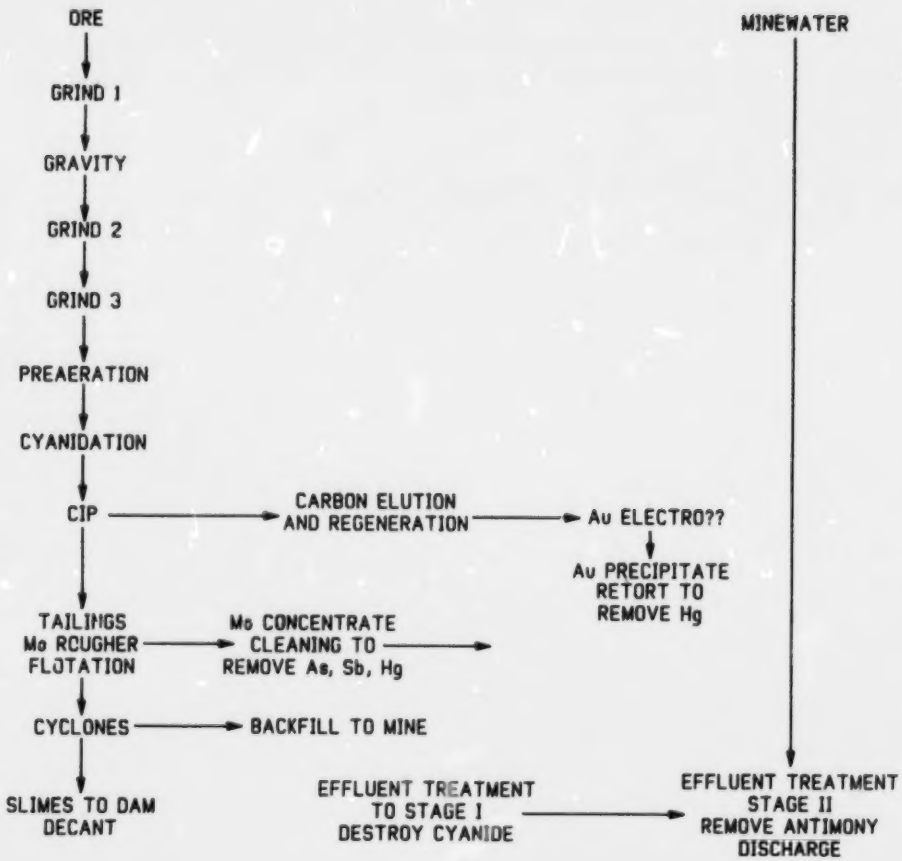
These major mills will treat their tailings and discharge effluents, and it will be interesting to learn how they propose to do so. The mines and mills are still under development, and it was not possible to get the full details as to how they propose to treat their tailings and how they will manage their effluents and water, although a rough outline of NORANDA's effluent treatment facility at Hemlo is shown below.

Hemlo gold ores contain relatively large amounts of environmentally undesirable metals. For example Noranda's Hemlo ore is rich in pyrite and has the following approximate level of metals:

Gold	4 - 16 g Au/t
Silver	0 - 2%
Mercury	16 g Hg/t (Ave.) as cinnabar
Molybdenum	0.03 - 0.04% MoS_2
Zinc	0.002% Sphalerite (Ave.)
Antimony	0.02% Stibnite (Ave.)
Arsenic	0.02% Arsenic (Ave.) 4-40 g/t Realgar

The metallurgical gold recovery circuit and effluent treatment plant design have had to take the ore characteristics into consideration as well as the environmentally sensitive location adjacent to a provincial park on one side and an Indian fishing ground on the other.

Water management for the operation requires an integrated plan including a partially lined tailings pond with seepage collection and return, mine backfill, tailings treatment to remove molybdenite with some of the arsenic, mercury and antimony sulfides, and finally effluent treatment for cyanide and residual soluble antimony and arsenic removal.


ORE
GRIND 1
GRAVITY
GRIND 2
GRIND 3
PREAERATION
CYANIDATION
CIP
CARBON ELUTION AND REGENERATION
Au ELECTRO??
Au PRECIPITATE RETORT TO REMOVE Hg
TAILINGS Mo ROUGHER FLOTATION
Mo CONCENTRATE CLEANING TO REMOVE As, Sb, Hg
CYCLONES
BACKFILL TO MINE
SLIMES TO DAM DECANT
MINEWATER
EFFLUENT TREATMENT TO STAGE I DESTROY CYANIDE
EFFLUENT TREATMENT STAGE II REMOVE ANTIMONY DISCHARGE

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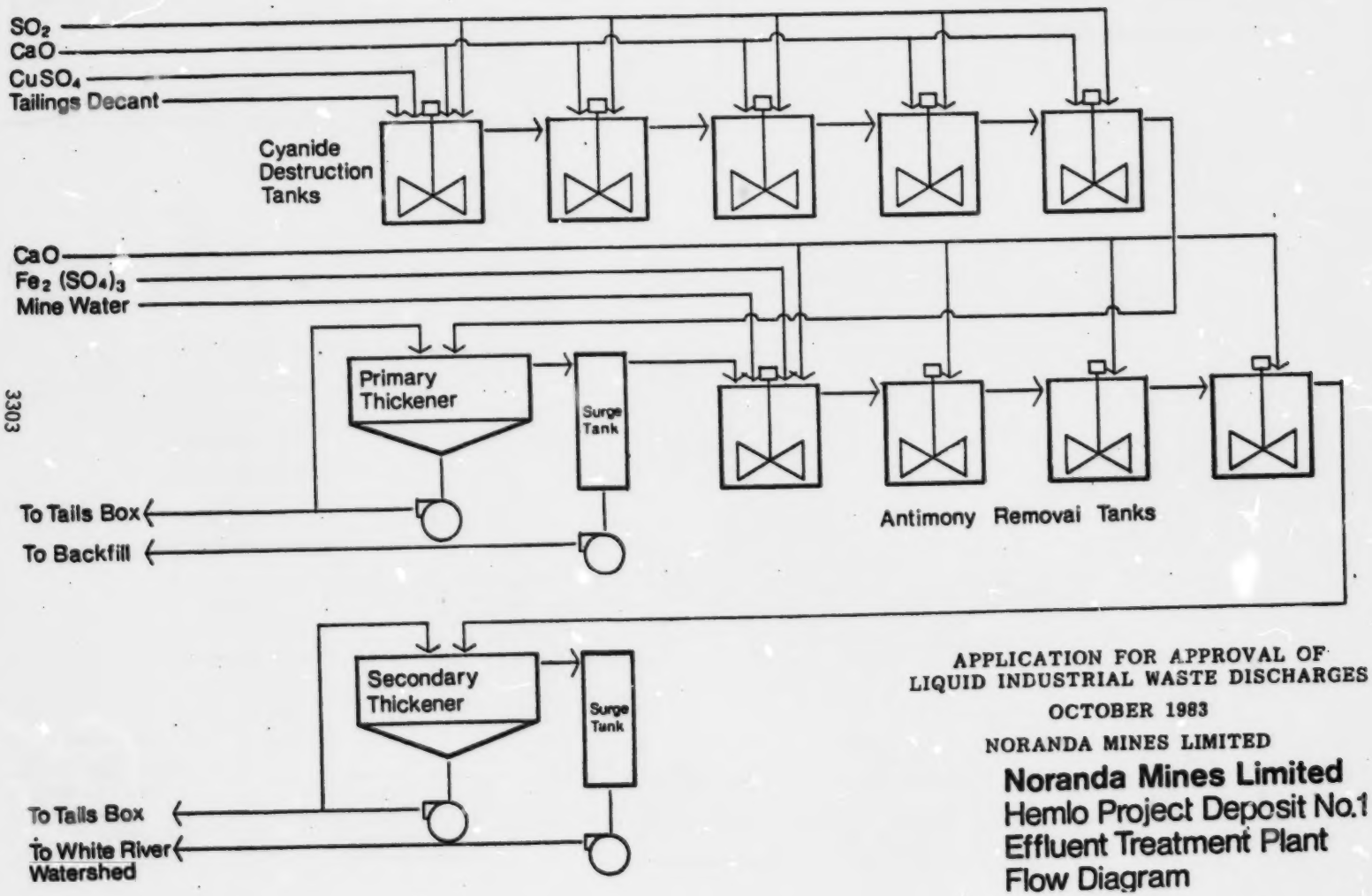


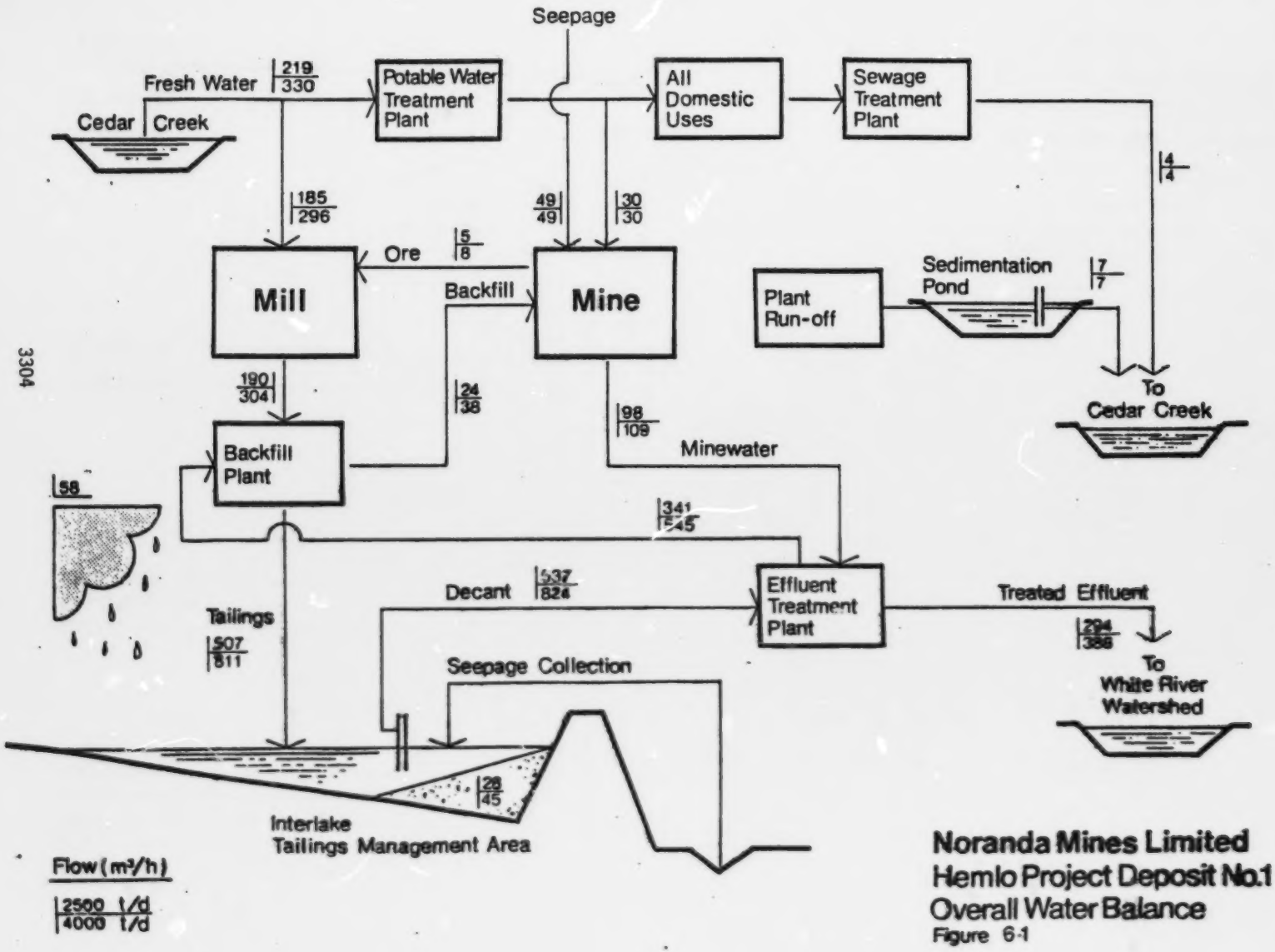
APPLICATION FOR APPROVAL OF
LIQUID INDUSTRIAL WASTE DISCHARGES

OCTOBER 1983

NORANDA MINES LIMITED

Noranda Mines Limited
Hemlo Project Deposit No.1
Effluent Treatment Plant
Flow Diagram

3303



Noranda Mines Limited
Hemlo Project Deposit No.1
Overall Water Balance
Figure 6-1

3304

TABLE 6.1

ESTIMATED WASTEWATER CONCENTRATIONS (TOTAL METAL IN mg/L)

Parameter	Influent Before Treatment (mg/L)		Final Effluent (mg/L)
Total Cyanide	20-60	25	<1.0
Thiocyanate	50-75	60	100
Cyanate	50-75	65	80
Thiosulphate	<10-100	Same	<10-100
Iron	20-40	30	<1.0
Copper	4-32	10	<0.5
Antimony	1-30	10	<5.0 - 2.0
Zinc	0.03-3.0	2.0	<0.5
Arsenic	<0.5-2.0	1.0	0.5
Molybdenum	0.5-3.0	2.0	<1.0
Nickel	<0.05-0.3	.2	<0.05
Mercury	0.001-0.01	—	<0.005
pH	4.5-8.5		10-11
Suspended Solids	10-50		15-25
Lead	<0.08-0.5	200.2	181.55
Vanadium	<0.1		
Bismuth	<0.5		.13 mg/L removed as avg.
Cadmium	<0.03		
Chromium	<0.01		
Cobalt	<0.02-0.1		
Manganese	<0.5	320	181.5
Tellurium	<0.1		
Aluminum	<1.0		130 mg/L removed.
Selenium	0.02-0.2		

16 - 130
Avg. 50 mg/L

NOTE:

Total cyanide measures the concentrations of free cyanide and metallo-cyanide complexes and does not include thiocyanate (SCN) or cyanate (CNO) compounds.

6.0 EFFLUENT TREATMENT

6.1 GENERAL

The mine and mill operation will produce four wastewater effluents: tailings decant, mine drainage water, runoff from the site, and sanitary sewage.

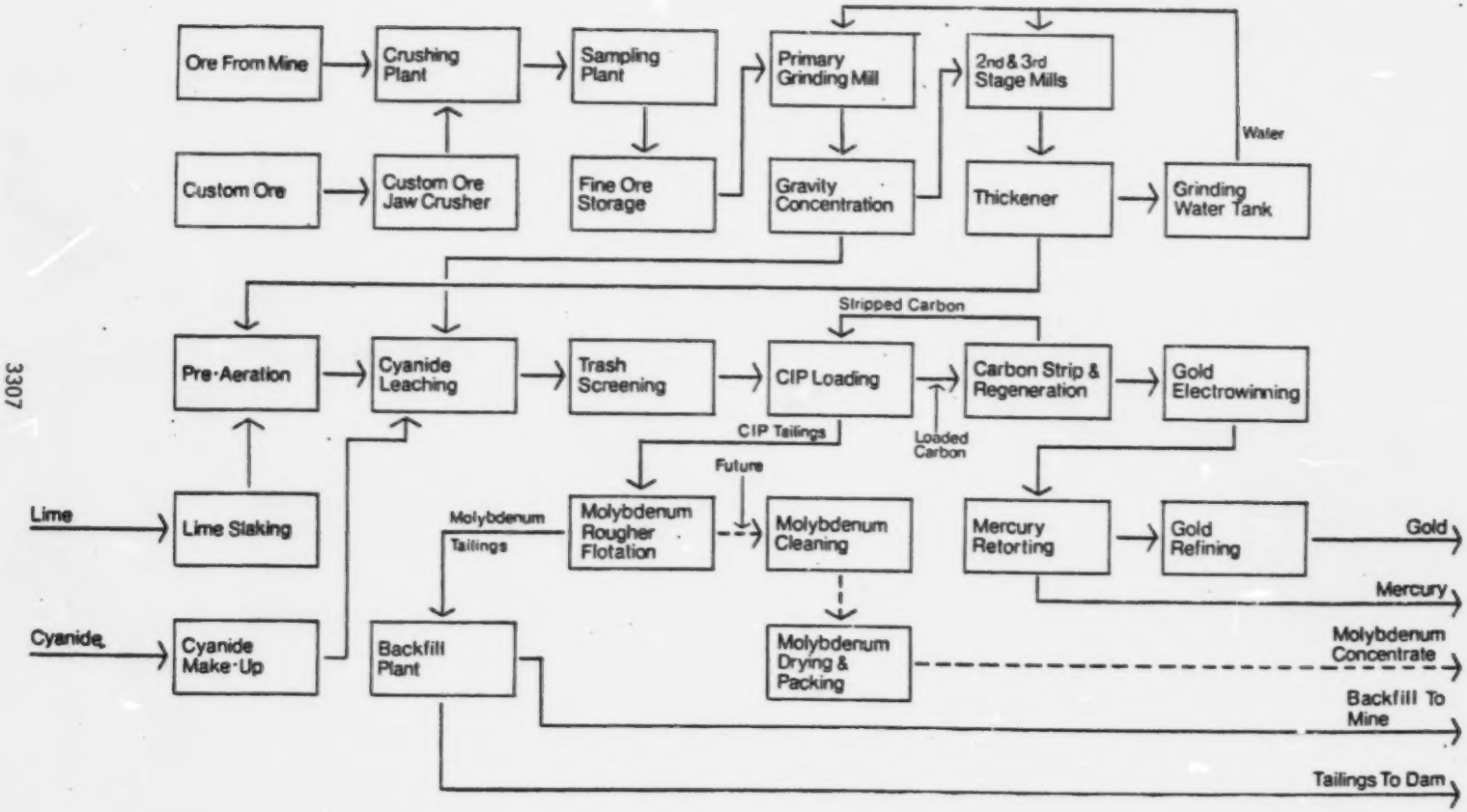
During operations, effluent from the tailings area as well as mine water will be treated in the effluent treatment plant.

Site drainage will be directed to a stormwater holding pond where it will be monitored and discharged when required to Cedar Creek. Sanitary sewage generated during construction and operation will be treated in a package treatment plant prior to discharge to Cedar Creek.

Tailings Effluent Treatment

The chemical characteristics of the tailings decant can vary considerably since the effects of natural degradation, dilution and chemical reactions in the tailings area will take place at varying rates throughout the year. Pilot plant test work was carried out at Lakefield Research of Canada on the gold extraction process, from which analyses of barren solutions from the carbon adsorption were made. The results of these analyses and leaching tests of the tailings material were combined to provide an estimate of the inflow to the effluent treatment plant, as shown on Table 6.1. The effects of aging in the pond and dilution were also considered to some extent.

Various processes which would reduce these chemical components to acceptable levels were evaluated. Preliminary conclusions are that a two step process will be required: the first one to treat for removal of free cyanide and metallo-cyanide complexes, and the second to treat the more persistent heavy metals. Minewater will be introduced for treatment in the second step of the process.



Noranda Mines Limited
Hemlo Project
Process Block Flow Diagram
Figure 4-1

Hemlo project

Proposed Pipeline Routings

noranda

3308

Noranda Mines Limited
Hemlo Project

JANUARY 1984

Introduction:
Noranda Mines Limited, Hemlo Project is developing an underground mine and milling complex to mine and process gold bearing ore. Located within 55km of Marathon, White River and Manitouwadge, the orebody has reserves presently totalling about 20 million tonnes, promising a mine life of some 20 years. The initial mining and milling rates will be 1000 tpd expanding to 3000 tpd. An expected workforce of 350 people will be required.

The proposal to mine the orebody and to treat the ore was developed over the past year as a result of studies in many disciplines including geology, mining methods, metallurgy, geotechnology and environmental science. Results from all of these studies form the basis of the present engineering design and operating plan. Ongoing discussions with the various government agencies and public are an important part in identifying the concerns that have to be addressed in the operating plan.

Noranda's final plan to develop and operate the Hemlo Project is now being discussed at public information sessions which are open to all parties concerned. Final Certificates of Approval, required under Section 24 of Ontario Water Resources Act, will be issued by the Ministry of Environment after consideration of public input and thorough review of detailed engineering plans.

A brief description of each area of the proposed operation is given below.

Project Development
In order to meet the target start-up date of January 1985, an ambitious engineering and construction schedule is underway. Construction manpower is estimated to peak at 700 men during the summer of 1984. Temporary housing facilities for this workforce is provided on site. Permanent manpower required for the mining and milling operations will increase gradually to 200 for the January 1985 start-up. This number is expected to increase to 350 in 1987. Housing will be provided in the existing communities.

Mining:
The orebody can be thought of as a long, thin rectangular book dipping northward at an angle of 70° to the horizontal. The planned mining method is blasthole stoping with delayed fill. A stope is an underground excavation that is made by removing ore from the surrounding rock following a detailed drilling and blasting plan.

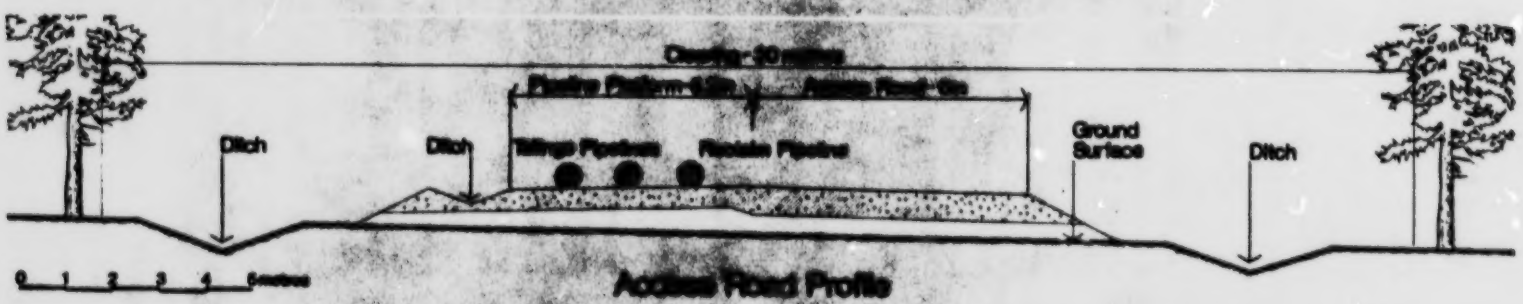
After each blast, the broken ore, falls to the bottom of the stope, where it can be recovered for transport to the underground primary crushers and crushed to less than 6 inch fragments.

After the ore has been drawn from a stope, the opening is filled with rock followed by cemented tailings which fill the voids and consolidate the rock fill.

A shaft is being sunk to a depth of 1,455 metres to access the ore. The shaft contains two 16 tonne productions skips, a 40-man single deck cage, a pipeway, manway and a counterweight. To supply fresh air to the working areas, a push-pull ventilation system will be used. Fresh air and exhaust fans will be located on surface. The fresh air supply will be heated during the winter with a propane heating system and waste heat from the mine compressors.

Hemlo project

Proposed Tailings Plan, Pipeline Route



Access Road Profile

noranda

Milling:
The on-surface crushing circuit reduces the ore to less than 1/2 inch. To form a slurry water is added and the ore is ground to a fine sand in the grinding circuit. The slurry is thickened before being pumped to the leaching circuit, a series of steel tanks located outside the mill building. Here the gold is selectively dissolved into solution. The leached slurry then flows to the carbon-adsorption circuit where the gold is adsorbed onto the activated carbon surface. The loaded carbon is stripped of the gold at high temperature and pressure to form a concentrated solution for the electrowinning circuit and refining step.

In addition to gold, the ore contains molybdenum which will be separated from the slurry by conventional flotation techniques. Pilot tests conducted to date have not been successful in producing a saleable molybdenum product and additional studies will be done when the milling operation starts up.

In addition to gold, the ore contains molybdenum which will be separated from the slurry by conventional flotation techniques. Pilot tests conducted to date have not been successful in producing a saleable molybdenum product and additional studies will be done when the milling operation starts up.

After separating the molybdenum, the tailings slurry is pumped to the backfill plant where the fraction of coarse sand (about 40%) is removed for use as backfill in the underground mine. The remaining 60 percent is disposed of in the tailings impoundment area.

Tailings Disposal
The tailings slurry is pumped to the impoundment area located about 2.8 km northwest of the plant. Out of a possible five sites, narrowed down from a total of twelve, this particular site was chosen since it offered the best combination of desirable features. The major criteria used to help evaluate the alternative disposal sites include:

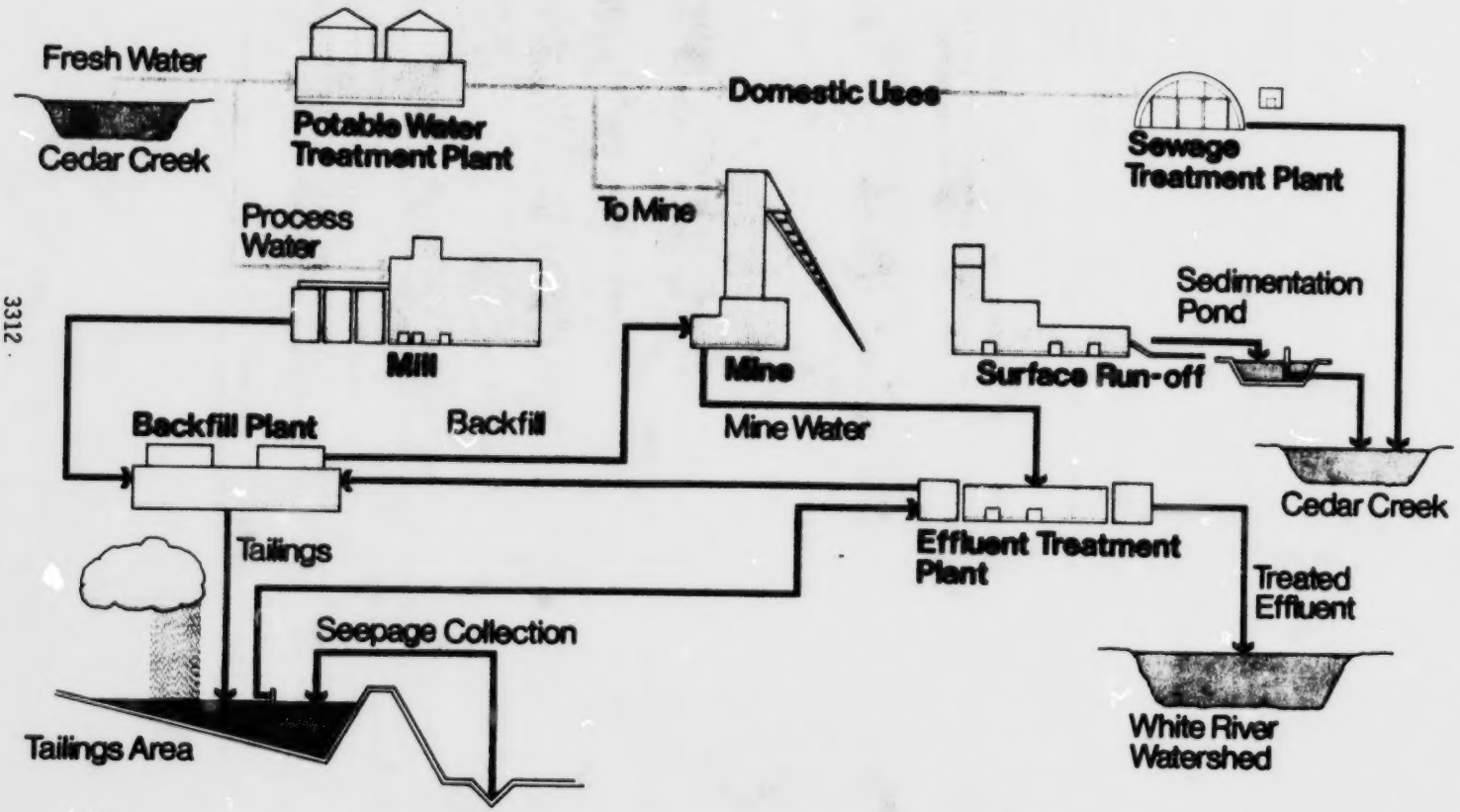
1. adequate capacity to contain the tailings produced during the life of the operation.
2. close proximity to the mine site.
3. minimal watershed area to reduce the quantity of water coming into contact with the tailings.
4. naturally occurring features to enhance the suitability of the site for containment.
5. status and land ownership questions had to be resolvable within reasonable time and economic limits.

The chosen tailings pond site is contained in a small valley just west of Cedar Creek. The main dam design ensures stability and minimum seepage. Techniques to achieve seepage control will include an excavated cut-off trench extending down to the bedrock, cement grouting of the bedrock and installation of a high quality seal, comprised of a synthetic liner and a layer of til on the upstream side of the embankment. Seepage which does by-pass the main dam structure will be intercepted in the seepage collection pond and pumped back to the tailings pond.

During operations, in addition to continuous computer monitoring, daily visual inspections of the tailings and reclaim water pipelines, pumps and dams will be carried out.

Hemlo project

Water Flow Diagram



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Water Recycle
Water recycle is an effective method of minimizing environmental effects by reducing total fresh water needs and by reducing the amount of water ultimately discharged to the environment. To this end, Noranda has been able to provide about a 70 percent recycle rate in the process.

Water Supply
Noranda, jointly with two other companies active in the area, is conducting a water supply study to formulate a proposal for government approval. The study will focus on the ability of the Cedar Creek system to satisfy the requirements and interests of the mining operations, and of the existing cottage owners within the Cedar Creek drainage basin.

Water Treatment Systems
Plant site run-off water will be channelled to the sedimentation pond by a system of ditches for the removal of suspended solids prior to discharge.

A biological treatment system is being used to treat sewage from all plant site services to meet the Ontario Ministry of Environment's guidelines. Water from the tailings pond will be returned to the plant site for recirculation and treatment in the effluent treatment plant. The proposed effluent treatment system uses the most up-to-date technology available to reduce contaminants to levels below the Ontario Ministry of Environment guidelines. Two treatment steps are being used to remove cyanide and heavy metals. The first step is the SO_2 process which destroys free cyanide and metallo-cyanide complexes. The second step removes the more persistent heavy metals using a ferric iron co-precipitation process.

The final effluent will be discharged to Lim Lake in the White River Watershed as requested by the Ontario Ministry of Environment.

Reclamation:
A program of reclamation and stabilization of the mine site and tailings disposal area will be carried out after decommissioning of the mine to ensure stability of the site, safety to man and wildlife and protection of the environment.

SCOTTIE GOLD MINES LTD.

Post Office Box 308
Stewart, B.C. V0T 1W0

Scottie Gold Mine is located at a high elevation in the Canadian Rockies near Stewart, BC. The mine is on a steep mountainside which is prone to avalanches in winter, consequently the complete mill has been erected inside a giant underground cavern.

Tailings from the 200 tpd high grade operation are discharged into a glacial lake. The outlet from the lake is shut off by a glacier for most of the time. However, in spring and summer as melt runoff fills the lake above a certain level, the ice is floats and releases the contents of the lake including the tailings into the river below. The river flows across the Canadian border into Alaska where it becomes a salmon stream which discharges into the ocean.

Scottie Gold leaches ground ore in cyanide and then filters the pulp. Gold is recovered by Merrill-Crowe and tailings were discharged to the lake. Up to 130 m^3/d barren bleed was treated by chlorination before being discharged to the lake.

Scottie gold ore contains quite high levels of pyrrhotite which results in a considerable ferrocyanide concentration which is not decomposed by alkaline chlorination. It ties up a considerable amount of cyanide which reaches the tailings pond reporting as CN_{Total}.

The filtration step, by all accounts, used to result in relatively poor washing of the filtercake which also resulted in some cyanide and even soluble gold values being discharged with the tailings, but the main metal and cyanide contamination was with barren bleed.

DISADVANTAGES OF ALKALINE CHLORINATION

1) Alkaline chlorination proved unable to achieve low total cyanide levels in the lake because it did not destroy ferrocyanide.

2) The chlorination process was installed underground and resulted in an unpleasant operator environment - watering eyes, etc. were one uncomfortable effect.

3) Solid chlorine forms such as $Ca(OCl)_2$ were used, and these had to be added in large quantities with the result that the tank would "freeze" solid.

4) Not enough chlorine could be added to kill all the cyanide without safety problems.

On account of cyanide (CN_T) buildup in the lake the operation was shut down temporarily by the BC government.

The existing alkaline chlorination tanks were converted by INCO Tech Ltd. to SO_2-Air cyanide removal to treat the barren solution. With the addition of one more air sparged tank the tailings pulp has been added into reactor II to treat it as well. Final effluent of 0.1-1 ppm CN_T with low metal values are achieved consistently which works out to a removal of over 99.5% of the cyanide in the incoming streams. The process has been described by DEVUYST & CONARD (1984).

The important point as far as water management is concerned in this case is that since the tailings are discharged to a lake, cyanide must be destroyed or removed in the total tailings and barrens and not just the tailings pond decant.

In this case the treated effluent from the cyanide destruction plant, although impressive, does not consistently achieve levels typically imposed on gold plant effluents. Regulatory authorities have undoubtedly taken into account the very large dilution of tailings by runoff water and snowfall.

CAROLIN MINES LADNER CREEK OPERATION

Carolin Mines Ladner Creek mill near Hope, BC treats about 1300 t/d ore at about 0.1 oz Au/t. A concentrate is recovered by flotation which was leached in cyanide. After cyanidation the tails were floated a second time to recover a graphite concentrate. Barren bleed was typically 150 m^3/d.

Process water is obtained by recycling tailings pond decant water. This requires removal of any cyanide which would otherwise depress pyrite in the flotation step.

Barren bleed was initially treated by alkaline chlorination, but washed tailings containing 5-10% of the cyanide bleed were discarded to the tailings pond without treatment.

Excess pond decant water was treated in a second alkaline chlorination circuit and then dechlorinated and pH adjusted prior to discharge to Ladner Creek. The permit to discharge tailings pond decant was limited to a maximum level of contained ferrocyanide. Iron cyanide levels were found to increase during winter months which created a serious problem for Carolin during spring runoff.

The problems were aggravated by the fact that Carolin Mines is located on the headwaters of the Fraser River. The British Columbia government was anxious about ferrocyanide in effluents to shallow streams in which they believed that free cyanide might be released by

UV in sunlight. With this restriction on discharge in force, the levels were building up and after a third tailings spill, the plant was temporarily shut down.

Carolin Mines had been accused of being responsible for fishkills in the stocked river in 1982. They were fined and temporarily shut down by the BC government.

The INCO SO_2-Air process was licensed in 1983. The existing alkaline chlorination process was converted for this process using auxiliary aeration agitation. Addition of $Na_2S_2O_5$ was in proportion to the barren flowrate and its cyanide content. In this case no copper sulfate addition was needed and lime was added on demand by means of a titrator-pH controller as described by DEVUYST & CONARD (1984).

Later on, tailings solids were also treated at Carolin. This was done by adding excess $Na_2S_2O_5$ to treated barren overflow as it entered the tailings box. Some $Na_2S_2O_5$ was also added to the aerated mix tanks for which flotation cells were employed.

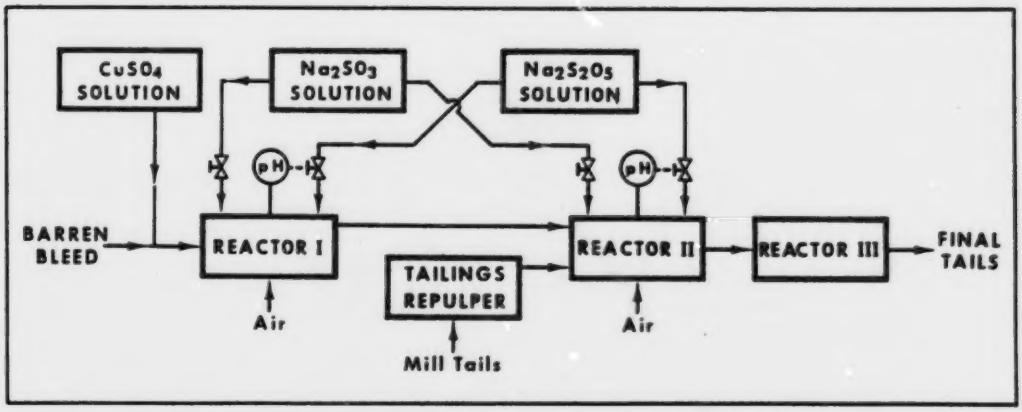
Subsequently, cyanide soluble iron levels increased dramatically in Carolin Mines ore and in the tailings to the extent that improved agitator tanks were needed. At that point, Carolin Mines elected to stop using cyanide and, instead, to ship their flotation concentrate to a smelter.

The costs of alkaline chlorination and SO_2-Air cyanide removal at Carolin Mines were not determined, but these must be quite substantial, including royalties, to justify shipping a concentrate with only ±1 oz. Au/t to a smelter.

The arrangement and results of the SO_2-Air process using the converted alkaline chlorination process are shown in the following table from DEVUYST & CONARD (1984).

Table No. II
Scottie Gold Results

Site	Stream	pH	Assays (mg/L) CN_T	Cu	Fe	Zn	Cyanide Distribution (%)
Plant	Barren Bleed		450	35	1.5	65	75
	Treated Barren Bleed	9.0	0.1-2	1-10	<.5	0.5-2	0.4
	Mill Tails (55% solids)		115	17	0.7	18	25
	Final Effluent (35% solids)	8.0	0.1-1	0.2-2	0.02-0.3	<.1	<.5
Lab	Barren Bleed		340	44	1.0	71	75
	Treated Barren Bleed	8.9	0.2	2	0.2	2	0.04
	Mill Tails (40% Solids)		48	12	1.4	10	25
	Final Effluent(32% Solids)	8.0	0.3	0.2	0.2	<.1	0.2

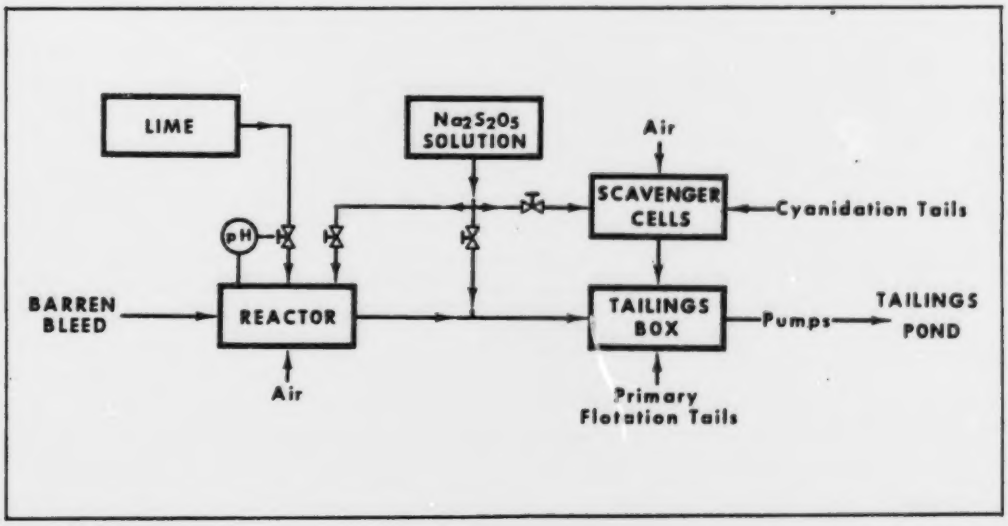


Conceptual Inco SO_2/Air Process at Scottie Gold

Figure 2.

Table No. IV
Carolin's Ladner Creek Mill Results

Site	Stream	pH	Assays (mg/L) CN_T	Cu	Fe	Cyanide Distribution (%)
Plant	Barren Bleed	11.0	1500	350	75	9 -84
	Treated Barren Bleed	9.6	3-10	5-15	0.1-0.3	1
	Mill Tails + Treated Barren	9.0	11-19	13-15	1.0-3.2	9-16
	Final Tailings to Pond	8.7	0.3-2	0.5-5	0.1-0.3	<2
Lab	Barren Bleed	11.8	2100	230	310	100
	Treated Barren Bleed	9.0	1.4	1.4	0.4	0.07



Conceptual Inco SO_2/Air Process at Carolin's Ladner Creek Operation Figure 4

DOME MINES, TIMMINS, ONTARIO

Dome Mines at South Porcupine, Ontario is one of the older mine-mill operations in Ontario and is of interest because they practice natural degradation of cyanide. This aspect has been extensively studied by Environment Canada as described by SCHMIDT et al. (1981) and SIMOVIC, et al. (1984).

Dome Mines constructed a separate impoundment for their "barren bleed" in 1975 so that this cyanide and base metal rich effluent could be retained and released only during the months April to November during which natural degradation takes place. The barren bleed pond was ultimately sized to contain 75% of the bleed discharged between December and March and was the subject of a joint assessment program. The Environment Canada report contains valuable information and is reproduced here in its entirety. Additional information on natural degradation is included in a more recent paper by SIMOVIC, et al. (1984).

It is concluded from this set of data that whereas separate impoundment of barren bleed does reduce cyanide and metal levels considerably in the final discharge, this process does not seem to be able to maintain the metal and cyanide removal consistently enough to be able to recommend relying on natural degradation alone to meet the anticipated regulatory limits in cold climates such as Canada.

The results of the monitoring program at Dome were:

(1) Cyanide content decreased from 65 ppm in March to 0.05 ppm in August.
(2) Temperature variation was 6°C.
(3) pH dropped from 10.5 to 7.0.
(4) pH drop was due to natural carbonation and hydrolysis of thiocyanate.
(5) Over 90% of the cyanide decrease was attributed to volatilization of molecular HCN.
(6) Some photodecomposition of ferrocyanides occurred.

The results are extremely important because they show that cyanide does not persist in the environment, and consequently, long-term effects are likely to be negligible (HUIATT, 1984). RANDOL INTERNATIONAL LTD. raises the question, "If natural degradation is due to CO_2 dissolution effects causing volatilization of cyanide, could this process perhaps be enhanced to speeded up through small CO_2 additions to decanted effluents in the pond or at the final discharge point?"

It is understood that the Ontario Provincial Government - Ministry of the Environment is relatively circumspect as to where they allow the sampling point for "final effluent" to be, depending on the sensitivity of the particular operation and its location as an environmental threat.

NATURAL DEGRADATION OF CYANIDES IN GOLD MILLING EFFLUENTS

J.W. Schmidt[1], L. Simovic[1] and E. Shannon[2]

Presented at the Cyanide and The
Gold Mining Industry Seminar
January 22 to 23, 1981

INTRODUCTION

Since 1973, Environment Canada has been concerned with the development and demonstration of suitable technologies for the removal of toxic contaminants from gold mine effluents. Contaminants of concern are cyanide, zinc, copper, nickel and arsenic. Several alternative technologies (alkaline chlorination, ozonation, ion exchange, electrochemical and others) which have potential for treating gold mill effluents have been outlined earlier in this seminar. In addition, The Environmental Protection Service (EPS) and Giant Yellowknife Mines (GYK) in a joint program have carried out pilot studies on alkaline chlorination and metal precipitation on various mine-mill effluents (Erkku and Price, 1979).

In early 1979, recognizing that natural processes may play a key role in determining the fate of cyanide and metal discharges from gold mines, EPS commissioned a literature review (IEC, 1979a) of the factors affecting the natural degradation of free and metal-complexed cyanides from gold milling effluents. It was apparent from this review that tailings pond or separate liquid impoundment areas had a high potential for cyanide removal from gold mill effluents on individual high cyanide stream (e.g. "barren bleed"), and in fact, several mines in Canada were using such a system.

One of these mines was Dome Mines at South Porcupine, Ontario, which had constructed a separate impoundment area for their "barren bleed" in 1975 (Pyke, 1978). The decision to provide separate barren bleed containment was based on observations (prior to 1975) that natural degradation of cyanide was occurring in a retention pond downstream of their tailings ponds. This degradation was found to occur primarily during the months of April through November. Under ice-cover little, if any, degradation was observed.

Although the Dome "barren bleed" impoundment experienced some operational problems during 1975 through 1979, the pond was ultimately sized to contain 75% of the bleed discharged between December and March. In 1978/79, the system operated successfully and in August 1979 the Wastewater Technology Centre (WTC) approached Dome Mines regarding a possible joint assessment program for the 1979/80 operating season as part of Environment Canada's program to develop suitable technology for the treatment of effluents from gold mills.

A cooperative study was agreed upon with Dome Mines Limited with the overall objectives of the study being:

1) to assist the mine in a better understanding of the processes ("natural degradation") which are occurring in their effluent treatment systems, and
2) to support the Gold Producers Task Force by examining the applicability of the Dome Mines technology for the removal of cyanide and other undesirable constituents from gold mill effluents, to other gold producers.

Specific study objectives relating to the operation of the "barren bleed" impoundment area and the tailings pond were:

1) To determine the degree of cyanide conversion/degradation in both systems;
2) To determine the extent of reduction of other undesirable constituents (e.g. metals) in both systems;
3) To examine the factors affecting the natural degradation of cyanides;
4) To relate the data generated by this study to the existing long-term data base (eg., data provided to the Ontario Ministry of the Environment over the years).

At this stage, this paper is a progress report for this project. Although data have been collected over a period of 14 months, results are still being assessed and correlated and it is expected that sampling will be undertaken again in 1981.

DEGRADATION MECHANISMS

Several studies on the fate of cyanide in the aquatic environment have documented that cyanide is not persistent. This natural degradation in receiving waters is generally attributed to a combination of physical, chemical and biological mechanisms including volatilization, oxidation, biodegradation, photodecomposition and conversion to thiocyanate. The relative magnitude of each mechanism appears to be governed by aquatic system variables such as pH, temperature, lake or stream morphology, and water chemistry.

Detailed literature reviews on the fate of cyanide (Ecological Analysts Inc., 1979) and on the natural degradation of cyanide as it relates

to gold mining effluents (IEC, 1979a) have been compiled and should be referenced for further detail on specific mechanisms. Factors which are potentially relevant to type of behavior observed during this study are discussed in the following.

Volatilization

Free cyanides exist in aqueous solution in a cyanide ion (CN^-) and hydrocyanic acid (HCN) equilibrium

$$HCN \rightleftarrows H^+ + CN^-$$

The dissociation constant for HCN is given in the following equation:

$$Ka = \frac{[H^+]\,[CN^-]}{[HCN]} = 4.93 \times 10^{-10} \quad (pka = 9.3)$$

The equilibrium and the relative distribution of CN^- and HCN is pH dependent. For example, at pH 7 to 8, 95 to 99.5% of the free cyanide exists as molecular HCN. Molecular HCN has a readily high vapor pressure and therefore, can readily be volatilized to the atmosphere, even from stagnant solutions. Dodge and Zabban (1952) and the Chester Engineers (TCE, 1977) have conducted extensive investigations of the factors influencing volatilization of cyanide. In general, reduced liquid depth to surface area ratios, decreased pH, increased temperature and increased turbulence will accelerate volatilization.

Metal cyanide complexes tend to dissociate into free metal ion and free cyanide. The extent of dissociation can be predicted from the appropriate dissociation constants. This approach is somewhat simplistic, as the hydrolysis of CN^- to HCN at the pH's found in natural waters will tend to shift the equilibrium so that more free cyanide (as CN^- + HCN) will be in solution than predicted by the use of the dissociation constant alone. However, the important factor in the rate at which cyanide bound in the complex exchanges with free cyanide in solution. MacDiarmid and Hall (1954a,b) observed that the rate of exchange of ^{14}C labelled cyanide was independent of CN concentration, which is consistent with a rate of exchange

governed by a step involving the slow dissociation of the complex. The rate of exchange was found to increase with a decrease in pH as well as by increasing the intensity of illumination by lights. In general two and four coordinate complexes exhibit rapid exchange rates while octahedral (hexa-cyano) complexes have slower rates. The time period required to achieve equilibrium ranges from approximately 1 day for $Ni(CN)_4^{-2}$ to 250 days $Fe(CN_6)^{-4}$.

Oxidation

Although chemical oxidation of free cyanide is a commonly employed treatment method for cyanide containing wastewaters, little data are available regarding the oxidation of cyanide in natural waters. Investigations by Pipes (1975) and Owerbach (1978) and others suggest that under aerobic conditions a certain amount of free cyanide may be converted to cyanate. It is not clear whether this conversion of cyanide to cyanate can occur non-biochemically.

If oxidation of cyanide were occurring, then the probable reaction product would be cyanate in accordance to the simplified equation:

$$HCN + 1/2\ O_2 \rightarrow HCNO$$

As shown by Hendrickson and Daignault (1973), cyanate can be hydrolyzed to carbonate and ammonia. This can occur at a pH of about 8.5.

$$HCNO + H_2O \rightarrow NH_3 + CO_2$$

Biodegradation

Biodegradation of cyanide can occur under either aerobic or anaerobic conditions Nesbitt and Wagner (1959) identified three bacterial types which were capable of cyanide decomposition. Later, Towill et al (1978) observed that there appears to be a wider variety of bacteria that degrade cyanide (generally free cyanide) rather than synthesizing it. Cyanide degradation at pH's as low as 5.3 and as high as 10.0 have been observed by Furuki et al (1972).

Under aerobic conditions cyanide biodegradation can be depicted simply as:

$$HCN + 1/2\ O_2 \xrightarrow{enzyme} HCNO$$

The resultant HCNO can then be further hydrolyzed as follows:

$$HCNO + H_2O \xrightarrow{enzyme} CO_2 + NH_3$$

A suggested pathway for the anaerobic decomposition of cyanide leads to thiocyanate formation followed by hydrolysis, i.e.

$$HCN + S \longrightarrow HCNS$$
$$HCNS + 2H_2O \longrightarrow H_2S + CO_2 + NH_3$$

Photodecomposition of Complex Cyanides

Cyanide forms complexes of varying degrees of stability with many metals. Metals of primary interest in gold mining effluents include zinc, copper, nickel and iron. Some of these complexes particularly those with iron, (ferro- and ferricyanide) are very resistant to decomposition.

It is evident from the previous discussion that most of the potential cyanide degradation or removal mechanisms apply to the free cyanide. In general, it is necessary to dissociate or break down cyanide-metal complexes to the metal and free cyanide components before cyanide removal can occur from an aquatic system. The rate and degree of dissociation of a particular complex is generally dependent upon pH and total cyanide concentration. Broderius (1973) showed that dissociation to free cyanide is greater for most cyanide-metal complexes under acid conditions. In a later study (Broderius, 1978) it was observed that ultraviolet irradiation accelerated the decomposition of the ferricyanide. The decomposition was relatively rapid, e.g. half-lives for iron-cyanide complexes of 50 and 20 minutes were observed for fall and summer mid-day conditions respectively for a lake surface in Minnesota.

Factors such as light penetration as affected by turbidity, color and depth, intensity and wavelength of light, angle of light incidence and cloud cover, will determine the impact of photodecomposition in a specific body of water.

Cyanide-Thiocyanate Reactions

According to Ford-Smith (1964) there are some 28 elements which are capable of forming complexes with cyanide with some 72 metal-cyanide complexes possible. The most important complexes in gold mining effluents appear to be those of iron, copper, zinc, nickel, cobalt and cadmium. Gold and silver are excluded since their effluent losses are minute compared to the referenced metals.

The formation constants (log k) for metal-cyanide complexes vary from a low of 5.48 for $[Cd(CN)_4]^{-2}$ to a high of 42 for ferrocyanide. The formation constants for metal-thiocyanate complexes tend to be much lower than the corresponding metal-cyanide complexes. It follows that if both cyanide and thiocyanate are present in solution the cyanide complexes will exist in solution preferentially to the respective thiocyanate complexes. In general, this is the case in most gold mill effluents.

In the absence of cyanide, the thiocyanate complexes will be present. Many of the metal-thiocyanate complexes are insoluble; therefore, this mechanism may play a role in the removal of zinc, nickel and copper in effluent holdings ponds.

Study Site

The Dome mine, located about 1.5 miles (2.5 km) southwest of the town of South Porcupine, Ontario, began operations in 1912 and except for two short delays, has been in operation continuously to the present day. Both gold and silver are recovered with the chief gangue minerals being quartz and ankerite with about 2.5% pyrite and/or pyrrhotite, (Pickett, 1978). The mill, with a capacity of 2 000 tons (1 820 tonnes) per day empolys the process of cyanidation and amalgamation to recover the gold. Approximately half the product is recovered in each process. The circuit is fairly conventional with crushing, grinding, amalgamation, leaching and gold recovery

by zinc precipitation (Figure 1). The tailings are discharged to a conventional tailings pond system (Figure 2) with approximately 30% being used as backfill underground. The waste barren or "barren bleed" amounts to 800 tons (730 tonnes) daily or 110 Igpm (0.5 m^3/min) and contains approximately 95 mg L^{-1} CN (Pyke, 1978).

The "barren bleed" is normally discharged with the tailings to the tailings pond except that during the colder weather, November through March, 75% of the barren bleed is discharged to a separate holding pond (Figure 2), as mentioned previously.

The "barren bleed" holding pond consists of two interconnected sections, a shallow section with a fairly large surface area and a deep section with about 10% of the surface area of the shallow section.

For this study sampling locations were established to obtain samples influent and effluent from each system as well as within the holding pond (Figure 2). The collection of grab samples was initiated on September 5, 1974 and continued until November 12, 1980. The tailings pond was sampled weekly and the shallow section of the "barren bleed" holding pond was sampled weekly from September 5, 1979 to June 25, 1980, then daily until the pond was discharged in early October. Sampling of the deep section of the pond was initiated on a daily basis on June 11 and also continued until October. All sampling was carried out by Dome personnel.

The selection of parameters to be measured was based upon the requirement for basic mean flow data and the assumption of potential degradation mechanisms. The specific parameters measured are listed in Table 1.

Meteorological data were obtained from the Timmins airport station located approximately 10 miles (16 km) away. However, it was decided to augment these data with on-site data and a "met" tower with specific measuring equipment was installed near the holding pond in late June. This station provided direct measurement of rainfall, wind velocity, solar irradiation and air temperature.

Samples for bacterial counts and metal analyses were unpreserved but these latter samples were acidified prior to anlaysis. Samples for the analysis of CN_T, CNO and CNS were preserved by adding NaOH to raise the pH to 12.

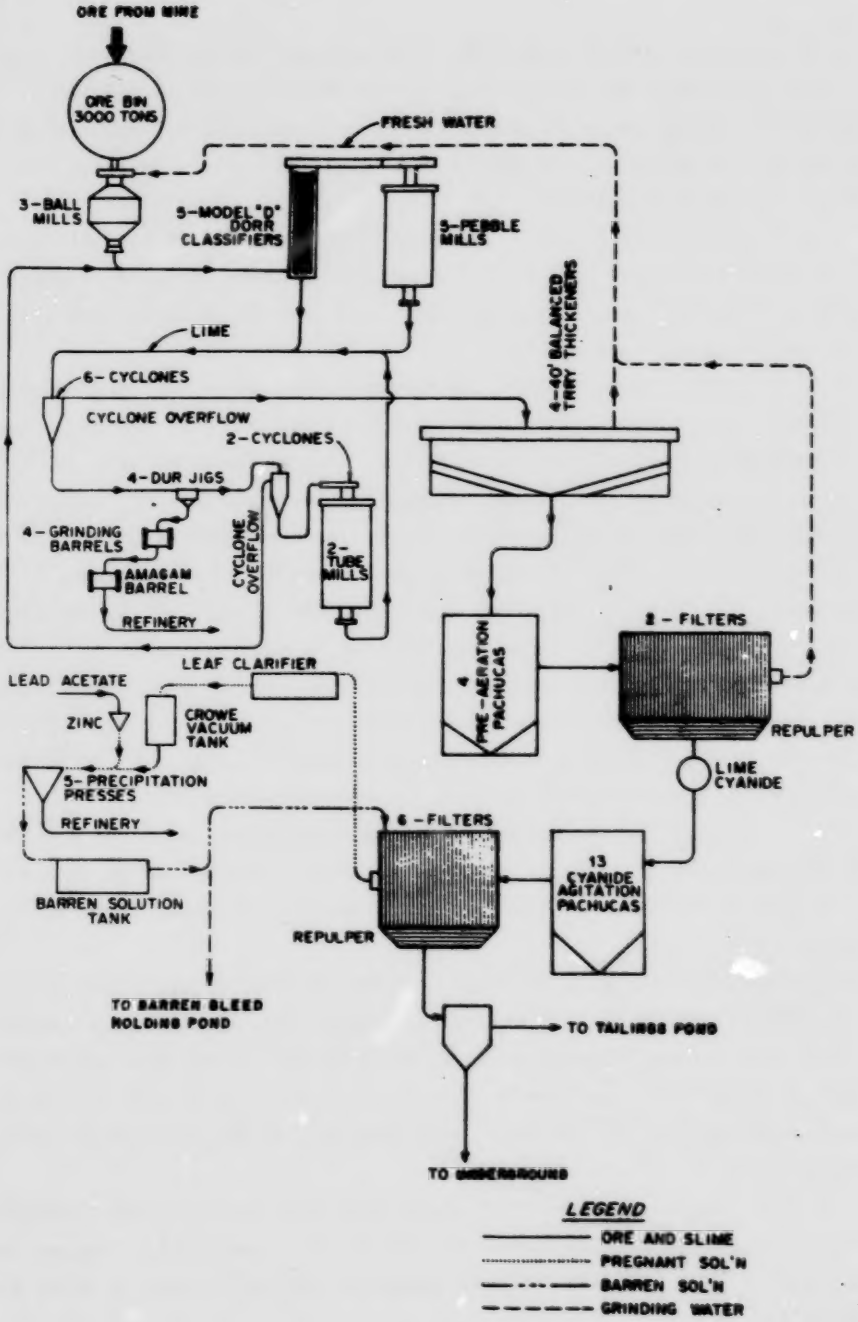


FIGURE 1 - SCHEMATIC DIAGRAM OF DOME MINES MILL CIRCUIT

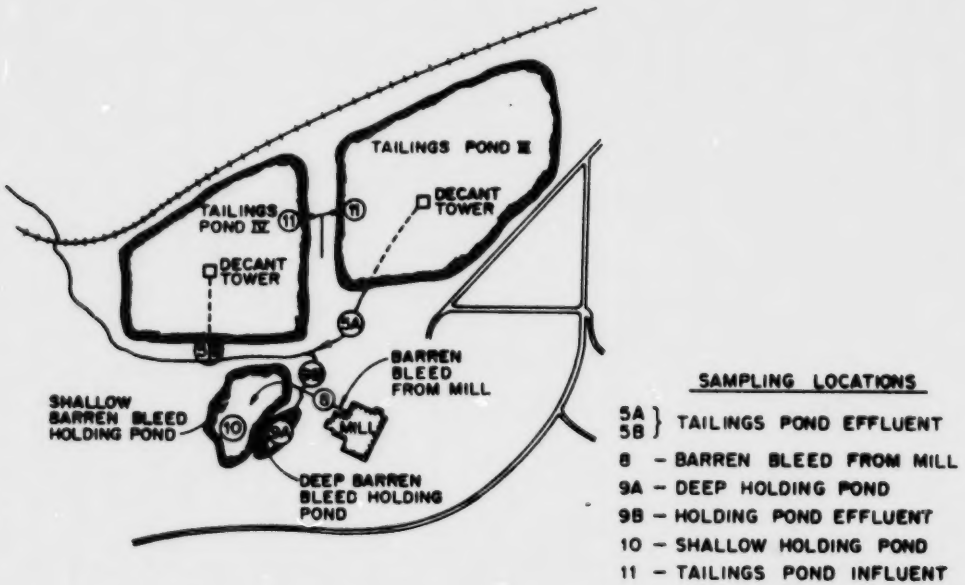


FIGURE 2 - LOCATION OF TAILINGS AND HOLDING PONDS AT DOME MINES

TABLE 1. PARAMETERS MEASURED DURING DOME STUDY

PARAMETER	COMMENTS
Cyanide - total (CN_T)	Rainfall
Cyanide - amenable to chlorination (CN_A)	Wind Velocity
	Solar Irradiation
Cyanate (CNO)	Air Temperature
Thiocyanate (CNS)	Flows
Metals: - total	
Cu, Ni, Zn, Fe, As, Pb	Residence Time in Tailings Pond
pH	
	Pond dimensions
Temperature	Pond depth at sample location
Total Suspended Solids	
Bacterial Counts	

RESULTS AND DISCUSSION

1. Tailings Pond System

Water Balance

The sole source of water to the tailings dam, with the exception of precipitation, is the mill tailings discharge. The volume of liquid discharged was computed on the basis of the tonnage milled and the "percent solids" pumped to the dam. Daily flows were calculated and converted to weekly mean values. Over the period of the study the weekly flow was found to be 845 $\pm$ 170 Igpm [3.8 $\pm$ 0.8 m^3/min]. Over the 61 week study period the total volume of liquid discharged to the tailings ponds was calculated to be 520 Igal (2.36×10^6 m^3).

The outflow from the ponds was not measured routinely. However, WTC personnel did conduct a one week tracer study to determine the residence time of the tailings pond and the volume of the outflow. The flow was

determined by measuring the velocity throughout a defined cross section in the outflow stream by using an "Ott Meter". It was found that the volume of the outflow agreed reasonably well with the inflow, therefore it was assumed that influent and effluent flow were equal over the duration of the study.

The residence time of the tailings pond was determined by injecting a lithium chloride tracer in the influent and measuring its concentration in the outflow. The results are presented in Figure 3. The mean residence time was determined as 70 hours or approximately 3 days.

Chemical Characteristics and Mass Loadings

Average and standard deviations data for the chemical and physical parameters measured on the tailings pond are summarized in Table 2. Data on the influent and effluent mass loadings for CN_T, CNO, CNS, Fe, Cu, Ni and Zn are presented in Table 3. In order to delineate the effects of not having the "barren bleed" discharged to the tailings pond, the data of Tables 2 and 3 have been divided into three seperate time periods. Mass loading plots for the tailings pond are presented in Figures 4, 5 and 6 for CN_T, Cu and Zn, respectively.

Removal of the "barren bleed" from the tailings pond influent tended to reduce the influent cyanide, thiocyanate, iron, copper, nickel and zinc concentrations by 37, 46, 27, 35, 57 and 65% respectively. However, effluent cyanide levels with and without "barren bleed" are not significantly different. This is probably due to the fact that most of the "barren bleed" is dicharged to the holding pond during less favourable conditions and the total "barren bleed" is only discharged to the tailings pond during a period when environmental conditions favour natural cyanide losses (degradation).

The influent cyanide loadings to the tailings pond are significantly higher during "barren bleed" periods (Figure 4). Effluent loadings tended to reach a minimum during June. The average cyanide removal through the pond was 65%. With the total barren bleed the cyanide loading reduction averaged 73% and without the bleed, 46%.

Effluent cyanate concentrations and loadings tended to increase during the warmer months suggesting that a certain amount of cyanide to cyanate conversion is occuring in the tailings pond. This effect is discussed later with respect to the holdings pond results.

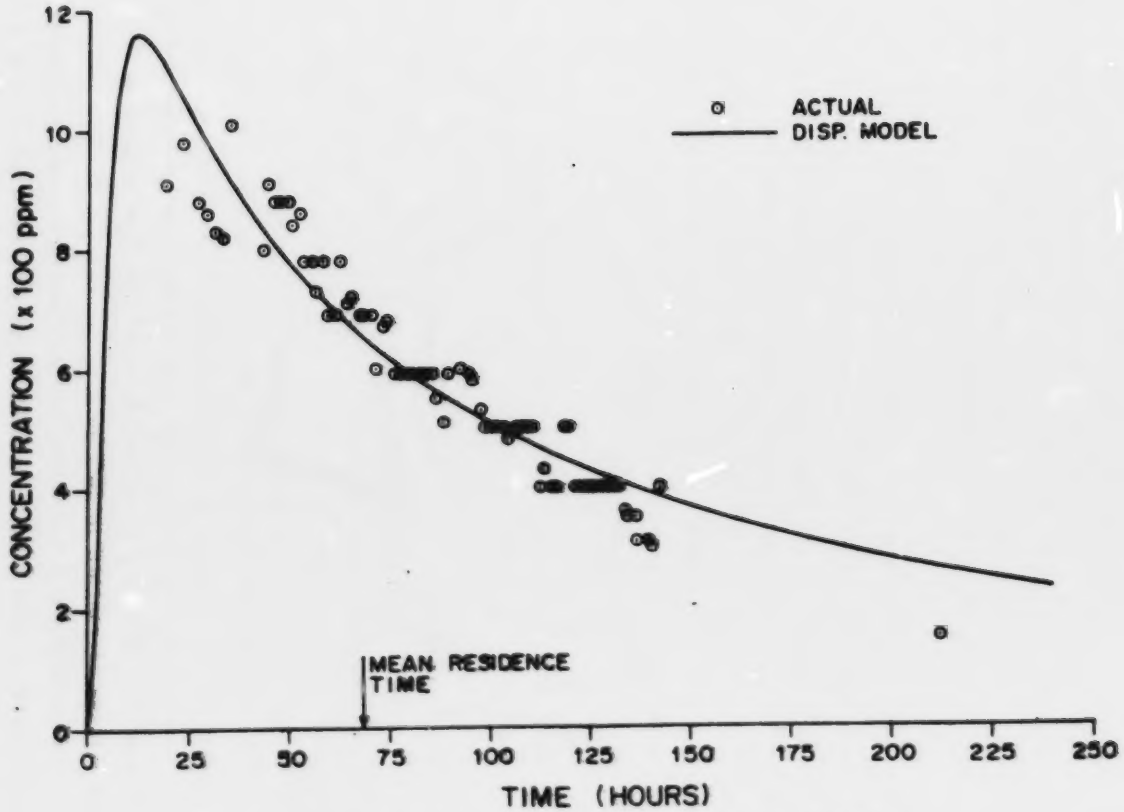


FIGURE 3—TAILINGS POND TRACER PLOT

TABLE 2. TAILINGS PONDS - PARAMETER CONCENTRATIONS* AT SELECTED SAMPLING STATIONS

	CN_T	CN_{PA}	CN_A	CNO	CNS	Fe	Cu	Ni	Zn	As	Pb	pH	TEMP °C	S.S.
1. COMPOSITE SAMPLES														
INFLUENT	18.2	19.9	17.9	2.4	11.5	1.3	3.2	1.0	1.5	0.1	0.01	10.3	17.2	19
	(7.6)	(9.4)	(7.3)	(4.8)	(6.7)	(1.2)	(1.3)	(0.8)	(1.9)	(0.2)	(0.03)	(0.6)	(4.9)	(19)
EFFLUENT	6.9	7.4	6.3	4.0	9.1	1.2	2.2	0.8	0.3	0.06	0.005	9.1	6.4	27
	(3.1)	(3.5)	(3.1)	(4.4)	(3.6)	(2.3)	(0.8)	(0.4)	(0.3)	(0.1)	(0.01)	(0.8)	(6.7)	(43)
2. WITH BARREN BLEED														
INFLUENT	22.3	24.8	20.9	1.8	14.2	1.5	3.8	1.4	2.0	0.1	0.01	10.3	20.0	19
	(7.1)	(9.1)	(7.6)	(1.3)	(6.9)	(1.5)	(1.1)	(0.7)	(2.3)	(0.2)	(0.01)	(0.7)	(4.0)	(21)
EFFLUENT	6.0	7.0	5.8	5.4	11.2	1.0	2.5	1.1	0.4	0.05	0.01	8.7	9.2	19
	(2.2)	(2.9)	(2.2)	(5.5)	(3.4)	(1.0)	(0.8)	(0.4)	(0.4)	(0.1)	(0.01)	(0.8)	(6.9)	(16)
3. WITHOUT BARREN BLEED														
INFLUENT	14.0	13.7	13.6	3.2	7.7	1.1	2.4	0.6	0.7	0.1	0.01	10.4	13.8	18
	(4.3)	(5.7)	(4.2)	(7.1)	(3.7)	(0.8)	(1.0)	(0.6)	(0.8)	(0.2)	(0.04)	(0.5)	(3.3)	(15)
EFFLUENT	7.9	8.2	7.3	2.2	6.4	1.5	1.7	0.5	0.3	0.1	0.01	9.7	2.0	39
	(3.8)	(3.8)	(3.7)	(1.5)	(1.1)	(3.4)	(0.6)	(0.2)	(0.1)	(0.2)	(0.01)	(0.6)	(3.8)	(62)

* Values are in mg/l, except as indicated; means and (standard deviations)

SAMPLE DATES: COMPOSITE SAMPLES: Sept. 9/79 to Nov. 15/80
WITH BARREN BLEED: Sept. 9/79 to Sept. 29/79; Apr. 6/80 to Apr. 26/80; May 18/80 to Nov. 15/80
WITHOUT BARREN BLEED: Sept. 30/80 to Apr. 5/80; Apr. 27/80 to May 17/80

TABLE 3. TAILINGS POND - INFLUENT AND EFFLUENT LOADINGS (kg)

	CN_T	CNO	CNS	Fe	Cu	Ni	Zn
1. COMPOSITE SAMPLES Sept 9/79 - Nov 15/80							
INFLUENT	47,150	5,400	29,550	3,450	8,100	2,650	3,750
EFFLUENT	16,550	9,350	23,250	3,500	5,400	2,150	850
REMOVAL (%)	65	-73	21	-1	33	19	77
2. WITH BARREN BLEED Sept 9/79 - Sept 29/79 Apr 6/80 - Apr 26/80 May 18/80 - Nov 15/80							
INFLUENT	33,050	2,400	21,950	2,400	5,600	2,050	3,200
EFFLUENT	8,950	6,800	16,450	1,300	3,600	1,650	600
REMOVAL (%)	73	-183	25	46	36	19	81
3. WITHOUT BARREN BLEED Sept 30/79 - Apr 5/80 Apr 27/80 - May 17/80							
INFLUENT	14,100	3,000	7,600	1,050	2,500	600	550
EFFLUENT	7,600	2,550	6,800	2,200	1,800	500	250
REMOVAL (%)	46	15	10	-110	28	17	54

Copper and zinc loadings increase during "barren bleed" addition periods (See Figures 5 and 6). In the case of copper there is a direct correlation between influent and effluent loadings. Nickel behaved in a similar manner as zinc, however, effluent zinc loadings were relatively insensitive to influent loadings over the study period (Figure 6). Overall zinc, copper and nickel reductions were 77, 33 and 19%, respectively.

The trend for iron appears to be one of warmer season iron retention and winter season losses with the net effect being no removal. This may be due to the carryover of stable iron-cyanide complexes during the winter when little or no photodecomposition occurs.

From the tailings pond data it is apparent that seasonal factors are playing a significant role in determining pond performance. Some of the potential natural degradation mechanisms which are probably important are discussed later with respect to the holdings pond data.

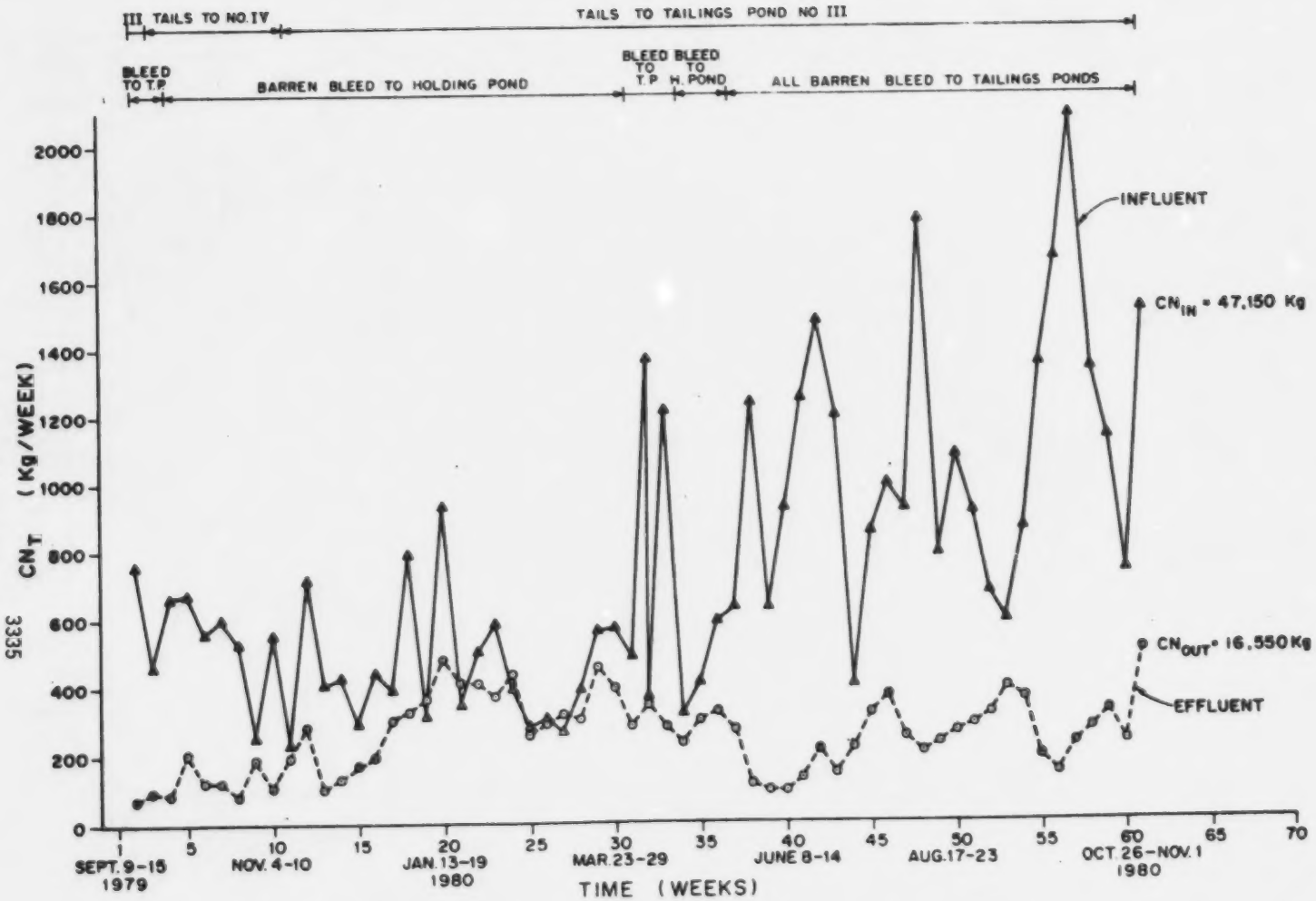


FIGURE 4 — TAILINGS POND TOTAL CYANIDE MASS LOADING

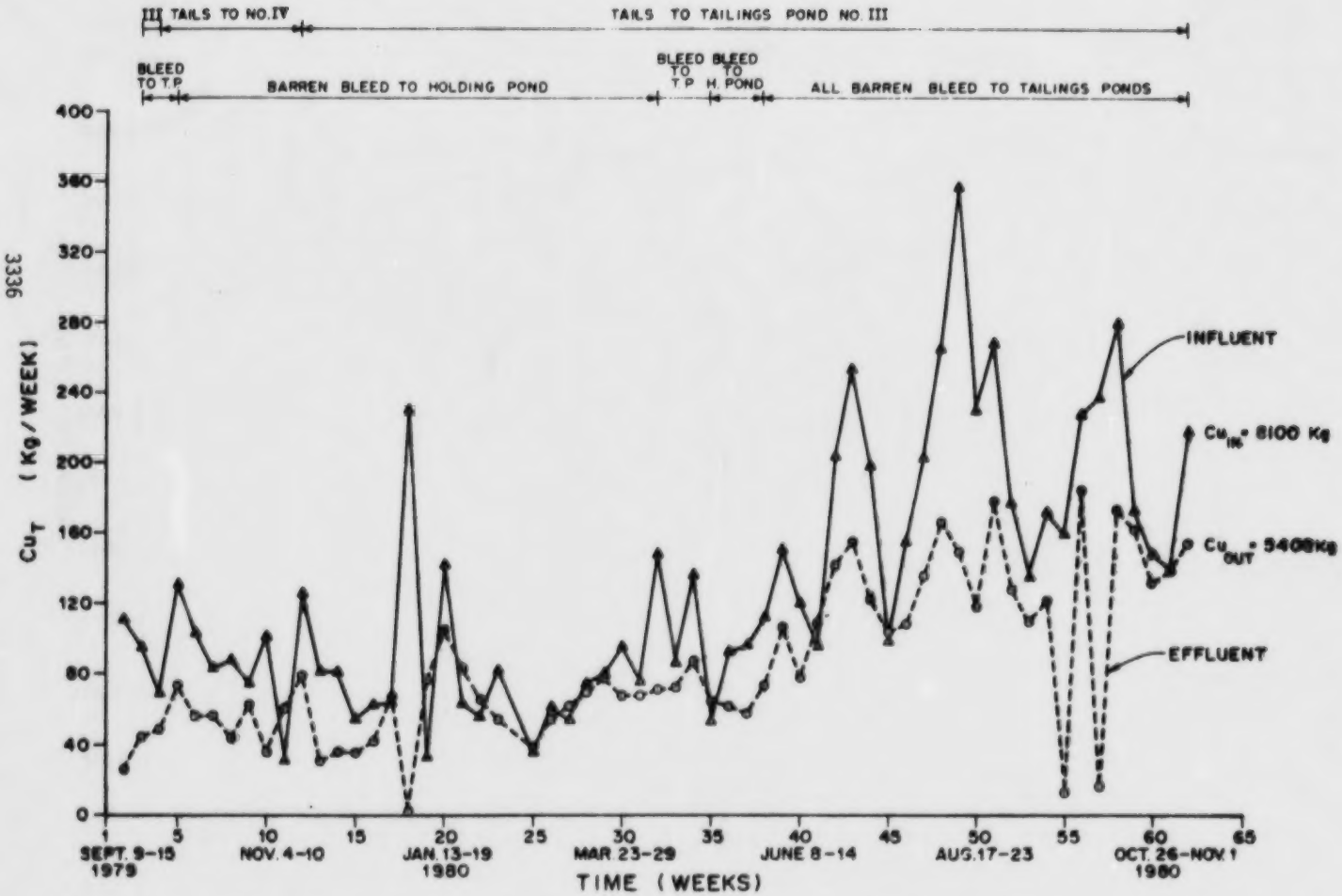


FIGURE 5 – TAILINGS POND COPPER MASS LOADING

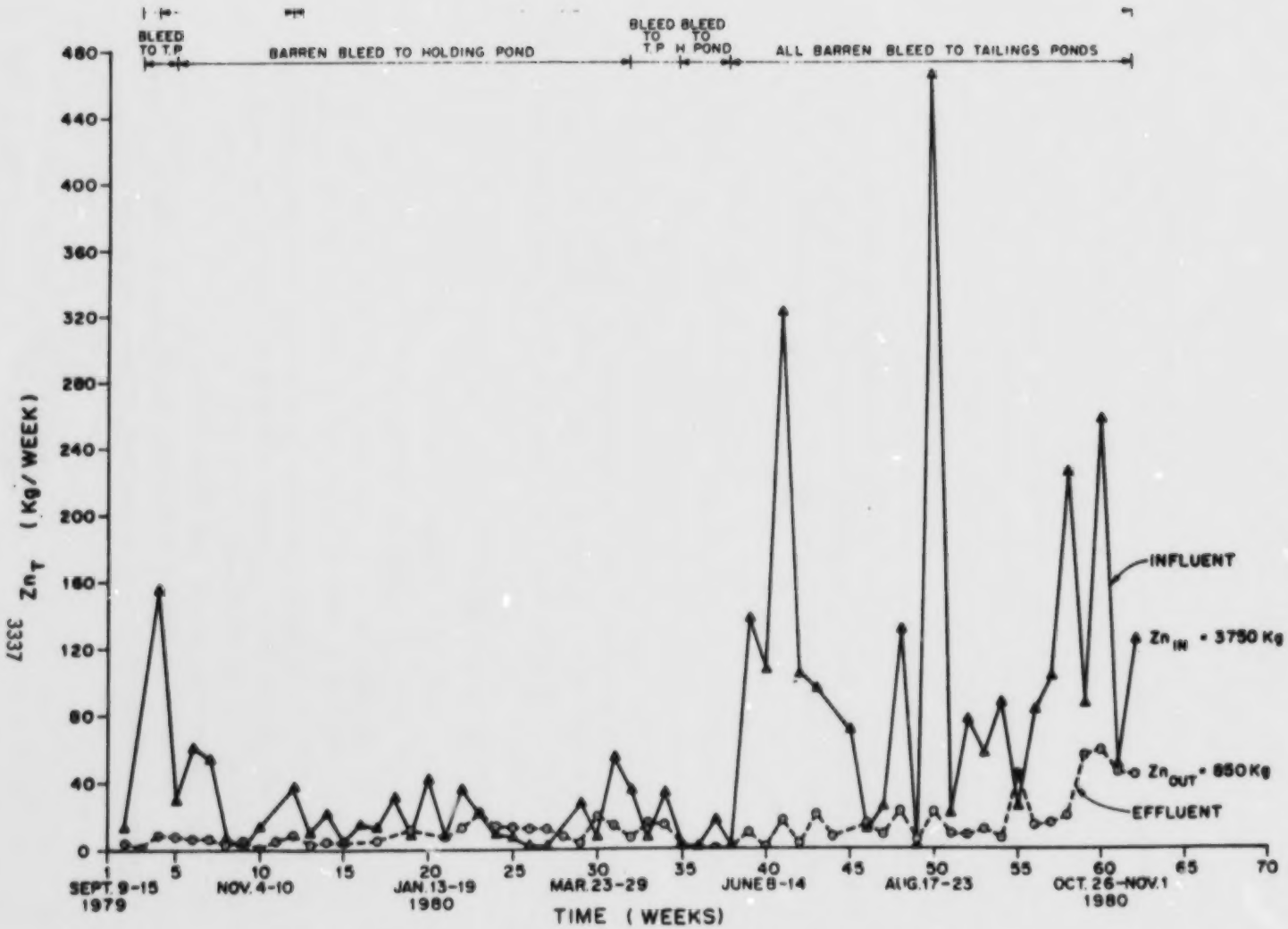


FIGURE 6 — TAILINGS POND ZINC MASS LOADING

2. Barren Bleed Holding Pond

Water Balance

The importance of obtaining a water balance was recognized in the design of the study. Unfortunately, however, all the data to compute a balance were not available at the time of writing the paper. Those values that have been calculated are described in the subsequent paragraphs.

The volume of the "barren bleed" discharged to the holding pond was not directly measured but calculated from the number of days of discharge to the holding pond and the difference in the flow to the tailings pond without and with the "barren bleed". This flow was estimated by preparing a probability plot of the mean weekly flow values (Figure 7). The flow was estimated at 205 Igpm [0.9 m^3/min] and was discharged to the pond for 184 days. Dome Mines recently installed a flow meter and for a seven day period in January (1981) a mean flow of 155 Igpm [0.7 m^3/min] was recorded which agrees reasonably well with the calculated value.

Measurements of rainfall were made while the meteorological instrumentation was on-site from June 28 through October 3, 1980. The quantity of evaporation was calculated from the meteorological data. It was calculated that there was a net evaporation loss of 5.4" (14 cm). However, to calculate these values for the remainder of the study additional data have to be obtained and analyzed. This will be done in the near future. Additional data to compute the discharge volume from the pond must also be obtained.

Chemical Characteristics

Data on the concentrations of the various chemical parameters measured, as well as pH, temperature and suspended solids, are summarized in Table 4. The most significant of these mean values are those for the cyanide discharge to the holding pond and, after degradation has occurred, the discharge from the holding pond. For example the cyanide concentration decreased from 68.7 mg/L to 0.08 mg/L indicating 99.9% removal. The residual concentrations of Fe, Cu, Ni and Zn were 0.4, 0.1, 0.4 and 0.3 mg/L respectively. Metal removals were 88, 98, 80, and 97% respectively.

The concentrations of various cyanide and metal species are plotted in Figures 8 through 12 for the holding pond influent and for the samples

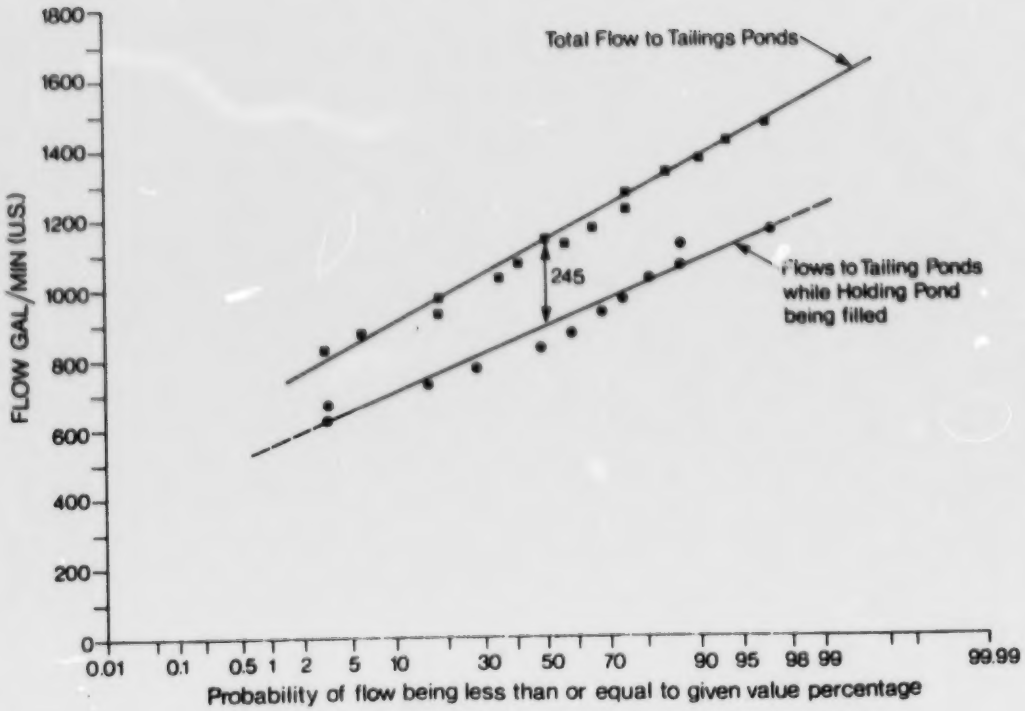


Figure 7 FLOW TO BARREN BLEED HOLDING POND

TABLE 4. BARREN BLEED HOLDING POND - PARAMETER CONCENTRATIONS* AT SELECTED SAMPLING STATIONS

	CN_T	CN_{PA}	CN_A	CNO	CNS	Fe	Cu	Ni	Zn	As	Pb	pH	TEMP °C	S.S.
BARREN BLEED DISCHARGE TO HOLDING POND [1]	68.7 (14.1)	73.5 (13.5)	68.4 (14.2)	3.0 (1.6)	35.1 (10.5)	1.9 (1.3)	7.3 (2.3)	2.1 (0.9)	10.7 (4.7)	0.5 (1.9)	0.1 (0.6)	11.7 (0.2)	16.1 (1.8)	37 (22)
SHALLOW SECTION SAMPLE [2]	17.0 (26.8)	39.3 (32.2)	16.9 (26.8)	5.9 (4.2)	18.8 (15.4)	0.5 (0.6)	2.9 (3.3)	1.4 (0.9)	3.3 (4.6)	0.05 (0.2)	0.09 (0.3)	10.2 (1.6)	7.0 (7.9)	14 (20)
DEEP SECTION SAMPLE [3]	3.0 (3.5)	5.1 (4.8)	2.9 (3.5)	8.6 (3.3)	18.5 (6.3)	0.2 (0.3)	2.3 (1.5)	1.33 (0.9)	1.3 (1.0)	0.02 (0.1)	0.01 (0.02)	8.2 (0.7)	16.7 (4.8)	4 (2)
DISCHARGE** [4]	0.08 (0.04)	0.1 ***		0.02 (0.03)	4.8 (2.8)	0.4 (0.2)	0.2 (0.08)	0.4 (0.06)	0.3 (0.03)			7.5 ***	3.0 ***	9 ***
REMOVAL**** (%)	99.9	99.9		99.3	86.3	78.9	97.3	80.9	97.2					76

* Values are in mg/L, except as indicated; means and (standard deviations)
** Only 3 sample results
*** One sample only
**** Calculated based on data in lines [4] and [1]

FILLING DATES BARREN BLEED: Oct 2/79 - May 15/80; Sampled weekly

SAMPLING DATES: SHALLOW SECTION: Oct 24/79 - June 25/80; Sampled weekly
June 26/80 - Sept 24/80 - Sampled daily
DEEP SECTION: June 11/80 - Oct 1/80; - Sampled daily
DISCHARGE DATES: Oct 10/80 - Oct 15/80

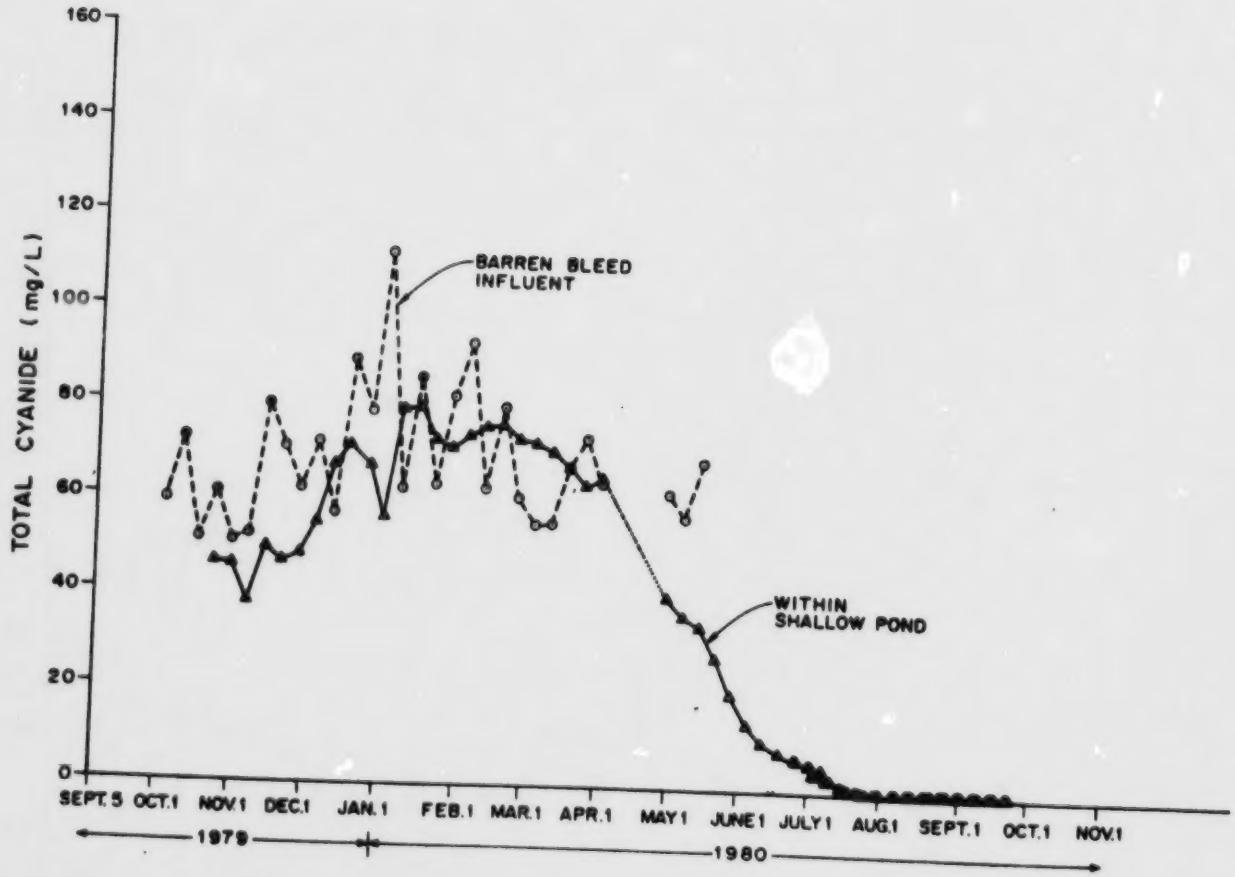


FIGURE 8 – TOTAL CYANIDE IN BARREN BLEED HOLDING POND

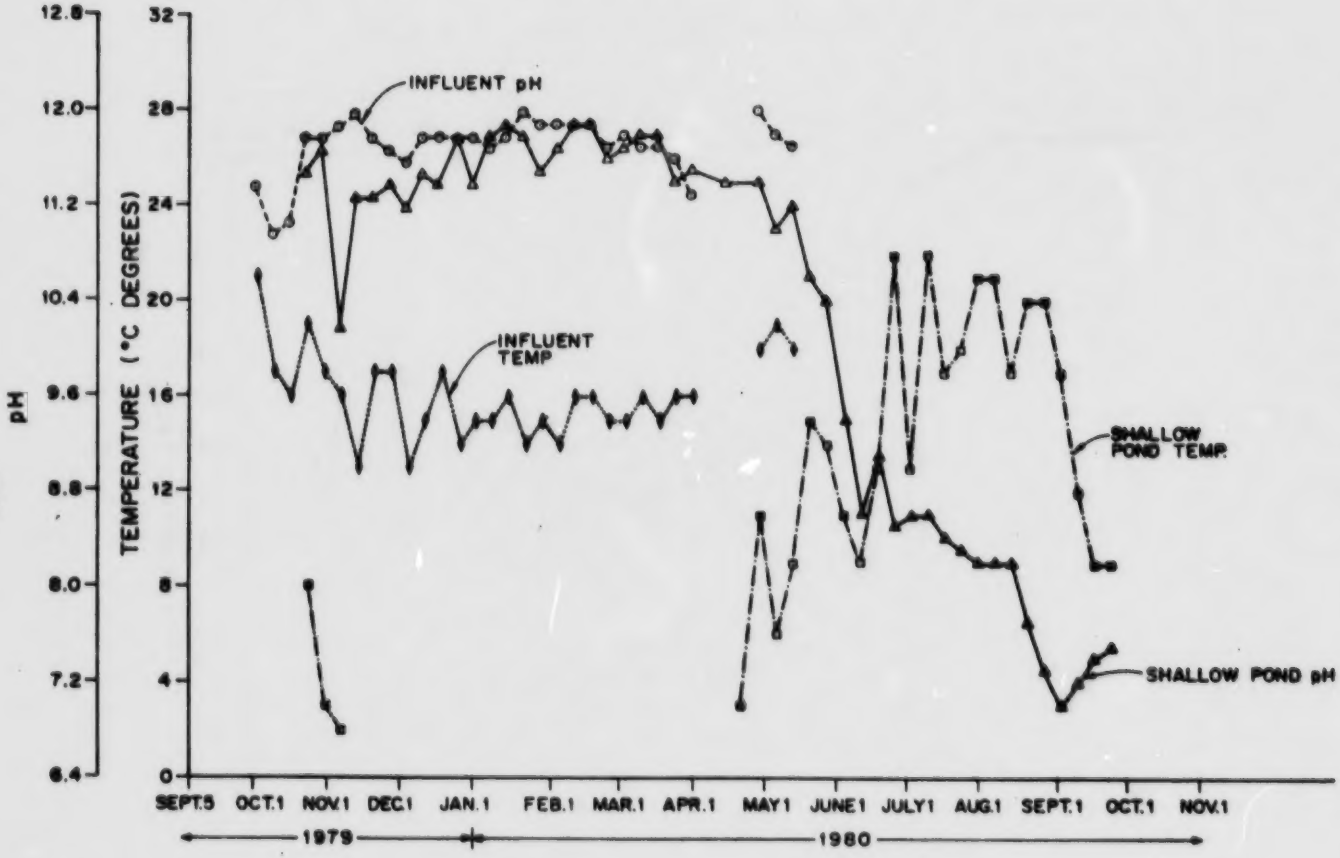


FIGURE 9 – TEMPERATURE AND pH IN BARREN BLEED HOLDING POND

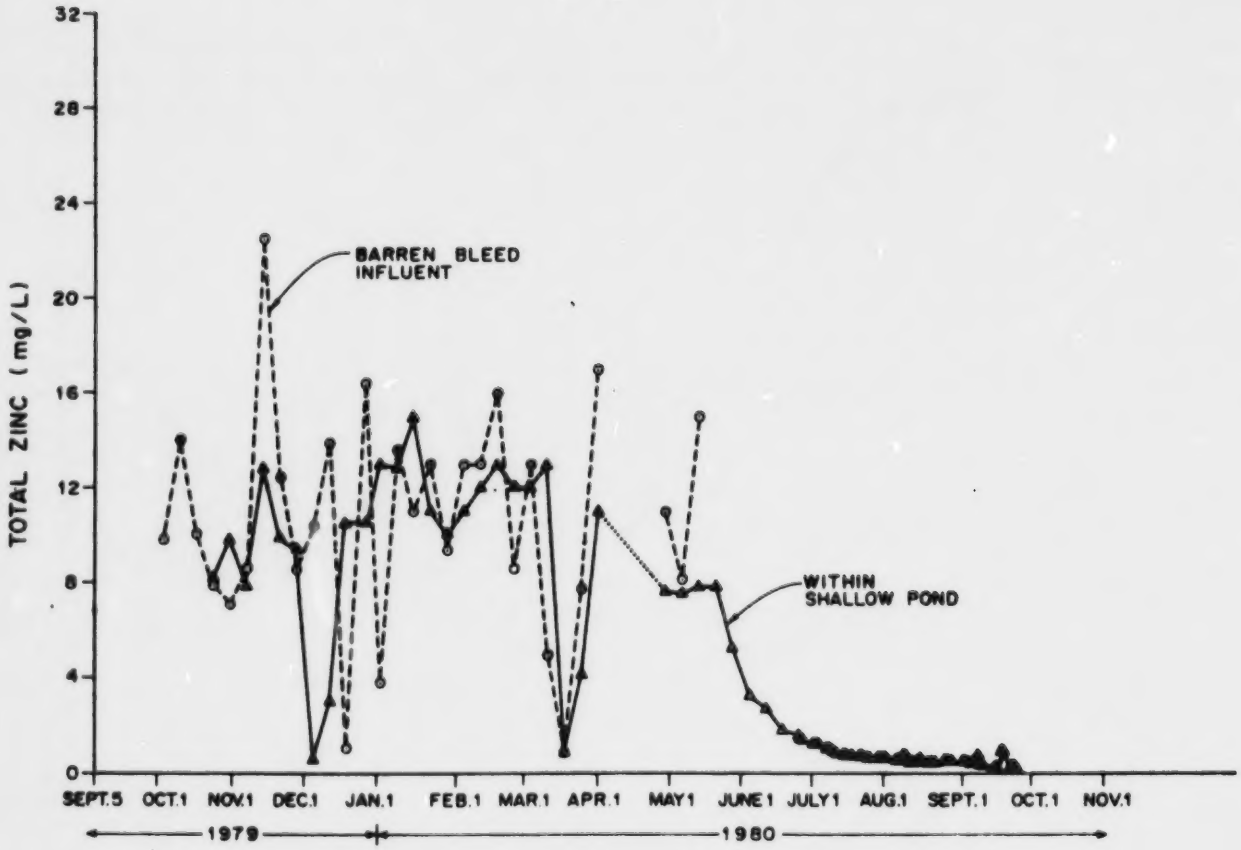


FIGURE 10 – ZINC IN BARREN BLEED HOLDING POND

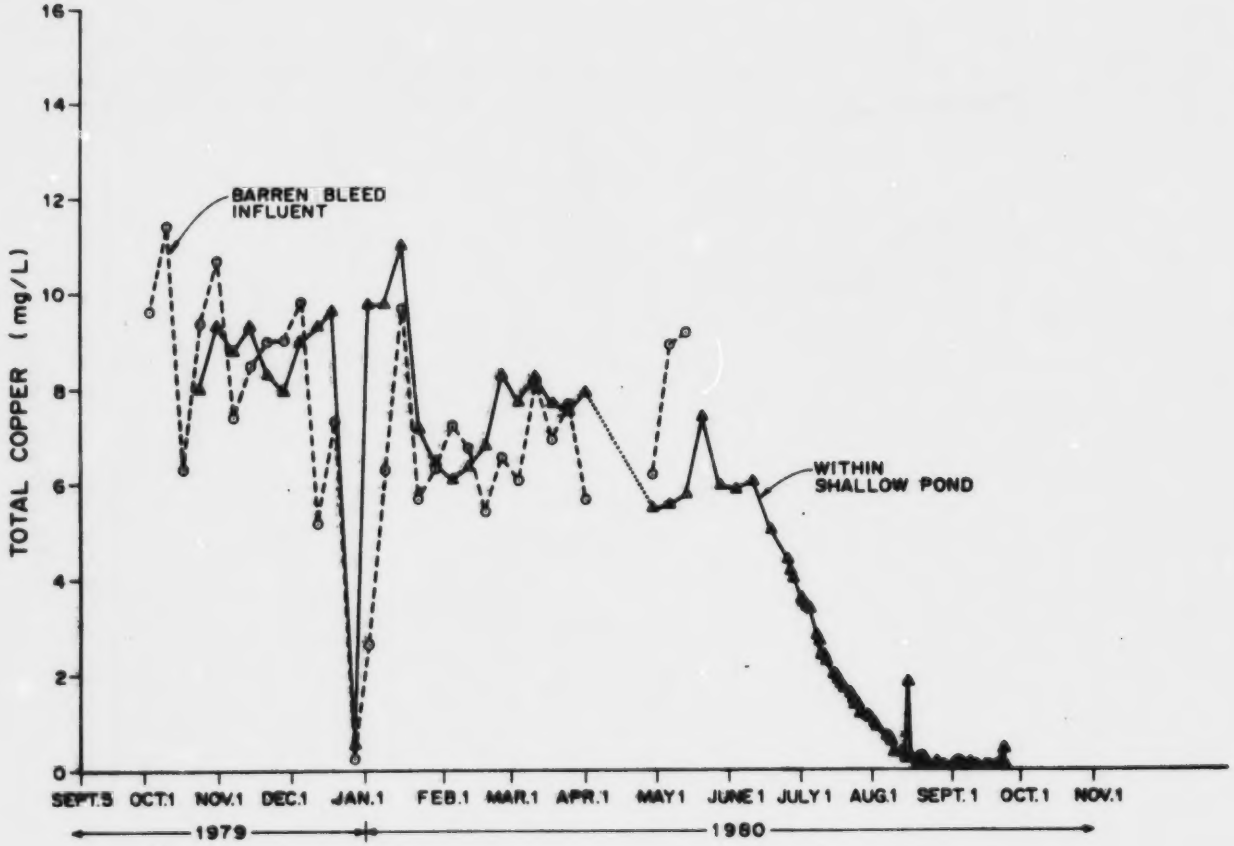


FIGURE 11 – COPPER IN BARREN BLEED HOLDING POND

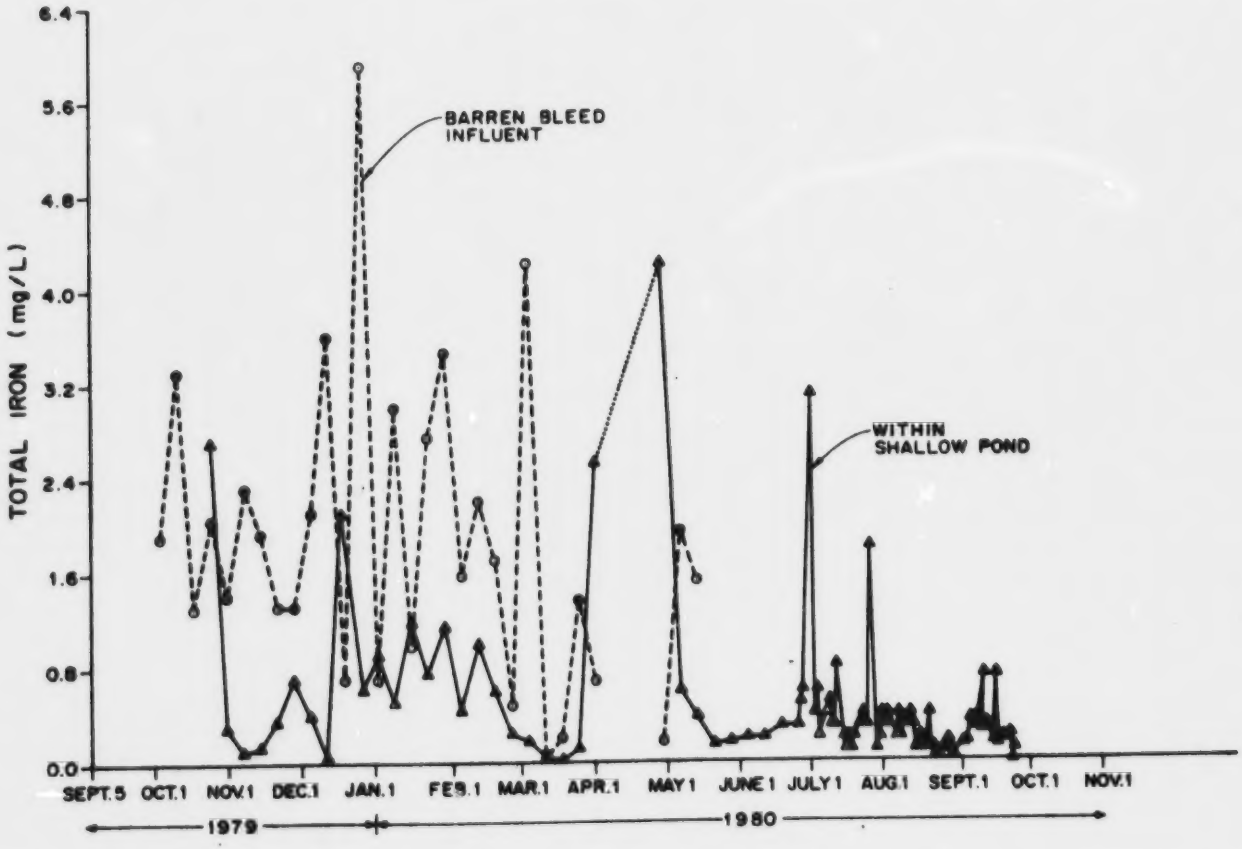


FIGURE 12 — IRON IN BARREN BLEED HOLDING POND

collected from the shallow section of the holding pond The striking feature of the graphs of the chemical concentrations is the decrease of the various constituent concentrations which occurs after filling of the pond has been completed. This phenomenon begins in April and continues throughout the summer and appears to be related to the rise in temperature and the drop in pH which occurs during the same period (Figure 9). Iron, however, does not appear to follow the same pattern. The rate of removal of constituents in the deep section paralleled, but lagged (by about 35 to 40 days) that of the same constituents in the shallow section.

Cyanide Removal

The removal process began almost immediately after discharge of the "barren bleed" ceased (Figures 8, 10 and 11). In an attempt to determine what was occurring during the initial stage of cyanide disappearance, data from April 2, (the initial point for the cyanide removal process) were compared with data from April 30, when the ice cover had largely disappeared from the pond. These data are presented in Table 5. To determine the amount of CN^- ion which might potentially be volatilized, it was assumed that the metals present existed as metal cyanide complexes and that the residual cyanide concentration was therefore "free cyanide" available for volatilization. (Although this assumption, strictly speaking, is not correct because total metal concentrations were measured on unfiltered samples, it was considered that this would provide a maximum boundary condition for the metal cyanide complexes). The metal cyanide complexes assumed to exist where $Fe(CN)_6$, $Cu(CN)_3$, $Ni(CN)_4$, and $Zn(CN)_4$.

It should be noted that the pH was very alkaline throughout this period; pH 11.5 on April 2 and pH 11.4 on April 30. Conceivably, a significant proportion of "free cyanide" could have accumulated while the pond was ice covered. The data in Table 5 suggest that 25.3 mg/L of the CN_T was volatilized. About 8.0 mg/L evolved from the dissociation of the metal complexes to produce free cyanide which was subsequently volatilized.

TABLE 5. HOLDING POND CONCENTRATIONS* DURING INITIAL CYANIDE REMOVAL

	2 April 1980		30 April 1980		Difference	
Parameter	Conc	Equiv. CN Conc.	Conc.	Equiv. CN Conc.	CN	Metals
CNT	65.3	65.3	40.0	40.0	25.3	
CNS	31.2		24.0			
CNO	4.1		4.6			
Fe	2.5	(3.5)	4.2	(5.9)		+1.7
Cu	7.9	(9.7)	5.5	(6.7)		-2.4
Ni	2.7	(4.8)	1.6	(2.8)		-1.1
Zn	11.0	(17.5)	7.6	(12.1)		-3.4
		(35.5)		(27.5)	(8.0	
CNF		29.8 (46%)		12.5 (49%)	17.3	

* all concentrations in mg/L

Figure 13 provides a perspective of the interaction of the various shallow pond parameters from April 2 through September 17. Trends are shown for cyanide, cyanate, thiocyanate, pH and metals. On August 6 the CN_T concentration reached 0.05 mg/L. After April 30, the pH of the system began to drop, reaching a value of approximately 8.3, the pH at which carbonate and bicarbonate are in equilibrium. The pH decrease is apparently due to the absorption of carbon dioxide from the air as follows:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3\downarrow + 2H_2O$$

At pH 8.3 the ratio of free cyanide (HCN) to CN^- is about 7 to 1. A continuing decrease in pH as a result of CO_2 absorption will be relatively slow due to the formation of the bicarbonate-carbonic acid buffer system.

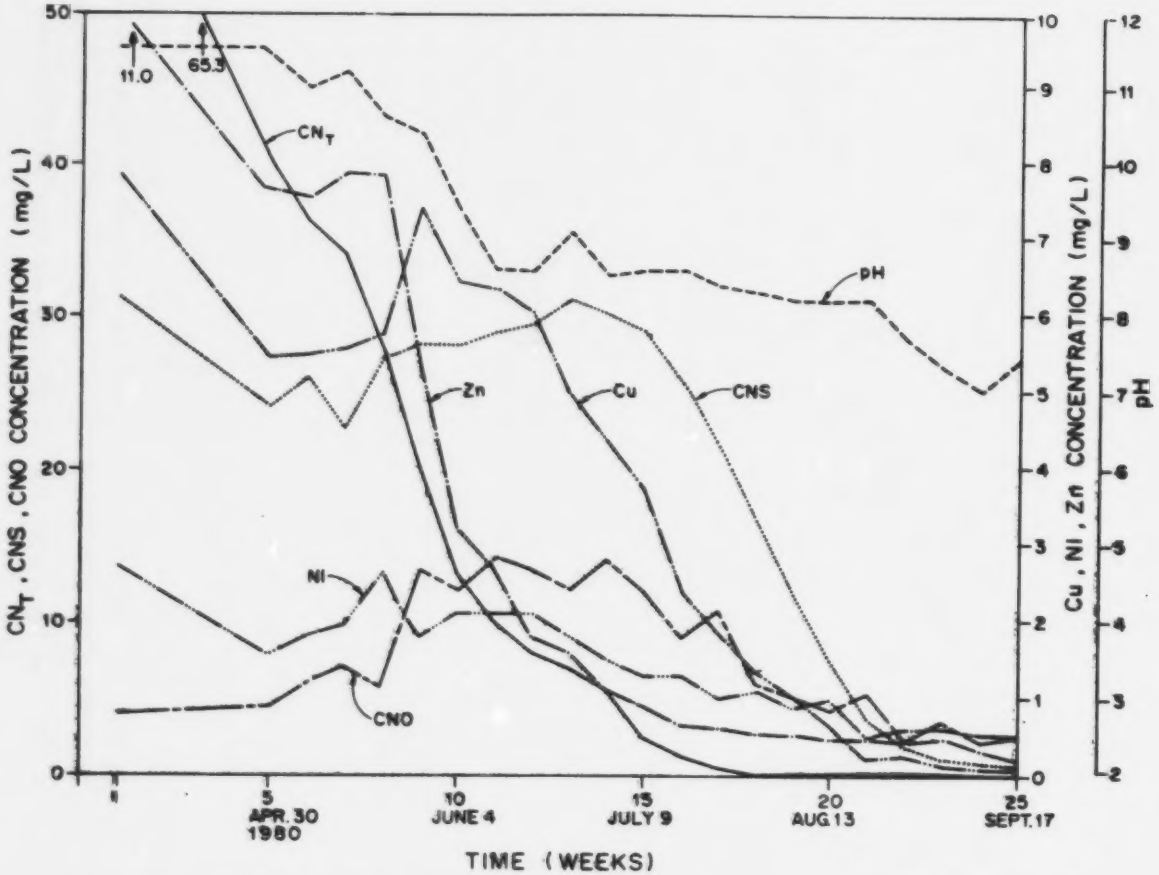


FIGURE 13-CONCENTRATION TRENDS IN SHALLOW BARREN BLEED HOLDING POND

(At equi-molar concentrations of H_2CO_3 and HCO_3^- the pH would be 6.5). Small changes in pH in this range, however, are reflected in large changes in the HCN/CN ratio. The gradual attainment of these low pH values and the corresponding increase in the available HCN will result in loss of cyanide to the atmosphere. Losses will be governed by Henry's Law.

Thus, after April 30, substantial volatilization of the cyanide likely occurred. Conducting the same computations as in Table 5 for the June 25th data showed that theoretically no free cyanide existed and that in fact, approximately 50% of the metals could not be complexed with cyanide.

Table 5 shows that a decrease in the concentrations of copper, nickel and zinc occurred from April 2 to April 30. It is likely that these metals precipitated as hydroxides. The slight increase in iron has no apparent explanation. Figure 14 depicts the solubility of various heavy metals as a function of pH. The minimum solubility for zinc and copper occurrs about pH 9 and increases as the pH decreases. However, even at pH 8.5, which was measured on June 25 in the pond, the zinc and copper concentrations of 1.60 and 4.39 respectively considerably exceeded the minimum solubilities indicated by Figure 14. This would suggest that these could still be precipitating as hydroxides, however, some may also still be combined with some cyanide.

Oxidation of Cyanide

From Figure 13 it can be seen that the concentration of cyanate increased from 4.1 mg/L on April 2 to a maximum of 14.3 mg/L on June 25; after which hydrolysis to ammonia and carbonate presumably occurred as the pH decreased. This increase of 10.2 mg/L of cyanate corresponds to the conversion of 6.3 mg/L of cyanide. Over the same period the cyanide concentration decreased by 58.3 mg/L from 65.3 mg/L to 7.0 mg/L. Thus the oxidation mechanism may have accounted for about 11% of the observed decrease in cyanide.

In terms of the driving force for this reaction photo redox processes are known to occur in aqueous solutions of metal cyanide complexes under illumination with ultraviolet (and sometimes, visible) lights. For example, the irradiation of ferricyanides with sunlight results in the

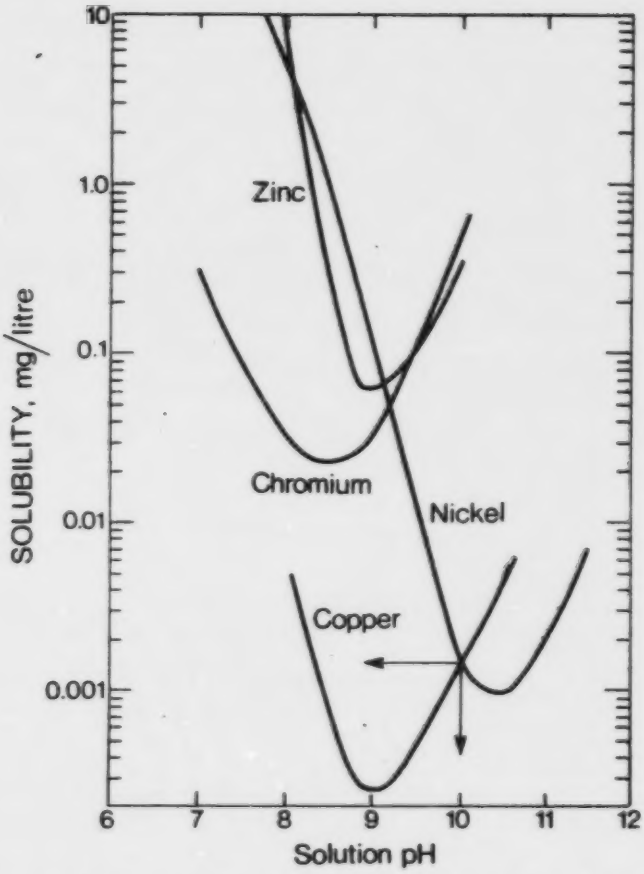


Figure 14 SOLUBILITY OF HEAVY METALS AS A FUNCTION OF pH

oxidation of cyanide to cyanate and the reduction of iron from the III (ferri) to the II (ferro) oxidation state. In this type of system the iron functions as a catalyst (Carey, 1981).

Biodegradation

The evidence with respect to the biodegradation of cyanide is inconclusive. Only the measurement of two parameters is germane; these are bacterial counts and dissolved oxygen. On July 2, the bacterial count was 2.0×10^5 cells/ml while at the same time the chemical data indicated that there was no free cyanide available for degradation. From July 2 to August 6, the count increased to 14×10^5 cells/ml which would tend to indicate that biodegradation of some substrate was occurring. Rather than cyanide being degraded, however, it seems more likely that the thiocyanate, which is quite biodegradable, is being degraded. Over this period, the thiocyanate decreased from 30.2 to 11.7 mg/L. The products of the reaction are carbon dioxide and ammonia, neither of which, were measured during this study. For the biodegradation of thiocyanate to occur, oxygen must be consumed. It has been estimated (IEC, 1979b) that 1.5 to 2.0 moles of molecular oxygen would be consumed per mole of thiocyanate degraded. However, in the report it was pointed out that a typical oxygen depletion in a natural stream with reaeration would likely be less than 1.0 mg/L. On August 11, the dissolved oxygen profile at two locations in the shallow pond was measured. A dissolved oxygen deficit of about 0.5 to 1.0 mg/L was noted in the water column. These data might tend to substantiate a biodegradation mechanism.

In addition, IEC (1979b), postulated that sulphuric acid could be produced by thiocyanate biodegradation. In this regard, Figure 13, it is shown that the pH of the system tends to drop slightly coincidently with the decrease in thiocyanate.

Photodecomposition

The significance of the mechanism of photo-decomposition in this study could not be assessed conclusively. Sunlight intensity was one of the meteorological parameters measured from June until early October. Correlation coefficients were calculated with the chemical parameters, pH and sunlight, however, none were found to be significant. It was hoped, based on

the literature that there might be a correlation with iron (and presumably iron cyanides). In Figure 12, it can be seen that the iron concentrations fluctuated continuously throughout the study with no discernable degradation trend although cyanate was produced perhaps as suggested in the previous section on oxidation.

Thiocyanate Precipitation

Examination of metal removal curves in Figure 13 suggests that copper may be combining with thiocyanate and precipitating in the insoluble form. There is some evidence that nickel may also be precipitating as thiocyanate. This mechanism and biodegradation may combine to account for the observed decrease in the thiocyanate concentrations. Again, however, the data are inconclusive.

Pond Geometry

As mentioned previously, the holding pond consists of two sections - a shallow section with an average depth of 3' (1 m) and an area of about 451 000 ft^2 (41 899 m^2) and a deep section with an average depth of about 20' (6.1 m) and an area of about 50 800 ft^2 (4 719 m^2). The ratio of the surface area of the shallow to the deep section is approximately 9:1. Samples were collected from the deep section of the pond from June 11. Selected parameters for the deep and shallow sections are plotted in Figure 15 (CN_T, CNO, CNS). Figure 16 (pH, temperature) and Figure 17 (Zn, Cu, Ni). In the deep pond the same phenomena appear to be occurring, however, the reaction rates appear to be slower and the constituents, with the exception of cyanide, do not appear to be removed to the same degree. These data, therefore, tend to confirm the desirability of shallow ponds for degradation.

Degradation Coefficients

Overall cyanide degradation coefficients were calculated for the shallow and deep pond data assuming a first order reaction of the form:

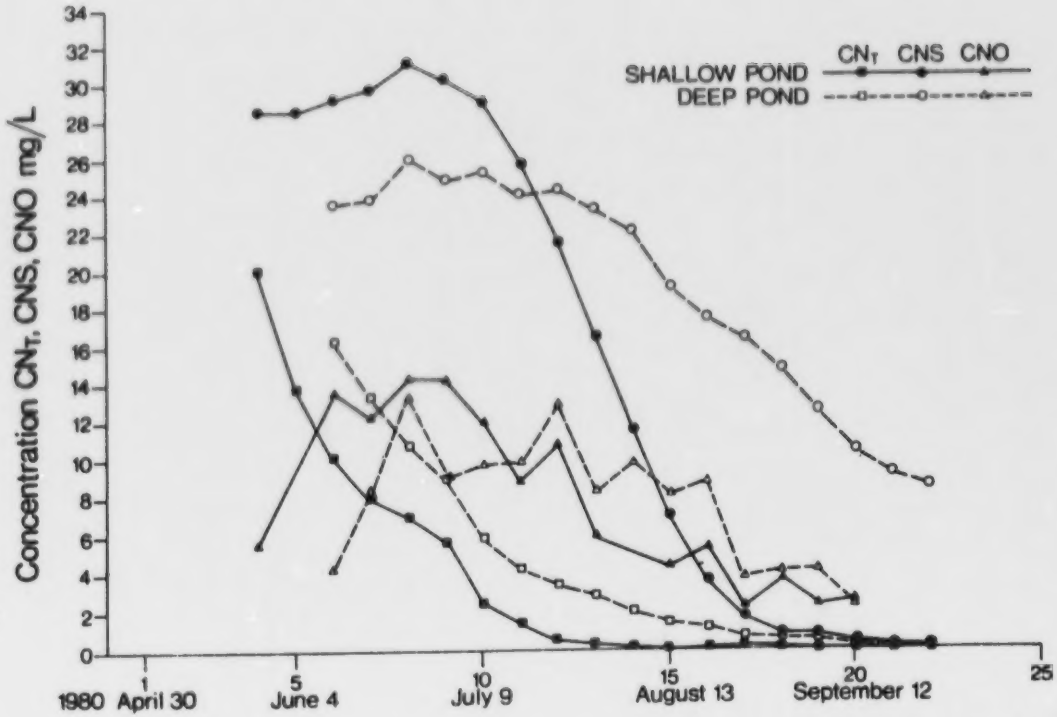


Figure 15 CONCENTRATION OF CN_T, CNS, CNO, SHALLOW AND DEEP SECTIONS

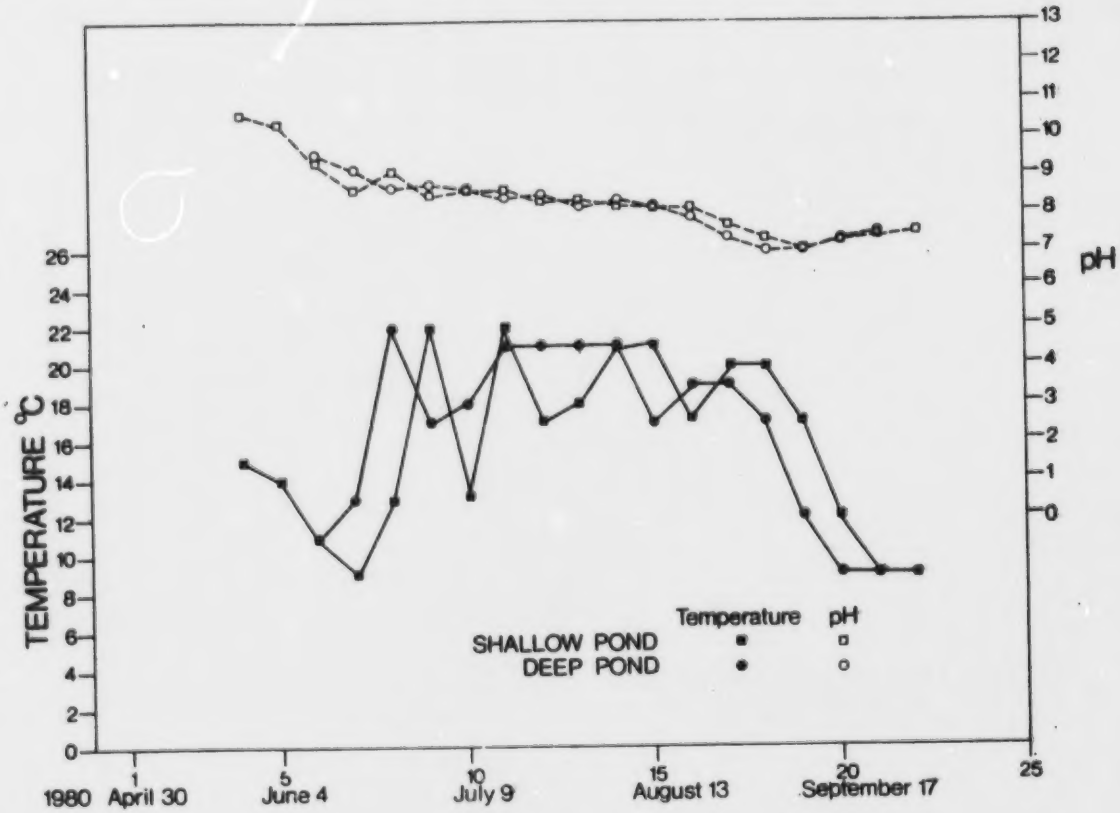


Figure 16 pH, TEMPERATURE, SHALLOW AND DEEP SECTIONS

3354

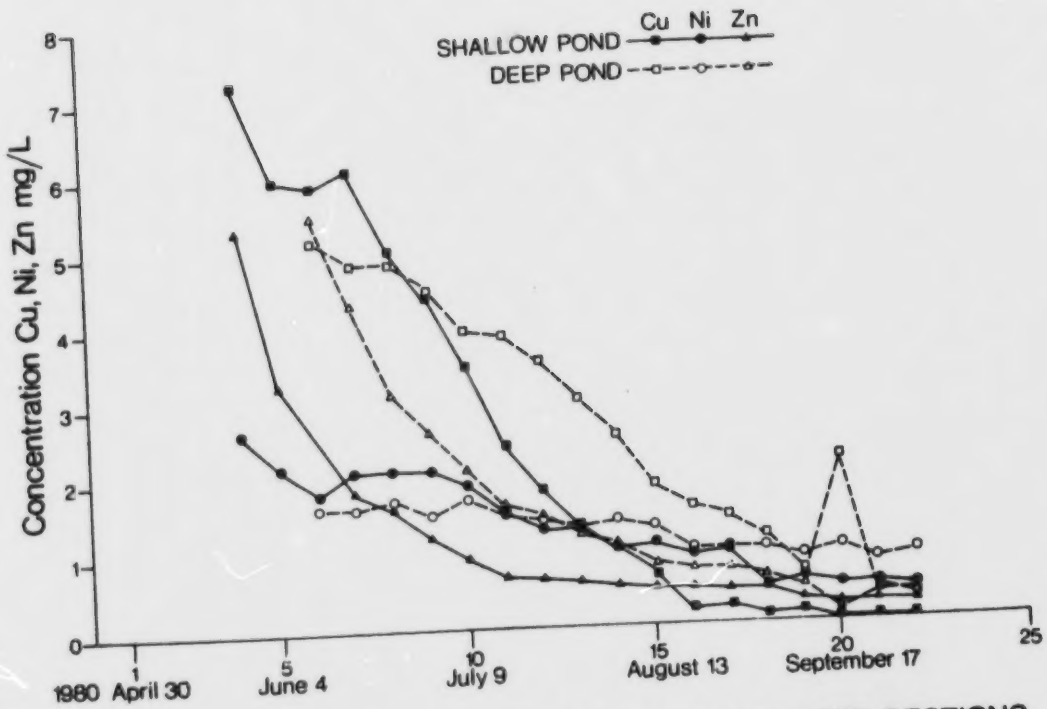


Figure 17 CONCENTRATION OF Cu, Ni, Zn, SHALLOW AND DEEP SECTIONS

$$C = Co\ e^{-Kt}$$

where C = CN_T concentration at time t
C_o = initial concentration of CN_T
K = degradation coefficient (t^{-1})
t = time

Data from the study, and data collected by Dome Mines during 1979 were subjected to separate calculations. The degradation coefficients obtained were:

1980 - Shallow Section
Initial Rate (First 90 days) - 0.0010 hr^{-1}
Final Rate (After 90 days) - 0.0052 hr^{-1}

1979 - Shallow Section
Initial Rate - 0.0010 hr^{-1}
Final Rate - 0.0045 hr^{-1}

1980 - Deep Section 1
Overall Rate - 0.0015 hr^{-1}

The degradation coefficients are similar for both years for the shallow section of the holding pond. The coefficient for the deep pond, as might be expected, falls between the two rates for the shallow section but is closer to the initial shallow pond rate.

Smith et al (1980) have recently published an article on the prediction of volatilization rates of volatile chemicals from natural water bodies. Using their equations and some simplifying assumptions a rate of 0.0014 to 0.0081 was calculated for stagnant ponds. The rates derived for this study fell within this range and suggest, that the observed removal of cyanide could be accounted for by volatilization.

Summary of Degradation Mechanisms

The possible degradation mechanisms as previously discussed are summarized in Table 6.

TABLE 6. SUMMARY OF DEGRADATION MECHANISMS

	Conditions	Mechanism
Stage 1 April 2 - April 30	Ice cover breaks up pH 11 - 11.5 Water Temp 2 - 5°C	CN_F volatilizes as HCN. Some Metal-Cyanide complexes dissociate CN_F - volatilizes Metals precipitated as hydroxides
Stage 2 April 30 - 25 June	Water Temp warms up to 20°C pH drops to about 8.5	CN_F volatilizes as HCN. Only complex CN remaining Some CN_T oxidized to CNO Metal cyanide complexes continue to dissociate CN_F - volatilizes Metals precipitated as hydroxides
Stage 3 June 25 to Oct	Water Temp remains in range of 17-21°C pH remains at about 8.5 slowly decreasing to 8.3 then rapidly to pH 7	No CN_F present CNO hydrolyzes to CO_2 + NH_3 CNS decreases probably as a result of precipitation with metals, probably Cu and some Ni and possibly bio-degradation Metal cyanide complexes continue to dissociate CN volatilizes as HCN Metals continue to precipitate

CONCLUSIONS

A preliminary analysis of data obtained from a 14 month study of the tailings ponds and barren bleed holding pond at Dome Mines has resulted in the following conclusions.

(1) The provision of a separate barren bleed impoundment at Dome Mines has been successful in reducing the discharge of cyanide from the tailings ponds, i.e. cyanide loadings from the

tailings ponds remain relatively constant year round, rather than the higher increasing substantially in winter loadings observed during pre-impoundment years.

(2) Natural degradation mechanisms in the barren bleed pond reduced the cyanide concentration from 68.7 to 0.08 mg/L (99.9% reduction) in the period April through September. The most important mechanism appeared to be volatilization of free cyanide. Oxidation of free cyanide to cyanate accounted for approximately 11% of the total cyanide conversion. The relative roles of photodecomposition and biodegradation could not be delineated.

(3) The tailings pond system at Dome Mines achieved average cyanide, copper, nickel, zinc and iron removals of 65, 33, 19, 77 and 0%, respectively.

(4) An important sbustantive data base has been developed on the operation of a tailings pond system and a barren bleed holding pond at a Canadian gold mine.

RECOMMENDATIONS

Although a substantive data base has been developed on natural degradation, the operative mechanisms and the implications for design purposes have not been sufficiently delineated.

Therefore, it is recommended that the following be undertaken:

- Completion of the analysis of the available data.
- Conduct further full scale studies to confirm the results of this study and provide data on additional parameters eg. NH_3, alkalinity
- Conduct appropriate "bench scale" studies on simulated effluents in an attempt to better identify possible degradation mechanisms and to assess the applicability of the "degradation process" to effluent from other mines
- Develop suitable design criteria in order that "natural degradation" may be used as an alternative technology or in combination with other technologies for cyanide and metal reduction

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GIANT YELLOWKNIFE MINES, NWT

Giant Yellowknife Mines is the subject of a detailed trip report in Appendix I.

The Giant Mine is located just south of the Arctic Circle on the north shore of the Great Slave Lake. In this part of the world there is no shortage of fresh water although its use is regulated by the Northwest Territory Water Board which allows a maximum annual consumption of 1,950,000 m^3 per year for the 325,000 tons mined and milled annually. This works out to 6.6 m^3 water per ton ore milled which reflects the plentiful availability of water.

Giant cyanide leaches a calcined flotation concentrate. The calcine is water washed before cyanidation. All effluents and tailings are commingled and pumped to a common tailings dam from which the decant is treated to remove cyanide and metals by alkaline chlorination and to remove arsenic by addition of ferrous sulfate and decanting.

The long frozen winters require that effluent be treated during the summer months only and accumulated in the tailings dam during winter. This requires a tailings dam with a large capacity and an effluent treatment plant capable of treating the whole year's liquid effluent in five to six months.

Although only the calcine and Cottrell precipitator dust from roasting are cyanided, i.e., only about 110 tons per day of material, the complete effluent from the tailings dam must be treated due to historical commingling. This arrangement does benefit from some natural degradation in summer.

If one were starting from scratch, undoubtably this operation would use roaster gas to detoxify just the cyanided calcine tailings which could be disposed of separately. Since these contain some residual undissolved gold, they would also represent a potential future resource if they were not commingled.

Seepage into the mine from the tailings decant pond downstream from the tailings pond resulted in a low level of cyanide in water pumped from the mine. Since the new cyanide destruction plant was installed to treat tailings decant ahead of this pond, cyanide has no longer been detected in minewater.

Giant Yellowknife recovers some incremental gold from treated effluent after decantation. Possibly residual cyanide contained in the commingled tailings helps in the leaching of some of this gold over a long period of time. It is not clear whether this opportunity would be lost through segregating the tailings as mentioned above.

Giant Yellowknife saves a considerable additional water treatment expense through careful housekeeping to keep arsenic flue dusts away from water.

Water management at Giant Yellowknife Mines is discussed in greater detail in a trip report in Appendix I.

CON MINE, YELLOWKNIFE, NWT

The Con Mine used to treat a refractory arsenopyrite gold ore which required roasting. For the last decade or more the mill has been treating a non-refractory gold ore by direct cyanidation. However, two sludge ponds containing arsenic flue dusts from the old, and now dismantled Edwards roaster remain and presented a threat of contaminating effluents and groundwater that ultimately could find its way to Great Slave Lake.

The Con Mine is also the subject of a trip report in Appendix I, and only a few features are mentioned here.

First, Rather than deal with the arsenic ponds as an environmental reclamation project, Cominco has developed a process and installed a $13 million plant to recover arsenic and a recoverable gold residue from the sludges.

Second, The tailings dam at the Con Mine is very large and shallow. Tailings are treated before leaving the tailings line by injecting excess lime, sodium sulfide and ferrous sulfate to precipitate most of the cyanide. Additional ferrous sulfate is broadcast over the decanted solution pond to further reduce cyanide and arsenic. Natural degradation does the rest.

Third, The water use permit allows the Con Mine also to use 1,950,000 m^3 water per year which reflects the abundant supply available.

Fourth, Like the Giant Yellowknife Mine the total volume of tailings are treated to remove cyanide and metals. Unlike Giant Yellowknife, the Con Mine process arrangement allows no opportunity for segregating various tailings streams. All the ore is cyanide-leached.

Finally, Performance data on the cyanide and metal removal performance of the Cominco patented cyanide removal process employed is impressive. Details of the $FeSO_4$ plus Na_2S cyanide destruction patent are provided in Chapter 10 on cyanide destruction.

CON MINE, NORTHWEST TERRITORIES

Wastewater Analyses (mg/l)

	Influent to Fe S Process	Tailings Pond Decant	License Conditions
As		0.3	0.50
CN_T Average	750	0.7	1.5
CN_T Max. Grab			3.0
CN_W		0.35	0.40
Fe	140		
Cu	50	0.30	0.30
Zn	155	0.04	0.30

Source: SCOTT (1984)

No effluent solutions are recycled to the Con Mine, it is all treated and discharged.

The cyanide levels in effluent allowed by Cominco's Con Mine operating permit are relatively lenient at 1.5 mg/l CN_T maximum average and 3.0 mg/l maximum in any grab sample, compared with some other parts of the world.

More information about the cyanide removal and arsenic recovery processes can be requested from:

MR. WALTER J. KUIT
Cominco Ltd.
200 Granville Street
Vancouver, BC V6C 2R2
(604) 682-0611

DR. LORNE BALL
Group Leader - Chemical Metallurgical Research
Cominco Ltd.
Trail, BC
(604) 364-4419

COMINCO LTD.
Con Mine
Yellowknife, NWT
Canada XIA 2R3
(403) 873-2783
Jim Gowans
Mill Superintendent

ECHO BAY MINES, LUPIN PROJECT

The Lupin Project treating 1000 tpd ore is located about 450 miles north of Yellowknife NWT about 125 miles north of the nearest tree. Managing water at an operation in such a cold climate presents a challenge or two. This property was not visited but some interesting aspects relating to water management were referred to by KARKLIN (1984). The ore characteristics require a unique processing step which affects water needs too.

The Lupin orebody is classified as a stratabound iron sulfide deposit. Gold particles average about five microns in size and are found in the iron rich sulfide layer bounded by quartzites. Gold occurs predominantly as microscopic grains associated with arsenopyrite and pyrrhotite. Other minerals in the ore include chalcopyrite, actinolite, silver, pyrite and minor rare earths.

AERATION

Because of the large amount of soluble sulfides and ferrous iron the ore after grinding to 90% minus 200 mesh is subjected to three stages of aeration at elevated pH using lime.

Three preaeration tanks each 24 ft Ø X 26 ft high are used to aerate cyclone overflow from the grinding circuit directly in 32% solids. After aeration the pulp is thickened to about 60% solids in a single 40' thickener and then diluted to 45% solids using barrens. One of the three aeration tanks has in the meantime been converted into a recycled water tank as part of an expansion program.

Lupin ore contains 18.8% iron, 3.8% sulfur and 3.6% arsenic, and after aeration the following assays in the thickener overflow are achieved:

S^{-2} - 2 ppm

$S_2O_3^{-2}$ - 4 ppm

SO_4^{-2} - 30 ppm

This step is necessary to maintain recovery and to conserve reagents. Unoxidized sulfide would preferentially consume cyanide and oxygen which would slow the dissolution of gold.

The thickener overflow is recycled to the grinding circuit. Presumably almost all the soluble iron that came with the oxidized sulfide will be in the ferric hydroxide state in

the aerated pulp. It remains to determine what effect this iron hydroxide has on the process. Is it cyanide soluble? If so, it would undoubtedly tie up a considerable amount of cyanide as ferricyanide complex.

The effectiveness of the preaeration step is demonstrated by the fact that even with recycle of the thickener overflow from the preaeration thickener, and recycle of barrens only 1.0 lb NaCN/t, .20 lbs $Ca(OH)_2$ and 0.65 lbs lead nitrate are required to achieve 90% leach recovery of gold. Level of arsenic in the leach solutions are kept down by maintaining a "low" pH at 10.3.

1,000 tpd ore yields 2800 m^3/d solution after filtration and washing. Much of which is recirculated as barrens.

Water brought into the plant must be heated so as much water as possible is recycled in the plant until fouling occurs, then the minimum amount is bled. In this sense water management also overlaps into energy management in this cold climate.

Tailings are pumped five kilometers over frozen tundra down to minus 60°C across two valleys to the disposal site. This requires a special pump arrangement described by KARKLIN (1984).

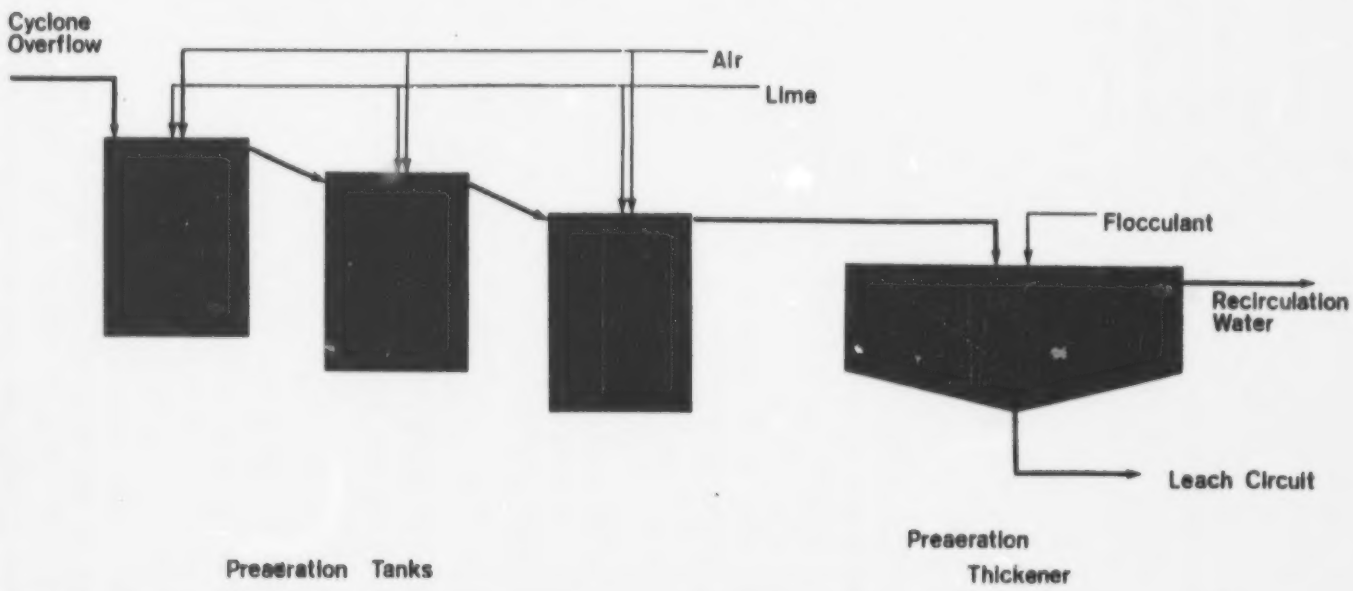
The tailings line is constructed of 6 inch, schedule 40 steel with flanged connections. The entire line has two inches of urethane foam insulation extruded around it, which is further protected with a 24 gauge galvanized metal jacket. The entire line is heat traced.

To enable line dumping in the event of power failure, dump valves are located at each of the two low points along the line. Vacuum breakers are fitted at the high points of the line.

The tailings pond is 250 acres in size and it is relatively shallow with low dam walls. Natural degradation of cyanide is found to be effective in such a large pond. Treatment of the final pond effluent is currently under study. The pond is designed to allow five years of retention prior to any effluent discharge. During the five year interval a program is underway to demonstrate that an environmentally acceptable effluent, as dictated by the terms of their water license, can be discharged. Two programs are currently underway. First is a detailed analysis of the aquatic environment that will receive the effluents. The second is a testing of various systems to determine the most effective process for treatment of pond effluents.

Washed filtercake is repulped with recycled water including high iron thickener overflow from the aeration step which presumably will tie up much of the cyanide as ferricyanide complex.

PREAERATION



KARKLIN

Additional information on the special water management considerations required for a mine-mill in such a cold climate can be obtained from:

ECHO BAY MINES LTD.
10180 101 Street
Edmonton, Alberta TSJ 3F4
(403) 429-5878
Graham Karklin

By 1985, the natural degradation phenomenon had been studied in great detail at the Lupin project. In winter, all effluent in the tailings pond is frozen solid. In spring, after the ice breakup, cyanide levels increase steadily in the decant solution until around mid-August when suddenly there is a dramatic reduction in cyanide levels. The steady wind and 24-hour sunshine over the shallow pond with a large surface area is ideal for natural degradation. It has not yet been firmly established whether the mechanism is CO_2 absorption to volatilize cyanide or a biological removal process of some sort, or both.

It is believed that ECHO BAY MINES plans to divide their pond into two areas; one for primary treatment in which ferrous sulfate will be added to precipitate arsenic, and a second polishing pond. It appears that the Lupin project will provide the first case study of a completely successful natural cyanide degradation demonstration in arctic conditions. To date, it appears that this operation will easily meet the North West Territories cyanide limit in their final effluent when their existing pond has to discharge effluent in a year or two. More information on this work could be requested from:

ECHO BAY MINES LTD.
10180-101 Street
Edmonton, Alberta T5J 3F4
(403) 429-5878
Hugh Wilson
Manager, Environmental Resources

LAC MINERALS - LA MINE DOYON

La Mine Doyon, a joint venture between LAC MINERALS LTD. AND SOQUEM, the Quebec Government owned mining company, is located in Quebec. This account is based on sketchy information but indicates a potentially useful way of enhancing natural degradation.

One of the challenges faced at La Mine Doyon on account of the cold climate is dust control. The ore is high in silica and dust could be hazardous to operators. Because of the very cold climate air must be preheated before it is brought into the mill. Also, for energy conservation reasons, the mill is well insulated and carefully winterized. Consequently the exchange of air required for dust removal is an energy drain. The La Mine Doyon mill has 30,000 cfm dust collecting capacity which the company would like to double.

At La Mine Doyon ore is ground and leached in cyanide then recovered by Merrill-Crowe. Barrens are recycled so most of the cyanide stays in the gold circuit except that which is not washed from the tails in the solid-liquid separation stage. Tailings are pumped to a pond from which the decant is discharged as a final effluent into Ruisseau Lac Bellot where it is diluted. This discharge of effluent resulted in an increase in cyanide and copper values in Lac Bellot. The discharge had to discontinued while ways cyanide destruction techniques were researched.

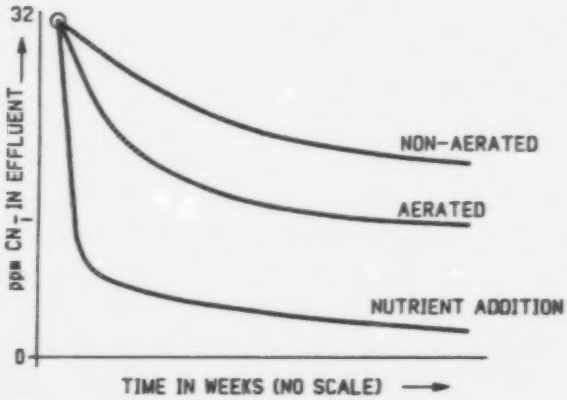
La Mine Doyon testwork, for which at this time only qualitative data were made available to this investigation, indicate that through aeration, and particularly through aeration and nutrient addition, natural degradation can be greatly enhanced.

No details were obtained on the nature of the nutrients nor on how the concept will be applied in practice, or whether it is temperature dependent i.e., seasonal in application. This work was still in infancy but appears promising.

More information on La Mine Doyon and the aeration-nutrient addition tests could possibly be obtained from Lac Minerals, bearing in mind that details may be considered proprietory until a process has been developed and tested.

LAC MINERALS LTD.
Post Office Box 670
Kirkland Lake, Ontario
Canada P2N 3K2
(705) 567-3358
Telex: 067-82515
George Hope
Chief Metallurgist

ENHANCED NATURAL DEGRADATION OF CYANIDE



LA MINE DOYON EFFLUENT
(Without Treatment)

	Tailings Dam Pond	Final Effluent[1]	Dilution in Ruisseau Lac Bellot	Lac Bellot After Effluent Discharge for Short Time
pH	11.9	11.6	10.5	6.99
Pb	0.05*	0.05*	0.05*	0.05*
Zn	1.15	1.09	0.13	0.01
Cd	0.005*	0.005*	0.005*	0.005*
Ni	0.5	0.67	0.05	0.05*
Fe	0.84	0.85	0.88	0.50
Hg^+	0.52	0.04	0.01	0.07
As	0.003*	0.003*	0.003*	0.003*
CN	39	38.5	3.3	0.24
S/S	1.0*	1.0*	5.0	1.0*
CN Available	39	38.5	3.3	0.20

Note 1: Before enhanced natural degradation was tested.

\+ in micrograms per liter

* less than

Information on the enhancement of natural degradation of cyanides in barren bleeds by aeration may be requested from:

WASTEWATER TECHNOLOGY CENTER
Environment Canada
Post Office Box 5050
Burlington, Ontario
Canada L7R 4A6
(416) 637-4370
J. W. Schmidt
L. Simovic

Information on test programs which engineered Typha Lalifolia "cattail" and other aquatic macrophyte bogs for relatively large scale tests for sewage treatment at Listerwell and Cobalt, Ontario, can be obtained from:

MRS. IVY WILE
Assistant Director of Hazardous Contaminants Division
Ministry of the Environment
40 St. Clair Ave. W.
Toronto, Ontario M4V 1P5

MR. GORDON MILLER
Ministry of the Environment
83 Algonquin Blvd. N.
Timmins, Ontario
Canada
(705) 264-9474

This marsh concept may prove valuable in developing an enhanced natural biological cyanide degradation system which would also help polish precipitated metals from effluents.

UNITED STATES

Water management for US gold and silver mining and milling operations focuses on each of the main aspects of water management, depending on the site specific nature of the operations:

Removal of suspended solids: Placer Mines in Idaho, Colorado, Alaska, California, etc.

Shortage of water and need to conserve: Heap Leaching operations in the Mojave, in parts of the Colorado plateau, and Nevada.

Removal of cyanide and metals from effluents: Homestake Mining Company, Lead, SD; Noranda Grey Eagle Mines, Inc., California Superior Mines, Inc., Stibnite, Idaho.

High TDS in available water: American Mining Co., Amboy, CA

Containment of effluents, zero discharge: Pinson Mining Co.; Freeport Gold Company; Cortez Gold Mines, Carlin Gold Mining Co.; Candaleria Silver Mine; McLaughlin project, California, and many others.

WATER MANAGEMENT FOR PLACER OPERATIONS

Placer gold recovery varies in size from very large dredging operations processing up to thousands of tons per hour down to one man part-time operations using sluices of all kinds.

Placer operations are frequently located in or alongside creeks and streams, for that is where most placer deposits were formed in the first place. Gravity concentration techniques require a lot of water and the stream is usually the best and most convenient source of the operation's water needs.

Sometimes there is not enough water in the stream and so water must be recovered and recycled. Other times water is drained from the placer tails and discharged back into the creek. In both cases suspended solids represent a problem. Recycled water builds up suspended solids, including clays and root particles, etc. until it may interfere with the recovery process - especially with some of the more sophisticated enhanced gravity centrifugal concentrating devices such as the Knelson Bowl Concentrator.

In the USA the Surface Mining Control Act SCMRA directly affects placer mining operations. It requires, among other things, that seepage or drainage from the operation must be treated to reduce suspended solids and that this water may not enter a natural stream unless it meets a series of standards. For most states these regulations require that suspended solids be reduced to below 35 mg/l (daily average) and below .70 mg/l for a 30-day sample.

The most convenient way to meet the suspended solids (TSS) criteria is to provide sedimentation ponds as needed to remove particulate matter. These ponds, however, often have a limited size and lifespan dictated by topography, the scope of the mining or processing operation and the quality of sediment in the water to be treated and discharged.

If the collected water has a higher SS than can be directly discharged, and if the flow rate is too high for a satisfactory detention and settling time, the mine or plant operator has to make some decisions about the ponds before a situation develops that could close down his operation or result in a fine. There are two main options:

- To build additional ponds.
- To install a flocculant treatment system to increase settling rates.

Building additional ponds may not be possible because of topographical constraints and may also be expensive. Addition of a suitable chemical flocculating agent to agglomerate fine particles into larger ones and increase their settling rate also results in improved sludge compaction.

The technology needed to set up a flocculant treatment system for a settling pond involves the need to know the flow rate, correct flocculant type and the correct dosage. Such systems involve metering pumps, mixing devices to prepare polymer solutions, etc. and may also therefore require a power supply and a source of makeup water at the site, as well as a suitable mixing zone where the flocculant and stream come in contact before dispersing into the pond. This can be both impractical and expensive, especially for a small scale mining operation. Time requirements to monitor and maintain the system, adjust dosage levels, replenish the polymer supply etc. can be excessive.

An innovative new flocculant polymer in gel form meets the following advantageous criteria:

- Does not require electricity, piping, pumps, tanks or other preparation and delivery equipment.
- Functions unattended for days at a time with minimal operator attention.
- Responds to changes in flow rates to keep dosages relatively constant.
- Shows visually when replenishment is needed.
- Is in a form that can be carried by hand to unaccessible locations.

The Hercofloc logs are available in a range of ionic functionalities and can be selected to match the needs of each system. Each gel log weighs 40 lbs and measures 18 inches long by 9 inches in diameter.

The application of Hercofloc logs mainly in remote coal mining operations was described by MOORE (1982) and these should be ideally suited for the medium and small scale placer miner and where suspended solids in recycled water interfere with the performance of equipment such as the Knelson Bowl Concentrator. More information on the product can be obtained from:

HERCULES INCORPORATED
Water Management Chemicals
90 Market Street
Wilmington, DE 19899
(302) 575-6500
James F. Moore
T. Davis
K. Fletcher

HERCLES INCORPORATED
One Maritime Plaza
Golden Gateway Center #1250
San Francisco, CA 94111
(415) 986-2535

HERCULES INCORPORATED
Water Management Chemicals
33092 Highway 550 North
Durango, CO 81301
(303) 247-0335

HEAP LEACHING AND MILLING

The industry is distributed mainly through the western states where the climate ranges from extremely arid - e.g., in the Mojave Desert, to arid with cold winters as in the Nevada highlands to warm as in Arizona, and wet with snowbound winters in Idaho.

Although there are currently no cyanide limits under the Federal RCRA regulations governing solid waste disposal at this time, it is expected that these will ultimately be developed under a new set of regulations designed to protect groundwater quality. Regulations do limit cyanide levels in effluents discharged to surface waters, however.

Incentives to practice water management and to apply water treatment at gold and silver mining and milling operations vary from the need to recycle every possible drop of water due to lack of availability, to the economic advantages of reagent savings through recycling to the need to comply with federal and/or state regulations. In addition some operators must make do with high TDS or hard water that must be treated before use.

Regulations that have an impact on water management range from the Federal "Clean Water Act" of 1977 with its BCT, BPT, BAT and NSPS regulations; the RCRA law and associated regulations governing solid waste disposal (applicability of which to mine and mill waste has been temporarily suspended). Discharge to surface waters is regulated by the EPA or the agreement states under NPDES regulations.

The trend is increasingly to transfer responsibility for regulating mining industry effluents and waste disposal to state governments as long as they are at least as stringent in their regulations and their enforcement as the Federal regulations. This has added greatly to the confusion and complication of securing permits for mining operations in many states because the state and local regulators often are not experienced in mining and metallurgical wastes and tend more often than not to try to get "unrealistic" regulations passed into state law which would make it impossible to mine or mill ore without becoming a criminal in the process. California is a trendsetting state and how this issue is resolved there - especially the rules dealing with "hazardous waste" disposal will have an influence on operations in many additional states - such an influence can already be seen in Washington, Montana, South Dakota, and even as far afield as Pennsylvania.

The problem is that different regulations are now emerging in each state and these are extremely complex. It would take a full time legal staff to keep up with the regulatory developments and since few of the regulators, the law makers nor the lawyers hired by the mining industry to fight their case have experience in mining and mineral processing, the whole ball of semantics wax seems to have got somewhat out of hand. In addition to the complexity of state regulations, the Federal CERCLA 'Superfund' regulations and the emerging EPA groundwater protection regulations are expected to have potentially serious consequences.

Examples of the severity and complexity of some of these regulations are provided in Chapter 7 on Regulations and Regulatory Trends. These include an excerpt from a California Regional Water Quality Control Board permit issued to ASARCO for the Waterloo silver operation in that state, and an NPDES permit issued to Homestake Mining Company

McCall, Idaho
Star-News
(Cir. W. 2,106)

APR 4 1984

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House panel probes wilderness mines

By Mike Stewart
The Star-News

A congressional inquiry into federal management of Thunder Mountain mining activities has been initiated, according to a congressional staff member.

The probe has been started by Rep. John Sieberling, D-Ohio, chairman of the House Subcommittee on Public Lands, according to Andy Wiessner, counsel for the subcommittee.

"We sent a letter to the Forest Service asking them about what happened there," Wiessner said.

While the inquiry is aimed at the events surrounding past spills of mining tailings into creeks in the area, it also addresses the broader issue of management policies toward mining operations located on lands adjacent to wilderness, Weissner said.

Sherry Wagner, public information officer for the Payette National Forest, said Friday that the forest had received the inquiry, but that it did not specifically address last fall's spill at the Golden Reef mine.

Rather, it requested general policy information on how such operations are managed from the federal government's point of view.

Information to be included in the response has been forwarded to Forest Service headquarters in Washington, D.C.

The Golden Reef spill took place last September or October, when several tons of sludge scooped out of settling ponds at the mine slid into Mule and Monumental creeks.

The sludge wiped out salmon and steelhead spawning beds in the creeks, according to Idaho Department of Fish and Game officials.

A settlement among Golden Reef operators, the Idaho Departments of Health and Welfare and the Idaho Department of Lands followed. The mine's operators paid a $5,000 fine and $20,000 for damage done to the streams.

While Sieberling's inquiry is directed at the Forest Service, that agency, with the state lands and health and welfare departments, are only three of the half-dozen or so agencies that have jurisdiction over different aspects of Thunder Mountain mining operations.

That fact helped foster claims made at the time by the Idaho Conservation League. The ICL said said government agencies were not watching the situation closely enough and were not being harsh enough in handing out penalties for violations.

Later, however, the ICL supported the settlement between the state of Idaho and the mine operators.

In criticizing the way the situation was handled, Wiessner said Sieberling was most interested in what was being done to prevent a repeat occurance.

for the McLaughlin project. Usually owners of a new mine and mill must apply for, negotiate and comply with numerous permits from various bureaucratic authorities. GUINIVERE (1984) pointed out that Homestake Mining Company had to apply for 281 permits in all for the McLaughlin project in California but not all of these related to water and effluents. The situation was complicated by the fact that the operation covering a 25 mile long project site extends into three counties each with their own regulatory authorities. GUINIVERE (1984) estimated that the overall environmental and permitting costs for the $250 million project which took four years to permit amounted to $22 million in all including:

$6 million:	EIR preparation and environmental backup.
$5 million:	Dams for sediment control.
$11 million:	Special design features, dust collection and runoff control during construction and operation.
$22 million:	Total

The McLaughlin Project is described in summary form in Appendix I based on published information. FERGUSON, et al. (1983) presented an interesting paper on how the water balance for this new operation was modelled. Their paper is inserted in Chapter 10.

Inserted below is an estimate by NORANDA of the additional costs incurred at the NORANDA GREY EAGLE MINES INC. 500 tpd operation in California to correct an unexpected minor cyanide seepage from their tailings pond which was in fact found to have resulted in negligible, if any, damage to the environment. The mitigating measures were estimated to cost an additional $10,498,000 on top of an original capital cost for the whole project of $20 million. The $10.5 million includes additional operating costs for the additional facilities and a contingency of 25%. This works out to an approximate cost of $11.66 per ton of ore for the remaining life of the mine.

Liquid effluents discharged to surface waters are governed by NPDES permit requirements.

Permits for all the gold and silver cyanidation plants in the USA located where it is climatically possible call for "zero discharge" of effluents. This is readily achievable in the low rainfall areas of the country where most of the gold mining operations are located.

Federal RCRA solid waste disposal regulations do not apply to mining and milling wastes for the time being, but the industrial states, led by California, apply their own hazardous waste discharge regulations to mine wasterock and mill tailings disposal.

8 July 1983

INFORMATION MEMORANDUM

FROM: M. Wasserlauf

TO: S. Wulf

SUBJECT: NORANDA GREY EAGLE MINE - PROJECT N-8321-3B - DESTRUCTION OF CN IN TAILINGS SLURRY - METALS STABILITY

SUMMARY

Leaching tests were conducted on Grey Eagle tailings after treatment for CN removal by SO_2 oxidation. Results of these tests indicate metal (Cu, Zn, Fe) levels of < 1 mg/L at pH 5.5. At a pH of 4.5, levels were significantly higher, with Cu and Zn concentrations ranging from 2.5 to 22.3 mg/L.

LEACHING TESTS

Grey Eagle tailings were treated for CN removal by SO_2 oxidation. Results of these studies were reported previously([1]). Metals anlaysis were subsequently carried out on filtered tailings decant before and after CN detoxification studies. The results were as follows:

	Sample	Cu (mg/L)	Zn (mg/L)	Fe (mg/L)
	Mill Tails Decant	228.6	11.35	5.4
Tails Decant	After Alkaline Chlorination	0.4	0.27	6.1
Tails Decant	After SO_2 Oxidation	3.1	0.11	0.5

The tailings after CN removal were then subjected to leaching tests. Samples of tailings solids (see Table 1) were placed in Erlenmeyer flasks, with volume then adjusted to 250 ml with distilled water. Sulphuric acid (1N) was added to adjust the pH to 4.5, and 5.5, and the flasks were placed in a Burrell Wrist Action shaker and agitated at 100 movements/minute for a 24-h period. The pH was monitored, and adjusted to the initial values continuously during the test. Subsequently, the liquid was filtered, and analyzed for Cu, Zn and Fe.

RESULTS

The results of the leaching studies are summarized in Table 1. As indicated, Cu and Zn levels were significantly higher at pH 4.5 levels than at pH 5.5 levels. Iron levels did not change.

Reference

1. Wasserlauf, M., Destruction of CN in Tailings Slurry, Noranda Research Centre, Information Memorandum, June 3, 1983.

TABLE I

RESULTS OF GREY EAGLE LEACHING TESTS

Item	pH 4.5 Tests		pH 5.5 Tests	
	Ratio *		Ratio *	
	2.5 : 1	10 : 1	2.5 :.1	10 : 1
Cu (mg/L)	22.3	6.8	1.1	0.7
Zn (mg/L)	7.9	2.5	<0.1	<0.1
Fe (mg/L)	<0.6	<0.6	<0.6	<0.6
Initial Volume (mL)	100	25	100	25
Dry Weight (gms)	90.4	22.4	67.7	25.2
Volume of IN H_2SO_4 added	20	5.1	10.0	3.9

* Ratio based on volume of slurry after dilution to initial tails slurry (at 50% solids).

NORANDA GREY EAGLE MINES

ESTIMATED COSTS OF REMEDIAL MEASURES

(1983 $)

	Capital	Operating	Total
1. Construct tailings dam third stage one year early $2,093,000 @ 10%	$ 200,000	$ -	$ 200,000
2. Flow reduction system	300,000	60,000	360,000*
3. New pumpback system	275,000	60,000	335,000*
4. Modification to water treatment plant	125,000	-	125,000*
5. Construction of toe-of-dam plant	1,900,000	4,500,000	6,400,000*
6. Sealing mine adit	75,000	-	75,000*
7. Water treatment costs due to pumpback system	-	200,000	200,000
8. Production interruption to install temporary pumpback	-	400,000	400,000
9. Engineering and research (Task force, consultants, and legal)	600,000	-	600,000
Sub-total	$3,475,000	$5,220,000	$8,695,000
*Contingency 25% of $7,210,000	650,000	1,153,000	1,803,000
Total	$4,125,000	$6,373,000	$10,498,000

Note: A. These costs exclude interest charges on the additional capital required to complete the program.

B. Approximate cost per ton: $\frac{\$10,498,000}{900,000 \text{ tons}} = \$11.66/\text{ton}$

There are no current Federal regulations governing cyanide limits in effluents or tailings, although heavy metals are regulated at low levels which indirectly regulate cyanide which must be removed to achieve the base metal limits. NPDES permits for effluent discharge, however include very strict cyanide limits in the few cases where they are granted for gold cyanidation effluents.

The Homestake Mine at Lead is of the few operations which is permitted to discharge an effluent subject to meeting extremely strict effluent limits for cyanide, metals, and ammonia as shown in the table inserted below. Despite enormous expense and effort these limits have yet to be met, although the performance of their new biological cyanide destruction plant using innovative technology will soon be known. Homestake Mining Co. has developed a new biological treatment process for cyanide destruction and metal removal. This is expected to be the "state of the art" in cyanide destruction where it is applicable. It is believed that an agreement has been reached with regulatory agencies whereby the final effluent permit requirements at this site will be tailored, if necessary, to the performance achievable provided in-situ bioassay shows that its effluent is environmentally compatible.

Homestake Mining Company discharges a combination of minewater and mill tailings decant effluent which requires a very expensive treatment facility to even approach the required effluent limits. Their plant and the new technology is briefly discussed in the chapter on cyanide destruction.

Duval Corporation's Battle Mountain operations which recover gold from an ore with relatively high levels of cyanide-soluble copper uses alkaline chlorination to decompose cyanide and precipitate base metals before discharging the tailings via a series of drop-boxes to the desert valley below the mine.

Some water management practices observed at US gold and silver recovery operations are summarized below.

HEAP LEACHING

Heap leaching of low grade oxidized gold and silver ores originated as a practice in Nevada. Agglomeration of fines requires that the ore not contain more than about 11% moisture which means that it must be pretty dry.

CANDALARIA SILVER HEAP LEACH, NERCO METALS, HAWTHORNE, NV

The Candalaria Partners operation was described by VAN ARSDALE (1984). 7500 t/d (metric) of ore are placed on the heaps which are irrigated with a 1.5 Kg NaCN/ton

solution at a rate of 14,500 t/d solution flow through the plant, or 0.012 m^3/h per m^2 (0.005 gpm/ft^2) through sprinklers.

In the fall, a wintertime leach area is constructed of new ore. This is fitted with 100 mm (4 inch) diameter perforated pipes on 9 m (30 ft) centers buried about 0.9 m (3 ft) into the ore. During freezing conditions solution is brought to these pipes by an above ground system similar to the normal spray system except that flexible rubber hose is connected from the spray points to the underground pipe. This permits a continuation of production at a reduced rate. Due to the solution flow configuration only 65-70% of normal production is maintained during extended periods of cold weather.

Candalaria uses NaOH for pH control.

Net water consumption is reported by VAN ARSDALE (1984 personal communication) to be 200 US gpm which works out to 1090 m^3/d of solution or 0.145 m^3 water per ton ore treated which makes this an extremely water efficient operation.

There is no barren bleed or effluent discharge of any sort. Heap pads are clay lined - and the drainage ditches and ponds are hypalon lined so seepage will be minimal. The operation is designed and operated for zero discharge.

The water source is 4.5 miles from the plant and it contains some carbonates.

Drew Chemicals Millsperse 802 is applied as a scale inhibitor at the rate of 50cc per minute to the barren pond to minimize scale formation in the heaps.

PINSON MINING COMPANY, WINNEMUCCA, NEVADA

Most Nevada heap leaching operations shut down for several months during the winter when the heaps freeze over.

PINSON MINING COMPANY operates a conventional CIP plant and, in addition, it heap leaches low-grade ore. What is most interesting is that they operate the heaps right through the winter, allowing a 3-4 foot ice layer to build up on top of the heaps. The ice is not a continuous sheet and allows the cyanide to reach the heap material and percolate through it.

To apply spray solution through the thick ice capping, sprinklers are mounted on 4' vertical stems so that the sprays can work over the ice.

Remarkably, cyanide does not seem to be locked up in the ice, possibly because some form of freeze-desalination is at work.

During the frozen months, the solution application rate is cut back slightly, and the production rate of gold from the heaps is slower than in summer. The important point is that cash flow from the heaps does not stop.

Because of the large inventory of water tied up in the ice cap, provision must be made to contain it during the spring melt. This means installing an adequate pond storage capacity. PINSON MINING COMPANY carefully computes their water balance and inventory.

PINSON MINING COMPANY
Post Office Box 192
Winnemucca, NV 89445
(702) 623-5036
R. Bruce Thorndycraft

AMERICAN MINING COMPANY, AMBOY, CALIFORNIA

AMERICAN MINING COMPANY operates a heap leaching venture in the Mojave Desert. Available water in this region is very high in dissolved solids, and this has brought most attempts at heap leaching in the area to their knees.

AMERICAN MINING COMPANY, however, is able to operate profitably using a water which is saturated in calcium chloride--to the extent that the salt crystallizes out in the drainage ditches. Carbon columns are used for gold recovery, but it has not been revealed how they keep the heaps and carbon beds from cementing up or the carbon from fouling. More information could be requested from:

AMERICAN MINING COMPANY HL
Post Office Box 75
Amboy, CA 92304
Telephone: Amboy No. 4

EDMUND CAMPBELL
Consultant
Box 178
Haileybury, Ontario
(705) 672-3460

CORTEZ GOLD MINE, CORTEZ, NV

This operation receives 5" of rain per year with an additional 9" per year rain equivalent as snow and 60" per year evaporation.

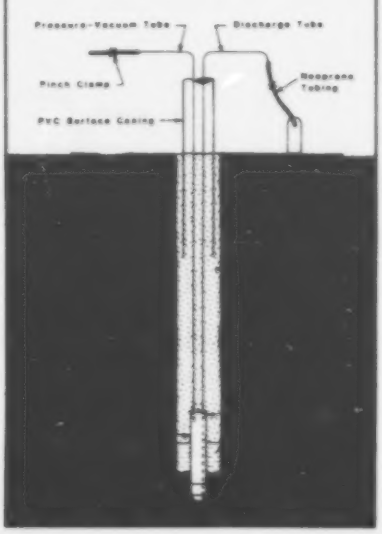
The operations treats a combined 2,000 stpd by a carbon-in-leach and 4,000,000 stpa by heap leaching.

USE OF PRESSURE/VACUUM LYSIMETERS FOR OPERATIONAL AND ENVIRONMENTAL MONITORING AT HEAP LEACH MINING FACILITIES

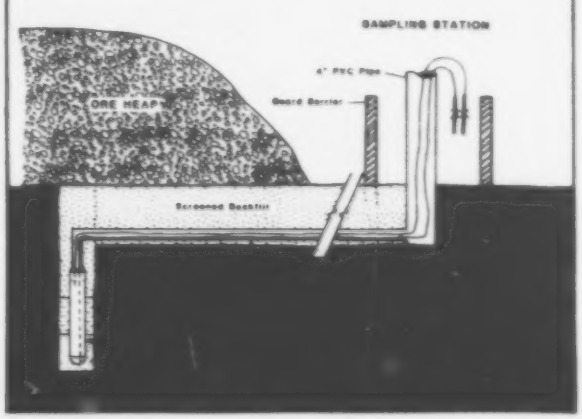
With the growing interest in heap leach techniques to recover precious metals from low grade ores, the monitoring of leach solution flow balance is a primary concern for both production efficiency and environmental protection. When leaching marginal grade ores, every drop of leachate becomes as precious as the metals themselves. In many cases, a loss of five or ten percent of leach solution through liner leaks can be the difference between success and failure. Leaks into the subsurface can result in extensive liabilities such as contamination of soils and ground and surface waters. Clean-up costs can be quite significant and future mining development may be prevented by concerned government regulatory personnel.

Envirologic Services International (ESI) has recently adapted an agricultural soil water monitoring technique as a method to detect the loss of leach solution. The pressure/vacuum lysimeter has proven to be a cost-effective monitoring tool that satisfies both leachate flow balance and environmental protection concerns. With proper planning, the installation of lysimeter units beneath the heap leach pads and solution ponds can give quick, reliable leakage detection. A lysimeter under a leach pad can detect a leak within several days or weeks, depend-

DIAGRAM OF PRESSURE-VACUUM LYSIMETER INSTALLATION



TYPICAL LYSIMETER INSTALLATION AT A HEAP LEACH MINING OPERATION



ing on the location and magnitude of the leak. The same leak may take months or years to be detected by perimeter monitor wells, and then only after contamination of vadose and ground water has occurred.

For maximum reliability and minimum cost, the installation of the lysimeters and their sample lines should be completed before the final emplacement of clay and synthetic liners. In most cases, the installations are shallow, three to five feet, and easily completed in a few hours. Sample lines are quickly laid in trenches dug by trenching machines. The lines can be covered with a sand backfill or run through one inch conduit prior to backfill. Permanent sample stations can then be constructed away from the leach pads, ponds and traffic right-of-ways.

Details on the installation and use of pressure/vacuum lysimeters were provided in a paper titled "Several Uses of Pressure/Vacuum Lysimeters at Mining Facilities and Hazardous Waste Sites" by William R. Bond and Jim V. Rouse, of ESI, presented at the October 1984 SME meeting in Denver. (Copies available upon request.) The paper stressed that pressure/vacuum lysimeter units are a cost effective, simple monitoring tool to be used for operational control as well as regulatory monitoring. At marginally operating heap leach mining facilities, lysimeter vadose monitoring can spell the difference between success and failure in today's unsettled metals market.

Envirologic Services International (ESI) is a division of J.H. Kleinfelder & Associates, a California-based geotechnical and environmental engineering firm specializing in hazardous wastes investigations, and materials and soils engineering. ESI provides environmental consulting services to the mining and minerals industries in the areas of baseline and site monitoring, pollution control, and geohydrologic/geochemical investigations for hazardous waste sites.

ENVIROLOGIC SERVICES INTERNATIONAL
A DIVISION OF J. H. KLEINFELDER & ASSOCIATES
2425 S. Colorado Blvd., Suite 200
Denver, Colorado 80222
303/759-2611

OTHER OFFICES
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Average net new water intake is 120 US gpm from wells at a pumping cost of $5000/year. The wells are located at the plantsite. This means that an average of 3142 stpd or 2856 t/d ore are processed using 655 m^3/d net fresh water or 0.23 m^3 water per ton ore net use. 500 gpm solution decant is recycled to the process from the mill tailings, and an average of less than 5 gpm barrens is bled to maintain a solution balance.

The operation is designed and run for zero discharge so no effluent treatment is required.

Because reclaim solution containing cyanide is used in the grinding circuit and because the ore is mildly preg-robbing Cortez is testing the use of NaOCl to destroy cyanide in the tailings reclaim solution. If installed, the cyanide decomposition step would cost $0.08 - $0.10 per ton ore.

Anti-scaling reagent Drew Chemicals, Millperse 802 is added at the rate of 2-5 ppm to the carbon elution circuit.

FREEPORT GOLD COMPANY

The Jerritt Canyon Mill near Elko, Nevada treats 3500 st/d (1,300,000 stpa) ore by carbon-in-pulp. The refractory preg robbing ore is first treated with chlorine and then leached in cyanide.

No water is recycled from the tailings dam and water costs $180,000 - $200,000 per year at a unit cost of $0.33/1000 gallons. Water is pumped from wells 2 miles from the plant, i.e. 600,000,000 US gpa = 2,272,000 m^3/yr which works out to a total net usage of 1.75 m^3 per ton ore.

Rainfall amounts to 12 inches per year with an estimated additional 12" as snowfall precipitation, and evaporation is 40" per year.

A barren bleed of 9,000 US gallons/day (34 m^3/d) is discharged 5 days per week from the eluate to bleed zinc.

Although no tailings decant solution is recycled to the plant, 1200 US gpm is pumped through carbon columns to reclaim some incremental gold.

The mill-tailings system is operated for zero discharge which has been achieved from 1981 to 1984. Since fresh water is used with no recycle, no anti-scaling reagents are needed or used.

Tailings decant solution is not recycled due to the high chloride levels.

GETTY MERCUR MINES, TOOELE, UT

The Mercur Mine was first worked one hundred years ago. The ore is refractory because of its preg-robbing characteristics. It also contains cyanide soluble thallium.

The Getty Mercur Mine's operation uses a carbon in leach process to overcome the preg robbing-nature of the ore. However, when water is recycled from the tailings pond, it contains residual cyanide which, if used in the ball mill, would start leaching gold which, in turn, would be robbed by carbonaceous species in the ore. Consequently, it is necessary to remove cyanide from the recycled tailings solution. This is achieved by reacting the solution with sodium hypochlorite before it is returned to the mill. The Getty Mercur Mine also is a zero discharge operation. In recycling solutions, cyanide is destroyed for the reason given. Thallium is removed from the system by washing it from the activated carbon used to recover gold, which is achieved with cold nitric acid. The acid washwater is neutralized and Na_2S added to make sure all thallium is precipitated. The precipitate is disposed of in the tailings pond.

This operation also has installed bentonite stabilized sand linings under its tailings pond which are super-impermeable. The Getty Mercur mill is described by WICKS and BREWER (1984). The authors can be reached as follows:

GETTY MINES LTD.
5250 South, 300 West, #300
Salt Lake City, Ut 84107
(801) 263-3850
Frank D. Wicks

GETTY MERCUR MINES
Post Office Box 830
Tooele, UT 84074
Robert E. Brewer

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CHAPTER 56

RECOVERY OF INCREMENTAL RESOURCE VALUES FROM EFFLUENTS

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RECOVERY OF INCREMENTAL RESOURCE VALUES FROM EFFLUENTS

During the course of this investigation, several examples of resource recovery from effluent streams were encountered. In some cases, the recovery process was installed solely with the motive of making a profit from the sale of the recovered resource--e.g., gold recovery from the effluent from gold mine-mills using activated carbon or the recovery of copper by SX from El Teniente's copper mining effluents in Peru. Another example is the recovery of uranium fr[illegible]water.

In other cases, metal values are recovered in sludges as a result of the treatment of effluents to meet discharge water quality limits, and the values in these sludges are recycled to metal recovery operations as a means first of gaining a credit for the metal values but, often more importantly, as the safest way of disposing of the sludges. Examples of this type of operation are COMINCO LTD., Trail, B.C., NORANDA at their Mattabi Division, Ontario, and several others.

In still other cases, resource values are recovered, but their value or the cost of recovering the values and possible metallurgical problems that would be introduced as a result of returning the precipitate sludges to the primary metal recovery process do not work out to be economically attractive--as, for example, has been found at AMAX's Climax Molybdenum operations in Colorado where molybdenum can be recovered in their water treatment plant by ion exchange.

Some examples of gold, uranium, and other base metal recovery are summarized below. The first of these is a purely speculative concept still at this stage and has not yet been studied in detail. It is a "long shot" but deserves attention because it seeks to recovery salable energy in transportable form from acid mine drainage and pyrite. Acid mine drainage and sulfides in tailings that cause it are the most serious causes of pollution that will seriously affect the economics of the mining and milling industry in some parts of the world where tailings impoundments and effluent treatment plants will require "perpetual" maintenance. Therefore, any concept that has even a remote chance of making a salable product to generate revenues that could offset the cost of tailings management and treatment of acid mine drainage has a very important possible impact. Therefore, although it is the least defined or developed, the concept proposed by Professor Al Stiller of the University of West Virginia deserves to be first on the list.

1. Hydrogen from Acid Mine Drainage and Pyrite: Concept

Professor Albert Stiller has proposed for further testing and development the concept of using acid mine water at pH 2, pyrite, and scrap iron as components of a galvanic cell that would generate hydrogen which would be recovered as a salable fuel resource.

PROFESSOR AL STILLER
Dept. of Chemical Engineering
University of West Virginia
Morgantown, WV
(304) 293-5398

Of all the resource recovery examples discussed here, this one is the least developed. Granular or briquetted pyrite would be immersed in AMD as one electrode and, when brought in electrical contact with shredded scrap iron as the other electrode, hydrogen would be generated. A process to collect this hydrogen has yet to be developed. Possibly the use of sonic resonance as proposed by Al Bodine of California would help release hydrogen bubbles from the pyrite surface, thereby keeping its surface more

reactive. Randol International Ltd. has no data on the possible economics or practicality of this process still raw concept.

2. Sulfur from Acid Mine Drainage: Concept

Biological processes have been suggested as one future way to treat acid mine drainage. Anaerobic biological processes yield H_2S from sulfate ions in acid mine drainage, but there are aerobic processes that would generate sulfur which, at least in some parts of the world, e.g., Brazil, is an imported raw material.

Although processes have been conceptualized for sulfur recovery from sulfate solutions, so far no commercial-scale process has been identified, and this possibility is identified as a concept for possible future investigation and development. At this time, not enough is known to be able to even start to evaluate the possible economics of such a process. The possibility of employing rotating biological contactors, for example, for such a process may offer some opportunity to make it more practical.

GOLD FROM MINE-MILL EFFLUENTS

3. Giant Yellowknife Mines Ltd.

Giant Yellowknife Mines Ltd. is located close to the Arctic Circle on the shores of the Great Slave Lake in the Northwest Territories of Canada. It processes 1,215 short tons of ore per day by flotation to yield just over 100 short tons/day of concentrate which is roasted. The calcine is washed and cyanide leached. The tailings pond receives flotation tailings, cyanide-leached calcine tails, and a cyanide leached fluedust tail. Tailings pond liquids are decanted and treated by alkaline chlorination to destroy cyanide and precipitate base metals, then treated with ferric sulfate to remove arsenic as ferro arsenate which is precipitated and settled in a final settling pond before being decanted and discharged to a creek flowing into Great Slave Lake. This final decant solution flows by gravity through three carbon adsorption columns in series for gold recovery.

Effluent Gold Plant Capacity:	312 million gallons (1,415,000 m^3/d) were treated in 1983, with a gold content of over 3,000 oz., clearly a worthwhile target.
Operating Season:	5 months during summer only. The total volume of solution is treated over a short season; this has been taken into account in the plant design.
Number of Adsorption Stages:	3 stages.

Design of Columns:	Upflow Cortez-type columns with 2% open area in the plate distributors.
Feed Solution Tenor:	pH 7.5 with 0.0008-0.002 oz. Au/t.
Carbon Loading:	65 oz. gold per ton carbon on loaded carbon shipped for elution.

Gold Recovery from Carbon:

Formerly loaded carbon was shipped to a smelter which worked out at a cost of over C$5,000 per ton carbon in road freight ($344/t), the cost of the carbon smelted, smelter charges, and recovery losses.

Giant is evaluating the cost of installing their own carbon elution and regeneration plant at the site. Meanwhile, the most economically attractive approach is to ship the carbon for elution to a custom elution plant in the U.S.A.:

N. A. DEGERSTROM, INC.
N 3303 Sullivan Road
Spokane, WA 99216
(509) 928-2987
James A. Bradbury
Chief Metallurgical Engineer

After elution, the carbon is sent for thermal regeneraion in Oregon before being returned to Yellowknife.

Discussion:

Gold recovery at Giant Yellowknife could be inserted before or after the cyanide treatment plant. In this case, it was inserted after water treatment with no detrimental effect on gold recovery. This indicates that gold cyanide is not decomposed in the alkaline chlorination step.

Recovering gold by carbon adsorption after cyanide destruction has other advantages. Firstly, most of the base metals are removed so the carbon adsorbs less of them, and there should be less interference with gold adsorption.

Giant tailings are frozen for much of the year. Even in summer, only the upper layers of the pond thaw so the decanted solutions drained from the tailings remain cold. At low solution temperatures, the density is higher, and this should be taken into account when designing fluidized bed adsorption units.

Giant has experimented with several carbon adsorption systems and found that unless carbon is fluidized correctly, adsorption recovery is poor.

The economics of elution and regeneration of carbon on a small scale is poor considering capital and labor requirements. For a conventional elution and regeneration plant to treat one ton carbon per week, the cost was estimated at C$400,000.

4. Vaal Reefs Exploration and Mining Co. Ltd.

In the South African gold mining industry, there are a number of process streams in which gold values of less than 1g Au/t solution are recoverable using carbon columns. DAVIDSON and STRONG (1983) reported a new fixed-bed carbon adsorption system in which barren solutions of less than 0.01 g/t can be achieved using activated carbon.

RANDOL (1983) described the fixed-bed carbon column installed at Vaal Reefs Exploration and Mining Company Ltd.'s West Plant where a Phase I commercial-scale test plant using the Anglo American Research Laboratories design was installed.

This carbon column plant operates in a downflow mode, and it has demonstrated that under certain conditions, very high gold loadings (to 30 Kg Au/t) can be achieved from very low gold tenors (around 0.15g Au/t). Operating large diameter carbon columns in a fixed-bed mode is a major breakthrough.

Phase I Capacity. The plant is designed to treat 150,000 m^3/mo of solution (5,000 m^3/d) based on results achieved in 3"Φ test columns in a pilot plant. Up to July, 1982, when this plant was visited, it had treated 80,000 m^3/mo or 110 m^3/h of solution. The limiting factor proved to be the screen panels in the columns which buckled at design capacity and will, by now, have been redesigned.

Feed Solution:

Gold plant tailings filtercake is repulped after drum filtration in the gold plant. On reaching the uranium plant, the pulp is dewatered again, and the solutions are returned for incremental gold recovery through the carbon columns.

Feed Solution Grade:	Typically 0.14-0.15g Au/t.
Suspended Solids:	10-15 mg/l.

Use of Column Barrens:

After residual gold recovery, the solutions are used as washwater on the gold plant filters.

pH Control:

Solution pH is adjusted in a feed solution reservoir to pH 7.5. This reservoir is located ahead of the carbon columns and receive solution at pH 10. Concentrated H_2SO_4 is added at the tank inlet, the rate of addition being controlled by a valve activated by a pH meter in the tank.

A dangerous situation arose when the level of solution in the reservoir dropped to a level where the pH meter was no longer immersed in the solution. Acid addition continued until the pH solution dropped to 1.5. The barren solution after the carbon columns was used as gold plant filter wash solution and, at this pH, filter operators were rescued from the effects of cyanide toxicity. This situation will not recur again but is mentioned to alert others who may be tempted to reap the attractive benefits of low pH carbon adsorption.

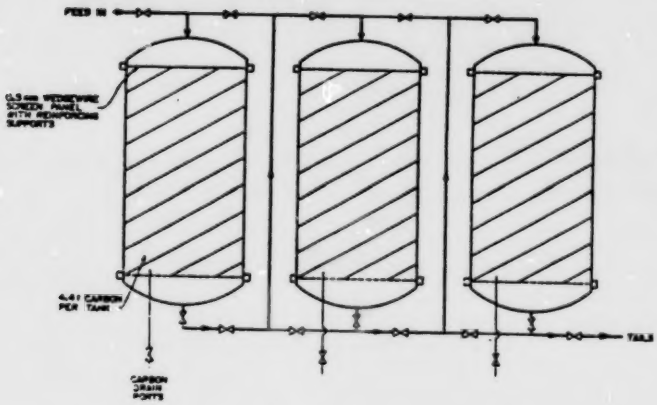
Solution Tanks:

The solution reservoir tanks and pipes are rubber-lined mild steel.

Carbon Columns:

Three rubber-lined steel ion exchange columns are used. The columns are 2.13m Ø. Carbon fills the space between the screen floor and a screen at the top of the column. The steel columns are 3.7 m high are are designed so that carbon can be drained from the bottom.

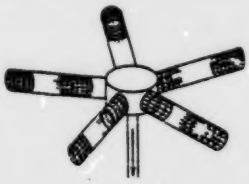
VAAL REEFS WEST
(FIXED BED CARBON COLUMNS)



Internal Screens:

Internal screens in the carbon columns are flat circular wedgewire screens fabricated from stainless 316 steel with nominal 2,130 mm diameter. Five panels are supported on a 25.4 mm x 6.3 mm frame made of stainless 304 steel plus interbars.

HUB-TYPE WEDGEWIRE SCREEN INLET & OUTLET



The screen aperture is nominally 0.5 mm. The lower wedgewire screen is covered by a 3" layer of plus 3/16" gravel to compensate for non-uniformity of the wedgewire screen gaps. Because the screens are not uniform and because the carbon contains a fraction of smaller particles, it was not possible to backwash the columns as had been planned. A flat screen of such a large diameter, even with reinforcement as provided here, has proven not to be a good idea. Initially, the screen panels buckled.

The plant staff were under the impression that a lateral hub-type screen with spiral windings of stainless wedgewire would be mechanically preferable to screen panels.

Representativs of Johnson Screens U.S.A. in South Africa were working on the fabrication of suitable hub-type screens:

S.A. SCREEN AND INDUSTRIAL SUPPLY
Post Office Box 82040
Southdale 2135
South Africa
(011) 68-5494/5

It is believed that CALGON CORP. supplies a carbon column for water treatment which probably would work well for this application as well.

Carbon Used:	Le Carbonne G210, 0.68 mm x 1.2 mm.
Carbon Capacity:	Each column holds 4.4 t carbon.
Pumps:	Pumps feeding the columns are designed to exert a maximum pressure of 220 k Pa.

Pressure Drop:

The pressure drop across the three columns when operated at 80,000 m^3/mo (110 m^3/h) was measured at 100 k Pa. The pressure drop across the three beds in variable. It drops immediately after each acid treatment of the carbon.

Acid Treatment:

In order to enhance the metallurgical performance of the columns and to prevent calcium carbonate fouling, provision is made to isolate any column as required and to fill it with acid and then for draining of the acid after the appropriate soaking period. At the time of the visit, the columns were being acid washed every two days using 4% HCl.

Several acid wash techniques were experimented with. For some time, the columns were washed with acid every two days using cold 4% HCl. Acid was injected through the bottom to fill the column with acid. If there were not problems in disposing of the acid, it would be desirable to inject a slug of acid daily.

At the time of the visit, acid washing had been reduced to once every week. The three carbon columns were simply filled with 12% HCl and allowed to stand for 24 hours before draining the columns to reclaim the acid before putting the columns back on line. The acid becomes deep blue in color indicating that base metals are stripped from the carbon in the process. No gold was detected in the acid effluent.

In pilot testwork, a slug of acid was simply pumped through the columns daily, and this had resulted in phenomenon gold loadings.

EFFECT OF ACID WASHING

It has been found that after acid washing, three changes occur:

- Enhanced gold loading on the carbon is possible.
- Incipient breakthrough of gold in the tailings solution is avoided.
- The pressure drop across the columns is reduced, and flowrate capacity is increased.

A negative aspect of acid washing is that it causes corrosion of the stainless steel screens.

Barrens:

Under optimum conditions, a barrens of 0.004g Au/t is achieved which was not typical of this plant, however. During the visit, tails ran 0.02g Au/t and, after a 3-day acid wash experiment, fell back to 0.011g Au/m^3. On the following day, gold levels in the barrens were back to 0.018 g/m^3. The test program showed clearly that more frequent acid washing with dilute acid has a more beneficial effect than less frequent, more concentrated acid washing.

Gold Loading:

In pilot plant tests, carbon loadings of 1.5 Kg Au/t can routinely be achieved from solutions with 0.15g Au/t. Acid washing every 5-6 days with one bed volume 5-6% HCl resulted in loadings of 2.5 Kg/t carbon at the time the third column broke through, achieving recoveries of 98% or more.

Later pilot plant tests with acid washing of the carbon on a daily basis achieved loadings to 30 Kg Au/t and 70 Kg Cu/t carbon.

At the time of the visit, carbon loadings up to 5.5 Kg Au/t carbon were achieved from the lead column before breakthrough occurred on the third column, also from 0.15g Au/t solutions.

Column Profile, July 4, 1982:

	Inlet	Solution Tail	C Loading Calculated
Lead Column	0.15g Au/t	0.10g Au/t	5.19 Kg Au/t
B Column		0.06g Au/t	2.24 Kg Au/t
C Column		0.020g Au/t	1.35 Kg Au/t

Elution:

The requirement for elution of 4.4t carbon would arise every 3-4 months. Carbon is simply drained from the lead column when this is needed.

Sampling:

A daily composite sample of feed and tail solution from each column is collected. These were assayed for gold.

It was anticipated that Phase II of the program would be implemented in which the full 250,000 m^3/month of solution available from the repulped gold plant could be treated for gold recovery using similar equipment.

More information could be requested on the design, operation, and performance of this type of carbon column from:

ANGLO AMERICAN RESEARCH LABORATORIES
Post Office Box 106
Crown Mines 2025
(011) 835-3251
Brian K. Loveday
Manager
Raymond J. Davidson

VAAL REEFS EXPLORATION AND MINING
COMPANY LTD.
Post Office Box 5010
Vaal Reefs 2621
South Africa
(018) 7141
W. A. Kretschmer
Manager Metallurgical
Roger Kelly
Metallurgical Superintendent

5. Welkom Division, Western Holdings Ltd.

At Welkom, a NIMCIX column using activated coconut charcoal rather than resin beads has been successfully installed to recover gold from up to 300,000 m^3/month dilute tailings decant solution as described in the following trip report extracted from RANDOL (1983).

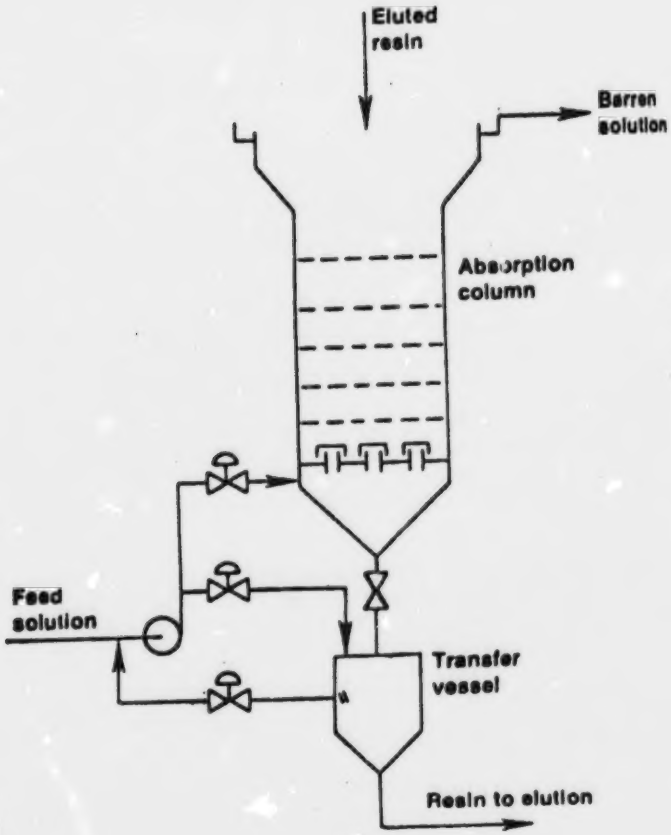
The multi-stage carbon column employed here was installed by:

DAVY McKEE SA (PTY) LTD.
Post Office Box 8608
Johannesburg 2000
(011) 28-5920

The basic principles of the NIMCIX design is depicted in the following diagram. Feed solution flows up the column which has nine stages located one on top of the other and separated by perforated plate distributors. The bottom plate distributor is believed to have been modified to incorporate "bubble caps" which are a patented design feature of the NIMCIX column owned by MINTEK. Information on NIMCIX columns can be requested from:

COUNCIL FOR MINERAL TECHNOLOGY MINTEK
Post Office Box X3015
Randburg 2125
South Africa
(011) 793-3511
David Boydell

UNIVERSITY OF STELLENBOSCH
Dept. of Chemical and Metallurgical
Engineering
Merriman Avenue
Stellenbosch
South Africa
Dr. F.L.D. Choete



The NIMCIX contactor

COMPANY

WESTERN HOLDINGS LIMITED - WELKOM DIVISION
(FORMERLY WELKOM GOLD MINING COMPANY LTD.)
P.O. BOX 1
WELKOM 9460
SOUTH AFRICA

LOCATION

Welkom, Orange Free State
Approximately four hours by car south of Johannesburg with daily airline connections.

TELEPHONE

(017) 25-331

CONTACT

Chris Harvey, Gold Plant Superintendent

MINING HOUSE

ANGLO AMERICAN CORPORATION OF SOUTH AFRICA LTD.
44 Main Street
Marshalltown 2107
South Africa

CONTACTS

V.J. Moore, Consulting Metallurgist, OFS
G.J.C. Young

DATE OF VISIT

11 June 1982

INTRODUCTION

Phase I of this report described the fluid bed carbon columns which were then being installed to recover gold from tailings reclaim water at the WELKOM millsite. This was described in Appendix 1 page 509-511.

This report update provides some actual operating information and relates some of the problems to be expected with this type of column during the startup phase. Not all this information came from ANGLO AMERICAN CORPORATION and some of it may not be accurate.

The column recovers gold from a low tenor solution at a low pH which results in enhanced gold loadings but also enhanced copper loadings. Teh high copper loadings seem to result in a more difficult elution of gold and ultimately in a high copper bearing cathode and dore bar.

PLANT STARTUP

Startup had been scheduled for September 1981, but actual commissioning took place in January 1982. The adsorption has functioned satisfactorily but there were initial problems with the elution and electrowinning steps.

TOTAL CAPITAL COST

R1.6 mm (about US $1.4 million).

COMMENTS ON COMMISSIONING:

ADSORPTION CAPACITY

It was found that the column which had been designed for 260,000 m^3/mo (356 m^3/h) of solution throughput could easily handle this volume - up to 300,000 m^3/mo had been tested successfully.

BED EXPANSION Carbon bed expansion of 100-120% is experienced at a flowrate of 120 l/s through the 3.0 m Ø column which works out to about 1 m/minute flow velocity. Initially some problems were experienced with elutriation of carbon platelets from the column, some of which were of the correct carbon granule size as specified based on pilot tests.

CARBON DENSITY

Density of dry carbon is 450 Kg/m^3. The column holds a total of 15 t carbon with 1.5 t in each stage except the top one, which holds 3 t carbon.

CARBON USED LE CARBONE G210AS , 0.6 - 1.7 mm particle size (mean 1.2mm).

Several carbons have been laboratory tested but only one, G210 AS , met the bed expansion test criteria.

FINE CARBON RECOVERY

A fine carbon recovery system consisting of a stainless steel screen and a pressure filter is installed to recover any fine carbon particles from the conditioning column and carbon prescreening sections plus any spillage containing fine carbon prior to the water leaving the plant. Fine carbon must not be allowed to recirculate back to the main gold plant.

CARBON CONDITIONING

Carbon as received is conditioned by placing it in an 80 cm column for eight hours in which the flow in the full scale columns is simulated. This gets rid of the platelets that are most likely to be elutriated before they get added to the system and to some extent also conditions the carbon particles. Overflow from the conditioning column is pumped via the fine carbon recovery system to prevent it from entering the gold plant process water.

NUMBER OF STAGES

The continuous adsorption column was designed to have ten stages. In fact, it was constructed with a double top stage, which means it has nine stages of which the top one has twice the capacity.

STAGE SEPARATORS

Perforated plates between each stage have holes sized for an upflow velocity of 120 l/sec. The holes in the separators have a 16 mm Ø.

pH CONTROL 5-10% H_2SO_4 is added as needed to the feed solution to adjust the pH of the feed to pH 7-7.5. On the date of the visit, the solution pH was 6.8. Sulfuric acid is mixed into the solution by an on-line static mixer. Since the pH of feed solution as received is 7.5 to start with, very little acid is added for pH adjustment.

ADSORPTION ENHANCEMENT

Based on findings of AARL, which have also been proven at the VAAL REEFS test columns, periodic flushing of the column with a slug of acid enhances gold loading capacity of the columns. WELKOM tested the use of 1 m^3 slugs of hydrochloric acid on a weekly basis using a three minute contact with 3% v/v HCl solution. However, this did not result in any noticable degree of improvement in adsorption and has been discontinued for the time being.

COLUMN CORROSION

The column is constructed of mild steel. Periodic checks are planned to monitor corrosion.

FEED SOLUTION TENOR

Feed solution to the columns were designed for 0.044 g Au/t solution based on typical values tested in the past.

After the plant was installed, grade of feed solution dropped to 0.026 g Au/t possibly because the operations feeding the recovery system had become more careful.

Cyanide concentration in the feed solutions is minimal at around 0.001% NaCN.

FEED IMPURITIES

Copper concentration in the feed solution is 2.5 ppm. The pH of the solutions as received, is around 7.5, so the H_2SO_4 dosing system need not be used most of the time.

SUSPENDED SOLIDS

Feed solutions with up to 2000 ppm solids, have at times been treated, which causes some problems.

CARBON FOULING

Silica adsorbs on the carbon to a degree, but did not seem to be adsorbing beyond a certain plateau level. SiO_2 is believed to be removed during elution in the caustic solution.

Calcium loads up to 4000 ppm on the carbon, but does not appear to interfere with gold adsorption.

GOLD ADSORPTION

Gold loading on carbon from 0.026 ppm Au solution were only around 250 g Au/t carbon. From 0.032 g Au/t solution feed loadings of 549 g Au/t were typical. Although acid treatment of carbon did not produce the expected results, close attention to the regeneration process has greatly improved recovery. Loadings of the order of 400 g Au/t C are now typical.

ADSORPTION PROFILE

A carbon adsorption profile for the adsorption column is shown in the following data - clearly taken on a day when gold solution tenor was closer to 0.03 g Au/t.

Copper loading in this set of data is reasonable at 7000 ppm. It has been reported that copper can load up to 22,000 ppm on the carbon on occasion.

MINTEK suggested adding cyanide to the feed solution to convert Cu^+ to $[Cu(CN)_5]^{-4}$ in order to reduce copper loading onto carbon. $[Cu(CN)_5]^{-4}$ loads very slowly onto carbon compared with CuCN and $[Cu(CN)_2]^-$, however this equilibrium between copper cyanide complexes is also cyanide dependent.

CARBON LOADING PROFILE

Stage	Au g/t	Cu g/t	Zn g/t	Ni g/t	Fe %	Ca g/t	SiO_2 %
1	436	7000	2700	2500	2.13	4200	1.26
2	342		2500	2400	0.92	3800	1.33
3	302		2700	2300	0.81	4200	0.71
4	325		2700	2500	1.02	3600	0.80
5	330		2700	2100	0.70	3600	0.56
6	324		2500	2500	0.70	2900	0.45
7	324		2500	2400	0.80	2800	0.47
8	248	5900	2500	2000	0.73	3000	0.51
9	225	6300	300	2100	0.99	3500	0.74

It is claimed by some, that carbon adsorption of copper is enhanced at the lower operating pH used here.

CARBON TRANSFER

The NIMCIX-type upflow column employed for carbon adsorption was basically designed for use with resin ion exchange beads which of course are more spherical than the carbon which has a platelet shape.

The sequence for carbon transfer in the NIMCIX-type column is described in the Appendix I trip report and basically includes a settling period followed by a brief backflush period during which a controlled amount of carbon is supposed to transfer down the column from each stage to the next. In this case, however, during the 45 minute period while the inventory from the bottom stage is transferred for elution, the complete carbon contents of the column settled to fill the first three stages leaving the rest empty.

When the column went back on forward flow, the carbon fluidised up the column again, but in the process, a considerable degree of backmixing resulted which probably reflects the design of the plate separators. One alternative was to fit bubble caps on each stage separator which would have been expensive.

The column has now been provided with provision to maintain upflow during carbon transfer. This is expected to prevent settling of carbon in the lower stages. Initial results look promising and it is hoped that interstage mixing problems will have been overcome by the time this report is printed.

CARBON RESIDENCE TIME

Carbon is transfered at the rate of 1.5 tons, twice a week. The operation does not wait for gold to break through before transfering a batch of carbon for elution.

RECOVERY

Tails from the carbon column are very low and about 70 - 80% of the gold in the feed is recovered at present. It is hoped that 90% recovery will be achieved when interstage mixing problems have been solved.

0.1 ppm Au solutions, yield tails at around 0.01 ppm Au and a carbon loading of 1 Kg Au/t carbon under standard adsorption practice at pH 7.5.

GOLD PROUCTION

5 Kg Au per month.

ELUTION

A ZADRA-type elution is employed and 90-95% of the adsorbed gold is eluted each cycle into 8-10 m^3 eluate from 1.5 t carbon.

After each cycle, about 25% of the spent electrolyte from the previous elution and electrowinning cycle is discarded and replaced by fresh eluant solution.

Elution follows the following steps:-

1. Transfer loaded carbon to elution column.
2. Drain the carbon, 6-8 hours.
3. Displace the transfer water with 2 bed volumes of process water to flush out any solids.
4. Pass hot NaCN/NaOH eluant through the column upflow. Collect the eluate in a tank. Recycle for 48 hours via a steady head tank.
5. Electrowin gold from the eluate.

In order to overcome problems with precipitation of solids in the heat exchanger it is necessary to wash the carbon with softened water to remove any entrained process water. It is worth recording that it is now usual to wash eluted carbon prior to regeneration as well as prior to elution. This reduces the level of entrained eluate with dissolved salts.

ELUTION CONDITIONS

1% NaOH, 0.1% NaCN at 95-98°C. At WELKOM, water boils at 95°C.

WELKOM were experimenting with a modified eluant of 0.3% NaCN and 2.5% NaOH.

Carbon batches of 1.5 t each, are eluted twice per week. Each elution cycle takes three days.

Elution rate is temperature dependent. One plan was to try to achieve 101-102°C by increasing the salt content of the eluate.

It is found that NH_3 is generated during elution as well as during electrowinning.

ELUTED CARBON

Carbon gold loadings after elution are around 30 g Au/t, which indicates an effective elution. However, the loaded carbon transferred to elution is loaded to only 300-400 g Au/t.

ELECTROWINNING

Initially, the NIM I cell (carbon granule electrodes) would not plate more than 5% of the gold per pass.

At a copper: gold ratio in the eluate of 40-50:1 copper plated onto the cathodes.

The NIM I cell that was designed to recover 3 Kg Au per cycle, ended up plating up to 40 Kg copper each cycle. There was also a rapid anode corrosion in the NIM I cell even when 2% NaOH was used in the eluate.

Many approaches were tried to overcome the problem, including the multiple reuse of the eluant, but copper still continued to build-up.

The operation produced copper bars with some gold content, which were sold to the RAND REFINERY.

The NIM I cell uses granular carbon chips as a cathode and produced gold and copper plated carbon chips. These did not smelt readily nor could gold be backplated onto titanium sheets with much success.

The results have greatly improved since the new version of the rectangular MINTEK cell has been employed.

MINTEK CELL

0.7 x 0.7 m cross section cathodes, of which there are six with seven stainless steel mesh anodes in a rectangular stainless steel bath. The cell tank is connected to the cathodes and serves as the busbar for the cathodes.

The cell is designed to treat 5000 l/h of solution.

In the new MINTEK cell, some corrosion of the stainless steel anodes was still being observed even at relatively high concentrations of OH^-.

Two sources indicated that only 3-6% Au was plating onto the steel wool cathodes. It was indicated that copper was still plating on the cathodes as would be expected. One industry source has suggested that by increasing the cyanide concentration in the eluate, copper plating would be inhibited.

WELKOM indicate, however, that cyanide is effectively destroyed in both the hot elution process and in the electrowinning cell.

According to two sources, only 3-6% Au was plating onto the steel wool cathodes. Copper was still plating on the cathodes as would be expected.

One industry source has suggested that by increasing the cyanide concentration in the eluate, copper plating would be inhibited. However, WELKOM indicate that cyanide is effectively destroyed in both the hot elution process and in the electrowinning cell.

There may be no cost effective solution to the problem other than to find a market for the gold that does not penalise heavily for the copper in the dore. Several factors could influence the copper content in the dore bar:-

1) Keep a high cyanide concentration in the feed solution to the column. At low operating pH, however, this is not likely to be possible.

   Carbon in the presence of copper in this low pH range catalytically destroys cyanide.

   High copper loadings seem to be part of the mechanism whereby high gold loadings are achieved.

2) Electrowin at below 2.5 volts. In Australia using cylindrical steel wool cells, gold has been selectively plated from eluates containing 2000 ppm and more Cu. It is noted that WELKOM's data sheet shows operation of their cell at 2.5-3.0 V but this requires confirmation as previous data showed a higher operating voltage.

3) It is not known whether it is relevant or not, but the Australian operation which plate gold selectively in the presence of high copper also use hot eluates which have not been cooled by a heat exchanger to preheat incoming eluant.

6. Homestake Mining Company, Lead, South Dakota

Homestake Mining Company is known to recover gold from reclaimed mill tailings decant solution. Although carbon columns are used for this purpose, no further details were obtained.

Appendix I also includes a description of the biological effluent treatment facility at Homestake's Lead operations. This facility uses rotating biological contactors with nutrient enhancement of the feedwater to oxidize cyanide and remove metals in the first stage followed by ammonia removal in the second. It is believed that low-level residual gold values in the effluent are also recovered with other metals in the biomass sludge generated by the RBC process. To date, no definitive data on this potentially useful aspect have been released by Homestake Mining Company.

HOMESTAKE MINING COMPANY
Post Office Box 875
Lead, SD 57754
(605) 584-1020
James L. Whitlock
Chief Chemist
Terry Mudder
Chief Environmental Engineer

7. Pinson Mining Company, Winnemucca, Nevada

Pinson Mining Company has installed fluid-bed multi-stage carbon columns to recovery incremental gold values from tailings return water reclaimed from their tailings dam for use in their milling circuit. No details were obtained on the performance of this recovery system, but these could be obtained from:

PINSON MINING COMPANY
Post Office Box 192
Winnemucca, NV 89445
(702) 623-5036
R. Bruce Thorndycraft
Mill Superintendent

The system installed at Pinson Mining is similar in principle to that installed at Giant Yellowknife in that the upflow fluid-bed carbon adsorption stages are located side-by-side and connected by gravity flow. At Pinson Mining, the loaded carbon is eluted and regenerated with carbon in their main CIP plant. The fact that no huge lead-times or freight bills are incurred means that Pinson Mining has less motivation to load gold to the maximum possible loadings on their carbon before it is eluted. In their case, inventory lockup would be a bigger factor.

8. Buffelsfontein Gold Mining Company, Stilfontein, South Africa

Buffelsfontein Gold Mining Company in South Africa also recovers low-grade gold values from gold mill tailings filtercake solution after it is repulped before being treated in their uranium leach circuit. In this case, the tailings are repulped in acidic water, and fine activated carbon is added to the pulp in the process. Final tails are floated to recover pyrite values, and residual gold values that were in the repulped tailings end up being recovered with the pyrite concentrate which contains the fine activated carbon. During roasting of this concentrate, the carbon is ashed, and gold is recovered in a subsequent step in which the calcine is leached in cyanide.

Details of this process were not released by Gencor Ltd., the mining house which manages Buffelsfontein operations. However, VAN ASWEGEN (1985) will describe the process and its performance later this year in Cannes.

The interesting aspect of this approach is that incremental gold that could otherwise be recovered by carbon columns such as at Welkom or at Vaal Reefs West, mentioned above, now is recovered out with the need for a special treatment plant. The only equipment needed is a device for addition of the fine carbon to the pulp. Because the carbon added is finely divided, adsorption kinetics are faster than for regular granular coconut carbon. However, it remains to learn what kind of recovery efficiency of the soluble gold in the pulp is achieved and what the flotation recovery of this carbon is, as well as what recovery is achieved in the concentrate roasting and leaching step.

The person at Gencor who has been deeply involved in the development of this process application at "Buffels" can be reached as follows:

GENCOR LTD.
Post Office Box 1820
Marshalltown 2107
South Africa
(011) 836-1121
Pieter Van Aswegen

URANIUM

9. Wyoming Minerals Corp., Bingham Canyon, Utah

The following trip report was excerpted from RANDOL (1980) and, undoubtably, many details regarding the contact, etc. may have changed. This operation employs a Higgins Loop ion exchange contactor illustrated below:

WYOMING MINERALS CORPORATION
BINGHAM CANYON

ADDRESS	Wyoming Minerals Corporation P.O. Box 311 Bingham Canyon, UT 84006
CONTACTS	Ron Platzke, Plant Manager Virginia Owens, Plant Chemist Ray Aitken, Purchasing Agent
TELEPHONE	(801) 364-1071
CORPORATE	Wyoming Minerals Corporation 3900 S. Wadsworth Lakewood, CO 80235
CONTACTS	J. C. Compton, Executive Vice President Fred Hohne, Vice President Carmine Mancuso Dr. Eric Tiepel Frank Ludeman
TELEPHONE	(303) 988-8530
RESEARCH	Westinghouse Research & Development Center Pittsburgh, PA
CONTACT	Mike Skriva
TELEPHONE	(412) 256-5035
CAPACITY	Three CHEM-SEPS units treat 6,600 US gpm solution (1500 m^3/h) i.e. 2,200 US gpm each or 500 m^3/h. This is average flow rate. Loading section ϕ is 8 ft. Since the units pulse 45 seconds every six minutes, the flow rate during the 'Run' mode must be 8/7 x 2,200 US gpm = 2500 US gpm (545m^3/h). This is considerably less than was originally designed based on pilot plant work.
SPECIFIC FLOW RATE	Originally the units were designed for 55 US gpm/ft^2 2200 US gpm average flow rate corresponds to 44 US gpm/ft^2 specific flow rate. 2500 US gpm flow rate during 'RUN' mode corresponds to 50 US gpm/ft^2.
NOTE	Wyoming Minerals Corp is sensitive about information on the HIGGINS LOOP operation. The information provided here should be regarded as confidential even when talking to Wyoming Minerals' staff.

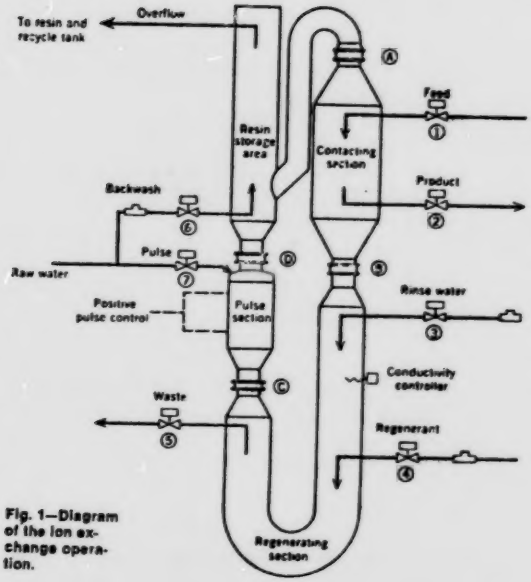


Fig. 1—Diagram of the ion exchange operation.

URANIUM GRADE	6-7 ppm U_3O_8 Grade may fluctuate to 5 ppm depending on the weather due to run-off dilution or depending on which tailings piles Kennecott Copper leaches that day. This corresponds with 6,600 US gpm flow rate for 365 days/year at 6.5 ppm head grade and 1.5 ppm barrens, i.e. 0.005 g/l extracted.
URANIUM PRODUCTION	140,000 lbs. U_3O_8/year
BARRENS	Used to be 1.7 ppm U_3O_8, now barrens of 0.9-1.2 ppm are experienced. The 1.7 ppm U_3O_8 average includes the third HIGGINS LOOP unit which doesn't run as well and gives higher barrens.
UNIT SIZE	8 ft.ϕ at loading section, the units are 55 ft. high. The three HIGGINS LOOPS fit into a remarkably small building.
LOADING STAGE	Originally the loading stages were 8 ft. high. Now loading stages have been reduced to 5 ft. height to reduce the pressure drop across the resin bed which was causing damage to the resin beads.
RESIN INVENTORY	750 ft.^{3} resin per unit (21.2m^3 each) Originally resin inventory was 1000 ft.^{3} (28.3m^3) prior to modification of the units.
RESIN TYPE	Macroreticular resin. Porous beads. DOWEX MSA 1 16-30 mesh (U.S. Std. Sieve)
RESIN COST	About \$125/ft.^{3} resin delivered \$4400/m^3 R 3500/m^3
RESIN SELECTION	DOWEX MSA1 was selected because it is both mechanically strong and resistant to osmotic shock. Ron Platzke claims losses are now such that the operation is economically viable. Gel type resins resulted in impossible resin losses to the extent that stable operation could not be achieved. DOWEX MSA1 has been used for the last 1½ years and has given a stable operation.
RESIN LOADING	1 to 2 g/l

RESIN LOSS

Resin loss in the CHEM-SEPS unit is high and is caused by:

-Osmotic Shock
-Mechanical Movement of the Resin
-Valves Closing on Resin
-High Pressure Drop Across the Resin Bed

Ron Platzke claims that resin loss is a result of valves closing on beads is low.

In the two years of their program with HIGGINS LOOPS to date Wyoming Minerals Corp. have used up about 12,000 ft.^{3} (340M^3) of resin in the three HIGGINS LOOPS WITH 750 ft.^{3} (21.2m^3) resin inventory each. This is roughly 270% per annum of resin inventory lost per year. A disastrous situation.

When Wyoming Minerals Corporation installed their first unit, the 1000 ft.^{3} resin inventory was destroyed within 6 hours. The unit had been started up under Chem-Seps supervision.

The resin inventory was replaced and it too broke in a day or so.

Then after performing some osmotic shock tests, the unit was filled with DOWEX MSA1 resin. This resin load lasted a week.

Each 1000 ft.^{3} resin load was worth $100,000, so in less than two weeks of running the unit, $300,000 worth of resin was destroyed. As a result, Wyoming Mineral's Corporation undertook a major resin test program, and modified the HIGGINS LOOP to downgrade its capacity thereby reducing the affects on resin loss.

Wyoming Minerals found that the resin breakage due to high osmotic shock and high mechanical shock applied t resin simultaneously was greater than the sum of the resin loss due to the two influences separately. In fact it was greater than the product of the resin losses from the two causes because the resin simply 'explodes'.

Mike Skriba of Westinghouse Research & Development has developed an RST (resin strength test) procedure and apparatus to measure resin losses on samples.

Resin losses now are believed to be around 100% PA of inventory or 54 PPM of flow rate of feed which is not bad at all.

Wyoming Minerals Corp. is actively searching for better resins and have developed a set of specifications which will enable resin to be manufactured for the HIGGINS LOOP that will last much better.

When comparing resin loss data for different CIX systems it is very misleading to compare on the basis of percent of resin inventory lost per year.

The HIGGINS LOOP treating 2200 US gpm has a resin inventory of only 750 ft.^{3} (21.2m^3).

NIMCIX at 1200 gpm requires a resin inventory of 5300 ft.^{3}. (150m^3).

Hence a 100% per year loss of resin inventory on a Chem-Seps unit at 2200 US gpm flow is equivalent to 5.3 PPM of flow.

5.3 PPM resin loss on a NIMCIX unit at 1200 gpm flow with 5300 ft.^{3} resin (150m^3) inventory would work out to 12.6m^3/year resin loss or 8.4% of the resin inventory.

It is therefore more appropriate to compare resin losses in terms of ppm of solution treated or volume of resin lost per unit of uranium produced.

Cost of resin loss per m^3 feed treated and per pound of U_3O_8 produced is compared below for 30%, 50% and 100% per year resin inventory losses on a Chem-Seps unit.

COST OF RESIN LOSS

21.2m^3 (750 ft.^{3}) Resin Inventory @ \$100/ft.^{3} per unit. Each unit produces 4.38mm m^3 x 5ppm x 2204.6 tbs = 48,280 lbs U_3O_8

At 30% Resin Loss Per Year

4.38 million m^3 solution treated per year per unit
= 6.36m^3 (225 ft.^{3}/yr) resin loss per year
= \$28,000 per year
= \$0.58 per lb U_3O_8 produced

At 50% Resin Loss Per Year

4.38 million m^3 solution treated per year per unit
10.6m^3 (375 ft.^{3}) resin loss per year per unit
= \$46,900 per year (\$125/ft^3)
= 0.97 per lb U_3O_8 produced

At 100% Resin Loss Per Year

4.38 million m^3 solution treated per year per unit
21.2m^3 (750 ft.^{3}) resin loss per year per unit

$94,000 per year cost of resin per unit ($125/ft^3)
$1.95 per lb U_3O_8 produced

RESIN DENSITY — The DOWEX MSA1 resin has an SG of 1.08 compared with SG = 1.1-1.2 for gel types. Resin density is not as important a feature for this type of contactor as for upflow systems.

FEED SOLUTION — Product of heap leached tailings dump rich in copper and high in particulates.
pH = 2.8 - 3.0 as received.

No resin poisons.

Very low SiO_2 content in feed.

ELUTION — Elute with three bed volumes of 150 g/l (3N)H_2SO_4
No copper gets carried over in the eluate.

ELUATE — 300-500 PPM U_3O_8

TEMPERATURE — 80°F or higher.

RUN/PULSE CYCLE — Resin is moved every 6 minutes. Each pulse lasts 10 to 15 seconds but the whole sequence including opening and closing valves takes 45 seconds.

SILICA — Very low SiO_2 buildup experienced--Less than 1% per year SiO_2 on the resin. pH is kept high enough to reduce the SiO_2 problem. At low pH's Ron Platzke believes that SiO_2 polymerises and "glues up."

RESIN REGENERATION — Not required at Bingham Canyon.

PARTICULATES — Suspended solids content of the feed solution at Bingham Canyon are high and vary considerably. Suspended solids of 1000 ppm are not uncommon. Variation depends on rainfall or snow melt runoff.

The particulates consist of flakelike particles of organics from the tincans used for precipitating copper cement.

In addition there are varying amounts of silt in the feed.

Particulates have a big impact on the HIGGNS LOOP operation. As particulates in the feed increase the pressure drop across the resin bed in the loading stages increases significantly.

Particulates also cause severe abrasion of pump.

PARTICULATE REMOVAL

Particulates are controlled as much as possible through three factors:

1. Installation of a one stage wooden settling tank ahead of the CIX unit.
2. Overflow solution is then filtered through sixty four ZURN strainers.
3. One section of the HIGGINS LOOP is used to backwash solids accummulated during the loading phase. The packed resin bed acts as a very good filter and will accumulate any solids present in the feed.

The HIGGINS LOOP is operated on a very short cycle of 6 minutes. The shorter the cycle, the less solids have a chance to build up in the loading stage between backwashes.

MAIN LOOP VALVES

21SSB Crane Monarch valves with squeegy disc wiper to reduce resin damage.

MAIN COST FACTORS

- Operators & Maintenance
- Resin Loss
- H_2SO_4 for Elution
- Na_2CO_3
- SX Chemicals
- Utilities e.g. Pumping Costs

MANPOWER REQUIRED

A total of 16 people plus three maintenance engineers are required to operate the plant.

5 foremen
6 process technicians
1 metallurgist
2 laboratory chemists
1 manager
1 clerk
16 Total

3 Maintenance Engineers

After Jacobs Constructors, who built the plant, left the site one of their crew left to go into business for himself and set up a small company that maintains the CIX units under contract.

OPERATIONAL AVAILABILITY

Now improved to 97-98%. Expected to drop to 90-98% as the new units get older and require more maintenance.

OPERATING SENSITIVITIES

All concerned emphasized that the HIGGINS LOOP is a very sensitive unit to operate.

When resin is pulse transported around the column in plug flow fashion it moves in what has been described as a "stick-slip" method. This leads to tremendous water hammer possibilities and enormous pressures seem to build up in the loop. Strain guage tests showed incredible forces in the column that could nly be explained by resin bridging effects.

At times when resin blinds the collector screens drawing barrens from the loading stage of the loop, tremendous forces build up which bend the collectors which are very robustly constructed. Forces up to 1000 PSI on the collectors are experienced at times.

WMC SATISFACTION WITH HIGGINS LOOP

Mike Skriba at Westinghouse Research & Development Center, Pittsburgh indicated that the HIGGINS LOOP could be developed into the best system for continuous ion exchange in the world for cases where:

(1) Feed rate is very high
(2) Recoverable grade is very low
(3) Value of recovered material is high
(4) Sophisticated operators with prior experience running a HIGGINS LOOP are available.
(5) There is a space constraint for the plant.

RESIN REGENERATION

If resin regeneration is required then a means would have to be built into the system to do so.

The resin regeneration cycle would be different to other CIX systems.

The whole hoop might be taken off line temporarily and the whole resin inventory regenerated simultaneously.

MODIFICATIONS

Numerous modifications were made to the units at Bingham Canyon.

1. The LOAD section has been reduced in size from 8' to 5' to reduce pressure drop across the resin bed.

2. The ferric strip stage was removed. Ferric is now stripped from the resin in a different manner.

3. Flow rates to the units were cut back to 2200 US gpm average.

4. Several piping modifications have been made by Wyoming Minerals Corp on the units.

5. Wyoming Minerals Corp have modified the solution tenor control system.

10. Cotter Corporation, Schwarzwalder Mine, Golden, Colorado

Cotter Corporation discharges minewater to a creek that ultimately gets into the Denver drinking water supply. The Colorado Dept. of Health has insisted on the most demanding effluent water quality limits for both uranium and base metals as shown below (from PALMER, et al., 1984). The water treatment plant is described in Appendix I.

Uranium is recovered from this minewater stream containing only 3-5 mg/l using a new design of a continuous downflow ion exchange adsorption unit resulting in extraordinarily low levels in the effluent of uranium (10 ppb) and base metals. In addition, eluate generated are concentrated enough (12g U_3O_8/l to be used as pregnant solution at Cotter Corporation's mill in Canon City.

This incremental resource recovery plant performance is quite remarkable and is a great credit to its designer:

HIMSLEY ENGINEERING
250 Merton Street
Toronto, Ontario M4S 1B1
(416) 485-4441
Alec Himsley

Element	Feed (mg/l)	IX Effluent (mg/l	Discharge Limit mg/l)
Uranium	3-3.5	LT 0.010	0.06
Cadmium	0.002	0.0004	0.0004
Copper	0.02	0.005	0.005
Lead		0.005	0.032
Zinc	0.0026	0.05	0.05
Radium (p Ci/l)	50-100	5	5 Total
Arsenic		0.05	0.05

11. Quivira Mining Company, Ambrosia Lake, New Mexico

At Ambrosia Lake, New Mexico, the Quivira Mining Company discharges large volumes of minewater from a series of underground uranium mines. Water seeps from the tailings dam (which is acidic) and, together with discharged minewater, finds its way into underground workings via drillholes and fractures. Underground, it leaches uranium from the stopes which, to comply with the NPDES discharge permit, must be removed before the minewater can be discharged.

This operation is described in an Appendix I trip report. It is, however, an example of how simple, one or two-stage upflow fluid-bed ion exchange adsorption units are less

effective in treating solutions containing high concentrations of ions that compete for sites on the ion exchange resins.

In this case, to achieve an efficient uranium recovery from minewater with the composition that is encountered at the Ambrosia Lake operations, a multi-stage system such as NIMCIX or a downflow CIX adsorption unit, such as designed by HIMSLEY, would be likely to give a greatly improved performance.

More information is included in the trip report and also may be available from:

QUIVIRA MINING COMPANY
Ambrosia Lake Operations
Post Office Box 218
Grants, NM 87020
(505) 287-8851
Charles F. Stanley
Mill Manager
Jonathan Ma
Metallurgical Manager

It is important to note that when the KERMAC CIX system consisting of one or two CIX stages for uranium adsorption were installed originally, the quality of the minewater was markedly different with much lower TDS and sulfate level, and the system performed more than adequately. Formerly, the resin needed to be eluted only 16 times a month to keep uranium levels in minewater below 1 ppm U_3O_8 for discharge. Now, due to the changed water quality underground, 40 elutions per month are required, and eluate tenor has also dropped due to the lower loading on the resin when sent for elution.

12. UNC-Homestake Partners, Grants, New Mexico

United Nuclear-Homestake Partners operates a uranium mine and mill complex at Grants, New Mexico. Ion exchange is used to recover incremental uranium values from underground minewater and from tailings dam recycle water. Uranium levels in 1980 were 16-23 ppm U_3O_8 in minewater and 20-30 ppm in reclaimed tailings water.

Significant quantities of uranium were recovered from both types of solution using in-house ion exchange systems. As solution chemistry changed with time, it became increasingly difficult for their simple ion exchange system to reduce uranium values to below 1 ppm as required by the NPDES discharge permit.

It is known that around 1981, UNC-Homestake Partners installed a NIMCIX ion exchange plant to improve their uranium recovery performance for mine and tailings return water. No published data on the performance of this plant was located. However, more information would be available from:

UNITED NUCLEAR-HOMESTAKE PARTNERS
Post Office Box 98
Grants, NM 87020
(505) 287-4456
John Turner
Metallurgist
Ken Skiff
Metallurgist

BATEMAN URANIUM ENGINEERING COMPANY
Irongate I
777 South Wadsworth Blvd.
Lakewood, CO 80226
(303) 989-4921
Peter Sutherland

One of the world experts on NIMCIX installations for uranium recovery of this sort who was directly involved in the installation of the plant at UNC-Homestake Partners, Anton Hendricksz, has now relocated as follows:

ANTON R. HENDRICKSZ
Bechtel Civil and Minerals, Inc.
Fiftv Beale Street
San Francisco, CA 94119
(415) 768-3686

COPPER

13. Cerro de Pasco, Peru

According to Delgardo Oscar of Centromin Perie at Cerro de Pasco, a 4,000 gpm acid mine drainage stream at pH 1.3 is treated to recover copper by SX and electrowinning. No further information on this installation or its performance was obtained. However, possibly more details could be available from:

INGO DELGADO OSCAR
Centromin Peru
Carabaya 891
Casilla 2412
Lima 1 Peru

COPPER

14. El Teniente Minewater

The copper recovery circuit at El Teniente is summarized by Dr. Maurice Cocquerel of Davy McKee Corporation below:

Davy McKee Corporation
2303 Camino Ramon
P. O. Box 5500
San Ramon, CA 94583
Tel.: (415) 838-1166
Telex: 337635

September 4, 1984

Hans Von Michaelis
21578 Mountefield Drive
Golden, Colorado 80401

Dear Hans,

Further to our telecon I enclose some data on the El Teniente mine water solvent extraction project.

	Aqueous Flow Rate	Copper Production
Minimum	250 m^3/h	<1000 tons/year
Nominal	612 m^3/h	4060
Maximum	900 m^3/h	4611

At nominal flow rates and below the plant operates in a conventional counter current two extraction two strip mode. For higher flowrates the plant can operate with the agueous feed in parallel through extraction.

The flow is seasonal and in place with the spring snow melt. High copper tenors >2 gpl often coincide with high flows at the beginning of the run off.

I hope you find this brief description of use in your survey.

Sincerely yours,

DMC Engineers and Constructors
A Division of Davy McKee Corporation

M. A. Cocquerel, Ph.D.
Vice President - Technology

MAC/djt

Davy McKee Corporation
A Davy Corporation company

LEAD-ZINC

15. Cominco Ltd., Trail, British Columbia

At Cominco's Trail, B.C., plant, an award-winning water treatment plant was installed to treat thirteen effluent streams from their zinc operations and some from the lead smelter. This plant treats 6,500 m^3/d of effluent, including flows from various sewer systems from 20 separate areas at the Trail metallurgical complex, as described by WATSON and TURNBULL (1983).

At Trail, effluents are treated by the high density sludge process to yield a precipitate sludge containing zinc and lead which is returned to the lead smelter for zinc and lead recovery.

The plant recovers 98.9% of the zinc, 99.5% of the lead, 97.5% of the cadmium, and 92.9% of the suspended solids in the feedwater. Although there is no return on the capital invested (C$9 million), the recovered metal values have been found to offset much of the C$720,000 annual operating costs according to WATSON and TURNBULL (1983) which, in itself, is a remarkable achievement. More information could be requested from:

COMINCO LTD.
Trail, B.C.
Canada V1R 4L8
(604) 364-4222
R. H. Watson
Manager

COMINCO LTD.
200 Granville Street
Vancouver, B.C. V6C 2R2
(604) 682-0611
Walter R. Kuit

ZINC

16. Noranda, Mattabi Division, Ignace, Ontario

Mattabi Division of Noranda Mines Ltd. operates a mine-mill complex recovering copper, lead, zinc, and silver from massive sulfide orebodies north of Lake Superior in Ontario.

Decanted solution from their large tailings dam, which is rich in sulfides, is collected and treated at a rate of 600 lgpm by lime precipitation. The water is treated by lime addition and aeration, followed by flocculant addition and settling in a plate pack thickener yielding a sludge containing 5-10% solids. The sludge contains zinc values and was returned to the zinc concentrate thickener where it was believed to be squeezed by the

weight of the concentrate and further dewatered before being shipped with the zinc concentrate, to a zinc refinery.

Certainly the revenues generated after freight by zinc values in the sludge that had been added to the concentrate would be minimal, and it has been learned that Mattabi no longer adds the sludge to their concentrate, but rather they are said now to add them back into the mill tailings.

In considering the value of zinc in precipitate sludges which may have to be shipped over many hundreds of miles to be treated, the cost of freight, not only of the zinc unit, but also of their contained moisture content, must be taken into account.

More information might be available from:

MR. G. VEILLETTE
Mill Superintendent
Mattabi Mines Ltd.
Ignace, Ontario
Canada
(807) 934-2291
NORANDA MINES LTD.
240 Hymus Avenue
Point Claire, Quebec
Canada H9R 1G5
(514) 697-6640
Ken Wheeland
Chief Environmental Engineer

NICKEL

17. Impala Platinum Refinery, Springs, South Africa

A flotation concentrate is smelted and then leached to recover copper and nickel hydrometallurgically, leaving platinum group metals, primarily in a sludge of undissolved metals.

The acidic process solution is submitted to a variety of processes for nickel and copper recovery and, in the final step, is neutralized to settle gypsum leaving an effluent solution that can be discharged or recycled. Randol Internationa Ltd. did not investigate details of any processes relating to platinum recovery operations as these are considered company confidential.

It is, however, believed that the gypsum precipitate so generated contains enough nickel values for it to be recycled back to the leaching step for incremental recovery.

18. Falconbridge Limited, Falconbridge, Ontario

At Falconbridge, Ontario, plant runoff water from the smelter and mill area was, for years, collected in a small shallow lake area alongside the plantsite where it was decanted to discharge water as an effluent with the mill tailings effluents that, in turn, discharged to the lake and river system. After many years, it was found that potable wellwater from a nearby well contained levels of nickel and other base metals. It was found that solids settling from plant runoff water contained relatively high metal values which had built up as a sediment in the impoundment. When these started to oxidize, base metals were leaking into the aquifer from which potable water was being pumped.

Falconbridge reclaimed the sediments, which were high enough in metal values to justify adding them to feed to the mill to benefit from recovery of incremental values to the tune of $1.5 million.

More information could be requested from:

FALCONBRIDGE LIMITED
Falconbridge, Ontario P0M 1S0
(705) 693-2761
John K. Weglo
Director, Environmental Control

BASE METALS

18. Piccalinna (Sardinia) Mine

GHIANI and TONETTI (1983) described the treatment of acid mine drainage from the Piccalinna Mine in Sardinia and the recovery of separated metals. Unfortunately, a copy of their paper was not obtained, and no details were obtained.

CYANIDE REAGENT RECOVERY

Several gold ore deposits have not been economically exploitable because the ore contains too much cyanide-soluble copper. When leaching this type of ore, so much copper goes into solution as to cause metallurgical problems and to require such large quantities of cyanide reagent addition that the gold recovery process is made uneconomical.

Although, many years ago, a cyanide recovery process was employed by the Hudson Bay Mining and Smelting Company at Flin Flon, Manitoba, no such operations have been identified in recent times. The Flin Flon process involved acidification of the effluent to volatilize HCN gas which was then redissolved into an alkaline solution for reuse.

Recently, a process has been announced for the recovery of cyanide reagent from effluents containing quantities of cyanide associated with base metals to the extent of being significant to the economics of the operation.

Details of the cyanide recovery process have not yet been released, but they have been promised for RANDOL (1985). The process, when treating tailings solution from an ore requiring 11 Kg NaCN/ton, was said by BERGMAN, et al. (1984) to cost $1.00/ton for cyanide recovery. The BERGMAN, et al. (1984) is inserted into Chapter 40 on cyanide treatment.

Additional details may be available from:

MNR REPROCESSING, INC.
Postfach 24
D5940 Lennestadt 17
West Germany
(02721) 835-303
Dr. Arthur Bergman

GEORGE M. POTTER
40 South Calcite Avenue
Tucson, AZ 85745
(602) 884-9609

REFERENCES

BERGMANN, A., GUZMAN, A., and POTTER, G.M. (1984) Regeneration of Cyanide - A Case Study: Pilot Cyanidation of a High Copper Gold Ore from Centinela, Chile. Proc. Conference on "Cyanide and the Environment," University of Arizona, Tucson, Arizona, December 11-14, 1984.

DAVIDSON, R.J., and STRONG, B. (1983) The Recovery of Gold from Plant Effluent by the Use of Activated Carbon. J. South African Institute of Mining and Metallurgy, August 1983, pp181-188.

GHIANNI, M., and TONETTI, E. (1983) The Purification of Acid Drainage Water in the Mine of Piccalina (Sardinia) and the Recovery of Separated Metals. Proc. International Mine Water Hydrology Conference 1983, c/o Dr. Rafall Fernandez-Rubio, Dept. of Hydrogeology, University of Granada, Apdo de Correos 556, Granada, Spain.

PALMER, C., HIMSLEY, A., and BENNETT, J.A. (1984) Design and Operation of Continuous Ion Exchange Process for Treating Uranium Mine Water. 45th International Water Conference, Pittsburgh, Pennsylvania, October 22-24, 1984.

RANDOL (1980) Continuous Ion Exchange and Resin-in-Pulp for Uranium Recovery. Randol International Ltd. Multi-Client Report, June 1980.

RANDOL (1983) Innovations in Gold and Silver Recovery, Phase II, Multi-Client Report, Appendix 2, pp398-403.

RANDOL (1985) Gold and Silver Recovery Forum 85 - Conference to be Held in Santa Fe, New Mexico, October 14-15, 1985.

VAN ASWEGEN, P.C. (1985) Recovery of Dissolved Gold from Rotary Filter Residues by the Addition of Fine Activated Carbon Powder Followed by Flotation. XVe Congris International de Mineralurgie, Cannes, France, June 2-9, 1985.

WATSON, R.H., and TURNBULL, J.D. (1983) Cominco Ltd.'s Effluent Treatment Plant at its Trail, B.C., Metallurgical Plant. The B.C. Professional Engineer, May 1983.

CHAPTER 57

SCALE, CORROSION, AND ABRASION CONTROL

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INTRODUCTION

Scale, corrosion, and abrasion can directly and indirectly account for surprisingly large expenditures on mine-mill complexes. The full extent of these costs are not always recognized by an operator as they are paid for from different departments under headings such as reagents, maintenance, replacement parts, pipes, pumps, water treatment, service supplies, etc. MOKKEN (1964) used a systems approach to evaluate the cost of pipe, pump, and valve replacement on Witwatersrand gold mines. His estimate of replacements in this area exceeds the total cost of milling and extraction. Much of these replacement costs are the result of corrosion which is directly attributable to water quality and abrasion. Scale control incurs direct costs for scale-inhibiting chemicals and physical scale removal measures. The indirect cost of scale includes the reduction in capacity due to reduced flow rates in pumps and pipes affected and in replacement and maintenance costs.

Water is recycled to an increasing degree as a means of reducing net water consumption and/or reducing the volume of effluents to be discharged or treated, and this trend will continue well into the future. As this occurs, scale and corrosion effects will become even more noticable, and increasingly costly measures will be required to counteract or control them. In addition, those that build up the knowledge and experience to predict and reduce these effects in advance will save costs and headaches as well as achieving a more efficient operation with less expensive downtime.

This investigation was able to carry out only a partial industry survey of water treatment chemicals used in mines and mills. Despite an effort to do so, it failed to establish definitive data on what the range in annual costs for water treatment chemicals and services at mines and mills actually amounts to. The results of a survey of copper, copper-moly, and gold and silver recovery operations is shown in the tables below. The impression gained is that the total cost of scale and corrosion inhibitors varies greatly but can be significant. On the other hand, some very large operations that recycle as much water as they can and are zero discharge, such as Vaal Reefs Exploration and Mining, do not need any scale-inhibiting chemicals in their gold metallurgical processes. Large copper and copper-moly mills employ water treatment service companies to prevent scale and control corrosion in their boilers and elsewhere.

Mining and milling companies would be well advised to survey their expenditures on this type of service and on water treatment chemical purchases throughout their operations. Once it is known how much is spent in this area and the extent to which pumps, parts, pipes, valves, etc. are replaced due to scale and corrosion effects, then they can draw some conclusions and set goals as follows:

- Should more or less attention be given to scale and corrosion control?
- Is the amount spent in this area large enough to justify investing in research and development into fundamental aspects of the phenomena to provide in-house services and expertise aimed at reducing overall costs?
- Are the answers to be found in material selection, water treatment, or both?

SCALE INHIBITION

One way to reduce scale problems is to use a plastic pipeline with a smooth inner surface, e.g., HD polyethylene, but this does not always work. In one case, a flexible rubber pipeline was being tested as it allowed scale to be easily removed after it had formed by simply driving a pickup truck over the line. In another case, a HDPE pipe was suspended across support towers and as it expands and contracts with temperature differences, the scale layer breaks loose due to the flexing motion.

Two innovative ways of reducing scale problems in metallurgical plants that use recycle solutions were identified. The first involves how fresh water is added to the circuit. Metallurgists have observed that, quite often, scale forms locally near the point at which fresh water is added to the circuit. The logical approach, therefore, has been to add fresh water to recycled mill solution in a separate tank or pond allowing it to precipitate species therethat would otherwise have formed scale in the plant. Some operations allow their process water to age for some time after adding fresh water. Examples of such operations include Cities Service, Pinto Valley; Cyprus Bagdad; Cyprus Pima; and Pinson Mining Company, and scale inhibitors are not needed as a result or are needed much more selectively.

A second approach to scale reduction involves an understanding and manipulation of the bicarbonate-carbonate equilibrium and its pH dependence. If, through CO_2 dissolution or any other cause there are bicarbonates present in recycled solution, then when lime is added to raise the pH, the $CaCO_3$ formed may far exceed its solubility at that pH. Even if NaOH is added for pH adjustment, $CaCO_3$ in solution may still be precipitated because at high pH, its solubility is much lower than at a low pH. At Bethlehem Steel Corp.'s Panther Valley Division, thorough aeration has been found to remove much of the CO_2 from solution resulting in less reagent requirement to raise the pH and much smaller quantities of precipitate to handle, i.e., a correspondingly less scaling water quality.

PHYSICAL SCALE REMOVAL

One way that is frequently employed to remove scale from the inside of pipelines is by passing a plastic "pig" through the pipeline, which has an abrasive carborundum coating which literally scours the scale from the inner surface of the pipe. This pigs vary in size up to 26" in diameter. A "crisscross" coated pig 26"Ø costs around R750 (U.S. $375), and a hand-made pig with a wire brush coating costs R1,000 ($500). These are supplied with launchers equipment or as a custom pipecleaning service by:

RSA PIPECLEANING (PTY) LTD.
Post Office Box 1568
Pitchefstroom 2520
South Africa
(01481) 254475
Mr. D. Arendt
General Manager

GIRARD POLYPIG
Houston, TX
(Address Not Found)

KNAPP
Houston, TX
(Address Not Found)

POLYMOLCH GmbH
Wupperthallerstr 257
5650 Solingen-1
West Germany
(2122) 592909
Heinz Lantzen

R. J. SPARGO LTD.
Post Office Box 3793
Alrode 1451
South Africa
(011) 864-2744
Telex: 4-20365
Jimmy van der Birgh

At Delta Managanese, steel pipes are beaten with sledgehammers by a crew that works full-time to dislodge scale from pipes. At Zincor, steel pipes used to be burnt in an outdoor fire in which the rubber lining is burnt away to release scale which then slides out of the pipes. Delta Managanese had considered using scale inhibitor chemicals but were not sure of the effect that these might have on their electrolytic manganese recovery process.

Brunswick Mining was experimenting with a very flexible pipeline in which scale could be dislodged and broken into pieces by simply driving a pickup truck over it. More information on this experiment would be available from:

BRUNSWICK MINING AND SMELTING CORP. LTD.
Mining Division
Post Office Box 3000
Bathurst, N.B. E2A 3Z8
(506) 546-6671
Telex: 014-24582
John S. G. Martin
Concentrator Superintendent

SCALE CONTROL

In the course of this investigation, it was found that scale and corrosion control services and reagents are widely used in metallurgical operations. For example, virtually every gold heap leaching and several successful CIP plants for gold recovery use a scale control additive to reduce carbon fouling which, in turn, enhances the efficiency of gold adsorption.

Carbon fouling in columns and CIP tanks generally seems to involve a carbonate scale, and acid washing of carbon is standard practice as a means of removing scale that blocks the carbon pores. For this, nitric or hydrochloric acid are used.

CALGON CORPORATION and NALCO have both recently completed studies on the fouling of carbon by scale in carbon columns and CIP tanks and now are in a position to make advanced scale inhibition recommendations.

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Bennett P. Boffardi

NALCO CHEMICAL COMPANY
1801 Diehl Road
Naperville, IL 60540
(312) 961-9500
William J. Roe
Mining and Mineral Processing Research

The formation of calcite scale occurs as a series of aqueous chemical reactions, ultimately leading to the precipitation and deposition of calcium carbonate under alkaline conditions. The process can be likened to any other crystalization from solution in that it initially involves nucleation to form fine seed crystals followed by crystal growth, agglomeration processes, and in this case, deposition on surfaces. These processes can be altered by certain chemical additives which either inhibit nucleation, modify crystal structure, or both. The result of such chemical addition can be one of complete scale inhibition. As such, aqueous systems can be stabilized with respect to scale formation even though their water chemistries would normally indicate instability.

Scale inhibition can also be used to prevent pipes, pumps, and screens from scaling up. Scale can be a problem in Merrill-Crowe filter screens, in barren lines, in carbon desorption circuit heat exchangers, and at several other points in the circuit. Getting back to the fouling of carbon, one operation of Cambrai Mining Co. in Zimbabwe was unable to achieve even a reasonable gold recovery by CIP because the carbon was severely fouled by a carbonate scale before the gold could load.

In the table below, only three heap leaching operations are listed, and only one of these uses a scale inhibiting chemical. In fact, in informal discussions with many heap leaching operations not listed, most of them rely on some form of scale inhibiting chemical.

The survey of gold and silver recovery operations lists more that do not use reagents than those that do. Those that use no reagents include several that recycle water extensively. It is possible that the quality of available water may have a major effect on scaling.

Operations that treat ores containing sulfide minerals and recycle tailings decant solution invariably find a buildup in sulfates and particularly calcium sulfate, a notorious scale former. Gypsum scale can also be very effectively controlled through the use of chemical additives, one of which, sodium hexameta phosphate, is wellknown. In desalination

CALGON
CORPORATION

SUBSIDIARY OF MERCK & CO., INC.

CALGON CORPORATION CALGON CENTER BOX 1346 PITTSBURGH, PA 15230 (412) 777-8000

Writer's Direct Dial Number
412-777-8525

December 20, 1984

Randol International Ltd.
21578 Mountsfield Drive
Golden, Colorado 80401

Dear Hans:

The problems at the Cambrai Mining Co. in Zimbabive are related to carbonate/sulfate scale being deposited in the carbon pores.

Calgon has scale inhibitor treatments capable of controlling these deposits. Two that are most appropriate for gold mine circuits are SCM105 and SCM205.

I have contacted our subsidiary Floccotan (Pty) Ltd. in South Africa about this problem. They will pursue this matter with your friend Ron Edington. Our representative is:

Mr. James Smith
Floccotan (Pty) Ltd.
P. O. Box 211
Hilton 3245
Natal, Republic of South Africa
Phone 27 331-33265

Let me know if I could be of anymore assistance.

Very truly yours,

CALGON CORPORATION

Ben

B. P. Boffardi, Ph.D
Senior Research Associate

/tt

processes, it is claimed that fouling can be prevented on surfaces in contact with solutions that contain gypsum up to 3-4 times saturation.

An operation that has experienced severe gypsum scale problems in monitor water pipelines is ERGO (East Rand Gold and Uranium Company) on the Witwatersrand which reclaims old gold mine tailings for recovery of pyrite containing gold and uranium by flotation followed by uranium leaching by sulfuric acid. A new CIP plant to treat the entire 1,600,000 tons per month of feed material has been installed. The partly oxidized sulfide-containing tailings material and sulfuric acid used in the process, as well as high TDS minewater used in the process, result in a high $CaSO_4$ level in recycled process water, but surprisingly, little scale problem is encountered in the tailings return solution lines, although serious scaling occurs in the lines taking water to the monitor stations where tailings are repupled. Several scale inhibiting chemicals were being tested at the time of the 1984 visit. Of particular interest is a dynamic scale monitoring device developed by CALGON CORP., whose address was shown above, and supplied in South Africa through their local agents:

FLOCCATAN PTY LTD.
Post Office Box 4578
Randburg 2125
South Africa
(011) 789-3823
Telex: 4-26994
Jack Hallows

This dynamic scale monitor allows scale inhibiting chemicals to be screened and also for dosages to be optimized for a given process solution.

Copper and copper-molybdenum mills in the desert southwest of the U.S.A. recycle tailings water extensively as a water-saving measure. These operations make extensive use of scale control chemicals, and some apply an innovative way of blending fresh water with recycle solution to reduce scale by allowing a precipitate to form and settle outside the plant.

Many mines and mills operate boilers to generate steam and heat. In boilers as in cooling plants, scale inhibition is essential to preserve the efficiency of heat exchanger surfaces lest their performance drops below design resulting in adverse process effects or equipment damage. Once again, the addition of chemicals is a common way of controlling scale in this area. Another way is to use demineralized water as boiler feed water, which is an application for R.O. and ion exchange.

Most typical scale encountered in metallurgical circuits is composed primarily of carbonates and sulfates, usually of calcium although scale can also contain a wide range of other species including magnesium, silica, iron, manganese, aluminum, etc. Bacterial scale

depositions akin to jarosites may be rich in metals and can lead to enhanced localized corrosion due to electrolytic effects.

Scale may be quite soft and easily removed as long as it is submerged. After exposure to the air, it can become very hard and difficult to remove. Sometimes this results in severe scale difficulties at the waterline in tanks, thickeners, etc.

$CaSO_4$ scale has been a problem, particularly where sulfide-containing tailings are involved or where sulfuric acid is used as a reagent and where the ore contains soluble calcium or where lime is used to neutralize tailings. Gypsum scale is commonly inhibited using chemical additives such as NL Baroid Division's S35 which is a hexa-meta phosphate. In operating plants, gypsum scale quite often is enhanced where there are local hot spots, e.g., in heat exchangers. In evaporative desalination, for example, temperatures of solution are sometimes kept below 80°C, above which gypsum seems to be particularly unstable.

It is of interest that if an excessive dose of sodium hexa-meta phosphate is used, then the excess converts to orthophosphate which may then exceed effluent limits. Also, excess Na hexameta phosphate itself converts to orthophosphate which results in phosphate scale formation under certain conditions, so it must be carefully dosed.

Two other operations that experience excessive gypsum scale problems include Delta Manganese Co. and Zinc Corporation of South Africa Ltd., both of which use sulfuric acid as a lixiviant for manganese and zinc leaching respectively. These operations are discussed in Appendix I. In both cases, sodium hexa-meta phosphate might prove useful in modifying the gypsum scale, but concern has been expressed as to the possible effects in their electrolytic cellhouse.

In general, where gypsum scale occurs, sodium hexa-meta phosphate is often applied to inhibit it. Where the scale is a carbonate, then maleic acid derivatives or polyacrylates can be applied. Just 2 ppm of a low molecular weight polyacrylate is found to be effective at inhibiting calcium carbonate scale as it has a marked effect on the $CaCO_3$ crystal structure. Suppliers of polyacrylates are the Nalco Chemical Co., Allied Colloids, and American Cyanamid. In Canada, a company called Alkaril Chemicals Ltd. also manufactures polyacrylates. Polyacrylates are potentially much less expensive to make than the maleic acid derivatives. Phosphonates inhibit both gypsum and $CaCO_3$ scale. WIECHERS (1975) discussed some of the scale inhibiting principles.

A variety of scale inhibiting chemicals are offered to the mining industry by:

N. L. INDUSTRIES
Baroid Division

CALGON CORP.
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Frank Daniher

DREW CHEMICAL CORP.
Drew Chemical Plaza
Boonton, NJ 07005
Joe Roti

NALCO CHEMICAL COMPANY
2901 Butterfield Road
Oak Brook, IL 60521
(312) 887-7500
Robert E. Finch

ALCHEM LTD.
Mississauga, Ontario

UNION CARBIDE CORP.
Solvents and Intermediates Div.
K436 Old Ridgebury Road
Danbury, CT 06817

ANIKEM PTY LTD.
Post Office Box 67817
Bryanston 2021
(011) 706-6106
Telex: 422256
Merwyn S. C. Wilson

ALLIED COLLOIDS (SA) PTY LTD.
Post Office Box 48775
Roosevelt Park 2129
South Africa
(011) 782-5335
Telex: 4-24410
Robert M. Page

FERSTE CHEMICALS (PTY) LTD.
Post Office Box 41109
Craighall 2020
South Africa
(011) 787-8857
Stuart Ferguson

FLOCCOTAN (PTY) LTD.
Post Office Box 4578
Randburg 2125
South Africa
(011) 789-3823
Telex: 4-26994
John Hallows

FLOCCOTAN (PTY) LTD.
Post Office Box 211
Hilton 3245
South Africa
(0331) 33265
James Smith

TESTING THE EFFECTIVENESS OF SCALE INHIBITION

Drew Industrial Division has developed a simple, yet effective means to test the effectiveness of scale inhibitors in recovery circuits. This method further enhances the data collected by the "PULSE" dynamic scale monitoring unit which produces data on a continuous basis. The combination of these two approaches further ensures up-to-the-minute evaluation of scale deposition in pipelines, pumps, and other water-related equipment.

This device, used by Drew Industrial Division consists of a retractable scale coupon which can be inserted into any system through a valve. Visual examination of this scale coupon can be accomplished in minutes.

Scale deposition can then be noted on the coupon to evaluate the effectiveness of the scale inhibitor in the system. This method can be used continuously to compare various products and/or dosage levels.

The advantage of the retractable probe lies in its simplicity, ease of use and reliability for measuring scale deposition visually in metallurgical and water treatment plants.

ALKARIL CHEMICALS LTD.
3265 Wolfedale Road
Mississauga, Ontario
Canada L5C 1V8
(416) 270-5534
Telex: 06 960179
Graham H. Gray

GIULINI CHEMIKE AG
Ludwigshafen
West Germany
(0621) 500310
Telex: 46484219
Dr. H. D. Nagerl
Fritz Thomas
Ronald Lehnert

Reagents come across in the course of this investigation which are used as dispersants include:

NL Industries, Bariod Division	S-35 Hexa-meta Phosphate
Drew Chemicals	Millsperse 802 Maleic Acid Derivative
Nalco	Nalco 8830
Alchem	Alchem 961
Allied Colloids SA	Antiprex
Anikem (Pty) Ltd.	Anikem 4393
	Anikem 7311 (For Compressor Coolers)
Floccotan	CL 4000
Ferste Chemicals	PC 40
Alkaril Chemicals Ltd.	Polyacrylates

Most of the copper and copper-molybdenum mills surveyed in the U.S.A. use recycle water. When recycled water is used, scale inhibitors of one kind or another are often applied, for example:

Operation	Treatment of Reclaim Solution (1980)
ASARCO, Sacaton	Hexametaphosphate for Scale Control
Phelps Dodge, Metcalf	Hexametaphosphate for Scale Control; Lime for pH Contol
Phelps Dodge, Morenci	Hexametaphosphate
Phelps Dodge, New Cornelia	Drew Co. "Amitrol"
Phelps Dodge, Tyrone	Calgon CL-50 (Inorganic Phosphate) and CL-95 (Dispersant), 5:1 Radio for Scale Control
Inspiration, Christmas	Calgon Reagents for Scale Control
Cities Service, Pinto Valley	Discharge water is put in a holding tank, and fresh water is added. Salts are allowed to settle out before water is recycled. No reagents are used.

Anaconda Co., Carr Fork, UT	Recycled water is not chemically treated.
Magma, Superior	Phosphate chemicals are added for scale control.
Anaconda, Butte, MT	Minewater and precipitation plant (lime) overflow is added to mill tailings underflow. Heavy metals from mine and precipitation plants waters are precipitated by alkaline mill tailings underflow. Tailings dam water is returned to plant at pH 10.5.
ASARCO, Mission	P_2O_5 Scale Control Additive Used
ASARCO, Silver Bell	Phosphate Chemical for Scale Control
Cyprus, Bagdad	Fresh water is added to recycle water in a tank and settled; no chemcals are used for scale control.
Cyprus, Pima	Tailings pond decant is mixed with fresh water. A precpitate is allowed to settle out. No chemcals are used.
Inspiration Copper, Inspiration	Decant from tailings pond is mixed with fresh water, and a Calgon reagent is added and the water recycled.
AMAX, Twin Buttes	NL Baroid chemical is added for scale control.
Duval, Sierrita and Esperanza	Mill tailings are thickened, and the overflow is stored in a reclaim water reservoir. Tailings pond decant solution is pumped to the reclaim water reservoir. Reclaim water reservoir is thickened, and overflow is recycled to the plant. A phosphate-based additive supplied by NL Baroid Div. is added for scale control.
Duval Corp.	Overflow from tailings thickeners is recycled to the plant with tailings pond decant. Water is chlorinated quarterly to kill bacteria.
Black Mountain, South Africa (Cu, Pb, Zn, Ag Flotation)	No Scale Inhibitors Used

SCALE CONTROL IN GOLD AND SILVER RECOVERY OPERATIONS

A recent survey of gold and silver recovery operations included questions as to the amount and type of scale inhibiting reagents used and where they are applied in the circuit. Responses to this questionaire are summarized as follows:

SCALE CONTROL IN GOLD AND SILVER RECOVERY OPERATIONS

Operation	Type	Location	Scale Inhibitor Used	Where Used	Dosage	Comments
Whim Creek Consolidated NL	HL, Au	Western Australia	Nil	N/A	N/A	$NaOH/Na_2CO_3$ Used for pH Adjustment
Hayden Hill	HL, Au	Susanville, CA	Nil	N/A	N/A	
Candelaria	HL, Ag	Hawthorne, NV	Drew Millsperse 802	Barren Pond	50cc/Minute	
Louis Moore G.M. Co. Ltd.	CIP, Au	Giyani, South Africa	Nil	N/A	N/A	
Major Witwatersrand Mill A	CIP/M-C	Witwatersrand	Yes	Boiler Feed	N/A	
Consolidated Modderfontein	CIP	Witwatersrand	Nil	N/A	N/A	
Major Witwatersrand Mill B	M-C	Witwatersrand	Nil	N/A	N/A	
Major Witwatersrand Mill C	M-C	Witwatersrand	Nil	N/A	N/A	
Vaal Reefs Exploration and Mining Co.	M-C	Witwatersrand	Nil	N/A	N/A	
Elandsrand G.M. Co. Ltd.	M-C	Witwatersrand	Nil	N/A	N/A	
South Roodepoort Main Reif Areas Ltd.	M-C, Au	Witwatersrand	Nil	N/A	N/A	
Western Deep Levels Gold Plant	M-C, Au	Witwatersrand	Nil	N/A	N/A	
Bracken Mines Ltd.	M-C, Au	Witwatersrand	Triple Polyphosphate	Pump Glands	10 Kg/d	None Used in Met. Process
Leslie Gold Mines Ltd.	M-C, Au	Witwatersrand	Triple Polyphosphate	Pump Glands	10 Kg/d	None Used in Met. Process
Mine A, Zim	M-C, Au	Zimbabwe	Nil	N/A	N/A	
Mine B, Zim	CIP, Au	Zimbabwe	Nil	N/A	N/A	
XYZ, Asia	M-C, Au	SE Asia	Nil	N/A	N/A	
Kiena Gold Mine	CIP, Au	Ontario	Nil	N/A	N/A	
Freeport Gold Co.	CIP, Au	Nevada	Nil	N/A	N/A	
Mercur Gold Mine	CIL, Au	Nevada	NALCO 8830	CIL Plant	13 lbs/t	
Cortez Gold Mines	CIL, HL, Au	Nevada	Millsperse 802	Strip Circuit	2-5 ppm	
Black Mountain	Flotation, AgCuPbZn	S. Africa	Nil	N/A	N/A	
BHP Gimlet South Project	CIL, Au	Australia	Nil	N/A	N/A	Keep Mg in Solution by Maintaining pH Below 9.8
Western Mining Corp.	CIP, Au	Kambalda, West Australia	Nil	N/A	N/A	
Lac Minerals, LTA Div.	M-C, Au	Quebec	Alchem 961	Thickener o/f	0.02 lb/t	
Lac Minerals, Macassa Div.	M-C, Au	East Canada	Alchem 961	Thickener o/f	0.01 lb/t	
Lac Minerals, Doyon Div.	M-C, Au	East Canada	Alchem 961	Thickener o/f	0.01 lb/t	
Lack Minerals, East Malartic	M-C, Au	East Canada	Alchem 961	Thickener o/f	0.01 lb/t	
FMC Silver Peak	M-C, Au	Nevada	Barold S-35	Leach and Barrens Line	Up to 0.05 lb/t	Projected
Giant Yellowknife Mines	M-C, Au	NW Territories	Alchem Balls	Clarifiers	0.004 lb/t	
Campbell Red Lake Mines	M-C, Au	Ontario	Alchem Balls	Clarifier	0.009 lb/t	
Hecla Mining Co.	M-C, Au	Republic, WA	Nil	N/A	N/A	

CORROSION

There are several mechanisms by which corrosion of metal pipes, structures, valves, and equipment can occur in mine-mill operations. These were described by BOFFARDI (1984) in a fascinating description, unfortunately not available in printed form. NALCO (1979) outlines some of the same aspects and shows some ways to control corrosion. Clearly, corrosion control is an art based on years of experience as well as a science. As solutions are recycled, this can result in a gradual increase in ionic species which cause an enhanced rate of corrosion. One of the most common of these is the chloride ion which, in an acid medium, corrodes carbon steel and even most stainless steels. Internal screens fabricated from stainless steel were corroded very rapidly in an ion exchange plant installed on the Witwatersrand. This corrosion was blamed on the presence of thiosulfate in the pregnant solution.

Corrosion of stainless steel autoclaves installed at Rustenburg Refiners to leach a base metal matte under pressure became a problem when the chloride level in the regional water supply started to rise during a drought. These metallurgical solutions are recycled extensively, and any chloride introduced in feedwater accumulates in the system. At Rössing Uranium Ltd., and Quivira Mining Co. uranium mills in Namibia and New Mexico, the extent to which acid tailings dam reclaim solution can be recycled to the mills is limited by corrosion of thickener rakes in the CCD circuit.

This corrosion is caused by chloride levels in the acid pulp solutions. In the case of Rössing, the need to increase the use of recycle solution was important enough to justify applying polyurethane coating to thickener rakes and the fabrication of stainless steel pump shaft sleeves to allow recycled water to be used in their lubrication. These measures and details are provided in the trip report on Rössing Uranium Ltd. in Appendix I. To date, the following suppliers and appliers of polyurethane coatings have been identified:

UNIROYAL INTERNATIONAL, INC.
World Headquarters
Middlebury, CT 06749

BAYER LEVERKUSEN AG
Leverkusen
West Germany

ATLAS FOAM (PTY) LTD.
Post Office Box 2268
Trekker 1547
Brakpan
South Africa
(011) 55-8504
Telex: 4-21137
Graham H. Pole

WEAR RESISTANT MATERIALS (PTY) LTD.
2 Kelsey Place
Asquith, N.S.W.
Australia 2078
(02) 476-5655
Ian Lyon
Managing Director

The cost of applying polyurethane coatings in South Africa works out to about R20 per mm/m² or R60 per m² for a 3 mm application. Polyurethane is much faster to apply than is rubber. Both require spark testing of coated surfaces prior to use.

At the Kloof Gold Mine, about 50 kilometers of underground piping reputedly had to be replaced due to corrosion that was enhanced by the presence of Cl^- in minewater.

Pitting corrosion is caused by galvanic effects and can be very rapid. Recycle of water results in a buildup of nutrients and metals and especially in an acid media, bacterial populations may thrive. At Rössing Uranium Ltd., when the use of recycled tailings water was increased, a biologically deposited "jarosite" scale containing relatively high concentrations of base metals was found to accummulate on the inner surface of steel pipes. Enhanced corrosion of the steel occurred under the scale layers due to an emf difference between the scale and the pipesteel. This is an example of a case where corrosion is enhanced by scale formation and where the use of an appropriate biocide would prevent both from occurring. A similar type of biological scale with high metal levels was observed at Bethlehem Steel Corp.'s Panther Valley Division coal mine in Pennsylvania in a pump used to lift minewater to the surface. Presumably, high density polyurethane pipelines resist this type of corrosion, although cement lines have been known to be attacked.

At Venterspost Gold Mining Co. Ltd. on the Witwatersrand, a steel pipeline is used to transport water pumped from the regional aquifer to a point at which it is reinjected 12 km away. This water was extremely corrosive, and the problem was solved simply by adding a small amount of lime to the water which rendered it slightly scaling.

It is wellknown that chloride ions in water result in enhanced corrosion of both mild and stainless steel. Another less wellknown cause of corrosion, especially when heated, is fluoride. Apparently, just a few ppm of Fluoride can be very damaging. More information on details of fluoride corrosion effects would be available from:

JAMES D. MAVIS, JR.
CH2M Hill, Inc.
Post Office Box 91500
Bellevue, WA 98009-2050
(206) 453-5002

DETERMINATION OF CORROSIVITY

There are innovative ways to determine the corrosivity of water. One way is to analyze the water and to compute the corrosivity or scaling nature of water. There are several indices that are in use including the commonly used Langelier Index. Corrosiveness can also be measured using a variety of tests in the laboratoy. Dynamic corrosivity measuring devices are available from U.S. suppliers and consultants such as:

E, G & G PRINCETON APPLIED RESEARCH
Post Office Box 2565
Princeton, NJ 08540
(609) 452-2111

In general, corrosion can be avoided by appropriate use of materials of construction and coatings, and it is customary to have consulting engineers with specialized corrosion experience to survey the process and to advise on material selection. Although this approach is invaluable when corrosive solutions are to be used, it requires that the composition of solutions be known in advance. This, in turn, requires accurate salt balance modelling which, for most mine-mill complexes, is still an inexact science. Some idea can be gained from tests and analyses of the ore, a knowledge of the reagents to be used, and proposed operating pH to determine what corrosion phenomena may be expected. Some companies have more experience in water and salt balance modelling than others.

Calgon Corporation has developed a very effective computerized simulator for cooling water system performance prediction for electric power plants. This program uses a huge database of empirical data gathered from operating power plants all over the world. This program and database, called "Calguard," cost many millions of dollars and years of work to develop, and it relates primarily to power plant water cooling systems. This sytem is capable of reproducing the operating conditions of cooling water systems and diagnosing the problems which will be encountered from corrosion, scale, and deposition. The entire range of treatment options can be scanned and the results accurately predicted. Since the computer simulator is based on fundamental technology, it applies to both present and future cooling system requirements. This represents a capability that is dramatically distinct from data banks which rely entirely on past experiences to address present day needs. Although no similar system exists for mine-mill water systems, the approach applied in developing the Calguard program as described by BOFFARDI and SCHWEITZER (?) could be helpful to those wishing to attempt the task of developing one. More information on Calguard can be requested from:

CALGON CORPORATION
Post Office Box 1346
Pittsburgh, PA 15230
(412) 777-8000
Leo Weaver
Bennett P. Boffardi
Ron Losasso

Others with known experience in modelling salt and water balances for mine-mill applications useful in material selections for corrosion control are:

RESOURCES CONSERVATION COMPANY
3101 NE Northrup Way
Bellevue, Wa 98004
(206) 828-2400
Russell Vanderberg
Vice President

STEFFEN ROBERTSON & KIRSTEN
7510 West Mississippi Ave., #210
Lakewood, CO 80226
(303) 936-8254
Adrian Smith
Geochemist

It is prudent practice to carry out corrosion surveys both before a plant is built and after it has been in operation for some time to identify where corrosion protection measures are needed. The following company is wellknown in this field:

MICHAEL A. BRETT AND PARTNERS
Post Office Box 61872
Marshalltown 2107
South Africa
(011) 803-2273
Dr. Colin E. Alvey
Partner

MICHAEL A. BRETT AND PARTNERS
21 Verulam Road
St. Albans Herts AL3 4DG
England
Telephone: St. Albans 55254
Michael A. Brett

Desalination processes are increasingly being used to produce low TDS water for use as boiler feed, battery water, and even potable water. These processes include ion exchange, reverse osmosis, electrodialysis, and evaporation. Desalinated water with very low TDS levels is one of the most corrosive of all water, and a post treatment is necessary to prevent damage to pipes, pumps, tanks, and reticulation systems. Usually these involve contacting water with granular limestone.

Corrosion of cooling tubes in refrigeration plants at large mine-mill complexes has been associated with the presence of high Cl^- and $SO_4^=$ as well as ammonia in cooling water. This is one reason that reclaimed sewage water may not be desirable for use in cooling systems. However, Calgon Corp. offers an additive which they find inhibits corrosion of copper-nickel cooling tubes exposed to this kind of water. Enquiries can be directed to Bennett Boffardi at the Calgon address shown above. Elsewhere, corrosion studies conducted at the CSIR recommended a different metal alloy for use in cooling tubes exposed to this kind of water. An alternative is to employ a sewage treatment process that removes ammonia very efficiently.

CORROSION PREVENTION

As with scale, corrosion can be controlled by selecting non-corrosive materials. For example, stainless steel may be more corrosive resistant than mild steel, but it is also more expensive.

The mid-1980's sees the dawning of the age of plastics of which there is a wide range for use either for fabrication of corrosion and abrasion resistant components or coatings. There are two aspects to corrosion resistant materials--first are the suppliers of the resins, etc., and developers of the materials such as DuPont, Uniroyal, etc. Usually, however, the mining company will be exposed to these materials through fabricators who manufacture plastic components and through service companies that offer to apply plastics.

Of course, one wellknown example of this is DuPont's high density polyethylene pipe known as Schlairpipe. Since it first became available less than a decade ago, a whole range of manufacturers and vendors have sprung up offering similar products.

On the Witwatersrand, for example, underground minewater after removal of suspended solids is treated with lime before it is pumped to the surface. This measure is adopted to minimize corrosion of pipes and pumps.

Belt filtration facilities are characterized by a lot of splash which creates a highly corrosive environment when corrosive solutions are used. Some belt filters have been constructed of stainless steel; others have been very carefully coated with plastics, e.g. epoxy coal tar or polyurethane. Where decks are employed in this type of environment, the use of conventional steel grating is asking for high maintenance needs. Consequently, this is one area where fiberglass grating, although initially more expensive, is likely to pay for itself over a short period of time.

Today, ceramic and plastic equipment items such as cyclones, valves, solution distributors, etc. are being used with increasing frequency. Suppliers include:

COORS PROCELAIN COMPANY
600 9th Street
Golden, CO 80401
(303) 278-4000
Telex: 45593
Ray Paricio

KRYPTONICS, INC.
5660 Central Avenue
Boulder, CO 80301
Michael J. Elliott

VESCO PLASTICS (PTY) LTD.
Post Office Box 47
Virginia 9430
(017) 3-3075
Telex: 8-4770
A. Leger

CORROSION CONTROL

Principle means of corrosion control that can be applied if it is not possible to select a non-corroding material include the following:

Insulation

The joining of dissimilar metals can lead to galvanic corrosion. If it is essential to use dissimilar materials, they should be insulated from one another. This can be accomplished by inserting non-conductive materials (such as plastic pipe) between them. When this is done, it may be necessary to put an electrical cable as a jumper around the isolated unit because the system may be used as an electrical ground.

Applied Chemical Inhibitors

In spite of the fact that many options exist to minimize corrosion by improved design or better construction methods, because of economics, the majority of systems are designed and fabricated in such a way that a chemical inhibitor program is needed to control corrosion. This applies to all types of water systems: potable water distribution systems, cooling water systems, boiler water systems, process water, and effluent treatment plants.

Corrosion inhibitors are commonly used in cooling water systems. Just as corrosion can be inhibited by interrupting either the anodic or the cathodic reactions, so any chemical applied to the water to stop the anodic reaction will stop corrosion. Any material that is added to reduce the rate controlling cathodic reaction will reduce corrosion. An effective corrosion control program usually depends on specific inhibitors to stop the anodic reaction, slow the cathodic reaction, or both. Typical inhibitors in use are:

Principally Anodic	Principally Cathodic	Both Anodic and Cathodic
Chromate	Calcium Carbonate	Organic Filming Amines
Orthophosphate	Polyphosphonate	
Nitrate	Zinc	
Silicate		

Of the anodic inhibitors, chromate is widely used and is a very strong inhibitor. Where many common corrosion inhibitors form a barrier layer on the metal surface, chromate reacts with the metal forming a hard layer of reduced chromate Cr_2O_3 and alpha iron.

Orthophosphate also forms a phosphate film, but it is not as tightly adherent or as long lasting as chromate. Ordinarily nitrate, orthophosphate, and silicate are less often used than chromate in open recirculating cooling systems because of costs and technical limitations, including the potential for deposits (tricalcium phosphate), nutrient effect on microbes, and limited effectiveness. Chromate, on the other hand, is considered environmentally very undesirable which has resulted in corrosion control formulations with lower $Cr^{(VI)}$ content.

Anodic inhibitors also carry risk: If applied in insufficient quantities, they do not properly passivate all anodic sites. Under these circumstances, the few remaining sites become the focal point of all the electron flow to the cathodic reaction area, and deep pitting can result. Therefore, it is important to maintain sufficient quantities of anodic inhibitor at all times.

Cathodic inhibitors generally reduce the corrosion rate by forming a barrier or film at the cathode, restricting the hydrogen ion or oxygen migration to the cathodic surface to complete the corrosion reaction. Overall rate of corrosion is under cathodic control so the corrosion rate is reduced proportionally to the reduction in cathodic surface area. Cathodic species zinc, polyphosphate, and calcium carbonate are all considered safe compared to the risks of anodic inhibitors.

ANODIC/CATHODIC INHIBITOR MIXTURES

Some inhibitors enhance the activity of others. By itself, 200-300 mg/l CrO_4 is needed to prevent corrosion in an open recirculating cooling system. However, when combined with zinc, various organic and inorganic phosphates or molybdates, equal or better results are achieved with 20-30 mg/l CrO_4. Some systems are effective at controlling corrosion with only 10 mg/l CrO_4.

ORGANIC FILMS

These materials form filming layers on metal surfaces to separate the water and metal. These include filming amines that work effectively only in significantly reduced oxygen environments. Copper and copper alloy corrosion is reduced by applying inhibitors mercapto benzo thiazole, benzotriazole, and olytriazole. Certain organo-phosphorous scale inhibitors used in cooling systems are aggressive to copper-type materials so the addition of a copper inhibitor film must be used when they are applied.

SACRIFICIAL ANODES

Sacrificial anodes reduce galvanic attack by providing a metal (usually zinc or magnesium) that is higher in the galvanic series than either of the coupled metals. The sacrificial anode becomes anodic to both metals and supplies electrons to these cathodic surfaces. Design and placement of these anodes is a science in itself.

BIOCIDES

Use of appropriate biocides removes bacteria that adhere to the wall of pipes, etc. and deposit metal layers under a layer of scale. The biologically deposited metal then forms a galvanic electrode in the corrosion process which results in corrosion unless the bacteria that deposit the scale can be prevented from acting.

MONITORING CORROSION

Most metallurgical systems are in continuous use so it is rare to be able to inspect the actual system to observe or to measure corrosion and corrosion inhibition. A number of tools have been developed to measure corrosion indirectly.

Corrosion Coupons: These preweighed metal samples are normally inserted into the system for 30-90 days. Following removal, they are cleaned and reweighed. The metal loss and type of attack is determined and reported.

Corrosion Nipples: Corrosion nipples are only visually inspected. A nipple consists of a single pipe that is installed in a bypass arrangement so that the nipple can easily be removed for inspection at any time.

Corrosion Meters: Corrosion meters provide long-term data. More immediate results are possible after 24 hours or less following the initial system insertion. The meter works by measuring an electrical potential across electrodes made of the metal being evaluated. The corrosion meter, once stabilized, can provide instantaneous corrosion reading which are useful for optimizing pH, TDS, inhibitor level, chlorine addition, and other control variables.

ABRASION

Abrasion is usually caused in pumps, pipes, etc. on account of the suspension of abrasive solids in water that is pumped through them.

On the Witwatersrand, underground minewater is first allowed to settle with the aid of flocculants as described in Chapter 12 on the removal of suspended solids. Once most of the suspended solids have been separated into a sludge, this water can be pumped to the surface with much less abrasion damage. To achieve this, several innovative devices have been designed and tested on a commercial scale and found to work satisfactorily.

Also, on the Witwatersrand, a new type of hydraulic power using water to power tools and equipment as opposed to organic hydraulic fluids or air in tools that are currently pneumatically powered. If water is to be used, it will be critical to remove fine suspended silica from the water used for this purpose, lest it cause abrasion wear of the hydraulic components. It is not known what the constraints on the hydraulic fluids are as far as suspended solids are concerned. In due course, information will be released by:

THE CHAMBER OF MINES RESEARCH
LABORATORIES
Post Office Box 91230
Auckland Park 2006
Johannesburg
(011) 726-3020

Throughout industry, there are numerous new developments that provide better wear resistance to solutions or water with abrasive suspensions. As mentioned before, this is the dawning of the age of plastics and ceramics in the mine-mill equipment business. A whole range of plastic and ceramic cyclones have been developed by:

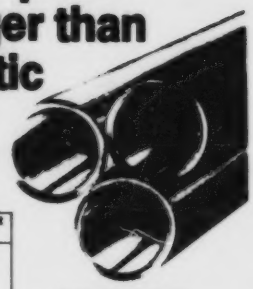
LINATEX CORP. OF AMERICA
Box 65
Stafford Springs, CT 06076
(203) 684-2756

KREBS ENGINEERS
1205 Chrysler Drive
Menlo Park, CA 94025

Uniroyal has announced a urethane slurry pipe which has unique abrasion resistance properties as shown in the table below in which it lost 8g weight in the time it took UHMWPE to lost 21g and carbon steel to lost 100g. More information on this urethane pipe is available from:

UNIROYAL, INC.
Slurry Pipe Products
Post Office Box 2008
Cathedral Station
Boston, MA 02118

Urethane slurry pipe lasts up to 8 times longer than steel, plastic or rubber



Relative abrasion resistance
Laboratory sand test (wet)

Materials	% Weight Loss*
Urethane	8
Ceramic Alloy	16
Nickel-Cast Iron	18
UHMWPE	21
Natural Rubber	55
410 Stainless Steel	65
304 Stainless Steel	75
Manganese Brass	84
Carbon Steel	100
Polyethylene (Low Density)	138
Polypropylene	275
Aluminum Alloy	310
Fiberglass Plastic	367
Polyvinyl Chloride	575
Hard Oil-Resistant Rubber	800

*Relative to 100

Actual applications and abrasion resistance tests show Uniroyal's urethane slurry pipe outlasts other types. Available: low-pressure solid urethane pipe; pressure-service Fibrethane™ pipe with a urethane liner and fiberglass cover; high-pressure urethane-lined steel pipe. For more information, complete coupon and mail card.

Uniroyal, Inc.
Slurry Pipe Products
P.O. Box 2008
Cathedral Station
Boston, MA 02118

Abrasion resistant ceramics are available as tiles or in castable form from:

MORGANITE CANADA, INC.
Abrasion Resistant Materials Division
3603 2nd Street N.E.
Calgary, Alberta
Canada T2E 3H6
(403) 230-1817
Telex: 03-826877

COORS PROCELAIN COMPANY
600 9th Street
Golden, CO 80401
(303) 278-4000
Telex: 45593
Ray Parica

Coors makes wear resitable components from alumina ceramics and also from wear resistant silicon carbide. Claims of outlasting ni-hard steel by 10 times at a cost premium of 30-40% are being made.

Even in carbon steel piplines, a way has been found to make pipe bends and fittings very much harder through a unique induction heat treating process to form a uniform hardened layer at the inner pipe wall at 600 Brinell hardness. The unhardened outer layer at 250

Brinell hardness ensures that the pipe has the strength and ductility required in typical pipe service. This type of pipe is available along with an innovative way to bend pipe using induction heating from:

NAS PIPE
North American Specialty Pipe Ltd.
5210-54 Avenue S.E.
Calgary, Alberta
Canada T2C 2V8
(403) 279-2222
Telex: 03-827514

POLYURETHANE COATINGS

Polyurethane coating are available from the same suppliers as were listed in the previous section on corrosion protection.

SPECIALTY ABRASION RESISTANT PLASTIC APPLICATIONS

Where recycle water containing fine solids particles is used, for example, in pump shaft lubrication as at Rössing Uranium or other such corrosive/abrasive applications, e.g., cloth roller bearings on belt filters, the need arises for specialty plastic components. One highly innovative company that formulates plastics and fabricates components to test or on small run production basis is:

VESCO PLASTICS
Post Office Box 47
Virginia 9430
(017) 3-3075
Telex: 8-4770
A. Leger

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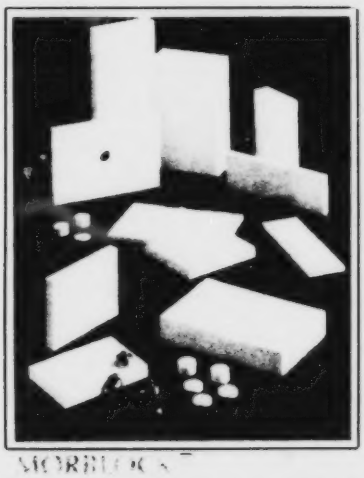
NALCO (1979) The Nalco Water Handbook, Chapter 20, Corrosion Control, McGraw Hill.

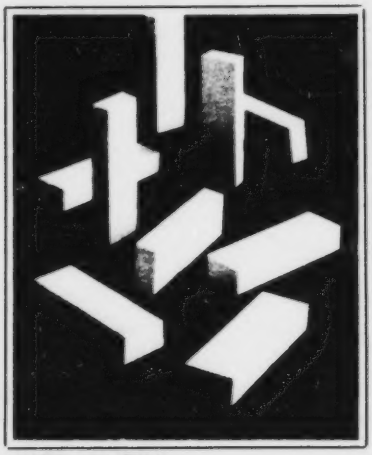
WIECHERS, H.N.S., STURROCK, P., and MARAIS, G.V.R. (1975) Calcium Carbonate Crystallization Kinetics. Water Research, Vol. 9, pp835-845, Pergammon Press.

Morganite®

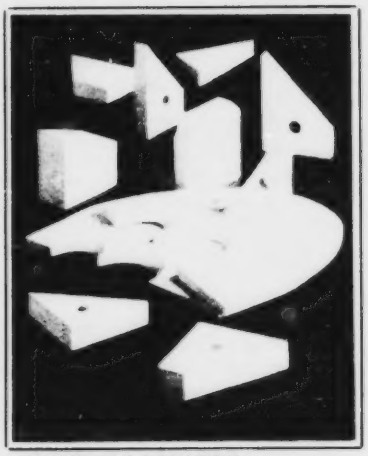
WEAR CONTROL CERAMICS



MORBLOCK™



PIPE LINERS



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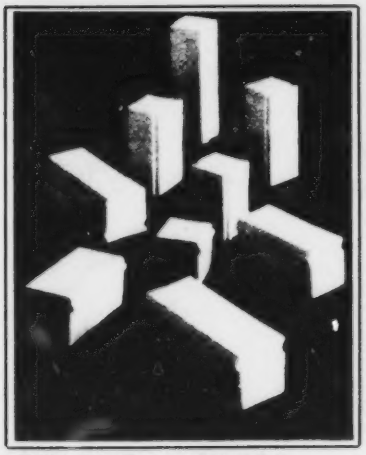

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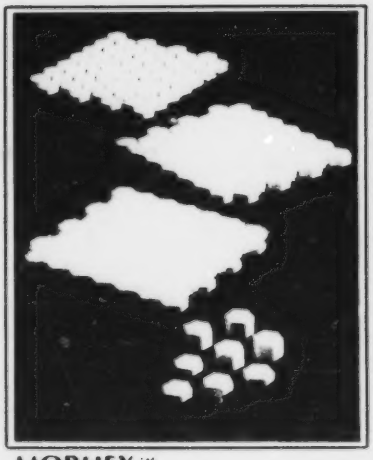

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Comparative Properties of MORGANITE High Alumina Ceramic

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PROPERTY		MORGANITE MATERIAL NUMBER	
		M[illegible]	M[illegible]
Alumina Content, Nominally	Al_2O_3%	87	94
Tensile Strength	Kg/cm²	1,265	1,800
	PSI	18,000	25,000
Compressive Strength	Kg/cm²	16,500	21,100
	PSI	235,000	300,000
Modulus of Elasticity	Kg/cm²	2.25×10^6	3×10^6
	PSI	32×10^6	43×10^6
Flexural Strength	Kg/cm²	2,990	3,160
	PSI	42,500	45,000
Impact Resistance, Charpy		6.3-6.5	6.5-7
Specific Gravity, Apparent		3.48	3.64
Porosity, Helium Mass Spectrometer		Gas Tight	Gas Tight
Water Absorption		0	0
Thermal Conductivity cal/sec/cm²/cm/°C @ 25°C		.03-.04	.05-.053
Average Coefficient of Thermal Expansion cm/cm/°C	25/200° 25/500° 25/700°	6.2×10^{-6} 7.09×10^{-6} 7.55×10^{-6}	5.5×10^{-6} 7.6×10^{-6} 7.9×10^{-6}
Hardness, Mohs Scale		9+	9+
Thermal Shock Resistance*		Good	Good
Firing Temperature, °C		1520	1675

* This quality affected by the size and contour of the part.

All data tests completed to ASTM Standards. Results are average for specimen tested and should be — but are not guaranteed to be — applicable to parts made of the material. Tests made on manufactured parts might vary slightly higher or slightly lower.

Packaging: Carton size: 6½" x 13" x 4". Approximate weight of packed carton is 35 pounds. Bulk packing on pallets available. Approximate pallet weight is 2500 pounds per pallet.

We invite inquiries for special sizes or configurations. Write or call: Morganite Canada Inc., Abrasion Resistant Materials Division, 3603 - 2nd Street N.E., Calgary, Alberta Canada T2E 3H6. Telephone (403) 230-1817 — Telex: 03-826877.

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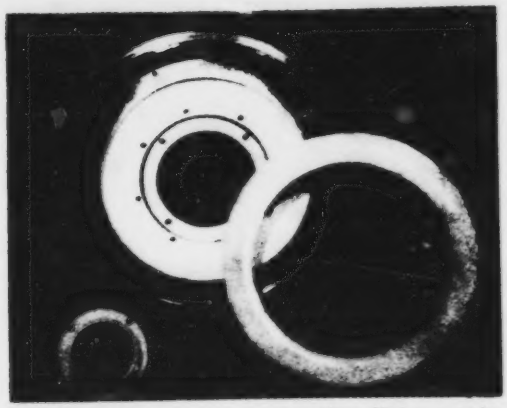
O.F.S. PIONEERS SAVING MINING INDUSTRY THOUSANDS

By combining their expertise two Free State entrepreneurs made a significant contribution towards underground pump maintenance.



Vesconite packing rings and protection plates fitted to a casing section of a high pressure multi-stage pump

When an 11 stage, 1100 Hp 825 kW underground centrifugal pump runs dry, roughly R25 000 goes down the drain. The resultant pump overall usually requires replacement of impellers, rings, diffusers, balancing disc, stationary disc and shaft.

A Welkom pump engineer, Doug Ray, has managed to bring this cost down to below R2 000 by introducing a packing ring and protection plates developed by South Africa's pioneer of engineering plastics, Alain Leger of Virginia, as a replacement for phosphor bronze parts.

This saving is being accomplished by fitting the multi-stage pumps with components made from Vesconite, a wear resistant thermoplastic polymer, which in the event of the pump running dry prevents metal to metal seizure.

Apart from outlasting similar phosphor bronze components and being resistant to erosion caused by water-borne abrasives, Vesconite melts harmlessly should a pump overheat. Hence it prevents the welding together of expensive metal components and eliminates the need for replacement of many thousands of Rands of spare parts.

The concept of the packing ring made from engineering plastics has been developed during many years of experimentation. Ray, who founded his Welkom pump service company in the late fifties, became increasingly aware of the need for a protection device in centrifugal pumps. He started searching for a material which could absorb the potential damage in a dry pump and initially fitted rings with laminated asbestos. The mud content in the water caused excessive wear and he subsequently tried moulded PTFE rings. However this material has the tendency of absorbing fine grit and consequently wears away the impellers.

Ray presented his problem to Alain Leger of Vesco Plastics in neighbouring Virginia whom he knew had been working for many years developing a thermoplastic polymer which would combine the load bearing capacity of white metal and long life of nylon. The resultant material, Vesconite, today is a sought after material as a replacement for bronze in bearings and bushes carrying high loads with small clearances under dirty, corrosive and poorly lubricated conditions. Its high dimensional stability and low friction coefficient even improve when the thermoplastic is immersed in water.

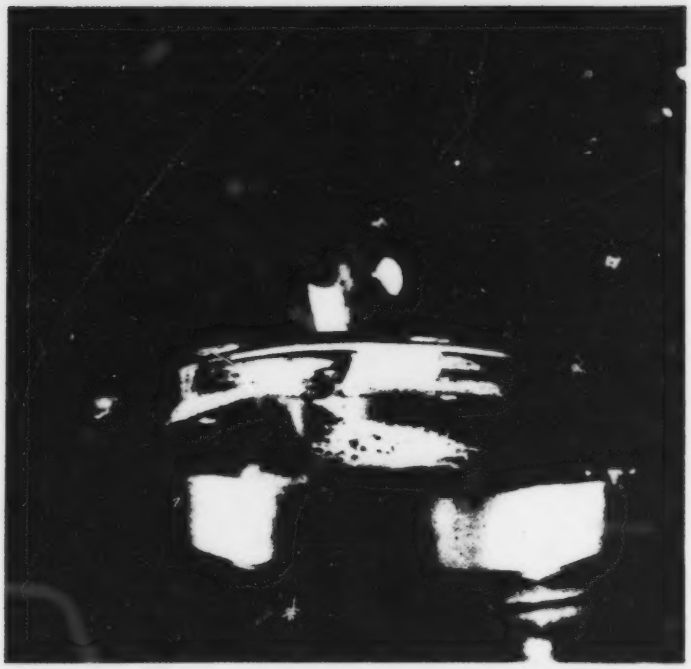
This was exactly the material Ray was looking for. The Vesconite component was put to the stringent test of lining a stationary disc subject to high velocity and friction. Early tests looked promising and with the co-operation of various engineers in Welkom mines a number of large and small packing rings and protection plates were fitted in a variety of pumps. It soon became apparant that the Vesconite parts would outlast those made from phosphor bronze.

Since 1970 the fitting of Vesconite rings and ceramic coating of the eye and boss of the impeller are standard practice for all pumps passing through the workshops of Rays Pump Service Company. Apart from two instances where a small packing ring failed owing to a large quantity of fine wood in the water, the mines have had most satisfactory results with this engineering plastics material.

The problem of pumps running dry is not only confined to the mining industry in South Africa. It is an international problem with which engineers throughout the world have to contend. This makes the achievement of Leger and Ray so much more remarkable.

Leger feels that the success largely resulted from a combination of Ray's every day involvement in pumping problems and possession of pump technology together with the availability of very large plastic parts in the right material for what was believed to be purely a metal application.

Doug Ray's packing ring development has not been his only engineering achievement. While building up his business as centrifugal pump specialists overhauling multi-stage underground water pumps he found that he had to make innovations all the time. Pumps of this type cannot be out of commission for any length of time and non-availability of parts was the order of the day. This led him to gradually equip his workshop with NC-driven lathes, milling machines, etc. which enable him to manufacture most parts in-



In many respects the workshop is self-sufficient for the provision of spare parts. A double shrouded diffuser cast in the company's own foundry is being jig machined.

house. With the addition recently of a foundry to make pump castings he has created a completely self-sufficient entity.

To minimise delays between breakdown and re-installation Ray has acquired an aircraft which he pilots himself to various mining areas in the Free State, Transvaal and Northern Cape. This means that within a few hours of a breakdown Ray can assess the damage, quote on the job and have one of his vehicles on the way to collect the pump.

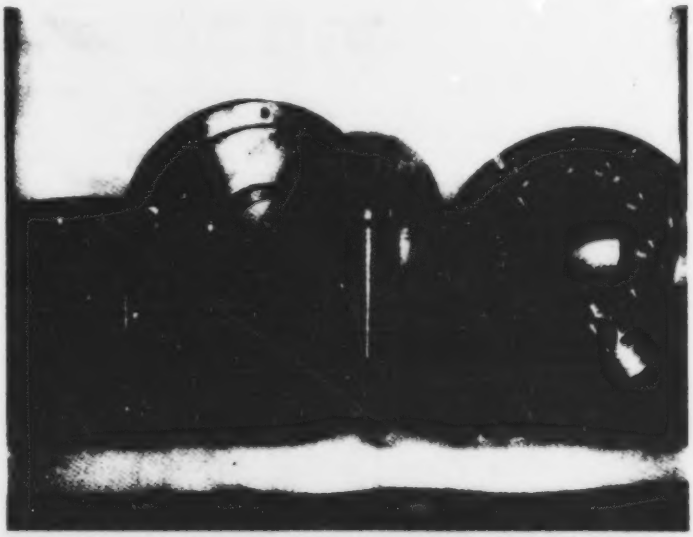
Alain Leger's development of thermoplastics makes equally interesting reading. A chemical engineer who, since 1967 was branching out from hardchrome plating into engineering plastics, found that the nylon he was importing did not have the versatility needed for a bearing material. Committing substantial resources from his existing business he started to develop extrusion techniques to produce rod and bushing from various polymers. There was no expertise to draw from either in South Africa or elsewhere. Eventually he found a thermoplastic with excellent dimensional stability and load bearing capabilities together with outstanding friction and wear resistance properties.

Recalls Leger: "Operating from the Free State didn't help either. Being far away from engineering facilities we had to design and produce ourselves, much of the tooling and equipment. In retrospect this isolation probably gave us the opportunity to explore a field which hadn't been tackled before and kindled the determination to succeed."

Initially there was buyer resistance to his new product. People thought of engineering plastics as being a cheap material incapable of accepting loads and of resisting wear or even lubricants. However resistance was gradually overcome as the material proved itself and today Vesconite can be found in heavy vehicles, front-end loaders, ships and in mining equipment.

Leger made considerable investments in plant and machinery to produce thin walled bushing stock and finished components to provide a wide choice of machinable materials to firms with machining facilities or to end users requiring ready to use parts.

Not only is Vesconite recognised as a prime engineering material in South Africa but already 10% of total production is destined for overseas markets, no mean feat for a Free State company.



A display of a number of bronze and stainless steel components manufactured by Ray's Pump Service Company. The gland and throttling sleeves have been ceramic coated.

Vesco Plastics, P.O. Box 47, Virginia, O.F.S. 9430.
Rays Pump Service Company (Pty.) Ltd., P.O. Box 506, Welkom 9460.

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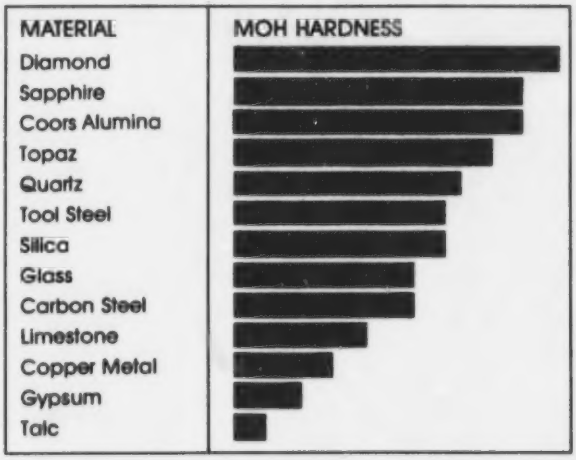

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Crystal Size Average	in x 10^{-6}	[illegible]	[illegible]
Water Absorption	ASTM C373-72	0	[illegible]
Gas Permeability	Helium test	[illegible]	[illegible]
Compressive Strength	kpsi	[illegible]	[illegible]

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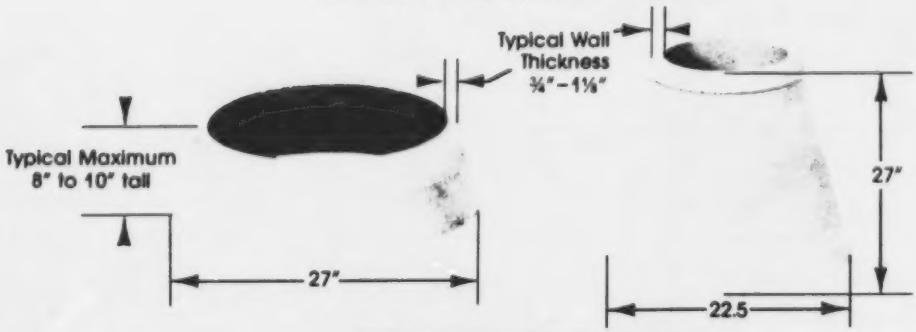

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Volume 7

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FOR

MINING & METALLURGICAL OPERATIONS

1 JUNE 1985

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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.).....	Milligrams per liter.....	17.12
Milligrams per liter.....	Grains per gallon (U.S.).....	0.05841
Milligrams per liter.....	Tons per acre-foot.....	.001360
Tons per acre.....	Metric tons per hectare.....	2.217
Grams.....	Ounces (avoirdupois).....	.03527
Ounces (avoirdupois).....	Grams.....	28.35
Gallons (Imperial).....	Gallons (U.S.).....	1.2009
Acre-feet.....	Gallons.....	325,851
Acre-feet.....	Cubic feet.....	43,560
Cubic feet.....	Cubic meters.....	.028317
Cubic feet.....	Gallons.....	7.481
Cubic meters.....	U.S. Gallons.....	264.2
Cubic meters.....	Imp. Gallons.....	220.0
1,000 m^3/d.....	I gpm.....	152.8
1,000 m^3/d.....	U.S. gpm.....	183.6
U.S. gallon.....	Cubic meter.....	0.3785

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TAILINGS IMPOUNDMENTS

INTRODUCTION

Tailings impoundment design, installation, and maintenance are a most important integral part of water management in mine-mill complexes and must be considered in any attempt to apply a systems approach.

The objectives of this chapter are to:

1. Provide an insight into the needs of tailings disposal methods within the framework of emerging environmental protection regulations.

2. Emphasize just how great the impact of tailings disposal techniques are on the economics of the mining industry, especially in some climatic regions.

3. Establish goals and objectives for tailings impoundment design to best meet regulatory requirements.

4. Outline several advanced and innovative techniques for tailings disposal which can reduce the overall costs and do a better job taking also into account post-operational requirements.

5. Identify sources of expertise in the technologies involved.

6. Provide some guidelines and identify some pitfalls associated with plastic membrane applications in water impoundments.

IMPORTANCE OF TAILINGS IMPOUNDMENT DESIGN IN THE IMPACT OF MINING AND MILLING ON THE ENVIRONMENT

At startup, that is before a significant volume of tailings have accumulated and while they are still fresh, the impact of tailings impoundments on the quality of water recycled to the mill or discharged to the environment is at first usually negligible. As tailings grow in volume and as they oxidize (especially if they contain sulfide minerals), their impact on water quality increases until the mine is worked out and closes and milling operations cease. Thereafter, the tailings impoundment and old evaporation ponds, wasterock piles, etc. are the main source of pollution from the site and can inflict very serious damage unless properly managed.

Considering that the life of a mine and mill may typically range between 10-50 years, but that the potential for environmental impact from the site exists for centuries thereafter,

the potential impact on the environment from minewaste and mill tailings after a mine shuts down is usually greater even than it is during the life of that mine and mill.

Environmental protection constraints may require that the tailings impoundment be maintained and that seepage and runoff be collected and treated to meet discharge quality criteria "in perpetuity." The cumulative cost of doing so for hundreds of years is awesome; therefore, better ways of disposing of tailings are needed that cost less to maintain and possibly avoid the need for a treatment plant.

What is the nature of the damage caused by tailings and water impoundments on the environment? The answer to this question requires site-specific answers and is not straightforward. Clearly, the impact of tailings will be minimal if the sites are managed and if effluents therefrom are treated before they are discharged. In climates with a net precipitation, the environment is usually different to that in climates with net evaporation. Also, liquid effluents will be generated in excess of evaporation losses, and containment can be an accumulating problem. Tailings containing sulfide minerals will have a different impact to those that do not. In net evaporation climates, tailings can be dewatered or simply allowed to stand and, gradually through evaporation, they will dry out. All that is needed is an impermeable base to contain seepage and a means of preventing erosion as well as collecting runoff. In some cases where geochemical attenuation of dissolved species in soil and rock beneath a tailings pond site occurs, even the impermeable liner may be dispensed with. In net precipitation areas, the installation of an impermeable liner to contain seepage may compound the problem as the volume of water in the impoundment will steadily accumulate.

Unless they are controled, tailings which contain sulfides impact the environment through release of water of low pH due to acid generation and also a variety of dissolved species such as base metals at levels that are toxic to aquatic life or which render groundwater aquifers non-usable as potable water. There are four ways sulfide tailings can impact the environment: Seepage; runoff, airborne dust; and pond failure.

Seepage of tailings pond water or runoff water results in contaminated water getting into groundwater aquifers. In some cases, seepage through an impoundment wall may surface again and get into surface waters, e.g., a stream running alongside the impoundment.

Runoff refers to precipitation on the tailings impoundment itself and also to precipitation draining onto the tailings site from the surrounding area which becomes contaminated as it comes into contact with the surface of the tailings impoundment. Superficial examination would lead to the conclusion that once the surface of dried out tailings has been "washed" through contact with runoff, its salt content would steadily be depleted until it becomes inert. This is not, however, the case as vertical transportation of salts to the surface continues from the pond interior through capillary action. If the tailings are submerged,

KAM KOTIA ABANDONED MILL TAILINGS SITE
TIMMINS, ONTARIO

then ion migration by diffusion occurs from below the solids surface into the surface water.

Airborne dust. When tailings materials are deposited in an impoundment, some configurations call for removal of free liquids by decantation or controlled subsurface drainage or seepage. The dry surface tailings may be subject to a dusting problem as was observed, for example, at an Elliot Lake site. This dust, which contains sulfides if these are present in the tailings material, then gets distributed over a wide area where it rapidly oxidizes and releases acid and metals to surface runoff.

Pond failure. Improper pond construction and inadequate control of the phreatic pressure (water table) inside the pond can result in pond failure. Likewise, in areas with net precipitation, if the pond is impermeable and no provision is made to draw excess water from the pond, liquids will accumulate in the pond until it overflows. Once that happens, erosion of the dam wall may damage it to the extent of impoundment failure. Pond failure, apart from the release of toxic metals and reagents, also causes severe silt damage to the drainage in its path.

GOALS IN TAILINGS IMPOUNDMENT DESIGN

- The impoundment must be strong enough to be physically safe. This is a function of the site and how it is designed and built, which may have to take earthquake probabilities into account.

- It must be affordable.

- It must be large enough to impound all the tailings which it is designed to hold.

- Seepage must be prevented where this is required to protect groundwater quality or to meet environment protection regulations and permit requirement.

- A goal is to find a site where the soils and substrata are already of low permeability or which are able to geochemically attenuate contaminants in seepage so that no additional clay or plastic membrane linings are required.

- The tailings pond may be used as a solution aging and storage impoundment during the life of the operation. It may fulfill a function in overall water conservation.

- In net precipitation areas particularly, the impoundment must be large enough to accommodate a growing water inventory if precipitation exceeds evaporation plus seepage. It may be necessary to draw excess water from the tailings pond for use

particularly useful. Uranium tailing disposal for some reason has been scrutinized more than any other, and these symposia brought together top people in this field. The proceedings are available from:

COLORADO STATE UNIVERSITY
Civil Engineering Dept.
Fort Collins, CO 80523
(303) 491-6081
John D. Nelson
Dirk Van Zyl

Alternative sources of information on tailings disposal are the environment impact statements submitted to regulatory agencies in support of permit applications. These are usually available for scrutiny at selected libraries in the area where the mine-mill-tailings are proposed.

The CHAMBER OF MINES OF SOUTH AFRICA (1979) issued a comprehensive manual on "The Design, Operation, and Closure of Residue Deposits," which shows many of the engineering aspects of tailings disposal. Copies of this document can be requested through:

THE CHAMBER OF MINES OF SOUTH
AFRICA LTD.
Post Office Box 809
Johannesburg 2000
South Africa

An excellent review of various techniques of tailings disposal showing how important the management of water becomes, especially in wetter climates, was prepared by CALDWELL and WELSH (1984) from which several illustrations inserted below were taken.

Because tailings disposal holds the key to so many environmental problems, major studies are underway to try and find better techniques. Several of these are group studies, presumably with government and industry funding, and information may be available from:

1) The Canadian uranium industry faces the same problem and has, for several years, also been working on tailings disposal techniques with a research center for the purpose at Elliot Lake. This work has been largely undertaken by:

CANMET
555 Booth Street
Ottawa, Ontario
Canada K1A 0G1
(613) 995-4124
Gordon M. Ritcey

CANMET has also gathered important data on base metal mill tailings disposal, and Gordon Ritcey and M. Silver are intensely interested in this aspect.

in the mill as an auxiliary source of water or for separate disposal by evaporation or for discharge after appropriate treatment.

- The surface of the impoundment must be made stable enough to resist erosion by wind and water.

- On closure, the site must remain stable and measures adopted to preferably inhibit or prevent acid mine drainage. If this is not possible, then the goal must be to provide means to control its impact on the environment.

- The most desirable goal is to be able to abandon the site after completion of the operation in an environmentally acceptable manner requiring no further maintenance and especially avoiding the need for a water treatment plant.

- If the tailings contain low-level resource values which may potentially be recovered profitably in the future, then the tailings impoundment should be such that will allow practical reclamation of the tailings for future processing if and when the need arises.

- The goal of all tailings designs should be to achieve an impoundment requiring a minimum of ongoing maintenance.

SELECTION OF APPROPRIATE TAILINGS DISPOSAL METHOD

In most cases, there are several possible alternative ways in which tailings can be disposed of. There is no clear-cut universally "best" method. Selection of an optimum alternative depends on the topography, geology, location, and climate at the site and the nature of the tailings themselves. It also depends on the naturally available materials for use in impoundment construction and for linings. The usual approach is to retain a firm of expert tailings disposal engineers to survey the possible sites and then to prepare cost evaluations for several alternatives specifically for the operation under consideration.

SOURCES OF INFORMATION ON TAILINGS DISPOSAL

Information on tailings disposal is available in the literature and from the various geotechnical engineering companies that specialize in this field that are listed at the end of this chapter and referred to throughout.

As far as literature sources are concerned, the proceedings of a series of annual symposia on uranium mill tailings management held at the Colorado State University are

2) A Group Study on Sulfide Tailings has been started by the Canadian Mining Association with participation by COMINCO LTD., INCO LTD., KIDD CREEK MINES LTD., and NORANDA MINES with input from FALCONBRIDGE LTD. Information may become available through:

NORANDA RESEARCH CENTER
240 Hymus Blvd.
Point Claire, Quebec H9R 165
(514) 697-6640
Dr. Ken Wheeland

FALCONBRIDGE LTD.
Falconbridge, Ontario P0M 1S0
(705) 693-2761
John K. Weglo

3) A third group interested in sulfide-bearing tailings disposal is the Atomic Energy Control Board in Canada:

ATOMIC ENERGY CONTROL BOARD
Ottawa, Ontario
Canada
Al Dorey

ALTERNATIVES FOR TAILINGS DISPOSAL

1) Mine Backfill
2) Above Ground Tailings Ponds with Controlled Release of Liquids
3) Above Ground Tailings Ponds with Impermeable Lining
4) Below Grade Impoundment
5) Combination Above and Below Grade Impoundment
6) Robinsky Thickened Tailings Method
7) "Dry" Tailings Disposal
8) "Semi-Dry" or Subaerial Tailings Disposal
9) Submarine Tailings Disposal
10) Deep Lake Disposal

All of the above alternatives have been applied with several variations. Regulatory requirements, ore characteristics, mill process design, and physical and environmental conditions at each specific disposal site are probably the four most important factors influencing construction and operating costs of modern mill waste disposal facilities. Some comments on each of the alternatives listed above may be in order, particularly as they apply to water management and treatment in mine-mill complexes. These observations are, however, made by an author with limited experience in this field.

Mine Backfill

Underground mine backfill is practised at several operations including Homestake Mining Company at Creede, Colorado, and Lead, South Dakota; The Black Mountain Mineral Development Co. at Aggeneys, South Africa; Kidd Creek Mines, Timmins, Ontario; Noranda Geco Division, Ontario, and many more.

the way backfill is applied also varies depending on the nature of the underground cavities and the height of the support needed. For example, in some of the massive sulfide mines in Ontario, backfill may have to support a mine roof hundreds of feet above the floor as described by YU and COUNTER (1983). At the Kidd Creek Mine, however, crushed wasterock is used as backfill because of the strength it offers when cemented and because the mine is located some distance from the mill which would require hauling tailings back to the mine. PATCHET (1977) reviewed testwork which indicated that cemented tailing slimes could successfully be used for deep underground backfill on Witwatersrand mines, and further development work in this area is currently being undertaken on the Witwatersrand.

At the Black Mountain Mineral Development operation which mines and mills a Cu-Pb-Zn ore in the arid norther Cape Province of South Africa, cemented tailings backfill is applied. It is interesting that at this site where water costs $1.20/m^3 (about R4.80/$2.40 per 1,000 U.S. gallons), fresh water is used in the backfill plant. This is because it is believed that if reclaimed tailings water were to be used, the strength of the cement could be adversely affected by organics in the water.

When ore is mined, it is not always possible to avoid getting cemented backfill into the muck, and sometimes a small quantity of cemented fill may reach the mill mixed in ore. Possibly because of dispersants used in the cement or because of other species introduced with the cement, flotation results appear to be impacted as a result. No quantitative data were available to confirm this.

Backfilled tailings bonded with cement usually result in minewater from those sections of the plant having a high pH, and metals in seepage from backfilled parts of the mine are usually at low concentrations.

In gold mills, i.e., those using CIP, it appears that a little cement addition to mill feed will not be detrimental to the process. For example, ANDERSON (1984) mentioned that at Battle Mountain operations of Duval Corp., a small amount of Type V portland cement is deliberately added to improve metallurgical performance in the presence of some cyanide-soluble copper.

In South Africa, the Chamber of Mines Research Laboratories had conceived the idea of an underground milling and flotation process which would preconcentrate mineral values underground which would be pumped to the surface, while tailings would be backfilled. Backfill can accommodate only 60% of the rock removed from the same cavity because of the 40% expansion factor when ore is milled.

One major drawback to backfilling is that today's tailings may well become tomorow's ore, just as today, tailings from past milling operations are also profitably milled, sometimes for the second or third times. If tailings are disposed of underground, these will not be available as an above ground resource for future recovery. On the other hand, tailings that have been backfilled underground with cement are unlikely to generate acid mine drainage.

Several massive sulfide ores contain large percentages of pyrrhotite, marcasite, and pyrite. If disposed of in conventional tailings impoundments, these become particularly bad acid generators. It would be logical to dispose of the high sulfide fraction underground in backfill. However, these materials can catch fire and are prone to spontaneous combustion underground which, of course, would be highly undesirable. Consequently, high sulfide material is not used as backfill.

At the Wedge Mine in New Brunswick from which ore was milled elsewhere, the mine cavity was backfilled with wasterock, and the site was very successfully restored thereafter. This solved some serious previous acid mine drainage problems.

Generally, in the U.S.A., minewater can be discharged under an NPDES permit, whereas mill and tailings decant solutions cannot except in exceptional circumstances in the U.S.A. It is interesting that since mill tailings have been used as underground backfill at Homestake Mining Company's Lead, South Dakota, operation, cyanide values started to appear in the minewater.

Many operations carry out a sand-slime split using cyclones. The sand is used for cemented backfill whereas the slimes are disposed of in above ground impoundments. Nonetheless, PATCHET (1977) showed that slimes could also be used satisfactorily as long as the moisture content can be controlled.

Emperor Gold Mines in Fiji deslime their tailings prior to backfilling. The cyclone overflow contains slimes which are disposed of in the slimes dam on the surface. The cyclone underflow is further washed in a rake classifier which produces an essentially slime-free sand which makes a very stable backfill material.

Denver Equipment Company has developed a centrifugal dewatering device which has been demonstrated at several mines for emplacement of tailings underground. Presumably, the

'tailspinner' also reclaims some water, but details would have to be obtained from the manufacturer:

DENVER EQUIPMENT DIVISION
Joy Manufacturing Company
5500 South Syracuse
Woodside 1, #105
Englewood, CO 80111
Michael Jensen
(303) 779-5586

Meanwhile, in South Africa, cement additives and improved pumping devices are also being evaluated so that the slimes tailings can be pumped with the lowest possible water content to the stopes for fast curing to be strong enough for roof support.

In this respect, it is known that lignin sulfonate can be used to keep cement fluid at lower moisture contents, but some caution is required if it is to be used where the cement, the additive, or water that has been in contact with the additive can get anywhere near a flotation circuit as lignin sulfonate is a dispersant that interfers with froth flotation.

Backfill Experiment: President Steyn Gold Mining Company:

Flotation tailings are neutralized and then submitted to the following procedure, all performed underground:

1) Addition of 120g nonionic flocculant (Allied Colloids Magnafloc 351 (PAM) is one that has been used).

2) The slurry is dewatered to 80% solids on a belt press supplied by:

MACHINERFABRIK ANDRITZ AG
Postfach 24
A 8045 Gracz-Andritz
Austria

3) Viscosity of the filterpress cake is reduced by adding tripolyphosphate. A small amount of cement is mixed in.

4) The viscosity modified high pulp density slurry is pumped via a Schwinn pump (positive displacement piston) which can pump the slurry 100-150m before it hardens up.

5) At the discharge end, a little Ca^{2+} is added as lime to destabilize the viscosity modifier by precipitating $Ca_3(PO_4)_2$.

6) Activated bentonite is added to the water recovered by the belt press to "kill" the excess flocculant. The water then goes to a thickener where the clay solids are recovered.

With 40 Stopes applying backfill at 10 tph for 8 hours per day, a total of 3,200 tpd solids would be disposed of. Water would be recovered, and the need for timber supports avoided. 27l/s water recovered would be lost in the 500 l/s machine water supply required in such a typical operation.

Names of Experts in Underground Backfill:

DR. S. J. PATCHET
Head, Rock Mechanics Dept.
Anglo American Corporation of S.A. Ltd.
Technical Development Services
Post Office Box 3
Welkom OFS 9460
Phone: Welkom 2-2151
Telex: 8-8243

DR. T. R. YU
Chief Engineer, Rock Mecahnics and Backfill
Kidd Creek Mines Ltd.
Bag 2002
Timmins, Ontario P4N 7K1
(705) 267-2161

ABOVE GROUND TAILINGS PONDS WITH CONTROLLED RELEASE OF LIQUID

The controlled release of liquid from above ground tailings has been used for many years. Operations such as Rössing Uranium in Namibia lose water from their tailings pond through seepage. This seepage is collected in trenches and recycled to the plant. After being in contact with the metamorphosed carbonate substrata, the seepage solution improves markedly in quality. Its pH is raised, TDS dropped, and radionuclide levels and iron are dramatically lowered. This type of tailings pond, however, does not allow quite the degree of control of solutions lost as would be desired in many cases. Even at Rössing in 1984, a hydrological study was underway to determine where some of the seepage was escaping to. At mines such as Noranda's Mattabi and Brenda, tailings ponds seepage is collected by a trench and pumped back to the pond.

More controlled liquids release is achieved through the use of underdrains at the foot of the dam through which solutions can escape and be collected. This keeps the phreatic level on the inner surface of the tailings pond wall down. Examples where this system is used include AMAX, Inc. at their Climax mill tailings where AMAX claims the system was invented; at Rustenburg Platinum Mines, Transvaal; and at ERGO, Transvaal, amongst many others.

There are numerous configurations of surface tailings impoundments including those that use cyclones to separate sand and slime. When the spigotted sand fraction is used to build the wall of the impoundment and the slimes flow toward the interior of the impoundment, the wall will invariably be somewhat porous.

In some designs, tailings are discharged "downstream," allowing solids to settle at the inlet end and relying on the impoundment wall to contain the decanted solution. In others, tailings are released "upstream" from the dam wall, thereby forming an advancing beach which extends from the impoundment wall. ROBERTSON and VAN ZYL (1980); ROBERTSON, SHEPHERD, and VAN ZYL (1980); ROBERTSON, BAMBERG, and LANGE (1978), and VAN ZYL and ROBERTSON (1980) discuss these features of site selection and design of uranium tailings impoundments.

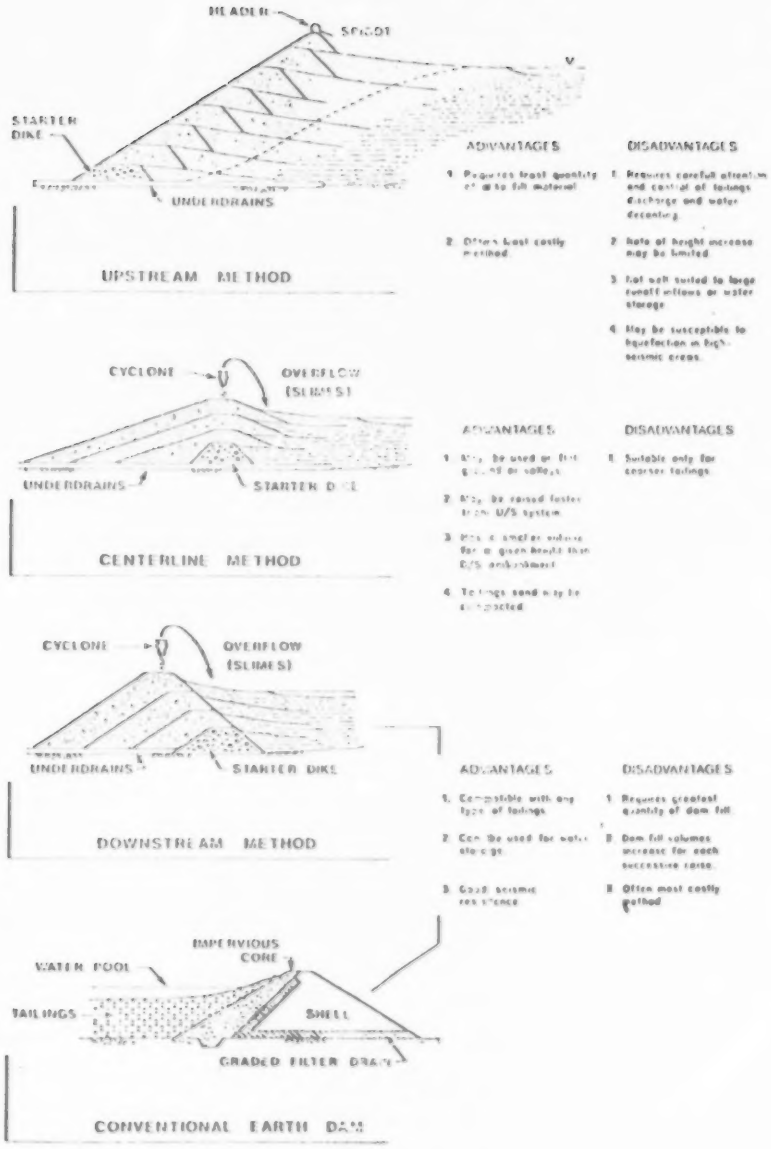
Subsurface drainage of tailings impoundments improves their stability, reduces hydraulic head on liners, improves water return to mill, and keeps the tailings better stabilized. VAN ZYL and ROBERTSON (1980) discuss the design, construction, and tailings management considerations involved. Poor control during construction of drains and during first filling with tailings can lead to the loss of dewatering capacity and even complete clogging of drains by the tailings themselves. Some practical consideration are discussed such as the influence of bottom surface slope of tailings impoundments, depositional procedures to minimize drain clogging, and installation of subsequent drains at higher levels in the tailings impoundment. More information can be requested from the authors who are specialists in this field:

ANDREW MacG. ROBERTSON
Steffen Robertson and Kirsten
#801, 1030 West Georgia
Vancouver, B.C.
Canada V64 2Y3
(604) 681-4196
Telex: 04-352578

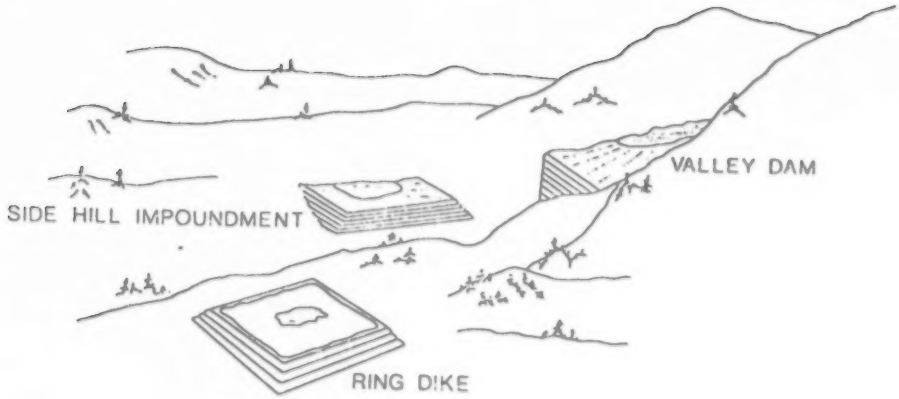
DIRK VAN ZYL
Civil Engineering Dept.
Colorado State University
Fort Collins, CO 80523
(303) 491-6081

JACK A. CALDWELL
Steffen Robertson and Kirsten
#801, 1030 West Georgia
Vancouver, B.C.
Canada V64 2Y3
(704) 681-4196
Telex: 04-352578

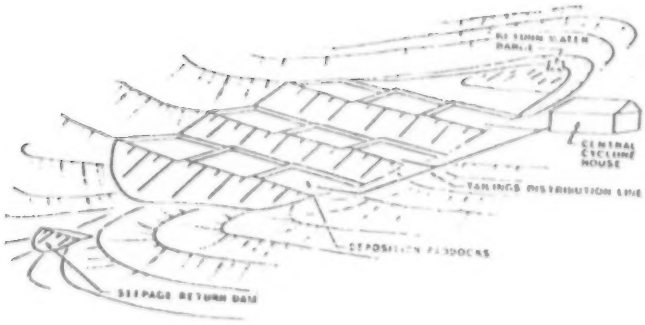
The use of geotextile fabrics in the construction of underdrain collection sites and in the stabilization of impoundment structures is becoming routine. Other techniques include chimney drain configurations. Geotextile underdrains are installed, for example, in the huge new $30 million tailings impoundment constructed to contain East Daggafontein and



Types of embankments.



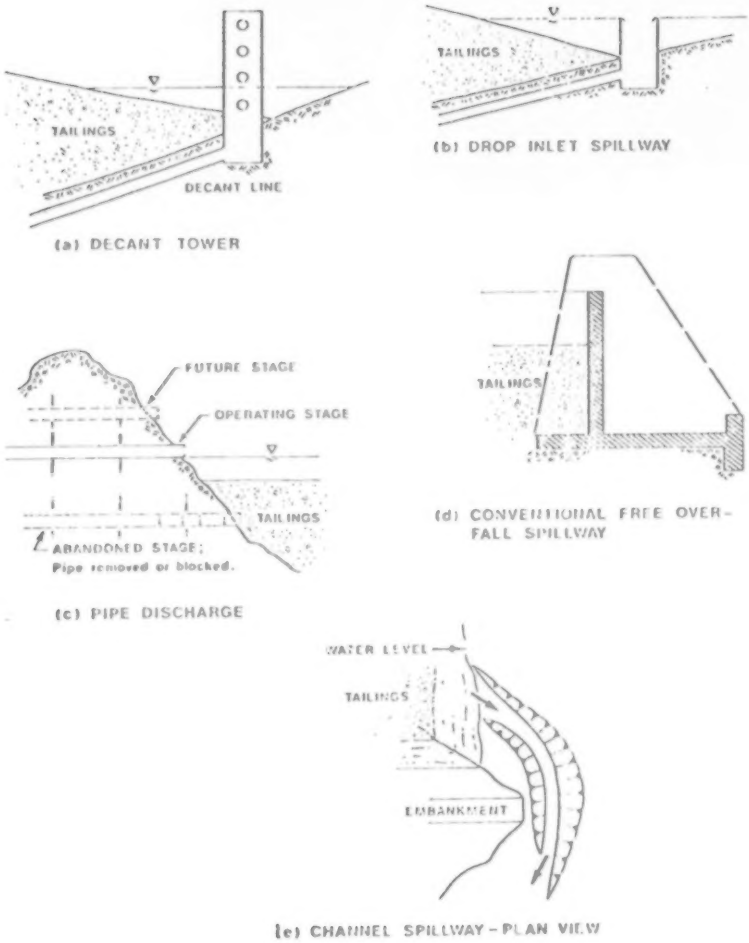
Impoundment location types.



(a) CENTERLINE EMBANKMENT CONSTRUCTION WITH PADDOCKS AND CENTRALLY LOCATED CYCLONE STATION

(b) SCHEMATIC OF CENTERLINE CYCLONE OPERATION - CYCLONES ON DAM

Examples of centerline construction.



Spillway types.

ERGO tailings east of Johannesburg. Older techniques involved the recovery of solution from the top of the pond through adjustable height penstocks connected to pipes that drain through the impoundment wall. A problem was presented when a very tall penstock connected to drains beneath the impoundment at INCO's Copper Cliff tailings pond was broken off at the base by a shift in the surface ice on the tailings pond. The total solution inventory was released to the Copper Cliff Creek with some damage. The question was how to replace the broken penstock. In the end, by far the most economical and practical way was to plug the original hole and to install a huge siphon over the dam wall. This has worked extremely well and offers a degree of safety not possible with very tall vertical penstocks in such a large deep impoundment. More details of the 3,200 foot long syphon arrangement are provided in the trip report on INCO, Copper Cliff, in Appendix I and can also be requested from:

INCO LIMITED
Copper Cliff, Ontario
Canada P0M 1N0
(705) 682-8341
H. R. Butler
Supervisor, Environmental Control

As environmental requirements (i.e., regulations governing discharge of effluents) have forced much greater recycle of tailings solutions and greater care in preventing seepage losses, so the TDS levels including species such as gypsum can build up in the pond until a point is reached where severe scaling may occur in the underdrains. This can result in clogging of underdrains and, although to date few cases have been ide[illegible] where this has actually occurred, the possibility has become an item of increasing concern to some operators who rely on underdrains to remove solution from their impoundment to keep the structure stable.

As mentioned above, one other way of "controlled" release of liquids is through construction of a porous impoundment which allows seepage through seepage which can then be collected by trenches or a wellfield installed around the perimeter of the impoundment as at Rössing and some of the southwestern U.S.A. copper recovery operations.

At Rössing, seepage collected in this way reduces the contaminant load in recycled water. The same applies at Quivira Mining Company in New Mexico where seepage reacts with the lime-rich aluvia and is partially neutralized by the material with which it come in contact.

ABOVE GROUND TAILINGS WITH IMPERMEABLE LINING

Increasingly, permits now call for lined tailings impoundments, particularly where geotechnical surveys do not indicate the [illegible]ce of virtually impermeable base material

or of conditions that will geochemically attenuate the migration of contaminants contained in seepage from an unlined impoundment.

California, for example, is a state that has insisted on double plastic membrane linings for impoundments unless very firm evidence is brought to bear that this is unnecessary, as has been the case for Homestake Mining Company;s new McLaughlin project where tailings are being disposed of over a natural clay base with 10^{-7} cm/s permeability.

Examples include Getty Mercur Mine at Toelle, Utah, where a bentonite stabilized sand has been used very effectively. More information on this innovative lining system may be available from:

GETTY MINING COMPANY
5250 South, 300 West, Suite 300
Salt Lake City, UT 84107
(801) 263-3850
Frank D. Wicks

Dawn Mining in Washington state is located in a climatic region with net precipitation. Formerly, this uranium mill discharged acidic tailings to an unlined pond which had a convenient leak allowing a bleed of undesirable species from tailings pond solution as well as a convenient loss of liquid to balance the incoming net precipitation.

However, once forced to line the pond (HDPE from Gundle Plastics was used), their operation was affected in several ways. Firstly, to keep the liquid level from rising too rapidly in the now leakproof pond, more tailings solution had to be recycled back to the mill in the place of fresh water that had previously been used. Secondly, without the salt bleed and with less dilution by fresh water, dissolved salt levels started to build up in the mill solutions. These then resulted in increased silica fouling of ion exchange resin and in a deterioration in ion exchange uranium recovery also due to higher levels of competing ions. In the end, the operation became uneconomic with falling uranium prices, and it has been shut down. In this case, excess high TDS mill solution cannot be disposed of by evaporation (as at Quivira Mining Company) because of the net precipitation climate, nor can excess salts be bled through seepage (as at Rössing Uranium) because of the impermeable tailings lining. In such a case, the only alternative appears to be the expensive route of desalination and the seeded slurry R.O. process which would appear to be particularly well suited. Alternatively, deep well injection of raffinates might be looked into.

WULFF, et al. (1980) described the new uranium mill tailings impoundment for Cotter Corporation in Canon City, Colorado. This operation recycles no tailings solutions so these have to be disposed of by evaporation from the tailings pond. Since the solid and liquid wastes from this mill were deemed to be toxic, a most important concern in the design of the new tailings disposal facility was containment, i.e., seepage control to prevent the degradation of downgradient waters. This was particularly critical at the

Cotter site which is only 2-3 miles upgradient from Canon City and the Arkansas River. The older millsite and existing mill tailings in the old permeable impoundment (not designed to be impermeable) have resulted in groundwater contamination problems, and the new tailings pond is to accommodate material moved from the old site in the reclamation thereof and the the old mill area. The materials underlying the new tailings site tested to have very high permeability rates on the eastern flanks. It was decided to line the entire pond with a membrane. The selected design was an above grade disposal system consisting of zoned earth embankments, a sophisticated lining system for the impoundment area, subdrains below the liner, and tailings dewatering drains above the liner as illustrated in the idealized section in their figure II-3 inserted below.

The foundations for the embankments and lined impoundment areas are excavated to or into bedrock. The embankments have an upstream sloping clay core backed by a continuous sloping drain and a horizontal drain in the valley area. The portion of the embankment downstream from the sloping drain consists primarily of random fill. The lining system consists of three layers: a compacted 0.46m (18 inch) clay subliner; a Hypalon membrane liner; and an 0.30m (12 inch) soil cover. The clay subliner is provided as a cushion for the Hypalon to prevent rock perforating the membrane and to act as a secondary liner in case the membrane is inadvertently perforated. The Hypalon thickness varies from 0.91 mm (36 mils) for the shallower areas, to 1.14mm (45 mils) for mid-depths, to 1.52mm (60 mils) for the greater depths. The membrane liner has a reinforcing fabric scrim. The 0.30m (12 inch) soil cover was provided to protect the Hypalon until it is covered by tailings.

The underdrain system consists of trenches excavated into bedrock, PVC pipe, and gravel backfill. The purpose of the underdrains is to collect seepage emanating from areas of the bedrock and transport the collected seepage beyond the toe of the dam so that there is not a buildup of hydrostatic pressures that could displace the liner.

To further reduce concerns about seepage over the very long term (i.e., after reclamation), the regulatory agencies requested that there be included a system to dewater the tailings to the greatest extent practical after the pond is decommissioned. Dewatering the tailings reduces the importance of the lining system in long-term containment of the waste. The dewatering system selected consists of a network of finger drains installed on top of the linings as shown in WULFF, et al.'s figures II-4 and II-5. the dewatering system is to function only during reclamation and after the free water in the ponds has evaporated.

The pH is adjusted in the mill from 1.7 to 4.2. Raising the pH has the following benefits:

1) Reduces the concentration of contaminants in the liquid hence decreasing the potential for contamination by seepage.

2) Reduces the potential for precipitates clogging the dewatering drains.

3) Reduces precipitates covering surface of tailings after evaporation, and reduces problems of placing reclamation cover. Costs for raising the pH were not included in their study.

Cotter Tailings System Quantities and Costs

The disposal system was designed to be constructed in stages. The ultimate height of the dam will be 35m (115 feet) with a crest length of about 1,524m (5,000 feet) and a tailings storage capacity of about 9,250,000 m^3 (7,500 acre-feet). The first stage embankment is 31m (101 feet) high, has a crest length of 1,497m (4,910 feet).

The total tailings solids storage capacity of the first stage impoundments is 3 million m^3 (2,400 acre feet). The first stage tailings storage will provide for approximately 3.4 million tonnes (3.8 million tons) of ore. Construction of the first stage tailings disposal facilities commenced in the summer of 1978 and was completed in 1979. Transfer of liquids from the old tailings impoundments began in the fall of 1979, and the new mill started operating in September, 1979, with the disposal of tailings in the new main impoundment at that time.

Mountain States Engineers were the designers and constructors for the mill Wahler Associates designed the tailings disposal facilities, and Stafford Construction Co. served as the construction subcontractor for the earthwork.

All earthwork materials for the embankments and liners were derived from the reservoir area and an area downstream of the dam except for sands and gravels for the various drains. Sand and gravels came from a commercial plant located near Canon City.

The first stage main and secondary embankments consisted of about 2.2 million m^3 (2.9 million cubic yards) of fill. Including clearing, grubbing, stripping, foundation preparation, embankment materials procurement and placement, and elimination of two old tailings ponds, the first stage embankments costs were about $13,000,000, which is an average of $5.86 per m^3 ($4.48 per cubic yard) of fill.

There were about 3,960m (13,000 lineal feet) of subdrains installed at a total cost of $190,000, or $47.97 per m ($14.62 per foot) of subdrain.

There were 623,000 m^2 (154 acres) of lining installed for a total cost of $5,300,000, including subliner, membrane liner, and cover. This is a cost of $8.50 per m^2 ($0.79 per square-foot of liner.

The tailings dewatering drains consisted of 8,930m (29,300 lineal feet) of drains and two sumps for installation of pumps. The total cost of the first stage tailings dewatering system was $303,000, for an average cost of $33.93 per m ($10.34 per lineal foot) of drain.

Construction of the remaining stages will provide 6.3 million m^3 (5,100 acre-feet) of additional storage. Data for storage provided by second stage construction and total storage are presented in Table II-1.

TABLE II-1

Future Stages and Total Tailings Storage Capacities

Future Stages		Total	
m^3	Metric Tons of Ore	m^3	Metric Tons of Ore
6.3 Million (5,100 Ac.Ft.)	7.3 Million (8 Million s. tons)	9.3 Million (7,500 Ac.Ft.)	10.7 Million (11.8 Million s. tons)

BELOW GRADE IMPOUNDMENT

Below grade impoundments have been considered in several cases for disposal of uranium mill tailings. To date, no example of the use of this method has been identified. WULFF, et al. (1980) evaluated four below grade disposal alternatives along with six other tailings disposal possibilities for Gulf Minerals' Mount Taylor uranium project in New Mexico. Below grade disposal involves excavating pits or trenches as shown in their figures III-1 and III-2.

advantages of trench disposal of tailings is that the tailings site can be reclaimed as trenches are filled rather than waiting until the very end as for large above grade disposal impoundments.

Below grade trench disposal was also considered for the pioneer Uravan operation proposed in Colorado which, like the Mount Taylor project never went ahead to production, for Homestake Mining Company's Pitch project in Colorado, and United Nuclear Corporation's Morton Ranch project in Wyoming.

Below grade disposal of tailings is generally the most expensive approach. This way may have particular appeal when ore is to be mined in a series of open pits which provide adequate room to accommodate at least 60% of the tailings below grade. To dispose of the balance, either additional pits must be excavated or above ground disposal in addition to the mine pits is necessary. Dry tailings, i.e., belt or rotary filter cake, have a lower

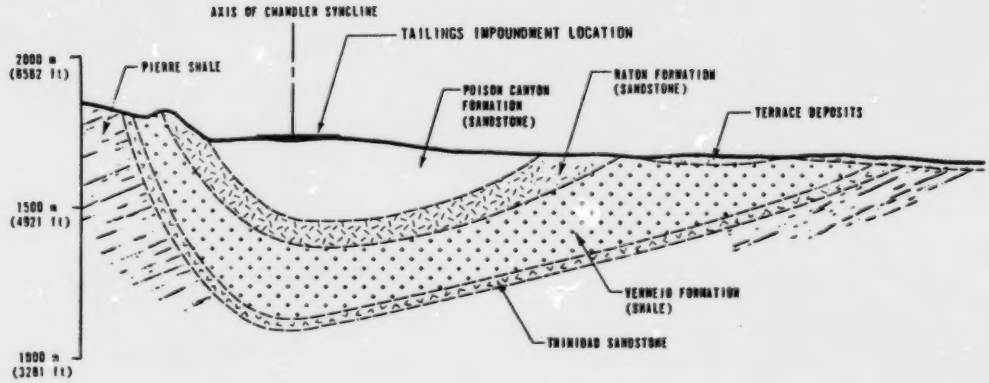


FIGURE II-2

SITE CROSS SECTION

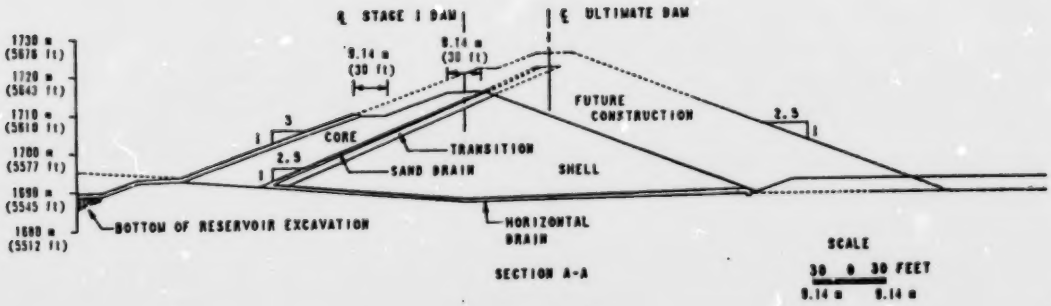


FIGURE II-3

TYPICAL MAIN DAM SECTION

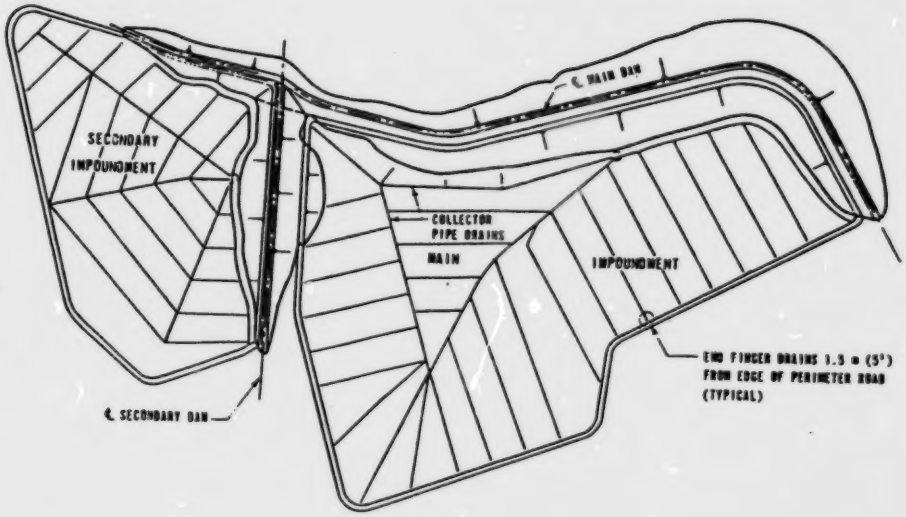


FIGURE II-4

TAILINGS DEWATERING DRAINS
LAYOUT PLAN

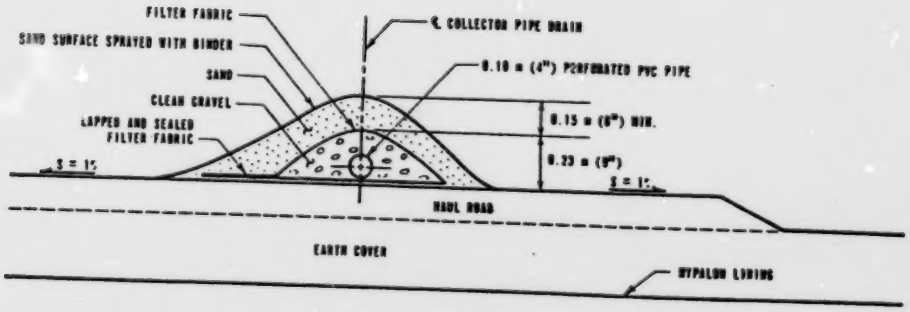


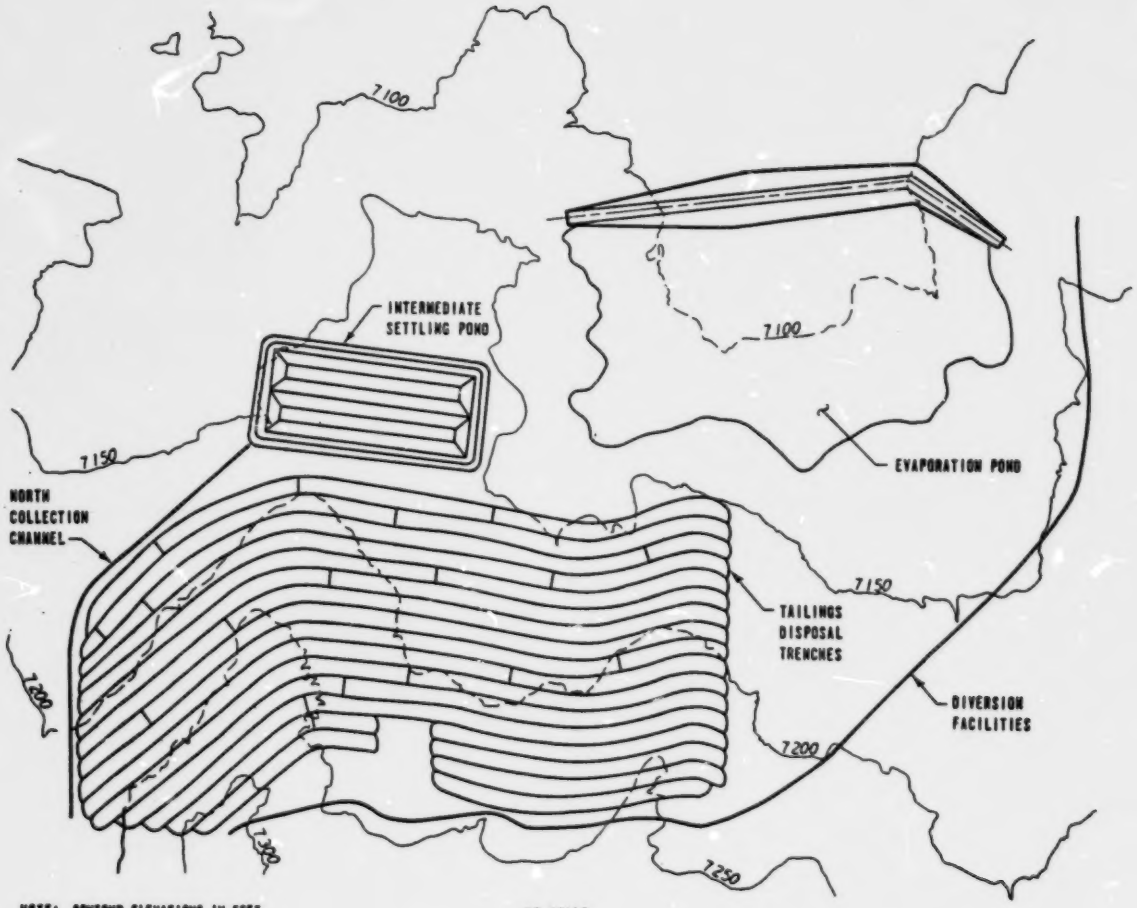
FIGURE II-5

TAILINGS DEWATERING DRAINS
DETAILS

TABLE V-1

SUMMARY COMPARISON OF SIGNIFICANT PROJECT FACTORS

PROJECT CHARACTERISTIC	PROJECT: COTTER	PROJECT: MT. TAYLOR	PROJECT: HANSEN
Location	Located at existing mill 3 to 5 km (2 to 3 miles) from nearest populated area (Canon City, Colorado). Approximate elevation 1680 m (5,500 feet).	Remotely located approximately 10 km (6 miles) from mill site, 16 km (10 miles) from San Mateo, 50 km (30 miles) from Grants and 100 km (60 miles) from Albuquerque, New Mexico. Approximate elevation 2160 m (7,100 feet).	Remotely located approximately 1.6 km (1 mile) from mill site, and 30 km (20 miles from Canon City, Colorado. Approximate elevation 2470 m (8,100 feet).
Mill Rated Capacity	1360 tonnes/day (1500 tons/day)	3810 tonnes/day (4200 tons/day)	4080 tonnes/day (4500 tons/day)
Tailings Impoundment Capacity	9,250,000 m^3 (7,500 acre-feet) (20 years of operation)	11,220,000 m^3 (9.100 acre-feet) (20 years of operation; 50 percent of tailings, as sands, to underground mine backfill).	13,300,000 m^3 (10,800 acre-feet) (15 years of operation)
Site Geology	Located in middle of bowl formed by Chandler Syncline. Site underlain by 240 m (800-feet) thick Poison Canyon Formation (primarily sandstone interbedded with shales and conglomerates.) Site underlain at depth of about 300 m (1000 feet) by mined out coal seam. Shallow alluvial soil cover.	Located in Colorado Plateau geologic province on the San Mateo Dome. Rock units are complex sequence of folded and tilted sedimentary formations. Bedrock units beneath site and generally flat-lying sandstone, siltstone, and shale. Thick, collapsible alluvial soil cover in some locations.	Located in Thirty-Nine Mile Volcanic Field, with rock units of Precambrian, Paleozoic, Tertiary and Quaternary ages. Site overlies thick Echo Park sedimentary formation, which is principally friable to poorly indurated claystone with lenses of silty sandstone and clean sand. Echo Park slump blocks rim the site valley. Stability of these is one primary consideration.
Groundwater Conditions	Seepage from old unlined tailings pond was causing concern for groundwater degradation. New facility will provide for reclamation of leaking ponds. Deep water table exists in old mine workings. Groundwater monitoring program in progress and for foreseeable future to verify expected quality improvement.	Near-surface geologic units are unsaturated to depths of several hundred feet. Major groundwater model study was conducted to predict performance.	Artesian conditions exist in deep aquifer, producing hydrostatic pressures to near natural ground level at some locations. Minor groundwater in shallow alluvium along streambeds.
Approximate Drainage Area Above Disposal Site	2.3 km^2 (0.9 Square Miles)	10.1 km^2 (3.9 Square Miles) (total above evaporation pond)	3.1 km^2 (1.2 Square Miles)
Method of Waste Liquid Disposal	Evaporated from tailings pond	Evaporated from separate evaporation pond for all alternatives except Alternative 1.	Waste liquids recycled - no evaporation facilities required.
Method of Handling Natural Basin Runoff During Operation	Small Diversion ditch and catch basin above tailings pond. Impounded water pumped past tailings dam. Tailings impoundment still designed to retain PMF series.	Diversion facilities to route PMF past disposal facilities for all alternatives.	Various methods, depending on alternative. Single dam, head of valley impoundment would retain PMF series. Cell and total burial schemes would require major diversion facilities around disposal sites.
Maximum Height of Tailings Retention Embankment Above Natural Ground	35 m (115 feet)	Alt. 1 33 m (107 feet) Alt. 3 19 m (61 feet) Alt. 5 14 m (47 feet) Alt. 6 No retention embankment Alt. 8 19 m (61 feet) Alt. 9 No retention embankment Alt. 10 No retention embankment	Total Below Ground - No embankment Deep Excavation, Multicell Disposal - 24 m (78 feet) Shallow Excavation Multicell Disposal - 27 m (87 feet) Single Dam, Head of Valley Impoundment - 55 m (180 feet)
Tailings Impoundment Lining Provisions	0.5 m (18 inches) of compacted clay, overlain by 0.9 to 1.5 mm (36 to 60 mil) Hypalon, overlain by 0.30 m (12 inches) of soil cover throughout reservoir. Subdrain system beneath compacted clay.	Limited areas of impoundment require compacted clay liner in Alt. 1. Cell bottoms would be scarified and compacted in Alts. 3, 5 and 6. Cell sides and bottoms scarified and compacted in Alt. 8. No lining in Alts. 9 and 10.	Compacted clay liner proposed at selected locations to be determined during construction for all alternatives.



NOTE: CONTOUR ELEVATIONS IN FEET.

NO SCALE

FROM DESIGN DRAWING
BY THE PACE COMPANY

FIGURE III-1

TAILINGS DISPOSAL CONCEPTUAL PLAN

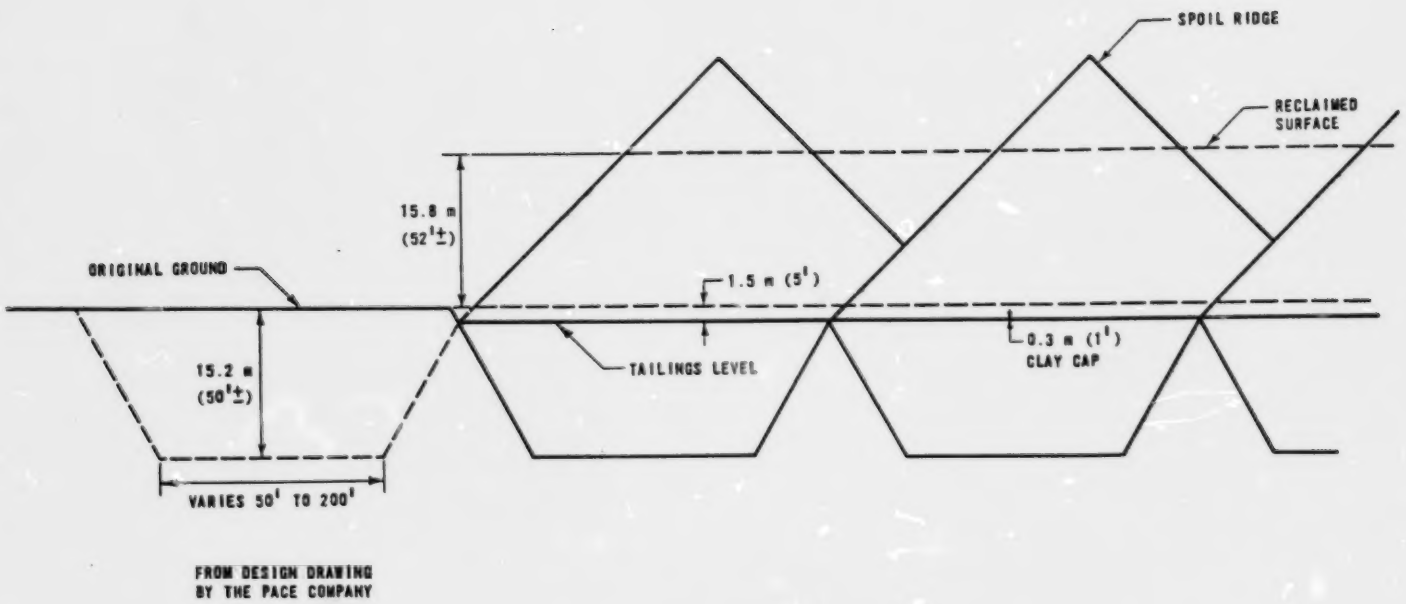


FIGURE III-2

TYPICAL TRENCH BURIAL SECTION

volume than when disposed of as a pulp and would be considered in conjunction with below grade disposal.

When using below grade disposal, one of the problems is how to line the sides of the pits which are conceptually steep.

WULFF, et al. (1980) showed that the cost of blow grade tailings disposal at Mount Taylor for the first stage ranged between $5.46-$45.55 per metric ton of ore. This alternative was considerably more expensive than the other alternatives evaluated.

COMBINATION BELOW AND ABOVE GRADE DISPOSAL

Above and below grade disposal of tailings may be an attractive alternative when ore is mined in a series of open pits and where the tailings provide a convenient way of filling the pits to reclaim the area.

In Colorado Springs, a sand and gravel quarrying company evaluated the possibility of retreating a 10 million ton pile of gold mill tailings with a view to disposing of tailings from the retreatment process in their sand and gravel pits. WULF, et al. (1980)'s evaluation found that even this alternative worked out marginally more expensive than in a single dam impounding tailings in the head of a valley.

ROBINSKY THICKENED TAILINGS METHOD

The Robinsky thickened tialings method uses a thickener to dewater tailings before they are discharged to a the central point of a large single impoundment area. As tailings are discharged, they are intended to spread out into thin layers from which solution decants and runs downgradient to retaining water impoundments on the outer perimeter of the tailings area. Six advantages are claimed:

1) The cone-shaped tailings pile can support a greater angle of repose than unthickened tailings. Consequently, the same size impoundment area can accommodate a greater volume of tailings.

2) Since solution decants to a pool along the outer perimeter of the area, there is a larger evaporation area and being shallower, the height and size of the impoundment wall can be a simpler structure.

3) Since solution is reclaimed from the tailings in a thickener, it can be returned to the mill without spending time in the tailings area. This is useful if recyclable reagents,

Figure 1 Comparison of the conventional and thickened tailing disposal systems

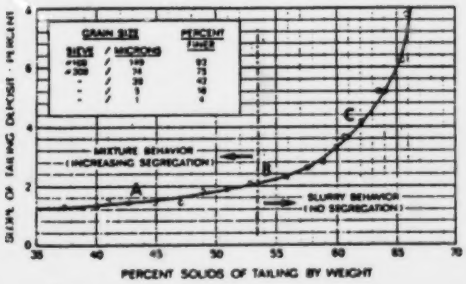


Figure 2 Typical laboratory tailing deposition test results

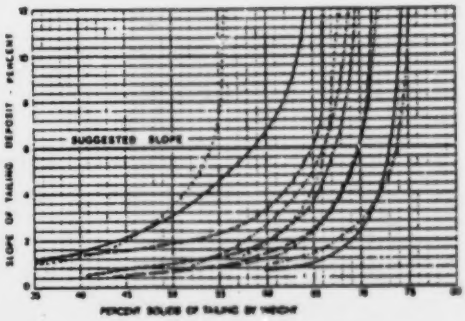


Figure 3 Laboratory test results showing tailing deposition curves. Tailing samples were obtained from different mines

Source: ROBINSKY (1981)

e.g., cyanide in a CIP tailings, are contained in solution which would be lost in a large open pond.

4) Because the tailings area covers a smaller area than conventional tailings in areas with net precipitation, less runoff and precipitation will be collected.

5) The Robinsky thickened disposal site is quicker to construct than most conventional tailings impoundments.

6) The possibility of scale clogging underdrains does not arise.

Critics of the Robinsky tailings method point out that many ores would yield a tailings that would not be stable to earthquakes. More information is described by ROBINSKY (1981) or can be requested from:

E. I. ROBINSKY
E. I. Robinsky Associates Ltd.
66 Lytton Blvd.
Toronto, Ontario
Canada M4R 1L3

One disadvantage of the Robinsky thickened tailings method at Kidd Creek Mines Ltd., Timmins, appears to be the problem of dusting during dry months when the wind blows. By building conventional tailings impoundments in sections, one at a time, each one, when full, can be vegetated as the next one is operational.

"DRY" TAILINGS DISPOSAL

"Dry" tailings disposal refers to the emplacement of dewatered tailings by conveyor belt, or dewatering them at the tailings site using a filter or belt press to recover water and reagent values for recycle.

The Nuclear Regulatory Commission insisted that uranium mills for which permits were applied in the U.S.A. evaluate this alternative. In this respect, belt filtration was considered to offer major advantages at one point. If the filters are to be installed with a view to washing the leached pulp as well as dewatering of tailings, then probably belt filters or the more expensive rotary filter should be considered. If, however, the filter is primarily there to make dry tailings and to recover solution (possibly with reagent and/or incremental resource values), then a disc filter would probably be more appropriate because they cost less. For the lowest possible cake moisture, belt presses could be considered. There are several on the market including those offered by EIMCO (Salt Lake City), DRAVO CORP. (Pittsburgh), PARKSON (Fort Lauderdale), and ARUS-ANDRITZ CORP.

ARUS-ANDRITZ CORPORATION
Arlington South Industrial Park
1010 Commercial Blvd. South
Arlington, TX 76017
(817) 465-5611
Telex: 794053

The United Nuclear Corporation evaluated dry tailings disposal for the Morton Ranch Project in Wyoming and rejected it for two reasons: Conveyor transport of dry tailings in winter would require convered and heated conveyors; and secondly, during the hot, dry, and windy Wyoming summers, there would be a real possibility of windblown losses. The cost of covered conveyors would be exorbitant.

Two dry tailings operations were identified, both disposing of uranium tailings, and it is known that a western U.S.A. silver recovery operation is considering dry tailings. Motivation of the two uranium operations is to maximize water recycling and to minimize water pollution. The silver operator's motive is to recover as much cyanide value with the tailings solution as possible.

1. Rudnik Urnana Zirovsky VRH
   Skofja Loca Slovenia
   Yugoslavia

   This 600 tpd operations installed two 50 m^2 units made by Filtres Philippe (France) in parallel. This operation also selected belt filters for the lower capital cost and expected superior wash efficiency.

   Details of the degree of success achieved could be requested from Dusn Pensa and Smargo Logar at the operation or from:

   FLUOR MINING AND METALS, INC.
   10 Twin Dolphin Drive
   Redwood City, CA 94065
   (415) 595-6000
   Don Skufka

   Also involved at the time was Brian Haydon, who visited the site but who has subsequently moved to:

   THE RALPH M. PARSON COMPANY
   100 West Walnut Street
   Pasadena, CA 91124
   (213) 440-3863

2. COMPAGNIE MINIERE DONG-TRIEU
Le Cherbois
87890 Jouac
France
(55) 68-21-09
Telex: 580-796
Christian Duchamp
Mill Manager

This 250 tpd mill also employed the latest Philippe belt filter to produce dry tailings for below ground disposal. The plant was visited just as the filters were being commissioned, and it was too early to determine how effective the dry tailings disposal was, i.e., what cake moisture is achieved, etc.

"SEMI-DRY" OR "SUB-AERIAL" TAILING DISPOSAL

The principle behind subaerial tailings disposal is to apply a tailings slurry in thin layers. Then the fluid is decanted off for recycle or evaporation, and the upper surface allowed to dry. When this occurs, it shrinks and cracks. The next layer of tailings then fills the cracks in the previous layer. It is also decanted and allowed to dry and crack, etc. Underdrains also remove any free moisture from below the impoundment.

"Semi-dry" tailings disposal are applied at numerous Witwatersrand gold-uranium tailings slimes disposal sites with excellent success. Of course, there is a warm, net evaporation climate and abundant, not yet too expensive labor to help make this sytem work.

Subaerial tailings disposal were first introduced in North America by Bruce Knight of Knight and Piesold in Vancouver.

A wellknown, successful application of subaerial tailings in Canada has been at:

KEY LAKE MINING CORPORATION
229 4th Avenue South
Saskatoon, Saskatchewan S7K 4K3
(306) 665-7000
Bernard Rosner
Engineering Manager
Joe Anderson
Environmental Manager

At Key Lake, a 12-inch layer of bentonite-stabilized sand (12 Kg bentonite per m^2) privides a satisfactory lower seal for the tailings pond. The bentonite-stabilized lining is covered with 3 feet of porous sand covering a system of perforated pipe to drain any fluids from the sloped lining. The tailings impoundment base slopes at 1/2-1° in two directions to drain fluids to a corner sump.

A very important aspect of the sub-aerial tailings technique practised at Key Lake is their disposal of precipitated arsenic and heavy metals sludges from the water treatment plant as well as precipitated $BaRaSO_4$. Because the precipitates are mixed with tailings and encapsulated, it is felt that they will be significantly more stable than when precipitates are mixed with tailings for disposal to a conventional tailings pond which allows diffusion of liquids throughout the submerged material. The Key Lake tailings, after subaerial deposition, are designed to be extremely impermeable and will not allow water containing CO_2 to reach the precipitate encapsulated in the mass of tailings. The importance of this lies in observations referred to in Chapter 29 that ferric arsenate precipitates may not be stable long term in the presence of CO_2 dissolved in water, just as the same observation has been made about $BaRaSO_4$. Therefore, the encapsulation of these and amphoteric base metal precipitates is likely to be very much safer than simply mixing them into conventional tailings. That is provided sub-aerial deposition works as well in their climate as laboratory simulation indicated.

BLIGHT and CALDWELL (1984) and WATES (1983) show how in South Africa the top surface of the subaerial deposited slimes are divided into paddocks for day and for night tailings addition. They also show that the retention of water on the top surface of a tailings as well as measures such as erosion protection by the covering of slopes with rock may lead to instability of the slopes under some circumstances.

The maximum practical rate of rise and hence the minimum cycle time required for effective desication, stable phreatic surface conditions, and access requirements is commonly thought to be a unique value for a given climatic region. For gold and uranium tailings impoundments in the Transvaal and Orange Free State, WATES (1983) points out that a value of 2.5m per year has been adopted as a maximum rate of rise. He points out, however, that it is not unique and that cycle time, which depends on the relative density of the tailings (i.e., water content), should be limited. He pointed out that about 1 ton of water goes to the dam for each ton of solids in a tailing with a specific gravity of 1.45, while about 3 tons of water goes with each ton of solids in a tailing with an SG of 1.18. Since the capital, maintenance, and running costs of pumps and piping are approximately proportional to the volume of slurry pumped, the cost of disposal per day can be significantly greater for slime of low solids content.

It is of interest that the tailings at the McLaughlin property of Homestake Mining Company will use a modified version of the subaerial tailings deposition technique.

Also of interest is the observation that Western Mines at their Myra Falls operation on Vancouver Island, British Columbia, is reputedly testing subaerial tailings deposition for tailings containing sulfides. Certainly, the problem of acid mine drainage generation from tailings containing sulfide minerals has yet to be resolved. The question is whether "sub-aerial" or "semi-dry" tailings disposal of this type of material could be adapted to provide adequate encapsulation of the sulfides in a low porosity material to limit the

migration of water into the tailings once lain down, or to limit migration out of acid. It will be most interesting to learn more about the experiments carried out by Western Mining on sulfide-bearing tailings and "semi-dry" tailings disposal techniques, because this operation is located in a net precipitation climate which will likely require some adaptation of the technique.

The Key Lake Mining tailings disposal method was designed with the help of Bruce Knight whose address is shown above and tested at:

SHERRITT-GORDON MINES LTD.
Fort Saskatchewan, Alberta
Canada T8L 2P2
(403) 898-6911
Herbert Veltman

Similar tests in which seasons over several years were simulated for Midwest Lake uranium ore (ESSO) were carried out in Mississauga by:

ONTARIO RESEARCH FOUNDATION
Dept. of Metallurgy
Sheridan Park Research Community
Mississauga, Ontario
Canada L5K 1B3
(416) 822-4111
V. Lakshmanan

The interesting aspect is that sub-aerial tailings disposal works also in parts of the world with very cold climates.

Certainly, in Witwatersrand slimes dams, the generation of acid from pyrite in the tailings seem to be inhibited relative to older sand tailings despite the fact that the more finely divided pyrite should oxidize faster--according to SMITH, et al. (1984). The question remains to what extent this inhibition can be enhanced were this feature important, possibly through an additive or some other approach.

Surces of expertise in "sub-aerial" or "semi-dry" tailings include:

KNIGHT AND PIESOLD
409 Granville
Vancouver, B.C.
Canada V6C 1T2
(604) 685-0543
R. Bruce Knight

STEFFEN ROBERTSON AND KIRSTEN
#801, 1030 West Georgia
Vancouver, B.C.
Canada V6E 2Y3
(604) 681-4196
Telex: 04-352578
Andrew MacG. Robertson

STEFFEN ROBERTSON AND KIRSTEN
7510 West Mississippi Avenue, #210
Lakewood, CO 80226
(303) 936-8254
Jack A. Caldwell

JONES AND WAGENER, INC.
Post Office Box 1434
Rivonia 2128
South Africa
J. A. Wates

FRASER F. ALEXANDER
Post Office Box 236
Benoni 1500
South Africa
(011) 54-6312
Telex: 8-2240
F. W. A. Daly
Chairman

The strong South African influence in "sub-aerial" expertise is due to the fact that this technique was developed there and is still quite new in North America where it is relatively experimental due to the different climatic conditions and objectives for its use.

SUBMARINE TAILINGS DISPOSAL

According to HAWLEY (1975), submarine disposal of tailings is practised by Bougainville Copper on Bougainville Island in the South Pacific (78,000 tpd); Utah Mines Ltd. operations at Rupert Inlet, Vancouver Island; and at Atlas Consolidated Mining, Toledo City, Cebu, Philippines (64,000 tpd) and also by the nickel recovery operations on New Caledonia. AMAX also deposits tailings from a molybdenum recovery operation in British Columbia into the sea, and one of the very largest of all submarine tailings disposal cases is planned by U.S. Borax and Chemical Company for their Quartz Hill molybdenum mine in southeastern Alaska.

The advantage of submarine tailings disposal is that there is no tailings site that requires maintenance or post-operation closure. Also, there is no acid mine drainage generated that can be treated for discharge. To date, information available on the effects on the marine environment of submarine tailings is not comprehensive. It is believed that Professor D. V. Ellis, editor of a book on the subject of marine tailings disposal, may have additional observations:

PROFESSOR D. V. ELLIS
Dept. of Biology
University of Victoria
Post Office Box 1700
Victoria, B.C.
Canada V8W 2Y2
(604) 477-6911
Telex: 049-7222

The economic advantages of submarine tailings disposal are great enough that it would be economically attractive to pump tailings over a considerable distance to be able to discharge them to the ocean.

The environmental impact of submarine tailings disposal is said to be minimal, but where is the study data to prove this. Jacques Cousteau investigated a submarine tailings disposal site off New Caledonia and reported very serious submarine environment damage.

Justification of submarine tailings discharge might be possible on environmental grounds through a study of the submarine environmental impact of doing so at existing sites. No such thorough study has been encountered. One of the problems is the lack of baseline data for such sites before the tailings were discharged.

Disadvantages of submarine tailings disposal include the loss of the opportunity to reclaim water or perhaps reagent values in tailings decant solution. On the other hand, if fresh water is available, this gives the operators grounds to use it throughout the plant which can have process benefits. Alternatively, tailings could be thickened prior to ocean dumping, allowing at least some water to be reclaimed.

DEEP LAKE DISPOSAL OF TAILINGS

Deep Lake disposal of sulfide tailings offers several advantages especially where these contain sulfide minerals. Firstly, the tailings are out of site and may never present a reclamation or AMD problem.

Not too many parts of the world have deep lakes--of those that do, the best known is Canada.

It is understood that, to date, licensing authorities have been against the issuance of permits for deep lake disposal of tailings. The reasons are not clear.

It is also understood that Hudson Bay Mining and Smelting used to dispose of tailings into a deep lake and that the environmental effects of doing so were found to be negligible. Details of the lake and identification of the operation that disposed of tailings in this way were not obtained. The study of environmental aspects was also not found--the hearsay comment is passed on for what it is worth in case the details can be tracked down through Hudson Bay Mining and Smelting.

At Westmin Resources' Myra Falls operation near Campbell River, B.C., on Vancouver Island, flotation tailings after alkaline chlorination for cyanide destruction were disposed of into the deep Buttle Lake from which the nearby townships draw their drinking water. It is reputed that this operation now employs subaerial deposition on an above ground

tailings pond which implies that they no longer dispose of tailings into the lake. No details were obtained on the subaerial tailings disposal nor if or why deep lake disposal ceased. Sponsors may wish to get in touch with A. G. Eccles, Mill Superintendent at this operation to learn more about deep lake disposal as well as subaerial deposition. A copy of his description of deep lake tailings disposal and cyanide destruction is included in Chapter 40 on cyanide destruction.

TO LINE OR NOT TO LINE A TAILINGS POND

Impoundment linings, whether clay or synthetic membranes (single or double), are very expensive. In some cases, lining a tailings pond upsets the water and salt balance as well, resulting in metallurgical recovery complications.

Whether or not to line a tailings impoundment depends on the answer to five questions:

1. What is the nature of the contaminants that will seep from the pond if unlined. That means what species in the tailings solution and what species will be generated as the tailings age, e.g., acid, base metals, reagents.

2. What is the nature of the material below the tailings impoundment. What is the porosity of the material--are there fractures which will leak.

3. Will contaminants in seepage be geochemically attenuated by the chemistry of the material underlying the tailings. Will this be adequate to protect aquifers and surface water quality.

4. What is the quality of water in the underlying aquifer that will be impacted. Is it already of such poor quality as to render it unusable and therefore not worth protecting. Can this be documented in a way that regulatory agencies will approve further contamination of the aquifer?

5. What do the local regulations require. Possibly, lining the pond is a prerequisite for a permit and, if so, what type of linings do they specify.

GEOCHEMICAL ATTENUATION OF SEEPAGE CONTAMINANTS

From a technical standpoint, geochemical attenuation of tailings seepage can be very powerful and a useful aid in tailings impoundment. In fact, this may be a most valuable criteria in selecting one of several alternative impoundment sites. Seepage from some tailings ponds is a desirable feature. One such example would be a tailings pond located at a site with net precipitation where a closed system recycle would interfere with

DOWNSTREAM DISCHARGE TAILINGS POND IN NEVADA

metallurgical efficiency (e.g., uranium recovery by ion exchange) located over a highly saline aquifer where the sediments over which the tailings are impounded have a chemistry that will neutralize the acid in the seepage and attenuate the contaminant migration geochemically.

The following are amongst the recognized experts in this area:

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GROUND WATER AND CONTAMINANT MIGRATION: PRINCIPLES, MONITORING, REGULATIONS, AND CONTROL MEASURES

Jim V. Rouse

May, 1984

INTRODUCTION

The state of awareness of the vulnerability of ground water to pollution, and the concern over such ground-water pollution occurrence and migration has come a long way since the days when a court ruled that the movement of ground water was such a mysterious and mystical process that it could not be known to mankind. Almost every present day technical publication deals with the real or supposed potential for ground-water contamination. EPA and the various state regulatory agencies are devoting significant amounts of time and effort to assuring that such migration does not occur.

Far from being a mysterious and mystical process which cannot be understood by mankind, the movement of ground water and dissolved contaminants obeys a series of rather straight-forward laws, and can easily be understood by a common sense approach.

The idea of "underground rivers" is totally out of place in virtually all situations of ground-water contamination. Available information shows that there are natural geochemical attenuation mechanisms at work to retard or prevent the spread of contaminants throughout the water mass. While it is not appropriate to depend solely on such natural attenuation, it does form a vital secondary line of defense beyond the engineered controls which man can emplace. It is appropriate to start

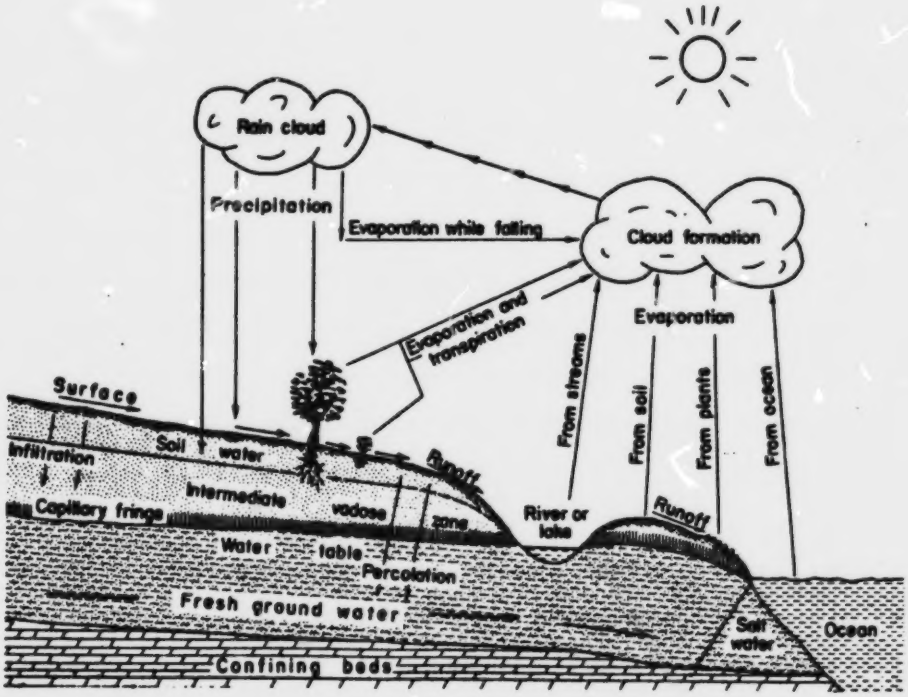
spreading this good news to regulatory agencies, that ground water does have certain natural geochemical purification processes.

GROUND-WATER HYDROLOGY PRINCIPLES

Far from being a separate, mystical and mysterious fluid, ground water is only one type of water which is interrelated to surface water and atmospheric water by means of the hydrologic cycle. This was very well summarized by King Solomon in the book of Ecclesiastes, when he stated that "all the rivers run into the sea but the sea is not full". Ground water includes only that portion of the overall hydrologic cycle where movement is through natural geologic media under saturated flow conditions. Ground-water recharge occurs when precipitation, in the form of rain or snow, infiltrates the soil and the unsaturated (or "vadose") zone to reach the ground water mass below the "water table". Additional recharge occurs from the infiltration of water from surface water courses, either permanent or temporary stream flow. All of this is schematically illustrated on Figure 1.

Ground-water movement occurs from areas of high potential energy to areas of lower potential energy. Thus, ground water moves "downhill", but the problem is defining what is "downhill". Flow generally occurs through a myriad of very small pore spaces between grains of mineral matter, and as such is extremely slow, with rates in the order of a few hundreths to a few tenths of a foot per day being quite common.

Figure 1 - The Hydrologic Cycle



From Groundwater And Wells, Johnson, 1975, p.16

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PREPARED BY: WTD DATE: 7/11/84	
CHECKED BY: CJR DATE: 7/12/84	PROJECT NO. Figure 1

Ground water discharges into streams to support the base flow of the stream, and also discharges into the atmosphere by means of direct evaporation of water at seeps, or by transpiration of water from phreatophytes (water loving plants) whose roots penetrate to the water table. Ground-water discharge thus rejoins the above-ground portion of the hydrologic cycle as either surface water or atmospheric water. Ground-water discharge also plays a major role in man's activities, with approximately half of the total water consumption in the United States being supplied by wells.

There are several units of measurement associated with ground-water hydrology which are quite important. One of the most simplest of these is the piezometric surface elevation, or the water table elevation for those aquifers which are at atmospheric pressure on the upper surface. Artesian aquifers are those aquifers which are confined on the upper surface by an overlying, impermeable strata. The piezometric surface for a confined aquifer is an imaginary surface significantly above the upper surface of the aquifer, and would be marked by the elevation to which water would rise through an infinite number of artesian wells penetrating the confining layer. Artesian aquifers are not necessarily flowing aquifers, but rather only flow when the piezometric surface is at an elevation higher than the land surface.

The piezometric surface, or water table elevation, is commonly measured by means of an electric sounding tape lowered down a

well until contact is made. The depth of water from a known elevation point is measured and is then converted into piezometric surface elevation by subtraction of the depth of water from the elevation of the measuring point. Water table aquifers generally show seasonal fluctuations in elevation; artesian aquifers frequently display rather marked variations caused by the passage of weather systems, the passage of a train near the well, or in response to nearby pumpage.

The permeability of a rock unit is the ability of that unit to transmit water under saturated flow conditions. Permeability is frequently stated in terms of velocity units such as feet per day but can only be converted to ground-water velocities by multiplication of the permeability times the ground-water gradient.

The transmissivity of an aquifer is the permeability multiplied by the vertical thickness of the aquifer unit. It is directly calculated by means of aquifer tests in which a measured quantity or flow rate is pumped from a pumping well over a period of time, frequently 24 to 48 hours, and the rate of ground-water decline in the pumped and/or monitor wells in noted.

CONTAMINANT MIGRATION AND FIXATION

Contaminants which enter the ground-water mass may move at the same rate as the ground-water particle, (in which case they are referred to as "conservative" contaminants), or they may be

retarded relative to the rate of ground-water flow, or may actually be immobilized within the aquifer. Contaminants with this latter form of behavior are referred to as "non-conservative" constituents. Obviously, the general situation is somewhere between behavior as a conservative and totally non-conservative constituent. Certain contaminants of concern tend to be very close to totally conservative, such as hexavalent chromium, organic solvents, and major ions such as chloride and sodium. Materials which are severely retarded in the ground-water environment include radionuclides such as radium. Most of the common heavy metals are retarded in a finite order which has been developed by studies through numerous areas of ground-water pollution.

CONCEPTUAL GEOCHEMICAL MODEL

Based on numerous studies, it is possible to develop a conceptual geochemical removal mechanism model to address the behavior of those contaminants which are retarded by geochemical reactions. The attached Appendix A summarizes the various geochemical reactions, which may take place in the subsurface, and provides additional details on the removal affecting an acidic, contaminant plume which is in reaction with the natural aquifer material. The following information, based on the various reactions, summarizes a conceptual geochemical model for contaminant mobilization, transport, and removal. This model is similar to that presented by Cherry, Shepherd, and Morin (February 14-18, 1982) and is based on the results of many

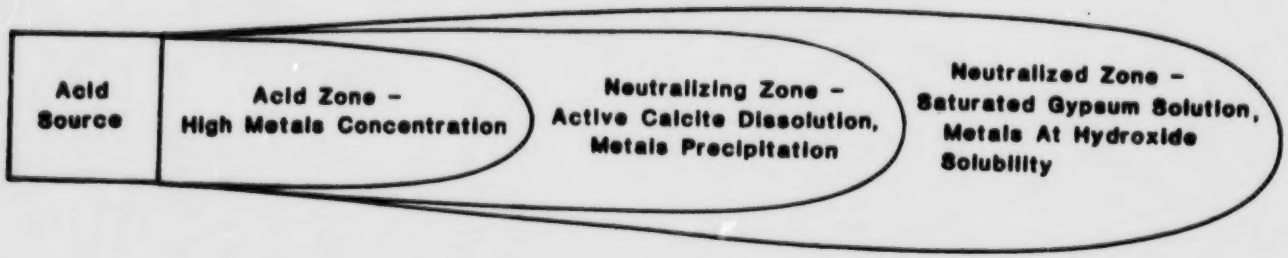
investigators in this field, as well as the authors' own field experience.

When a highly acidic water percolates from a process water impoundment, the initiation of calcite dissolution occurs at the advancing wetted front. As the plume proceeds downgradient, a total of three zones form, illustrated on Figure 2 and described in the following section.

The first zone, which may be termed the "acid" or "core" zone, consists of ground water with a quality virtually identical to that of the pond water. The water is characterized by extremely low pH, the presence of very high sulfate ion concentrations, often in the form of ferrous sulfate complex, and other contaminants including numerous heavy and toxic metals. Radiochemical contaminants are strongly sorbed on aquifer clays and rarely move more than a few meters.

The acid or core zone described above is characterized by an area in which all calcite minerals present in the soil or rock column have been dissolved and reacted and the ground water is similar in quality to that of the source. In areas with soil rich in carbonate minerals, such reaction, and the resultant acid or core zone, is often a few meters in extent. By contrast, the second conceptual zone, termed the "neutralizing" zone, is the site of active calcite dissolution and the formation of chemical precipitates, including metal hydroxides, calcium phosphate, calcium flouride, and gypsum. This zone is further characterized

Figure 2 - Conceptual Model Of Geochemical Zones



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by continuing high values of dissolved metals, in accordance with the order of metal hydroxide removal. The types of metals involved can be directly related to the resultant pH of the solution. The front and rear boundaries of this zone are not sharp lines, but rather tend to be zones which advance downgradient in response to chemical reactions. Radiochemical contaminants are generally absent, having been sorbed and coprecipitated in the acid zone.

Downgradient of the neutralizing zone is an area which can be termed the "neutralized" zone, characterized by high concentrations of total dissolved solids representing a saturated calcium sulfate solution. The area is further characterized by little in the way of calcite reaction, with virtually all of the calcite originally present in the soil or rock still remaining available for reaction. The upgradient boundary between the neutralizing and neutralized zones is gradational, depending on the metal hydroxide removal stage. The downgradient boundary of this zone is represented by increasing total dissolved solids concentrations.

GROUND WATER MONITORING

The design, installation, and operation of a ground-water monitoring system to adequately define the horizontal, vertical, and temporal variability of ground-water quality dictates a thorough knowledge of the ground-water flow system. Numerous extensive articles and manuals have been prepared on the proper design, construction, and operation of such a system, and should be consulted prior to the beginning of such activities. In addition, the appropriate state and Federal regulations for hazardous waste sites should also be considered, since they dictate facility location, construction, and operation, as well as the statistical analysis of the resultant data.

While any evaluation of the ground-water resource should utilize to the maximum extent practicable any existing well, all too frequently such wells are not located at suitable sites, are not completed in the appropriate horizon, or information does not exist on the construction techniques. In such cases, monitor wells must be drilled and completed specifically for the purpose of ground-water monitoring.

Monitor Well Construction

Extreme care must be taken during the construction of monitor wells to assure that the wells properly sample the aquifer of interest, and do not allow for the vertical migration of contamination from one zone to the other. Prior to monitor well construction, state agencies should be contacted for the latest requirements concerning permit and completion requirements.

General experience has shown that well clusters or "nests" are more suitable for routine monitoring in the vertical dimension than multiple-completion wells because of their simpler structure. However, each has its advantage under certain circumstances, as discussed in a following section.

Care should be exercised in selection of the material used in well construction, considering geochemical site conditions. PVC well casing is usually preferred over metal, unless samples are to be collected for organics. Sand or gravel for well packing should be checked for high concentrations of regional material. Johnson (1972) provides an excellent general discussion of wel' construction techniques.

The most common monitor well construction is one open over a vertical section of the aquifer, used to obtain ground-water samples from un-onsolidated sediments or semi-consolidated rocks. In consolidated rock, open bore holes without casing can serve the same purpose. Such a well is not effective in providing information on the vertical distribution of contaminants. Most existing wells converted to monitor well use are of the open section type. All too frequently, such open-section wells are completed to a depth just below the water table, which has the obvious major drawback that only the upper portion of the aquifer and the most recently infiltrated contaminant is sampled. In some cases, wells are screened over the entire aquifer thickness in an effort to counteract this shortcoming. This solution may mask contamination by excessive dilution, and provides no

information on the vertical distribution of the contamination due to the composite measure of the sample.

Piezometers are used to measure water pressure in aquifers and to obtain water samples from a specified depth. A piezometer is isolated from other pressure environments by an impermeable clay or cement seal. If the well screen is properly isolated by an impermeable seal placed immediately above the screen, a piezometer can also be used to measure vertical head differences under unconfined conditions. The important difference between a piezometer and a well screened over the entire vertical interval is the annular seal. Such a relatively impermeable seal will prevent downward movement of contaminant into uncontaminated zones of the aquifer.

Multiple piezometers with screen intervals set at different depths in a single location can be used to form a well cluster or "nest". Such a nest allows the definition of the piezometric elevation as a function of depth within the aquifer, and also allows the collection of water-quality samples from various depths. Contaminant plumes are often more dense than the receiving ground water, and sink to a lower confining layer with subsequent movement as a density current in the aquifer, with little mixing. Thus, a nest of piezometers or short-screen wells can define that portion of the aquifer which is contaminated, and allow for the development of remedial measures which limits the quantity of ground water which must be pumped and treated.

Aquifer Tests and Permeability Determination

By far the most common method of determining the permeability of an aquifer is by means of aquifer or pump tests. Water wells are generally tested for two reasons:

1) To obtain information about the performance and efficiency of the well, and
2) To provide information on the water-yielding characteristics of an aquifer or the interrelationships of different hydrologic units.

In the conduct of an aquifer test, it is assumed that a thorough pre-test site evaluation will be conducted by trained hydrogeologists. The details of such an evaluation are beyond the scope of this paper, but are discussed by Stallman (1971) and Fedora (1980). In general, this evaluation should include study of pertinent well logs and other data in order to determine and estimate as many of the characteristics of the aquifer as possible. Either of the previously mentioned test objectives will require collection of the following data:

1) Static water levels before pumping starts
2) Location of and distance between pumping and observation wells
3) Barometric pressure change during test
4) Pumping rate or rates of discharge from the pumped well
5) Dynamic water levels or pumping levels at various time intervals during the pumping period
6) Time of starting the pump

7) Time of any change in discharge rate and new pumping rate

8) Time of stopping the pump

9) Dynamic water levels after cessation of pumping

All equipment to be used during the tests should be checked thoroughly. If a test must be terminated prematurely because of mechanical failure, all of the previous efforts may be useless and require repeating. Prior to testing, the well should be thoroughly developed or its response to the test may not be meaningful. A pump of appropriate capacity should then be installed. Such a pump should be capable of continuously delivering one quarter to one half of the maximum well yield.

The pumping rate during testing should be kept as constant as possible, and should not vary more than 10% during the test. The best control is provided by a valve in the discharge line. The valve should be partially closed to restrict the initial discharge. Partially closing the valve tends to reduce any fluctuation in pump rate due to varying line voltage. As the water level falls during pumping, the lift increases and the discharge of the pump tends to decline. With the valve initially restricted, it can be opened as necessary during the test to maintain a constant rate.

Small pumping rates can be determined by observing the time necessary to fill a container of known volume, such as a 55 gallon drum or 5 gallon bucket. Commercial water meters may also

be installed in the discharge line. Subtracting two readings taken exactly one minute apart gives the pumping rate in gallons per minute. This apparatus has the disadvantage of delays in getting initial values at the start of a test when the rate is being adjusted. The water meter and volumetric methods for measuring discharge rate are most useful for flows of less than 100 gallons per minute.

Discharges from turbine or centrifugal pumps are often measured with a circular orifice plate. The discharge pipe must be straight and level for a distance of at least two meters back of the orifice plate (Johnson, 1972).

No matter what method of flow measurement is used, water discharged from the pumped well must be conducted away from the well head so that it cannot recharge the aquifer during the test. Depth of water in the pumped well must be measured several times during conduct of the test. Water level measurements should be recorded to the nearest 5 millimeters or 0.02 feet, depending on planned units of measurement. Measurements should be made at 30 second intervals during the first 5 minutes, 5 minute intervals for the first hour, and every 20 minutes for approximately 2 hours subsequently. Subsequent measurements can be made hourly for the first day of pumping and then at a lesser frequency. Measurements must be made from a fixed reference point such as the top of the casing to the water level. The actual elevation of the reference point should be determined to allow calculation of the water-table elevation.

Once the pumping test has been completed, water level recovery measurements should be made. This is simply the reverse process of the pumping time. After these data have been collected, appropriate data analysis should be made. Discussions of aquifer analysis are provided in numerous texts such as Freeze & Cherry (1979), Davis & DeWiest (1966), or Johnson (1972).

In situations where the cost of a full pump test is not warranted, and especially where low permeability sediments are encountered, "slug" or "bail" tests can be utilized. Both tests are initiated by causing an "instantaneous" change in the water level of the well by sudden addition (slug test) or removal (bail test) of a known volume of water. Recovery of the water level is then noted and recorded. An excellent discussion of the conduct of such tests is provided by Freeze & Cherry (1979).

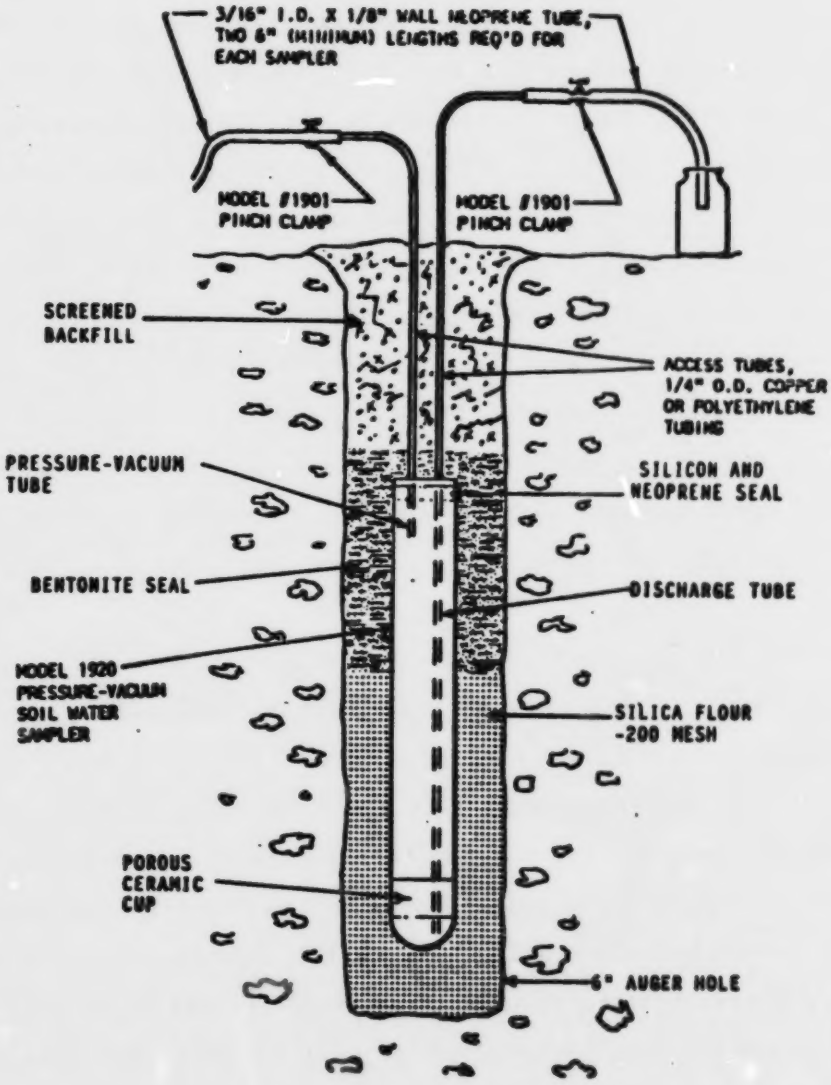
Slug and bail tests yield results that are, technically, only indicative of the area immediately surrounding the bore hole. As such, there are some limitations that must be considered. Accurate results depend on the response of the bore hole. Poor response due to incomplete development or screen clogging may result in inaccurate calculated values. Also, if the well was developed by surging or backwashing prior to the test, values may simply reflect the increased conductivity in the gravel pack surrounding the bore. If the wells are to be used for water quality monitoring, care should be used in selection of the water added during a slug test to avoid false water quality data.

Vadose Zone Monitoring

In many cases, it is desirable to know the concentration of potential contaminants in the soil moisture above the groundwater, so as to allow initiation of remedial measures prior to the contamination of the saturated zone. Such monitoring of the unsaturated or vadose zone can best be accomplished by means of pressure/vacuum lysimeters. Pressure/vacuum lysimeters consist of a porous ceramic or Teflon cup capable of holding a vacuum, a small-diameter sample accumulation chamber of PVC pipe, and two sampling tubes leading to the surface. Once the sampler is emplaced, a vacuum is applied to the cup, causing soil moisture to move into the sampler. The sample is then recovered by releasing the vacuum and applying pressure to the delivery tube, forcing the accumulated water to the surface through the sampling tube. Figure 3 illustrates a typical lysimeter installation.

Lysimeters yield a limited quantity of sample, generally less than one liter, depending on such factors as soil type and moisture content, sampler construction, and depth of installation. For installations at great depth, a lysimeter must include a check valve to prevent forcing the sample back out to the porous cup during sample recovery. Lysimeters have proven useful to depth in excess of 35 feet. Equipment costs are relatively low, but the equipment requires care and experience in proper installation. Highly saline soil moisture can plug the cup pores as a result of chemical precipitate formation.

Figure 3 - Pressure/Vacuum Lysimeter Installation



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REGULATIONS CONCERNING GROUND-WATER QUALITY

In the past few years, a number of regulations have been promulgated at both the Federal and state levels which have an impact on ground-water quality and operations which might endanger such quality. These are briefly discussed below, along with their impact on the technical operation of a facility. They should not be considered as definitive legal discussions, but rather a technical summarization of the various pieces of legislation.

Federal Laws and Regulations

The development of recent ground-water protection regulations has been especially active at the Federal level in the past ten years with the passage of three Acts which severly impact ground-water quality.

The Safe Drinking Water Act has a marked impact on activities which might relate to ground-water quality, as a result of the Underground Injection Control (UIC) program. Many facilities in the metal finishing and electronics industry utilize "dry wells" for the disposal of water such as parking lot runoff. Such "dry wells" are under the purview of the UIC program. At present, such wells are "Class V" wells and are not regulated by permit, but rather are administered under a general rule. However, EPA intends to pursue the appropriateness of regulating the various wells, including "dry wells", which are presently incorporated under the "Class V" designation.

Dry wells do have the distinct potential for contaminating ground-water in those cases where toxic substances are spilled on the pavement, either through drips or by accidental plumbing failure. Thus, there is a need for consideration of the potential contamination associated with the practice of "dry wells".

A few metal finishing operations dispose of effluent by the intentional injection of such waste into deep disposal wells, or Class I wells under the UIC program. The permitting of a Class 1 injection well is quite extensive and expensive and can consume 12 to 18 months between the time of application and permitting.

The Resource Conservation and Recovery Act (RCRA) is a comprehensive bill which pays close attention to the potential ground-water pollution associated with the generation, transport, and especially treatment and disposal of hazardous waste. Regulations promulgated by EPA in response to RCRA specify the number and type of monitor wells which must be emplaced around a hazardous waste disposal facility, and also the type of statistical evaluation of the resultant ground-water quality data. If monitoring under RCRA determines that a contamination situation exists, a phased program of additional, extremely expensive, ground-water monitoring steps must be inaugerated.

The Comprehensive Environmental Response Compensation and Liability Act (CERCLA) deals with the clean up of inactive hazardous waste disposal sites. CERCLA allows EPA to oversee

such clean up and then to charge the costs of such clean up, including EPA administrative costs, to the responsible parties. Under the "joint and several" provisions of CERCLA, EPA can bring enforcement action against any one of a number of responsible parties involved with waste disposal.

Much of the CERCLA activities deal with potential ground-water contamination. The EPA Hazard Ranking System (HRS or MITRE Model) does not incorporate the concept of geochemical attenuation in the subsurface environment. The MITRE Model also does not pay any attention to the direction of ground-water flow, but rather postulates a flow in any direction toward a potential source of supply. While the MITRE Model might be acceptable in a ranking system for organic contaminants in a human environment, it is not pertinent for either metals contaminations or arid zone environments.

State and Local Regulations

In general, the state and local regulations have tended to follow those specified by the Federal legislation. One notable exception is the area of Leaking Underground Storage Tanks (LUST) in which southern California has taken the lead requiring extensive ground-water monitoring around underground storage tanks containing petroleum products or hazardous wastes. Vadose zone sampling techniques are ideally suited for monitoring of LUST.

REMEDIAL MEASURES

Remedial measures aimed at ground-water control can be extremely expensive and time consuming. In general, remedial measures take the form of either recharge prevention, discharge prevention, or recovery and treatment. These general techniques are listed in decreasing order of preference and increasing order of cost. The concept of recharge prevention aims at preventing the movement of either water or contaminants into the subsurface. For example, if the soil in a site is contaminated with mobile contaminants, recharge prevention might take a form such as capping the site with an impermeable clay or membrane cap, or installation of a slurry cutoff wall upgradient of the site, to deflect ground water around the zone of contamination.

Discharge prevention is aimed at preventing the movement of ground water and/or the contaminants from the site. Contaminants may be immobilized by enhancement of geochemical phenomena which tend to provide for fixation. Ground-water discharge itself may be prevented by features such as the emplacement of slurry walls or grout trenches to reduce or retard the movement of ground water from the site.

Techniques for recovery and treatment generally involve capturing the contaminated ground water for pumping to the surface with subsequent treatment and discharge either back to the aquifer which served as its source or directly to surface water sources. Such recovery and treatment can be extremely costly both in capital and operating costs, and must continue until the contamination source has been totally cleaned up. As a result, this can be extremely costly in both time and money.

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Appendix A

Summary of Major Geochemical Reactions

By far the single most significant geochemical reaction is that of calcite dissolution, wherein the acidic contaminant reacts with calcite or other carbonate material present in the soil or rock. The reaction is calcite reacting with hydrogen ion to liberate calcium ion and form bicarbonate ion. This results in the gradual downgradient movement of an acidic reaction front, and an acid-front retardation in the saturated zone, relative to the rate of water travel. Hydrogen ions in the acidic plume are consumed by calcite dissolution. The retardation of the advance of the acid front is a result of the number of pore volumes of water with a specified hydrogen ion concentration that must react with a representative volume of the porous media to completely remove the total mass of calcite in the volume (Cherry, Shepherd, and Morin, February 14-18, 1982). Since the rate of ground-water flow is slow relative to the rate of calcite dissolution, the result is a slowly moving displacement acid front.

Calcite dissolution may also take place by means of an anaerobic reaction wherein calcite reacts with ferrous iron to form ferric carbonate (siderite) with the resultant liberation of calcium ion. By this means, calcite reacts with ferrous iron to remove iron from solution by the in place precipitation of ferric carbonate.

Geochemical precipitation pathways are, of course, reversible by dissolution, but in many instances the chemical conditions necessary for the reversal (such as pH of 2) are extremely rare or unlikely in natural geochemical environments (Wilson and Rouse, May 2, 1980). Precipitation of metal hydroxides as a result of increasing pH has been studied by a number of investigators. Rouse (October, 1976) presents a summarization of the process and notes that the various metals are sequentially removed as a result of elevated pH. Figure 1 indicates that iron is the earliest metal hydroxide to be removed as a result of elevated pH values, followed in turn by aluminum, copper, zinc and finally manganese of the common metal contaminants present in the acidic plume. In recent work in the Globe-Miami area of Arizona, several such sequential precipitation plumes have been identified downgradient of copper mining operations (Rouse, in press). Radiochemical pollutants, such as radium, tend to coprecipitate with the metal hydroxides.

Although not commonly recognized, it is possible for hydrogen ions in an acidic contaminant plume to be removed and pH increased by the process of ion exchange, wherein hydrogen ions replace other cations on ion exchange sites such as clay mineral surfaces. This process, while increasing the pH and possibly precipitating other metals, does not reduce the total dissolved solids but rather liberates other major cations and produces an alkali earth-rich solution. However, such major cation

liberation may, in some cases, be countered by the process of gypsum precipitation.

Both the process of calcite dissolution and the ion exchange with clay can result in the presence of high concentration of calcium ions in acidic contaminant plumes such as are common to phosphate acidulation operations. The use of sulfuric acid for many industrial practices results in the presence of extremely high sulfate concentrations. These concentrations of calcium and sulfate ions will, in an aqueous solution, result in the precipitation of gypsum in the subsurface, with subsequent reduction in rock or soil permeability. Note that the precipitated gypsum occupies more volume than the dissolved calcite. Radium has chemical behavior similar to calcium, and hence is coprecipitated with the gypsum.

As was previously noted calcite dissolution can take place by means of calcite reaction with ferrous iron to precipitate siderite. Subsequent to the removal of all calcite mineral from a soil column, this siderite may, in turn, react with acidic contamination plumes to consume acid with the side reaction of dissolution of ferrous iron. This results in the consumption of hydrogen ions and an elevation of pH from an acid plume, but with the undesirable side reaction of dissolution of previously precipitated iron.

All of the above reactions have the desired effect of removing hydrogen ions from solution and raising the pH. Unfortunately, there are a number of competing geochemical reactions which result in decreasing pH by liberation of hydrogen ions.

Some acid contaminant plumes contain high concentrations of ferrous sulfate complex. Such ferrous iron can be directly removed from solution by the oxidation of ferrous iron to the ferric reaction state and the resultant precipitation of ferric hydroxide. The required oxygen can come from dissolved oxygen contained in percolating vadose water, or oxygen dissolved in the ground water. The resultant reaction liberates hydrogen ions, resulting in a pH increase.

Aluminum ion can hydrolize directly with water to form an aluminum hydroxide precipitate, with the subsequent liberation of hydrogen ion. Similarly, aluminum can react with water and dissolved silica to form amorphous alumino-silicate precipitates, with the liberation of significant quantities of hydrogen ion. Evaluation of water quality data in the vicinity of phosphogypsum facilities indicate relatively high concentrations of dissolved aluminum and silica. Thus, it is expected that the acidic plumes may be the site for precipitation of amorphous alumino-silicate precipitates and the generation of additional acidity.

TAILINGS IMPOUNDMENT WATER BALANCES

The following account is excerpted directly from CALDWELL and WELSH (1983). It is interesting that during plant visits, very few of the operating personnel actually are aware of their tailings pond water balance. CALDWELL and WELSH's description provides some insight into how a tailings impoundment water balance is calculated.

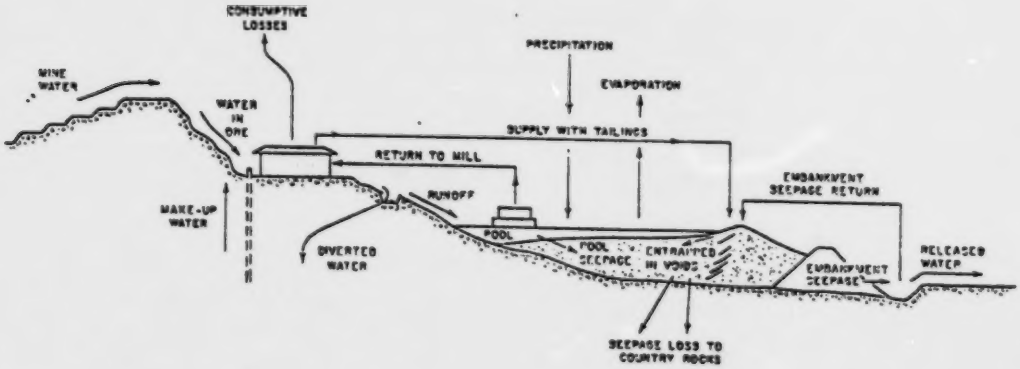
Tailings Impoundment Water Balances

Fig. 6 shows the components of a water balance model of a tailings impoundment. As shown, water flows into the system from a number of sources. It is stored within or on the tailings and is lost from the system by evaporation, seepage or discharge. The water balance system or model of an impoundment and mill can be analyzed as three interlinking cycles:

- the mill water cycle;
- the tailings impoundment mill cycle; and
- the tailings impoundment natural cycle.

The first cycle deals with the water input to the mill with the ore, from make-up water and by way of return flow from the impoundment. The tailings impoundment mill cycle deals with water input from the mill, the amount trapped in the deposited tailings and returned to the mill. The impoundment natural cycle deals with rainfall, runoff, evaporation and seepage. It is the only one of the three cycles that deals with stochastic, that is randomly variable, processes. Statistical methods are usually required to deal with this cycle.

Table III summarizes the results of water mass balance studies on three typical tailings impoundments which are either being designed or constructed in the U.S.



Water balance components.

Typical Average Annual Water Balances

Water Balance Item	Case		
	1. Wet	2. Moderate	3. Dry
1. Ore production - tonnes/year	127,000	1,600,000	8,300,000
2. Mill water - L/min			
2.1 Input			
ore	25	170	
fresh make-up	45	60	
tailings return	380	2,000	
2.2 Output			
tailings discharge	450	2,230	
2.3 Mill balance	0	0	
3. Tailings impoundment - mill cycle L/min			
3.1 Input			
tailings discharge	450	2,230	32,200
mine dewatering	7,660	0	3,200
3.2 Output			
trapped in tailings	70	600	3,700
return to mill	380	2,000	35,000
3.3 Mine cycle balance	7,660	-370	-3,300
4. Tailings impoundment - natural cycle L/min			
4.1 Input			
precipitation	1,300	920	4,000
runoff	2,380	1,440	
4.2 Output			
diversion	2,300	650	0
evaporation	170	460	300
seepage	0	0	400
4.3 Natural cycle balance	1,210	1,250	3,300
5. Discharge from tailings impoundment L/min	8,870	880	0

The values listed represent the average annual water volumes over the life of the impoundment. Many of the values vary from year to year and show trends with time. Such details are not shown.

Case 1 is a very wet natural cycle as the precipitation at the impoundment is high. The mill cycle has a large surplus of water from mine dewatering activities; this is discharged into the impoundment. Consequently, a relatively large volume of 8870 L/min must be discharged. Even without the mine dewatering component, the impoundment generates excess water at the rate of 1210 L/min and 70 L/min per thousand tonnes.

Case 2 represents a slightly drier natural cycle. The mill cycle has a slight deficit balance (370 L/min) which means the mill removes more water from the impoundment than it contributes to surface storage. Overall, there is a slight surplus of 0.5 L/min per thousand tonnes which must be discharged.

Case 3 represents a relatively dry natural cycle with a small surplus coupled with a mill cycle which has a slight deficit balance. In this case, a zero total balance has been achieved and the system is, in fact, a closed circuit.

Water balances such as those shown in Table III can be evaluated very easily using regional hydrologic and climatic data, preliminary information on the mill process, and time averaged impoundment and catchment areas.

As the more detailed studies proceed, the mass balances computational process becomes correspondingly more detailed. The tailings impoundment system can be divided into subcomponents such as the main tailings impoundment, the tailings embankment and the seepage return dam. Computer models are used to perform stepwise solutions to the mass balance equations, thus simulating a time sequence that shows how the tailings impoundment develops.

TAILINGS DISPOSAL COST COMPARISON

The following table from WULFF, et al. (1980) shows the relatively wide range in tailings impoundment costs from $1.57 per metric ton to $45.55/metric ton calculated for the disposal of the same tailings at a western U.S.A. site. This indicates the importance of undertaking engineering cost studies for several alternatives. These should, however, be applied using a systems approach. If, for example, below grade disposal was estimated to cost $5.00 per ton compared with $2.50 per ton for conventional above grade disposal, the difference might well be justified if the below ground disposal method avoided the need for a "perpetual" maintenance program and operation of a water treatment plant to treat acid seepage from the tailings in a wet climate; it would hardly be likely to b justified in a dry climate or for disposal of inert tailings where acid mine drainage will not become a problem.

Disposal Alternative	Stage		Range of Costs* Per m^3 (Acre Foot) of Tailings Storage	Range of Costs* Per Metric Ton (Short Ton) of Ore
Total Below-Grade Disposal (Pits or Trenches)	First Stage	High	$ 38.91 ($48,000)	$ 45.55 ($41.32)
		Low	$ 4.31 ($ 5,322)	$ 5.46 ($ 4.95)
	TOTAL	High	$ 4.95 ($ 6,100)	$ 4.55 ($ 4.13)
		Low	$ 4.04 ($ 4,978)	$ 3.64 ($ 3.30)
Combination Below-and Above-Grade Disposal (Cells)	First Stage	High	$ 6.03 ($ 7,434)	$ 6.97 ($ 6.32)
		Low	$ 2.50 ($ 3,084)	$ 1.83 ($ 1.66)
	TOTAL	High	$ 3.84 ($ 4,736)	$ 3.96 ($ 3.59)
		Low	$ 2.49 ($ 3,077)	$ 1.83 ($ 1.66)
Principally Above-Grade Disposal (Single Dam, Head of Valley Impoundment)	First Stage	High	$ 6.35 ($ 7,829)	$ 5.45 ($ 4.94)
		Low	$ 3.76 ($ 4,638)	$ 3.04 ($ 2.76)
	TOTAL	High	$ 3.49 ($ 4,299)	$ 2.85 ($ 2.59)
		Low	$ 2.06 ($ 2,540)	$ 1.57 ($ 1.42)

*Costs used to develop this table include capital costs for all applicable features of a given disposal scheme, excluding tailings and water conveyance facilities.

CLOSURE OF MILL TAILINGS

Closure of mill tailings impoundments at the end of an operation is critical. How this is achieved could well determine whether a perpetual maintenance program with acid mine drainage treatment plant is required or not. How a tailings impoundment site can be restored largely depends on how it was designed in the first place and the nature of the tailings.

The greatest single environmental problem facing the mining industry today must certainly be acid mine drainage control, i.e., the disposal of wasterock and mill tailings that contain sulfide minerals, particularly after the milling operation has ceased.

BLIGHT and CALDWELL (1984) state, in connection with Witwatersrand tailings disposal sites, "It became abundantly obvious during these investigations that no maintenance-free solution exists to the abatement of pollution from abandoned dams. Maintenance efforts can be minimized by careful design and construction, but the onslaught of the elements ensures that maintenance and aftercare can never be eliminated."

Discussion of several aspects of tailings site stabilization and revegetation is included in the following excellent papers. Sponsors are also referred to trip reports on the Wedge

Mine, INCO at Copper Cliff, Waite-Amulet site in Quebec, as well as Falconbridge at both Falconbridge and Onaping, Ontario, for additional discussion of site restoration in Appendix I.

Despite BLIGHT and CALDWELL's conclusion, and the same basic conclusion drawn in the course of this investigation, it is a worthwhile goal to set, i.e., development of a method of disposing of tailings and restoing the site to avoid the need for future perpetual maintenance and, especially, for effluent treatment.

This discussion brings to mind the Atlas Minerals tailings site alongside the Colorado River at Moab, Utah. When looked at philosophically, perhaps the cleanest and safest way to permanently dispose of those tailings would be to let them wash down the Colorado River the next time it comes down in flood. When in flood, the municipal water plants downstream shut down anyway, and the ultimate destiny of the tailings would be in a thin layer of sediment spread across the floor of the Boulder Dam. That would solve all safety, environmental, and aesthetic aspects of these otherwise unattractive tailings.

In Canada, the revegetation of highly acidic iron sulfide-rich tailings has been accomplished by trial and error, largely to reduce the dust and aesthetic problems. At INCO, Sudbury, very large areas of reclaimed tailings are planted with grass and harvestable crops annually and, in effect, the reclaimed tailings have been converted into farmland. This type of vegetation is, however, not self-sustaining. Neither of these have yet proven to inhibit AMD generation in the underlying tailings, however.

At Waite-amulet, Noranda has achieved a lush, dense vegetation cover which is self-sustaining year after year, directly over a high iron tailings site.

Falconbridge, at the Onaping and Falconbridge sites in Ontario, have used crushed wasterock as a capillary barrier over high sulfide tailings in some cases; in others, town garbage and sewage sludge is used over the capillary barrier; and in yet others, low sulfide tailings are applied as a cover over the high sulfide tailings before revegetation.

At not one site visited is there yet evidence of a sulfide-containing tailings pond which could be left unattended without the need for site maintenance and/or installation of a water treatment plant, although progress is being made in that direction.

JONGEJAN and RITCEY (1981) described a way to produce compost from municipal wastes of Canadian Mining towns which could be used for enhanced revegetation of mill tailings sites.

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Jan. 1984. pp. 1–9.

The abatement of pollution from abandoned gold-residue dams

by G. E. BLIGHT* and J. A. CALDWELL†

SYNOPSIS

The metropolitan area of the Witwatersrand has grown up around the Witwatersrand gold mines. Most of the mines have now been abandoned, but deposits of waste material remain and have been surrounded, and in some instances covered, by urban and industrial sprawl.

This paper describes the development of geotechnical measures for the abatement of air and water pollution from abandoned gold-residue dams in the Witwatersrand area. The measures include the stabilization of the surfaces of the dams to prevent wind and water erosion, the terracing of slopes to minimize erosion, and the construction of catchment walls and dams.

The measures were developed in terms of the set of guidelines for environmental protection adopted by the Chamber of Mines of South Africa in 1979.

SAMEVATTING

Die metropolitaanse gebied van die Witwatersrand het om die Witwatersrandse goudmyne gegroei. Die meeste van hierdie myne is tans verlate, maar die afsettings van afvalmateriaal is steeds daar en is deur wydlopige stedelike en industriële uitbreiding omring, en in sommige gevalle selfs daardeur bedek.

Hierdie referaat beskryf die ontwikkeling van geotegniese maatreëls vir die vermindering van lug- en waterbesoedeling afkomstig van verlate goudresiduddamme in die Witwatersrand-gebied. Die maatreëls sluit in die stabilisering van die oppervlakte van die damme om wind- en watererosie te voorkom, die aanlê van terrasse teen hellings om erosie tot die minimum te beperk en die bou van keermure en opvangdamme.

Die maatreëls is ontwikkel in terme van die riglyne vir omgewingsbeskerming wat die Kamer van Mynwese van Suid-Afrika in 1979 aanvaar het.

Introduction

Unlike the United States of America and Canada, the Republic of South Africa has no legislation specifically directed towards the protection of the environment from the effects of mining. However, there are a number of statutes that affect the design, operation, and abandonment of residue deposits. These are the Atmospheric Pollution Prevention Act, the Health Act, the Mines and Works Act, the Soil Conservation Act, and the Water Act. To comply with the requirements of these Acts and to achieve effective environmental control over the tailings deposits owned by its members, the Chamber of Mines of South Africa in 1978 commissioned the authors to draft a comprehensive set of guidelines for the design, operation, and closure of tailings deposits[1]. These guidelines were revised in 1983.

After a brief description of the guidelines pertaining to the closure and aftercare of tailings deposits, this paper describes measures put into effect to bring a number of abandoned gold-residue dams in the Witwatersrand area into compliance with the guidelines. The measures incorporate a number of interesting features. First attempts at compliance with the guidelines were based on tried and tested, but conventional, geotechnology. Because of the characteristics of gold slimes, the measures met with mixed success. Apart from describing the protection measures, the paper recounts the difficulties experienced and points to solutions to these difficulties.

It became abundantly obvious during these investigations that no known maintenance-free solution exists to the abatement of pollution from abandoned dams. Maintenance efforts can be minimized by careful design and construction, but the onslaught of the elements ensures that maintenance and aftercare can never be eliminated. The present paper represents an amplification and updating of an earlier paper on the subject[2].

Guidelines for the Closure of Tailings Deposits

The guidelines for the closure of tailings deposits require, prior to the closure of any tailings deposit, an inspection to be made by a professional engineer, who should report on the existing state of the deposit and list all the actions that are needed to ensure that the deposit complies with the provisions of the guidelines. In addition to the state of the tailings deposit itself, the report should note the presence of any adjacent structures or development, and the extent to which they may be affected by abandonment of the deposit. Recommendations to minimize the impact of abandonment or of possible failures of the deposit after abandonment should also be made.

Erosion of Top Surfaces

The Atmospheric Pollution Prevention Act requires that steps be taken to prevent the dust from any waste deposit becoming a nuisance as a result of its dispersion in the atmosphere. Regulations under the Mines and Works Act require that any waste deposit be dealt with in a satisfactory manner so as to prevent the dissemination of dust or sand from it. The Water Act requires all rain water precipitated on a waste deposit to be retained on that deposit, together with any of the waste material that becomes displaced by the action of the precipitation. To comply with these requirements, the guidelines require the best practicable means to be adopted to

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prevent erosion of top surfaces. Among the measures that have been suggested for the control of wind erosion are the following:

(a) the establishment of vegetation on the top of a deposit, either by planting directly into the tailings material or by first covering the surface with a layer of top soil of suitable thickness (the cost of importing topsoil usually rules out the latter alternative);

(b) covering the top of the deposit with a suitable thickness of broken waste rock.

Water erosion on top surfaces, as well as the requirement that all precipitation should be held on the dam, has been taken care of by a system of crest walls that sub-divide the surface of the dam into a series of paddocks. The crest walls also prevent precipitation on the top of the dam from cascading down the outer slopes and increasing the potential for slope erosion. The height of the crest and division walls is designed hydrologically so that the walls contain the maximum probable precipitation over a period of twenty-four hours with a frequency of once in a hundred years*. A freeboard of 0,5 m is required throughout the system above the predicted maximum water level. In the Witwatersrand area, as the annual evaporation from a free-water surface vastly exceeds the annual precipitation, there is usually no need to decant water from the top surface of a deposit.

The paddocks must be carefully shaped to prevent water from standing near the crest wall of a dam. Numerous cases of piping erosion[3] have occurred when water has been held on the surface near to the crest of a dam.

The penstocks used to decant water during the operation of a residue dam are plugged when the dam is closed because they otherwise tend to collapse and provide channels for piping erosion. Old dams often have a number of steel delivery or penstock pipes buried in them at various positions. The steel has usually corroded away and the resulting void been enlarged by erosion. Such a collapsed pipe can result in severe erosion, as illustrated in Fig. 1.

In practice, water and wind erosion are inextricably linked. Material loosened and collected in low spots by water erosion in the wet season may be picked up by the wind and dispersed as dust during the dry season.

Erosion of Slopes

The slopes of old residue dams are extremely steep (usually 35° or more), and the protection of these steep slopes against erosion is very difficult. Sheet erosion of the slopes can be reduced, and gulley erosion virtually eliminated, by the provision of crest walls, which prevent water from cascading off the top and down the slopes of a residue deposit. Slopes can be protected against erosion by being covered with a layer of waste rock. However, this requires a large quantity of rock because the angle of repose of the rock seldom, if ever, equals the slope angle. Vegetation has also been used to provide protection against erosion. This practice has not proved entirely successful: some of the steeper slopes are gradually denuded of grass as erosion progresses.

Fig. 1—Severe erosion caused by the collapse of steel penstock and delivery pipes buried in the residue. Voids left by a number of such pipes are visible

Containment of Precipitation and Eroded Material

Run-off and eroded material are contained by a series of catchment paddocks round the perimeter of a dam. These paddocks are designed hydrologically to ensure a freeboard of at least 0,5 m above the maximum predicted water level, which is based on the average monthly rainfall for the area concerned less the gross mean evaporation for the area plus the maximum precipitation to be expected over a period of twenty-four hours for a frequency of once in a hundred years. To this is added an additional capacity to allow for the siltation resulting from erosion off the slopes. Little information exists on rates of siltation, but it appears that, in extreme cases, a single storm can silt a paddock to the extent of encroaching on the freeboard, whereas more usually the siltation capacity is a number of years. Regardless of the actual siltation rates, provision must always be made for the desiltation of paddocks, or raising of their walls, once the required freeboard is no longer adequate.

Control of Access

It has been found essential to prevent access to abandoned tailings deposits by members of the public,

*On the Highveld, this is equivalent to 250 mm of precipitation.

especially those seeking recreation by horseriding or cross-country motor cycling. The trails left by these activities often reduce the freeboard of paddock walls and result in gulley erosion. It is therefore considered essential that each abandoned tailings deposit should be surrounded by a properly constructed, well-maintained security fence. Cutting of fences, and even the theft of whole sections of fencing, gates, etc., are common. Hence, frequent inspection and maintenance are essential if unauthorized access is to be prevented.

Stability of Slopes

The retention of water on the top surface of a tailings deposit, as well as measures such as erosion protection by the covering of slopes with rock, may lead to instability of the slopes.

The guidelines require an investigation of potential slope instability as part of the closure report.

Fig. 2 shows diagrammatically some of the features mentioned above, while Fig. 3 shows the crest and dividing walls on the top of an abandoned dam. (Note the urban development surrounding the dam and the severe surface erosion in the foreground.)

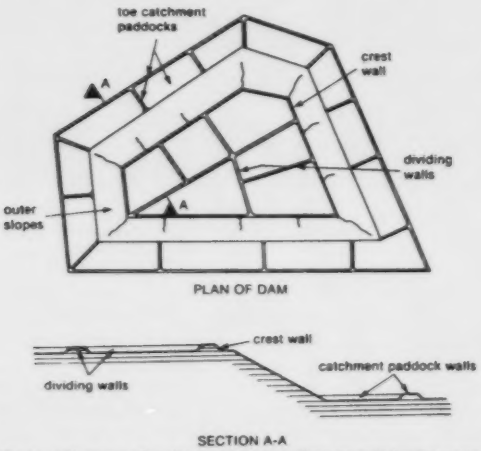

Fig. 2—Diagram showing measures taken to minimize water erosion of abandoned tailings dams

Geotechnical Developments in Pollution Abatement

A considerable number of abandoned gold-residue deposits exist within the Witwatersrand metropolitan area. The area has been almost completely built up, and the tailings deposits in question are surrounded by residential and industrial development. In most instances, the mining companies responsible for the tailings deposits are defunct, and the State has accepted responsibility for the rehabilitation of these dams to comply with the Chamber of Mines guidelines. To date, more than twelve dams have been rehabilitated. During the course of the work, a number of rehabilitation features were developed that differ from those envisaged when the guidelines were prepared. While the authors are convinced that the principles on which these measures were designed are correct, their implementation has not been completely successful, for a number of reasons. These measures and their shortcomings are described below, together with possible remedies.

Cement Stabilization of Top Surfaces

The Chamber of Mines considers the vegetating of the top surfaces of dams to be the best practicable means of stabilization, but this is subject to certain difficulties. The lack of success can be partly ascribed to the low pH of the surface material, and wind action may also undermine the root systems of the vegetation. Estimates by the Chamber of Mines at the time at which the guidelines were being prepared (1978) indicated that vegetating and the associated maintenance was costing upwards of R10 000 per hectare, while the cost of importing soil or waste rock was prohibitive, quite apart from the limited availability of these materials.

For these reasons, the chamber decided to stabilize the top surfaces of a number of dams on an experimental basis, using either slaked lime or Portland cement. Although the gold mine tailings that were being dealt with were highly acidic (pH of 3,5), Eades tests showed that relatively little stabilizer was required to raise the pH to a stable level of approximately 12,5. Fig. 4 shows typical results of Eades tests with ordinary Portland cement. It is also known that, although gold residue contains no clay minerals, it does contain a certain amount of amorphous silica, which can be expected at pH values above 12 to react with hydrated lime to form calcium silicates. The ability of slaked lime to stabilize residue sands had earlier been demonstrated when the surface of an access road to a sand dump near the Johannesburg market was stabilized. The surface remains in a remarkably good condition a decade and a half later, although the lime content of the material is very high. It was considered that stabilization should be even more effective with the gold slimes, which are finer.

In the case of cement stabilization, it was realized that sulphates contained in the residue might attack the products of cement hydration. However, at pH values above 12, the sulphates should be in the form of gypsum which, being sparingly soluble, is not as aggressive as other forms of sulphate. The use of sulphate-resisting cement could not be contemplated owing to its high cost. Because it is essential to keep the costs of rehabilitation as low as possible, and also because the object was the achievement of an erosion-resistant skin on the surfaces of the tailings deposits without the achievement of much strength, it was decided that experiments should be conducted with very small stabilizer contents.

Accordingly, a series of large test panels measuring 30 m in length by 5 m in width and stabilized to a depth of 150 mm were laid out using 2, 3, and 4 per cent by mass of both lime and cement. After the required quantity of stabilizer had been spread on the surface of the tailings deposit, it was mixed in by use of a rotary mixer. The moisture content was then adjusted to the optimum for compaction, and the panels were compacted by pneumatic rolling. The completed stabilized panels were

Fig. 3—Abandoned tailings dam provided with crest and dividing walls

moist-cured for six days by use of water sprays. The erosion resistance of the stabilized tailings surface was assessed with a portable Comet erosion tester, which directs a jet of water 0,8 mm in diameter at the surface from a distance of 25 mm. The pressure behind the jet is increased at a steady rate until the surface breaks up, the pressure at which the disruption occurs being recorded as a measure of the erosion resistance. The authors do not consider the Comet tester to be ideal for the measurement of the erosion resistance of residue surfaces. It gives a point measurement that, in their view, is not representative of the erosion resistance of a surface of large extent. Moreover, the relationship between the Comet index and actual rates of erosion has not yet been established.

Fig. 4 shows the measured erosion resistance plotted against percentage cement at times of 21 days, 42 days, and 2 years after stabilizing. It became apparent from these results that (at least in the early ages) cement was more effective than lime, and it was decided that the top surfaces of a number of tailings dams should be stabilized with cement (3 per cent) to a depth of 75 mm, and that the performance of these surfaces should be observed over a number of years. Twelve tailings deposits were stabilized in this way.

The test results in Fig. 4 show a considerable decrease in Comet readings after 2 years. The decrease can be attributed to at least two causes:

(i) the attack on the cement by sulphates proved to be more severe than expected; and

(ii) soluble salts, drawn to the surface by evaporation gradients and crystallizing out at the surface, disrupted material at the surface.

These effects may reinforce each other. Rising salts and acid may result in a lowering of pH and, hence, an acceleration of the attack by sulphates.

The Comet resistance of lime-stabilized panels showed a similar decrease after two years to that for cement-

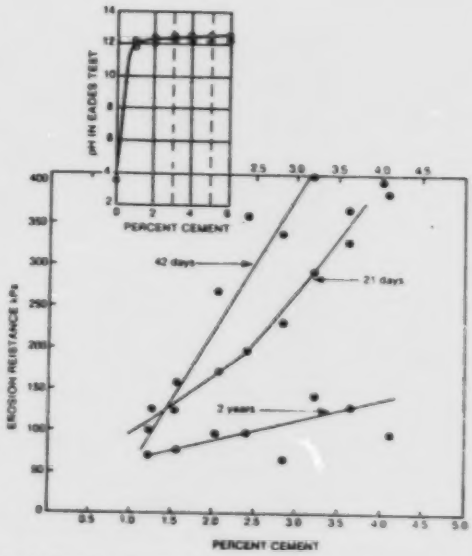

Fig. 4—Results of tests on the stabilization of gold residue with Portland cement

stabilized panels. As attack by sulphates can be ruled out in the former panels, disruption by salt crystallization and acid attack appear to be the major causes of the deterioration.

A visual assessment of the surface condition of twelve dams that had been stabilized with cement shows that similar deterioration has occurred there. 'Fluffy', raised surface crusts resulting from salt crystallization are much in evidence. The surface finish appears to be more important in maintaining erosion resistance than was previously appreciated. The smooth, almost-glazed surface

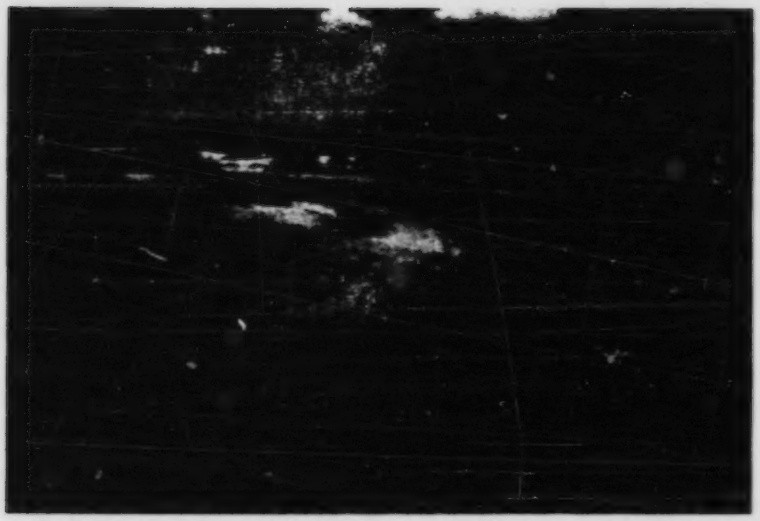

Fig. 5—Appearance of test panels of stabilized gold residue three years after laying

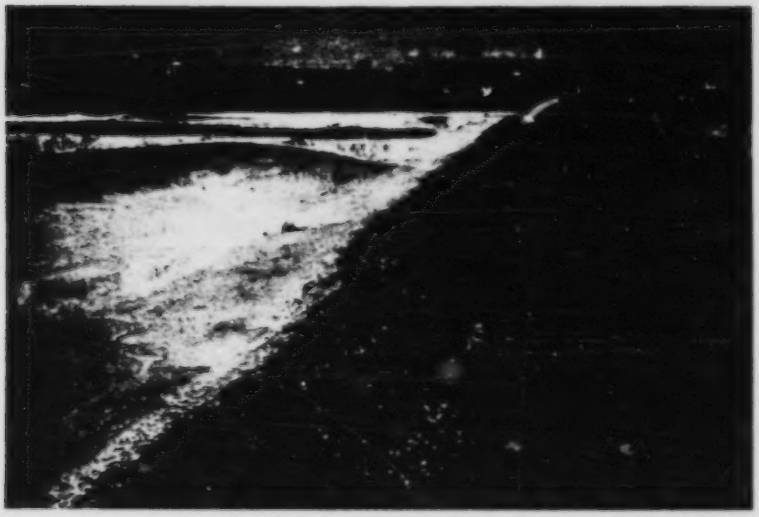

Fig. 6—Appearance of paddock walls protected against wind and water erosion by a single layer of 19 mm of crushed-stone chips. Photograph taken two years after laying

produced by a pneumatic compactor appears to deteriorate less than the rough, indented surface left by a tamping compactor. Fig. 5 shows the surfaces of the original test panels three years after being laid. The unstabilized strips between the panels show up as a result of their lighter colour. Even though the Comet resistance of the panels is low, they now stand proud of their surroundings, showing that they are more erosion-resistant than the unstabilized surfaces.

The effect of the surface deterioration is that loosened material is washed into the low spots of the paddocks during the wet season. Although this material crusts over as it dries, it is potentially available for dispersion by wind during the dry season if the crust is disturbed.

Successful alternatives to stabilization with cement or lime are not obvious. Potentially the most successful alternative is a process that was used for the stabilization of travelling sand dunes outside Walvis Bay. There, a

large dune that threatened to move into the town was successfully halted after its surface had been covered with power-station cinders. The layer was thin, only one particle thick, but successfully prevented the wind from picking up the underlying sand, thus halting the movement of the dune. This technique was tried on the slopes of the paddock walls of one of the twelve treated dams. There, a single-particle layer of 19 mm crushed-stone chips was spread on the slopes. Two years later, the treatment appears to have been very successful, with little evidence of the displacement of the stone or the underlying slimes by water or wind. Fig. 6 shows the appearance of this treatment two years after its application.

Grassing of Residue Deposits

Greig[4], from a study of the vegetation established on 27 slimes dams in the Central Witwatersrand area, concluded that, in general, the ratio of grass cover to slime exposure is 1 to 2 or greater, and that this cover ratio approaches that of the natural veld. He notes that there is no evidence that wind or water erosion from horizontal surfaces grassed up to fifteen years ago is a problem. The cost per hectare of grassing, leaching, and maintaining the top of a slimes dam where only the perimeter and contour wall are leached varied at that time from R3836 for a 40 ha site to R9321 for a 4 ha site. When the whole surface was leached, these costs increased to R10 024 and R14 859 respectively.

The average cost of cement stabilization at the twelve deposits so treated varied from R5000 to R8000 per hectare.Thus, the costs for the two types of treatment were similar at that time.

Terracing of Slopes

At a number of locations, the authors had observed that, where vertical faces had been cut in the slopes of tailings deposits, these faces appeared to be unaffected by erosion. The same phenomenon has been observed in natural vertical slopes. It was therefore decided that an experiment should be carried out in which the slope of a tailings deposit is terraced into a series of vertical faces separated by approximately horizontal steps or berms. To retain the precipitation, the berms are sloped back towards the dam, and are sub-divided at intervals by cross-walls so that all the precipitation on the berms is held and allowed to evaporate. Fig. 7 gives a design section of a terraced slope, and Fig. 8 shows an experimental terraced slope three years after the terraces were cut.

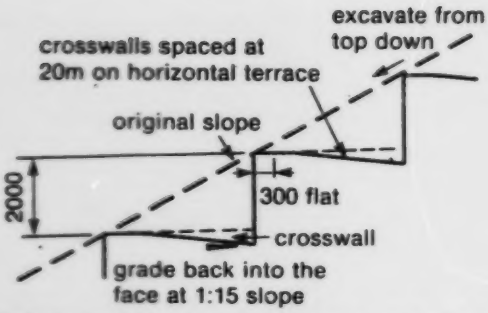

Fig. 7—Design section for terraced slope shown in Fig. 8

The state of these terraces is extremely good. In all cases very little erosion of the vertical faces has occurred, and in many cases a hard, dry crust has formed on the vertical face. Some eroded slime has accumulated in the paddocks formed by the back-sloping benches, and in a few instances exceptionally heavy rain has resulted in

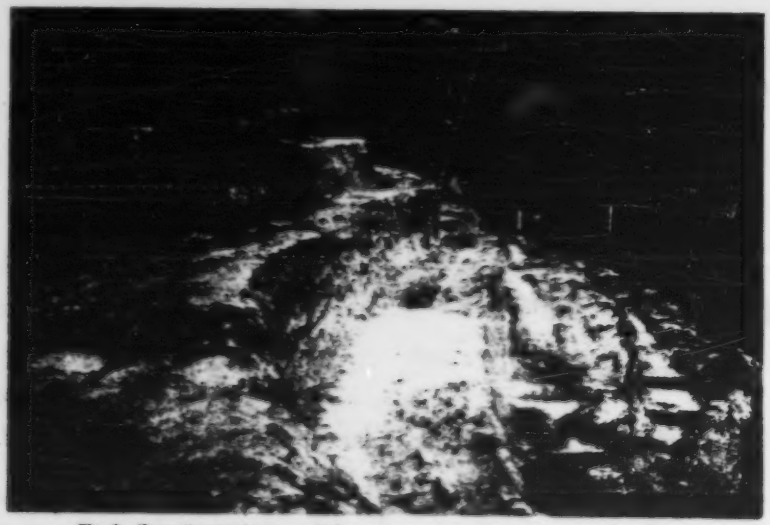

Fig. 8—Experimental terraced slope three years after the terraces were cut

Fig. 9—Vertical face of a terrace taken three years after the terrace was cut

overtopping of the benches. Fig. 9 is a close-up view of the vertical face of a terrace, showing the excellent condition of the surface.

On the basis of the observed behaviour of the terraces, it is concluded that terracing is a very effective way of reducing erosion from the slopes of residue dams.

Filter Dams

Run-off from tailings deposits that is polluted by material eroded from the deposit is retained at strategic positions by dams designed to retain the silt content of the run-off while allowing clear water to seep away. Although this water is clear, it contains dissolved solids, and only one component of pollution is removed. Fig. 10 shows typical details of such a filter dam. The upstream slope of the dam is underlain by a filter blanket that acts as a collection drain and filter for the polluted water retained behind the dam. After entering the filter blanket, the water gravitates to the central collecter drain and is allowed to escape downstream. Fig. 11 shows one of these dams, together with its emergency spillway, protected from erosion by means of a gabion mattress.

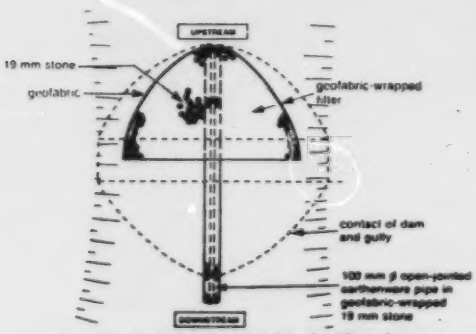

Fig. 10—Plan showing details of a filter dam

Fig. 11—Appearance of a filter dam with an emergency spillway

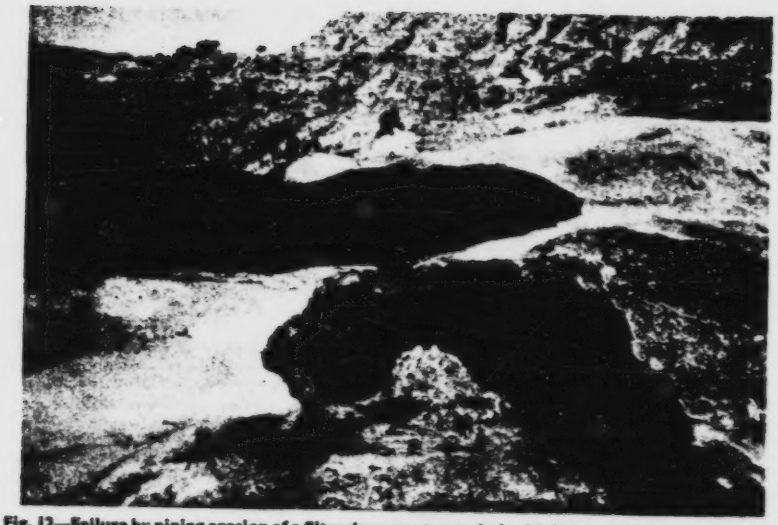

Fig. 12—Failure by piping erosion of a filter dam constructed of gold slimes and built on a slimes foundation

No problems have been experienced with these dams where it was possible for them to be constructed of natural soil. However, when constructed of gold slimes, especially when built on a foundation of slimes, numerous problems have been experienced with piping erosion. Erosion pipes have formed in the slimes under the dams, at the contact between the dam and the abutment, and at the interface between the embankment material and the geofabric-wrapped filter. Laboratory tests have shown that the erodibility of slimes is much reduced if the pH is raised to above 12 and the material cemented by the addition of lime. Future embankments should be constructed of lime-treated material. In addition, the embankment must be keyed into its abutments and foundation to lengthen the seepage path of potential pipes. Fig. 12 shows typical piping-erosion damage to a filter dam constructed of gold slimes and having slimes abutments.

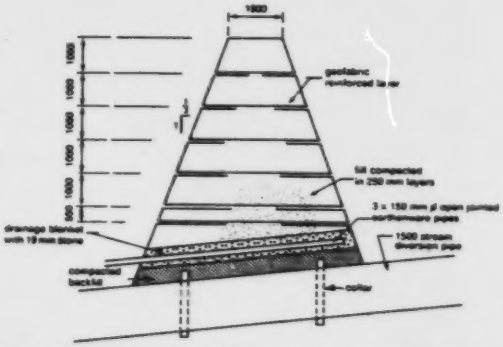

Fig. 13—Section through geofabric-reinforced gravity-section filter dam

Fabric-reinforced or Cement-stabilized Dams

In rehabilation work on tailings dams, it often occurs that a narrow valley with a limited capacity has to be crossed by a filter dam. If a conventional dam of compacted tailings is constructed, too much of the capacity of the valley is occupied by the filter-dam embankment. In situations like this, it is advantageous for the dams to have steeper slopes and, in fact, a gravity section is ideal in such instances. A gravity-section dam can be built either of cement-stabilized tailings or of fabric-reinforced tailings.

Fig. 13 shows the design of a fabric-reinforced gravity-section embankment. This embankment has been built and is illustrated by Fig. 14. The dam spans a valley between two tailings deposits down which a natural stream flows. The stream has been by-passed through a culvert that runs down the valley and under the gravity-section dam, while the gravity-section dam itself acts as a filter dam for precipitation running off the slopes of the tailings dams on either side of the valley.

When first filled, an erosion pipe large enough for a man to crawl through formed through the lower part of the dam abutment. The entry to the pipe is clearly visible in Fig. 14. The fabric-wrapped embankment bridged over the pipe with some deformation but was otherwise undamaged, as the photograph shows. The failure was repaired by the placing of a filter blanket over the hole on the upstream side and plugging of the hole with compacted tailings from the downstream side. The authors consider that any less flexible construction would have failed completely.

Aftercare of Tailings Dams

It must be recognized that the environmental protection measures specified by the guidelines of the Chamber of Mines require continual inspection and maintenance if they are to remain effective. There is no maintenance-free solution to the environmental protection of tailings dams.

(1) Any erosion damage to crest or dividing walls, filter dams, or catchment paddocks must be repaired.

(2) Catchment paddocks and filter dams must be desilted periodically, or must be raised in order to maintain their capacity.

(3) Continual inspection must take place lest problems of slope stability, the collapse of old drainage conduits, or penstock outfalls and similar degeneration should cause breaches in the anti-pollution defences of the protected dam.

(4) Access by animals and the public must be prevented. This last requirement contains something of a sociological problem. The existence of the large, abandoned, inaccessible areas represented by environmentally protected tailings dams within urban environments makes them attractive, not only as playgrounds for early-teenage children, but also as hiding places for the lawless element of the community.

(5) Dumping of litter adjacent to abandoned tailings dams is another social problem to which there appears to be no solution at present but periodic clean-ups.

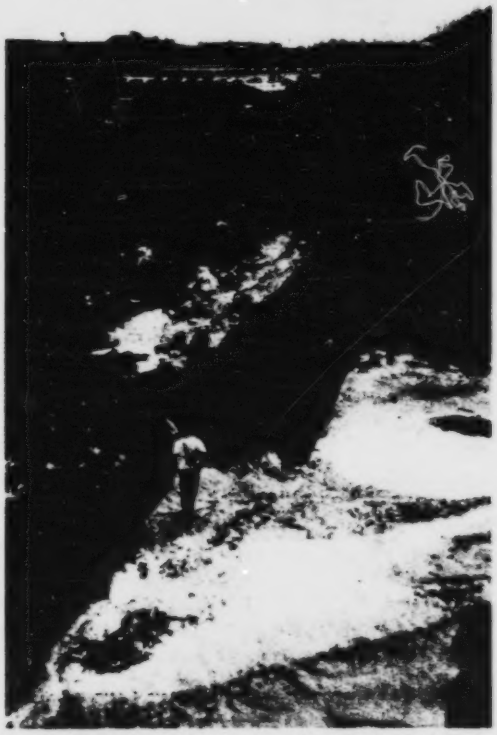

Fig. 14—Geofabric-reinforced dam after the formation of a pipe through the foundation. The entrance to the pipe can be seen to the right of the dam

Acknowledgements

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Even though there is no common method for establishing vegetation for tailings, a high degree of scientific and technical expertise is required to ensure a successful reclamation program Here are some ideas on how to implement successful programs

Tailings reclamation in eastern Canada

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Vegetation establishment on tailings in Canada has received widespread attention in the past decade. In Canada, few hard rock mine and mill waste products are considered to have any land use potential other than for wildlife purposes.

Isolation from densely populated regions and intensively farmed areas generally precludes development for recreational, agricultural, and commercial purposes. Specific characteristics of waste disposal areas, such as radionucleide contamination in uranium tailings, or physical site dangers represented by steep slopes of nearby "glory holes" are often sufficient reason to justify exclusion of the public from these areas.

Numerous studies have demonstrated considerable heterogeneity both within and between tailings disposal areas for all forms of metal mining. It is now recognized that a high degree of scientific and technical expertise is required to ensure a successful reclamation program.

Unfortunately, there is, from an industry viewpoint, no common method for establishing vegetation; every tailings disposal area requires individual assessment. Prime importance is now given to establishing vegetation directly into the tailings and not to covering with overburden—a technique of last resort.

For the majority of companies, reclamation by revegetation must veer toward a simplistic concept—the establishment of a permanent, self-sustaining and maintenance-free plant cover, which will achieve one or more of the following ends:

- Fugitive dust control
- Erosion control to prevent dam wall rupture
- Erosion control to prevent run-off of surface particles and subsequent sediment disposition in water courses
- A reduction in water volume seeping through acid and heavy metal contaminated wastes
- Aesthetic improvement of waste areas
- Acceleration of natural succession on waste areas.

Laboratory and field experience has established the following general principles for developing a tailings reclamation program:

- The need to form a reclamation team comprised of personnel with expertise in agronomy, engineering, hydrology, milling, and water quality
- To allow at least 2 years, preferably longer, for the development of an overall tailings abandonment program so that the necessary procedures can be developed and evaluated prior to implementation to ensure the most efficient cost selection
- To realize that a vegetation program is a biological system, subject to failures as well as successes, the causes of which cannot necessarily be predicted by "slide-rule" calculations
- The understanding that such a program requires the same intensive technical input as any other portion of a mining operation and, if not treated as such, will be subject to expensive failures.

Early Programs

One of the earliest tailings reclamation projects in Canada was that undertaken at Timmins, Ontario by McIntyre Mines Ltd. (now Schumacher Division-Pamour Porcupine Mines Ltd.) in 1932. Fertilizer and black muck were worked into non-sulphide gold tailings, and clover and timothy were planted to create a local park.

Several years later, tree planting and formal landscaping took place. In the same period the Hollinger Mine also embarked upon a tailings reclamation program using techniques similar to those of McIntyre. Today some tailings sections on this site have been built upon for commercial purposes.

Starting in 1968-69 all the operating mines in the Timmins region began tailings reclamation programs. Those involved at the time were Broulan-Reef Mines Ltd., Dome Mines Ltd., Hollinger Consolidated Gold Mines Ltd., Preston East Dome Mines Ltd., the Noranda group of companies, and Kidd Creek mines of United States-based Texasgulf Inc.

Many programs continue today, accepted as part of normal operations.[1]

The Birdsfoot Trefoil

Significantly, all these later programs contained a common ingredient for success, the legume birdsfoot trefoil (*Lotus corniculatus*). Since the early 1970's birdsfoot trefoil has formed the cornerstone of all successful reclamation programs for acidic, neutral, and slightly alkaline tailings.

This legume has widespread adaptation to tailings moisture conditions, is winter-hardy in most of the country and forms a self-sustaining and maintenance-free plant cover. If seeded in conjunction with correct fertilizer practice and specific grass species, no additional agricultural inputs are required from the day of seeding.

Where establishment has not been satisfactory, this can be attributed to incorrect fertilizer practice, its inclusion in unsuitable multiple species grass seeds mixtures, or poor bacterial inoculation technique.

General experience has shown that other legumes are not suitable for many tailings reclamation programs. Alfalfa, and white, red, and alsike clovers do not provide the self-sustaining and maintenance-free aspects that characterize the use of birdsfoot trefoil.

Crownvetch, while exhibiting many desirable characteristics, has not been used due to inconsistent establishment and high seed cost.

The first successful reclamation of sulphide tailings was achieved by the International Nickel Company (Inco) of Canada in the mid-1960's after almost 15 years of investigation, although the

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Table 1.
Partial listing of mines with sulphide tailings in eastern Canada having reclamation programs

Assigned Site Number	Company and location	Primary product	Tailings area Status	Number of samples investigated	pH Average (Range)	EC x 10⁶ Average (Range)	Agricultural limestone required tons per acre
1	Selco, South Bay Division, Ear Falls, Ont.	Copper Zinc	Closed	8	3.4(2.1-5.6)	n.a.[1]	45-70+
2	Rio-Algom, Elliot Lake, Ontario.						
	2A Nordic Mine[2]	Uranium	Closed	5	2.9(1.9-4.8)	1.8(.028-3.4)	0-15
	2B Lacnor Mine[2]	Uranium	Closed	5	4.7(2.3-7.5)	1.5(.007-2.4)	0-15
	2C Pronto Mine[2]	Copper	Closed	9	5.5(3.5-6.5)	2.7(2.3-3.7)	0-45+
3	Noranda Mines-Horne Division, Noranda, Que.						
	3A Waite Amulet	Copper	Closed	5	2.5(2.2-3.0)	3.2(1.8-3.7)	10-40
	3B No. 3	Copper	Closed	4	1.4(1.3-1.4)	5.9(5.3-7.0)	25-60
4	Noranda Mines-Geco Division, Nanitouwadge, Ontario[3]	Copper-Zinc	Active	15	2.1(2.0-2.1)	4.3(3.7-5.0)	25-40+
5	Noranda Mines, Brunswick Mining Division, Bathurst New Brunswick.						
	5A No. 6 Pilot Plant[4,6]	Lead-Zinc-Copper	Closed	1	2.6	6.5	Unknown
	5B No. 12 Mine[5,6]	Lead-Zinc-Copper	Active	9	3.6(2.0-6.5)	5.4(2.0-8.5)	Unknown
6	Not available[6]	Zinc-Copper	Closed	40	3.8(2.0-6.6)	4.8(1.6-8.0)	Unknown
7	Not available	Nickel-Copper	Closed	12	5.3(2.7-8.0)	2.1(1.5-4.0)	0-40+
8	Not available	Lead-Zinc-Copper	Active	20	1.8(1.6-2.1)	6.5(5.5-8.0)	60-80
9	Not available						
	9A	Copper	Closed	31	6.4(3.8-10.2)	n.a.[1]	25-125+
	9B	Lead-Zinc	Closed	3	3.1(2.6-3.5)	2.6(2.0-3.3)	20-80
10	Not available	Copper-Zinc	Active	18	3.6(2.3-6.8)		10-100+

1. n.a. data not available 2. Samples from treated areas where vegetation had not established 3. Samples from dam wall only 4. Composite sample 5. Tailings range in age from 3 months to 10 years 6. Unknown status ascribed since acceptable amendments not yet determined

company's general area reclamation program dates back to 1917. Numerous techniques were investigated before success was achieved; a technique permitting seeding of grasses direct into the tailings.

Methods and materials developed by Inco were almost immediately adopted by other mining companies, generally with poor results. As subsequent investigations have shown, each and every sulphide tailings area requires its own particular set of methods and materials.

In terms of iron sulphide content, the tailings deposited by Inco are now classified as low. The majority of the acid-producing iron sulphides (pyrite and pyrrhotite) in the original ore are moved during ore processing.

As the results of attempts to reclaim other tailings areas that had been formed by the milling of massive sulphide ore bodies were obtained, showing FeS content between 5 and 45 percent, it became obvious that new approaches and techniques would have to be developed for such areas if revegetation by direct seeding was to be successful.

pH and Tailings

As the environmental importance of acid tailings seepage was established in Ontario[1], and subsequently in eastern Canada, two companies developed major reclamation programs.

The Horne Division of Noranda Mines Ltd., in Noranda, Quebec, mining a massive sulphide deposit, expanded its work into a five-year research program at a Canadian university.

Rio Algom Ltd.'s Elliott Lake, Ontario uranium operation set up a program in cooperation with Canada Ener-

Table 2.
Sample pH within and between various tailings sites and agricultural limestone required to obtain plant growth

1		2A		2B		2C		4		6		7		10	
pH	Rate[1]	pH	Rate	pH	Rate	pH	Rate	pH	Rate	pH	Rate	pH	Rate	pH	Rate
5.6	70+[2]	2.5	15	7.5	0	3.5	15	2.1	25	6.0	40	7.0	0	3.2	10
3.8	60	1.9	15	2.3	15	5.9	45+	2.1	40	5.4	80	7.0	0	3.2	10
4.0	70+	2.3	15	5.4	0	6.2	0	2.1	25	6.1	40	3.4	30	3.0	10
2.3	45	2.4	15	2.6	0	6.5	0	2.0	25	2.4	80	3.3	20	5.8	25
2.4	70+	4.8	0	5.6	0	6.4	15	2.0	40	4.7	80+	8.0	0	5.4	25
4.3	70+					5.2	0	2.0	25	2.4	80+	7.8	0	6.8	100+
2.4	70+					6.1	0	2.0	40+	2.3	80+	7.6	0	6.8	50
2.1	70+					4.2	45+	2.0	40	2.2	80+	3.0	40+	2.3	20
						5.8	15	2.0	40+	5.8	80+	7.7	0	2.8	20
								2.1	40+	5.6	80+	2.7	10	3.4	10
								2.1	40	3.8	80+	2.7	10	3.5	20
								2.1	25	6.2	80+	3.0	20	4.5	10
								2.1	40	4.0	80+			3.1	100+
								2.1	40	5.1	80+			2.8	100+
								2.1	40	5.7	80+			2.7	20
														6.2	100

1. Tons per acre
2. A figure followed by + sign means a higher rate than this was not assayed

gy, Mines, and Resources.

Both of these programs attempted to correlate physical and chemical tailings characteristics with plant growth obtained in controlled environment studies. Neither was successful in this.

For example, under the auspices of the Noranda Mines (Horne Division)-University of Guelph research program, "Reclamation of Mine and Industrial Wastes," an attempt was made to correlate such factors as mineralogical analysis of iron sulphide content and form, other mineral constituents, X-ray analysis of heavy and light mineral fractions, X-ray analysis of water soluble constituents, chemical analysis of water soluble constituents, acidity of tailings and standard agricultural soil test analyses of a wide range of oxidized and non-oxidized tailings, with plant growth performance on such tailings.

No definite correlation was found between the above factors and plant growth potential. Only the total salt content of tailings provided any degree of correlation, but even in this case the variability was too great to be of any practical significance.

These studies, as well as others that were conducted by Mine Waste Reclamation, have confirmed the unreliability of present analytical procedures. Determination of the agricultural limestone requirement of acidic tailings by using plant growth as an indicator has revealed an enormous variation both within and between tailings disposal areas (see Table 1 and Figure 1). That variation cannot be correlated with the pH values obtained for the samples as depicted in Table 2.

The measurement of pH in tailings can only be approximate. Apart from the fact that there are no detailed research studies on what might be the most accurate method of measurement, even using any one constant method for determination will show that pH values vary considerably at any sample point in a single growing season.

At present, pH measurement should be considered only as a broad indication of the presence or absence of potential problems in the establishment of a vegetative cover.

Limestone Quality

Another problem shown in recent studies is concerned with the quality of agricultural limestone. In studies conducted under the previously mentioned Noranda-Guelph program and by Mine Waste Reclamation, a single source of agricultural limestone was and is being used to determine the amounts required to amend acid tailings so that vegetation can be established. In the field, agricultural limestone would be obtained from numerous sources, depending upon mine site location.

A standard evaluation was made of agricultural limestone in 1980-81. Understandably, the limestones vary widely in physical and chemical composition and in their efficacy as neutralizing agents (see Table 3).

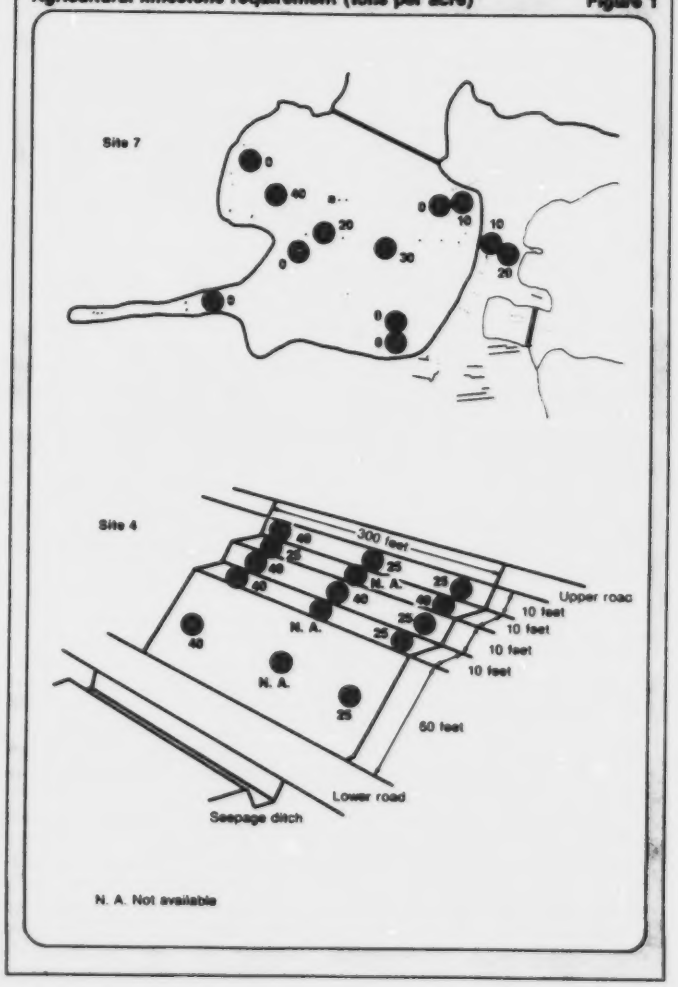
It is not possible to select agricultural

Table 3.
Variation in agricultural limestone

Character	1	2	4	5	6	8	9	10
Percent passing 5 mesh	100	100	37	62	100	—	100	
10 mesh	97	100	20	36	98	100	90	100
60 mesh	80	26	5	6	35	100	40	86
100 mesh	52	12	4	4	24	86	30	59
Percent total calcium	35	21	30	26	24	29	54	30
Percent total magnesium	3	0.2	0.3	0.2	4	0.3	45	0.2
Neutralizing value (pure $CaCo_3$ = 100)	84	100	84	93	92	91	100	94
Agricultural index[1]	73	56	9	17	55	91	60	86

[1]Agricultural index is a value calculated from percent passing 10 and 60 mesh and from neutralizing value. For agricultural purposes an index of 75 or above is generally recommended; it is not necessarily recommended for use on acid sulphide tailings where an index as low as 55 has proven suitable.

Agricultural limestone requirement (tons per acre) **Figure 1**



limestone solely on the basis of desirable characteristics and efficacy. Transportation costs preclude such choice. It is necessary, though, to give some consideration to the characteristics of the available material.

For example, material from sources 4 and 5 are too coarse as evaluated but would be suitable if they could be ground to finer particle size; whereas, source 8 is considered to be too fine, both in terms of applying it in the field and lack of sufficient coarseness to provide long-term buffering capacity.

The level of phosphorous fertilizer used in both laboratory studies and field programs has been found to be critical, particularly in obtaining adequate legume establishment. On one medium sulphide tailings area (Site 9A, with 45 percent FeS), where a wide range of agricultural limestone was required (see Figure 2), and where soil test analyses indicated virtually no phosphorous present, striking responses were obtained to phosphorous application (see Table 4).

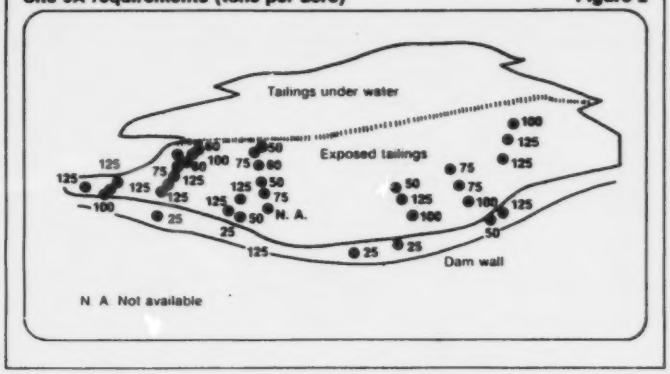
A base fertilizer of 1,500 pounds per acre 5N-20P-20K was applied with additional treatments of nil (low), 500 pounds per acre ON-46P-OK (medium) and 1,000 pounds per acre ON-46P-OK (high). A vegetative response was still recorded at the highest level of phosphate application.

Neutral non-sulphide gold tailings when seeded with birdsfoot trefoil alone also showed a high level of growth with increased phosphate. Because of the nitrogen fixation capacity associated with legumes, this increased growth is most probably due to the interaction between nitrogen and phosphorous and its effect on plant growth, a well-established phenomenon.

Tall fescue, which like most grasses does not have this nitrogen fixation capacity, does not respond to additional phosphorous when seeded alone. While emphasizing the effect of phosphorous on plant growth, the studies have also demonstrated that fertilizer requirements for plant growth are also species-dependent.

The widespread variation in agricultural limestone requirement exhibited both between and within tailings disposal sites and disturbed land areas is possibly a reflection of several factors, such as iron sulphide type and quantity, degree of oxidation of iron sulphides, distribution of tailings grain size in the tailings ponds, length of inundation of water on the tailings surface, and mineralogical composition of the ore body.

Site 9A requirements (tons per acre) **Figure 2**



At the present time it is not possible to determine the interrelationships between these factors by analytical means. It does mean, though, that a tailings disposal area is in most instances a very heterogenous area, with widely different plant growth potentials across its surface. Because of that variation, it is virtually impossible to conduct small plot trials in the field in order to determine plant growth potential.

To assess the surface variation and its varying requirement for agricultural limestone, fertilizer requirement, and suitable species would entail very extensive field plot work. In addition, such trials may take 18 months or more to complete, as at least two growing seasons would be required for a comprehensive evaluation.

If such trials were to take into account additional factors such as optimum seeding time, method of seeding (mechanical and hydroseeding), evaluation of different mulches, and their rates of application, then the field trials would become even more complex.

Without doubt, several field trials could be conducted in place of one large one. Such an approach, though, inevitably lengthens the evaluation period to at least 3 to 4 years, for until the basic requirements for vegetation establishment are known, factors such as time of seeding, mulch requirements, and other practical aspects cannot be adequately assessed.

Sampling

One approach to resolve the apparent complexity of field type evaluation that is finding increasing acceptance is to evaluate initial vegetation potential under controlled environment conditions. The basis of this technique is to take samples from a tailings area, then sample the selection being governed by visible variation on the tailings surface such as color (degree of oxidation), particle size, and different moisture levels.

Such sampling is subjective, but is the only known means at present. This particular approach has several important advantages over beginning the evaluation directly in the field.

Evaluation time is reduced to approximately 100 days, compared to 18 to 24 months. The evaluation concentrates on determining the optimum agricultural limestone and fertilizer specifications and results in the elimination of much subsequent field plot investigation.

Not all tailings or disturbed soils have an immediately recognizable vegetation potential. That may be due to the very high agricultural limestone levels required, which may be too costly, particularly if the agricultural limestone sources are distant or to an inherent low potential, which can only be increased by devising other methods of amendment.

Whatever the reason, a company rapidly becomes aware of the degree of ease or difficulty it will face in conducting the vegetation aspects of a rehabilitation program. If the evaluation indicates an acceptable level of vegetation potential, then the first field trials to be conducted can concentrate on the practical field aspects of vegetation establishment, unhampered by uncertainty as to whether or not the correct amendment levels have been chosen.

Such evaluation enables a company to rapidly assess the future financial aspects of the vegetation portion of the rehabilitation program, and at a cost considerably less than that required for conducting a two to three-year field testing program.

Reclamation programs utilizing the above approach are now being undertak-

en by a number of Canadian mining companies (see Table 1). Some programs are almost completed, others are still at the assessment stage prior to considering field trials, and others are presently in abeyance.

At Noranda-Horne, about 100 acres of level and sloped areas have been direct-seeded at the Waite Amulet property. Another 50 acres were covered with overburden, as physical site conditions would not permit access of reclamation equipment; overburden was spread during the wintertime on frozen tailings.

Although studies showed that the No. 3 tailings could be satisfactorily amended with agricultural limestone, which was confirmed by subsequent field trials, equipment access problems were encountered due to poor drainage in the center of the tailings area.

Presently, low-lying areas are being raised by filling with non-sulphide gold tailings from current milling operations at Noranda-Horne. The gold tailings will then be directly seeded. Revegetation has formed part of a continuing water quality control program being undertaken by the Horne Division. A history of the reclamation program has been extensively described.[4]

Portions of the experimental and field programs have also been recorded on a film, available to the public, entitled, "To Make the Wasteland Green". Rio-Algom has completed revegatation of major portions of three inactive properties. The sections not completed are again characterized by impeded drainage. Since a program was implemented in 1970, extensive invasion by native shrubs and trees has occurred in forage seeded areas.

The phenomenon of native tree and shrub colonization of revegetated tailings has been recorded at numerous mines in eastern Canada. The exact role of birdsfoot trefoil in influencing colonization is not known, for unfortunately, there has been little documentation of such colonization. It is now being investigated by Rio-Algom.

Table 4.
Effect of phosphate fertilizer on plant growth[1]

	Limestone	0-46-0 pounds per acre		
Neutral gold tailings[2]	tons per acre	0	500	1000
Birdsfoot trefoil	0	1.10	1.40	1.40
Tall fescue	0	0.35	0.37	0.39
Acid sulphide tailings[3,4] (Site 8A)				
Birdsfoot trefoil	50	0.01	0.22	0.24
	60	0.16	0.25	0.39
	75	0.23	0.36	0.50
	100	0.36	0.53	0.88
	125	0.41	0.65	0.93

1. Mean shoot growth per treatment
2. 10 sample average
3. 31 sample average
4. All 41 samples received base treatment of 1500 pounds per acre 5-20-20

The Long Term Approach

By initiating studies 2 years prior to mine closure, personnel at Selco Mining Corporation Ltd.'s South Bay mine were able to accurately assess reclamation procedures and costs and their relative importance in the overall mine closure program. Controlled environment studies provided a rapid indication that the use of agricultural limestone as a tailings amendment was not a practical method.

Extreme variation in amendment requirements was found between samples taken only a few feet apart. Consequently, a source of local overburden was evaluated and proven to be suitable for plant growth. The overburden was spread over frozen tailings in the winter of 1981-82, and seeded in May 1982. By some standards the work undertaken at South Bay could appear mundane. However, the approach taken enabled the company to make accurate planning schedules and costings with the confidence that tailings abandonment had been achieved in the most efficient manner possible.

Long term tailings reclamation planning is being emphasized at Noranda-Geco, Noranda-Brunswick Mining, and Site 6 and 8. At each, massive sulphide tailings with iron sulphide content, generally not less than 40 percent, occur. In the case of Noranda-Brunswick Mining, the iron sulphide content of the tailings is consistently in the 80 to 90 percent range.

Preliminary studies at Noranda-Geco have indicated that reclamation of the tailings dam embankment by direct seeding is a definite possibility. Controlled environment studies have shown that the agricultural limestone requirements are not excessively large, but that there is considerable variation in the limestone requirement along the face of the embankment, and that several problem areas could be present (see Figure 1). The extent of the variation still has to be fully determined before a practical field reclamation plan can be devised.

A serious atttempt is being made at Noranda-Brunswick Mining to devise methods for direct seeding of the very rich sulphide tailings. Sufficient overburden is simply not available to cover the estimated 3,000 acres of tailings that will be created by presently planned mining operations.

In addition to the tailings investigations, reclamation of all disturbed areas at the No. 6 pilot plant of the mine are being evaluated. Such areas include pyritic waste rock, water treatment sludge ponds, and sections from which all surface soils had been stripped.

At present studies have shown that such areas may be revegetated directly but field confirmation is required. Sites 6 and 8 present interesting contrasts, for they emphasize how misleading tailings characterization techniques can be.

Site 6 is particularly difficult, as it has not been possible to date to determine what would be suitable direct-seeding methods, even though initial tailings analyses using standard soil testing techniques do not indicate as severe a situation as has been encountered elsewhere.

By contrast, reclamation at Site 8, despite exceedingly acid conditions, would appear feasible from controlled environment studies. Again though, field confirmation trials are necessary.

Over the last 10 years reclamation of sulphide tailings in eastern Canada has made considerable progress. It is true to say that an understanding of the factors affecting plant growth on these types of tailings is very far from being understood in chemical and biological terms. From a management viewpoint, though, it has developed to the stage where costly and unsuccessful reclamation programs can be avoided.

Where large scale reclamation programs are or have been undertaken, they have been initiated with confidence that success will result considering that biological, not engineered, systems are being created. ■

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THE ESTABLISHMENT OF VEGETATION ON HIGH IRON-SULPHUR MINE TAILINGS BY USE OF AN OVERBURDEN

R. E. Michelutti 1/

ABSTRACT

Since 1971 numerous tests have been conducted at Falconbridge Nickel Mines Limited to establish vegetation on tailings containing high percentages of pyrrhotite.

The object was to produce a self-sustaining vegetative cover which would reduce or eliminate seepage long after the operations cease. This solution was not a simple task, however, due to the low pH (3.0), the heavy metal toxicity and the hard pan produced by the pyrrhotite.

Vegetation research, mainly on Nickel Rim Mine tailings, led to the use of overburdens as the most promising method of achieving the primary objective of a maintenance-free vegetative cover. The ideal overburden was found to be three inches of coarse material (1/4 inch) overlain with three inches of loam. The coarse material prevents the upward leaching of solubilized metallic salts, while the loam provides a suitable growth media for the plants.

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Introduction

The sulphide ores of the Sudbury Basin contain economic quantities of nickel, copper and iron, which occur mainly in the minerals pentlandite, chalcopyrite and pyrrhotite respectively. These valuable minerals are associated with a variety of igneous silicate host rocks.

In order to separate the metallic minerals from the waste host rock, the ore must be crushed and ground to at least minus 65 mesh. Separation t is effected by the process of flotation and wet magnetic separation. O ton of average grade Sudbury ore, once processed, results in the followi products:

1. 250 lbs. of copper-nickel concentrate
2. 500 lbs. of pyrrhotite (iron-sulphide concentrate)
3. 900 lbs. of coarse tailings (+25 microns)
4. 350 lbs. of tailings slimes (-25 microns)

The tailings are classified by hydrocyclones to produce a coarse fractic (70%) called sands and a fine fraction (30%) called slimes. The coarse fraction is returned to the mine as backfill and the slimes are discarde with the pyrrhotite. Falconbridge Nickel Mines Limited mines four milli tons of ore annually which results in 1,800,000 tons of tailings slimes pyrrhotite, occupying a volume of 30 million cubic feet. This waste material is pumped as a slurry containing 15% solids, to landlocked basi or low lying areas called tailings ponds.

Here the solids are retained behind dams and the water is decanted off a treated prior to re-use or discard. Once these tailings ponds are full, however, they must be reclaimed, to eliminate or reduce pollution arisir from them, as well as to improve the aesthetics of the area.

RECLAMATION PROBLEMS

The most acceptable method to date in reclaiming these tailings areas is by means of a vegetative cover. This, however, is no simple task for the following reasons:

1. The tailings acidify with time to pH 2.5 - 3.0
2. Heavy metal concentrations are high, especially upon acidification
3. The top 2 inches to 2 feet becomes rock hard due to a complex iron-sulphur matrix called a ferruginous cap
4. The tailings are devoid of nutrients and appropriate bacteria

EXPERIMENTAL WORK

(a) Fertilizers

Experiments were conducted in the laboratory and field with the objecti of establishing a maintenance free vegetative cover that would revert back to nature. Of the fertilizers tested, 6-9-6 with 50% urea formal

allows the nitrogen to be released slowly and should therefore reduce or eliminate maintenance.

(b) Neutralizing Agents

From the laboratory tests, the minimum amount of limestone required to sustain plant growth over the 3-month test period was 10 tons per acre. The limestone used was "Beachville feed-grade" which has a 70% coarse fraction (sand particle size) and 30% fine fraction (dust size). This was chosen over other neutralizing materials for its ease of handling as well as for the coarse fraction which would act like a buffer and maintain a constant pH. In the field tests, however, the test plots acidified in 2-3 months' time to pH values ranging from 3.5 to 4.5. This was believed to be caused by the upward movement of sulphuric acid by capillary action during hot dry periods. The acid would also dissolve metallic salts and concentrate them upon evaporation on the surface. This was evidenced by white and yellow crystals (mainly Ca and Mg sulphates) on the surface of our tailings. It soon became apparent that continued maintenance would be necessary to maintain a vegetative cover on our tailings area.

(c) Overburdens

Due to the initial difficulties encountered with direct seeding in the tailings, tests with overburdens were begun in the laboratory and field. The overburdens used, ranging from gravel to black loam, had a pronounced effect in increasing yields, as well as allowing legumes to become established for the first time. Of the soils tested, black loam resulted in the greatest yields in the 3-4 month test period. However, there was some concern as to the long term effects. Due to the fine particle nature of the black loam it was felt that the upward movement of solubilized metallic salts would not be halted by the black loam and that after several years the concentrations would become toxic.

Dr. G. Courtin of Laurentian University was consulted and a decision was made to conduct research toward a master's thesis on this problem with Falconbridge Nickel Mines Limited personnel assisting with materials, assays and labour. Tony Spires, who was performing this work, came up with some basic conclusions. First of all, the black loam did result in the best initial growth of plants, but also had the highest heavy metal accumulation at the end of the experiment. The coarse sand and gravel overburden on the other hand acquired very little if any metallic salts, but growth was mediocre due to lack of moisture. The ideal overburden in these tests was a 3-inch layer of 1/4 inch crushed slag overlain with 3 inches of black loam. The slag broke up the capillary action and the black loam provided a growth medium with a good cation exchange capacity (128.5 me/100g) and moisture retention capability (137g/100g).

As with some of our earlier experiments, Mr. Spires demonstrated that a solid barrier between the tailings and 6-inch overburden resulted in zero to poor growth due to a lack of moisture.

REVEGETATION PROJECTS

(a) Nickel Rim Mine

Nickel Rim Mine is an abandoned mine which was purchased by Falconbridge Nickel Mines Limited in 1964. With the purchase of this property, Falconbridge then became responsible for the pollution originating from the tailings area, covering approximately 30 acres. These tailings are composed predominantly of siliceous gangue (66%) and pyrrhotite (34%) and had been exposed since 1958.

After several tests with various overburdens, the results were sufficiently successful that we proceeded to reclaim 20 acres by use of an overburden. The overburden material used was a sandy loam located within one mile of the site. The cost of this project is outlined below.

Materials	Cost/Acre
Limestone	$180.00
Fertilizer	160.00
Seeds	90.00
6-inch Overburden (includes Labour)	660.00
Labour (liming, fertilizing and seeding)	100.00
Total	$1,190.00

A test plot with similar overburden material has been monitored since 1973 for pH to determine if re-acidification is taking place. The initial pH in September 1973 was 7.4 and as of March 1975 was 6.6. No maintenance on the 20-acre area has been conducted since it was established in 1975.

(b) Hardy Pyrrhotite Stockpile

In the Onaping area, 30 miles northwest of Sudbury, pyrrhotite had been stockpiled for future reclamation and recovery of values. This resulted in severe reclamation problems since the pyrrhotite containing 56% iron and 36.5% sulphur had not been diluted with tailings (siliceous gangue) as in other areas.

Adjacent to the pyrrhotite stockpile, a sandy gravel overburden was being removed from an open pit operation. This material appeared suitable as overburden and a 6 foot deep cover was placed over the pyrrhotite stockpile at no cost to the reclamation project, due to the close proximity of the pit operation.

This 17-acre area was seeded with the use of conventional farm equipment at a cost of $326.00 per acre in August 1973. There was some concern, however, that the sand-gravel overburden was so coarse that the nutrients would wash out faster than in a loamy sand overburden. To maintain a healthy vegetative stand an additional 300 pounds per acre of 12-18-12 40% sulphur coated urea fertilizer was applied during August of 1976 at a cost of $150.00 per acre.

The vegetation is doing very well and numerous unidentified weeds as well as several tree species, including trembling aspen and birch, have already encroached.

(c) East Mine Tailings

The East Mine tailings should have been relatively easy to vegetate since pyrrhotite was not discharged in to this area. These tailings were seeded in 1969 without the use of any overburden and the resulting grass cover was poor. Large bare areas were scattered throughout, without any vegetation whatsoever. It soon became apparent that the tailings were not homogeneous and that these bare areas had a very high iron content and a pH of 2.5. Unknown to the reclamation group at that time was that high iron waste products had been dumped into this area. These bare patches were covered with gravel at a cost of $404.00 per acre and re-seeded.

The vegetation cover initially was not very healthy and required annual maintenance for the first five years. This was possibly due to the proximity of the nearby smelter.

More recently, however, birdsfoot trefoil and alfalfa have begun to spread. Fertilizer requirements should be reduced since these legumes can produce their own nitrogen.

OBSERVATIONS

1. Tailings should be pumped over pyrrhotite stockpiles during the final stages of a tailings pond to eliminate the need for an overburden.

2. The use of domestic garbage, mine wastes, etc. as overburden materials should be investigated. This would result in one revegetation scheme for both the tailings and garbage.

3. Planning in conjunction with operating departments will save considerable dollars, e.g.- removal of overburden materials from open pits or dam construction, etc.

4. Finally, it should be kept in mind that continued monitoring of the vegetation is essential in order to determine the effectiveness of the overburden material in achieving a maintenance free vegetation cover.

CONCLUSIONS

Based on past and continuing research on tailing pond reclamation at Falconbridge Nickel Mines Limited since 1971, the following conclusions are reached:

1. Tailings areas containing high quantities of iron-sulphur and/or heavy metals can be vegetated successfully by use of an overburden material.

Conclusions (cont'd)

2. The ideal overburden should be coarse enough to reduce or eliminate upward leachate migration from the tailings while at the same time providing sufficient moisture retention and a cation exchange base for the vegetation.

3. Initial establishment costs by using overburdens are quite high but maintenance work is substantially reduced.

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Lysimeter investigations on uranium tailings at CANMET

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ABSTRACT

The processing of uranium ores produces tailings that could constitute environmental problems. At most operations the tailings are dumped into a designated area, with the ultimate acid drainage occurring if sulphides are present, together with the release of metal constituents to the rivers and streams. If the chemical reactions occurring within the tailings could be predicted, perhaps methods could be developed to either increase or decrease the rates of reaction. One such study has been in progress at CANMET during the past three years. The paper describes the use of lysimeters containing low-grade and complex uranium tailings to determine the effects and interactions of bacteria, sulphides and solvent extraction organics on the release of radionuclides and on acid production. A simulated rain cycle nine-fold the normal was used and the lysimeters were subjected to timed intervals of light and darkness. As a result, the tests simulated a 25-year period.

Introduction

Although Canadians derive major benefits from uranium, there are environmental and health consequences, not yet fully understood, from the associated mining and milling operations. A major project at CANMET (Canada Centre for Mineral and Energy Technology) has the ultimate goal of ensuring that any adverse effects on man and environment, now or in the future, resulting from the processing of uranium should be acceptably low. The magnitude of the task was exacerbated by the fact that the increased demand for electrical energy and the resultant increased prices for uranium oxide during the 1970s led to a rapid expansion in the industry. Annual world demand for uranium was expected to increase 12-15 fold in the next quarter century, with annual requirements of between 200,000 and 300,000 metric tonnes anticipated by the year 2000[1]. Currently, the demand is low and the prices for the oxide have decreased.

The major problems stem from the discarded materials, "tailings", which contain radioactive substances and other contaminants. Most of the existing uranium mills operate with an efficiency of greater than 90% uranium extraction. Any uranium not solubilized in the leaching process will be discharged to the tailings and will thus constitute a source for daughter products. Uranium tailings, resulting from sulphuric acid or sodium carbonate leaching processes, contain (after uranium recovery) much of the initial radioactivity of the original ore before processing. A uranium ore containing 0.1% uranium will contain 330 pCi Ra^{226}/g ore. Therefore processing of 1 million tonnes of such material will result in 0.33 kg Ra^{226}. Other long-lived radionuclides in equilibrium with the ore would be Th^{230} at 15.4 kg and Pb^{210} at 3.5×10^{-5} kg per million tonnes. Much of the tailings in Canada (Elliot Lake) are made up of quartz, pyrite and calcium sulphate (resulting from lime neutralization at discharge), metal hydroxides, and precipitated thorium and rare earths. Solu-

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M. Silver

Marvin Silver graduated from the University of Manitoba with a B.Sc. (1963) and an M.Sc. (1966) in microbiology. After obtaining his Ph.D. (1968) in microbiology from Syracuse University and a post-doctoral year at Indiana University, he was on faculty at Laval University for nine years. Most of his research work has been on the biology of the iron-oxidizing thiobacilli, and on the use of these bacteria for the recovery of copper and uranium. Since joining CANMET in 1978, he has been involved with research on the environmental aspects of base metal and uranium mining.

Keywords: Mineral processing, Lysimeters, Tailings, Uranium tailings, Environmental control, Elliot Lake, Rabbit Lake, Midwest Lake, Key Lake, Radionuclides.

tions accompanying these solids contain calcium sulphate, radium, ammonia and nitrate. Fresh tailings areas have a pH of 6.5-9.0, whereas seepage and runoff from abandoned tailings have a pH of 2-3.

Impoundment areas for tailings range in Canada from 35 to 400 acres. It is estimated that uranium tailings from previous operations in Canada amount to 100 x 10^6 tonnes covering more than 1000 acres[2]. In the U.S.A., in the Colorado River basin alone, more than 12 x 10^6 tonnes of tailings containing about 8000 curies of radium exist at abandoned mill sites[3]. Thus, with increased mining and processing of the existing uranium reserves, the environmental consequences of the disposal of such tailings wastes will increase considerably.

When uranium milling started in Ontario in the mid 1950s, tailings "disposal" areas were designed according to the best available technology and the methods used were acceptable to the federal and provincial regulatory agencies. Tailings, after neutralization to pH 8 with lime, were deposited in small lakes and swampy areas and gravel or mine-waste rock dams were used to contain the tailings within these areas. No particular problems were expected from the uranium-mill tailings areas. The tailings basin provided a settling area for the solids and the clear effuent flowed through the overflow decant for discharge into the receiving watercourse. Such ponds of radium-bearing mill tailings, typically containing 400 or more picocuries of radium per gram of solids, become repositories for large quantities of radium during the active mill operation. Abandoned tailings dams, unless maintained, may break and release tailings containing radionuclides to the streams where radium dissolves and contaminates the watercourse. Also, as the inactive tailings pond dries, radium-bearing dust is scattered locally by the winds[4,5].

After a few years of operation, it was found that the effluents and seepage from the tailings areas were becoming more acid and that the radium levels were increasing[6]. The acidity was caused by chemical and bacteriological oxidation of pyrite, which constitutes 5 to 8% of the tailings. Chemical oxidation would lower the pH to about 4, and bacterial action would then lower it to 2 or less.

In Canada, barium chloride was introduced in 1964 to precipitate radium as an insoluble barium-radium sulphate and has been effective in removing over 99% of the dissolved radium in the effluents from the active tailings areas. The addition of 0.07 to 0.11 lb of barium chloride per 1000 gal of discharge or seepage effluent from inactive and active tailings areas produces a barium-radium sulphate coprecipitate which settles out in a subsequent settling pond to give much reduced concentrations of dissolved radium. Typical values of 12 and 1000 pCi/L in the seepage and effluent are reduced to between 3 and 10 pCi/L in the settling-pond discharge. These can be compared with a federal limit of 10[7] and current Ontario and Saskatchewan objectives of 3 pCi/L of dissolved radium[8].

The present $BaCl_2$ treatment, although effective in significantly lowering radium seepage, produces a barium-radium sulphate precipitate which could eventually break down by bacterial action and thus release radium and barium compounds into the environment[9]. Thus, unless technology is developed for eliminating radium from the tailings, control must be maintained long after the mill ceases operation.

Recognizing this need for new technology, and aware that there is a lack of definitive data for correlation and prediction of the chemical occurrences in tailings as the tailings become weathered, CANMET began several years ago to determine the many factors affecting the environment due to uranium tailings. In addition to work on the tailings, research included the development of new alternative processing technology which is chloride-based to solubilize the radionuclides for subsequent isolation in the mill. The work includes the hydrogeologic examination of present tailings and old tailings impoundment areas by drilling, the characterization of seepage plumes, the production of compost from municipal wastes for tailings cover and the development of vegetation technology for those areas[3,6,10]. Laboratory studies of tailings, using various types of lysimeters, are being compared with on-site hydrogeochemical measurements to determine if a relation exists between the laboratory and the field results and if chemical and physical predictions of occurrences in the abandoned and current tailings based on laboratory studies are valid.

The word lysimeter is used frequently throughout the text, and the following is a composite definition[11, 12]: "a structure containing a mass of soil, and so designed as to permit the measurements of water draining through the soil. It consists of a basin, having closed sides and a bottom fitted with a drain. Quantities of material and/or artificial precipitation are measured, the deep percolate is measured and analyzed, water of evaporation is measured, water taken up to plants is weighed, etc."

This paper describes the results that have been obtained in continuing laboratory tailings studies[13] in various sizes of lysimeters and the comparisons with actual tailings areas. Simulated weathering-time cycles are described and correlations are made with measurements on actual tailings. The interaction of bacteria and organics on the oxidation of sulphides to sulphuric acid are studied, as well as the release of constituents such as Ra^{226}, $SO_4^{=}$, total iron, uranium and the effect on pH of the effluent. Because a study of tailings weathering is a long-term process, 9 times the normal rain cycle was arbitrarily used to determine solubility effects in a simulated 25-year period, in order to compare with old abandoned tailings that were laid down for about 25 years. Thus, it might be possible to predict i) the production of acid and the solubilization of metallic elements by the action of iron-oxidizing bacteria; ii) the effects of organic solvent extraction reagents (used in the uranium purification process) on these bacteria; and iii) the leaching of radium-226 and other chemical constituents caused by water percolation through a tailings area. The release of arsenic and nickel are also followed in studies on complex uranium tailings.

Previous work at CANMET had shown that there was a certain degree of toxicity to bacteria due to organic solvent extraction reagents[14]. These reagents were incorporated into the

TABLE 1. Chemical analysis of uranium ore tailings

Component	Elliot Lake	Rabbit Lake (H_2SO_4 leach, no oxidant)	Rabbit Lake (H_2SO_4 leach + oxidant)	Midwest Lake (small column)	Midwest Lake (shake flask)	Key Lake (H_2SO_4 leach)
Radium-226 (pCi/g)	170	1215	915	1650	6090	1090
Uranium (%)	0.007	0.128	0.013	0.395	0.05	0.004
Thorium (%)	0.025	0.002	0.001	0.007	-	0.0008
Iron (total) (%)	2.82	2.88	2.36	2.48	1.83	1.11
Sulphate (% S)	0.72	1.04	2.33	0.19	0.09	1.26
Total sulphur (%)	3.64	1.40	2.38	0.80	0.81	1.28
Nickel (%)	-	0.02	0.01	0.77	0.51	0.60
Arsenic (%)	-	0.04	0.20	1.21	1.08	0.34
Calcium (%)	0.45	1.33	2.33	0.11	-	2.23
Total carbon (%)	-	0.86	0.48	-	-	0.17
Carbonate (%)	-	0.04	-	-	-	0.02

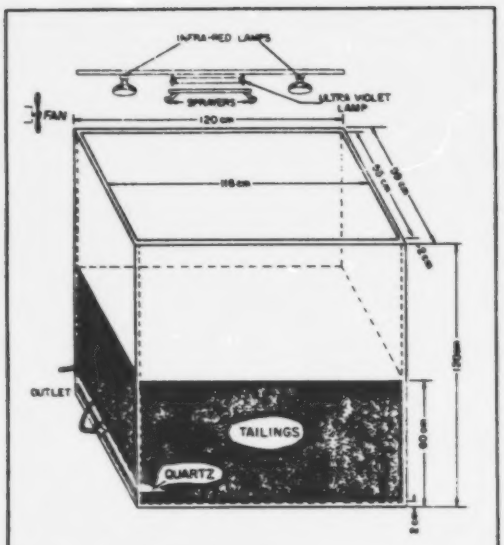

FIGURE 1. Lysimeter box details.

tests to determine whether there was sufficient quantity present to decrease the oxidizing effect of bacteria on sulphides.

Procedure and Experimental

Table 1 shows the chemical analyses of the tailings used in the various lysimeter tests. These samples were obtained from a conventional low-grade operation at Elliot Lake in Ontario and the Rabbit Lake operation in Saskatchewan. In addition, small-scale tests were performed on tailings resulting from the leaching of the complex high-grade uranium areas of Key Lake and Midwest Lake in Saskatchewan, which also contain appreciable arsenic and nickel. Because of initial blending with lower-grade material of those two ores before leaching, the Ra^{226} content is not perhaps as high as might be anticipated. The latter two properties are not yet in operation.

Early in 1978, three reinforced plexiglass lysimeter boxes (Fig. 1) with approximate dimensions of 120 cm by 55 cm by 120 cm (length, width and height) were constructed and loaded to a depth of approximately 60 cm with fresh solid uranium mine-mill waste. The tailings were obtained by decantation of the tailing neutralization discharge from the uranium milling circuit of the Rio Algom Quirke Mine at Elliot Lake, Ontario, immediately after addition of lime. A portion of the finer tailings was lost during this procedure and is the reason for the relatively low radium-226 content. This material contains, on a dry weight basis, 2.5-3.5% pyrite, 0.72% sulphate (as sulphur), 2.82% total iron, 0.007% uranium, 0.025% thorium and 170 pCi/g radium-226. The contents of each lysimeter box are described in Table 2.

The lysimeter boxes were designated 'A', 'B' and 'C' and each was loaded with approximately 1 tonne of tailings. To lysimeter box 'A', 175 L of water containing 90 mL/L of kerosene (Shell 140), 5 gm/L of Alamine 336 and 5 mL/L of isodecanol was added. After equilibration for 2 days, box 'A' was flushed with 175 L of water and inoculated with a washed 72-hour culture of iron-oxidizing thiobacilli isolated at Elliot Lake. Boxes 'B' and 'C' were flushed with 175 L of water, and box 'B' was inoculated similarly. The water level in the lysimeter boxes was maintained within 10 cm of the surface by a syphon tube from the effluent port, allowing water saturation and thus anaerobic conditions to exist below this level. Modified simulated conditions were automatically controlled with exposure to infra-red and ultra-violet lamps and a fan which were activated every 1½ hours, and 5.2 L of water which was sprayed on each box every 8 hours, resulting in an application rate 9 times the average annual precipitation of the Elliot Lake area (996.1 mm). Thus, if the leaching rate of the chemical constituents were dependent only upon the water applied to the tailings, a chronological acceleration of nine-fold should be achieved, and 40 days of experimental time would be equivalent to 1 simulated year as far as water application was concerned. Bacterial oxidation of pyrite would also be accelerated because of the higher average temperature and increased availability of water and oxygen. The water supplied to box 'C' contained 1-3 mL/L of hypochlorite solution (Javex bleach) containing 5% available chlorine to inhibit bacterial action, and thus sulphate generation, while maintaining oxidizing conditions. The experiment was conducted at ambient temperature (18 ± 4°C), with extraneous light being excluded by black curtains. The water level in the lysimeter boxes was maintained within 10 cm (or less) of the tailings surface by a syphon tube from the effluent port. Liquid samples, taken from the effluent ports at intervals of approximately 2 weeks, were analyzed for total iron, pH, sulphate, uranium, thorium and radium-226. The effluent and core samples taken from the centre and each corner of lysimeter box 'A' were periodically analyzed by gas-liquid chromatography for kerosene. Due to interference of the kerosene on the chromatographic spectrum of isodecanol, this latter compound could only be detected, but not quantified. Alamine 336 was analyzed by a colorimetric procedure[13]. Subsequently, a method has been developed at CANMET for kerosene using gas chromatography.

Note that all results are reported on the simulated time basis of 1 experimental year = 9 years of water application with a time cycle of light and darkness and drying. No freezing or thawing tests were carried out to complete a true weathering cycle.

Results and Discussion

Lysimeter Boxes

Figure 2 shows the pH and concentrations of radium-226, sulphate and total iron in the effluents of the three lysimeter boxes over a period of about 900 days, simulating about 22½ years during which time 13.8 tonnes of water were applied. No

TABLE 2. Lysimeter box contents

	Lysimeter box 'A' (bacteria and organics)	Lysimeter box 'B' (bacteria only)	Lysimeter box 'C' (bleach)
Dimensions (cm)	124.5 x 59.5 x 58.0	124.5 x 59.5 x 58.0	116.5 x 55.5 x 59.5
Volume (cm^3)	429 650	429 650	384 712
Weight (kg)*	1,047	1,047	938
Radium-226 (μCi)	178	178	159
Total sulphur	38.11	38.11	34.14
Sulphate (kg as S)	7.54	7.54	6.75
Uranium (kg)	0.73	0.73	0.66
Total iron (kg)	29.53	29.53	26.44
Thorium (kg)	0.26	0.26	0.23

* Calculated dry weight, specific gravity 2.65, moisture content 8.8%.

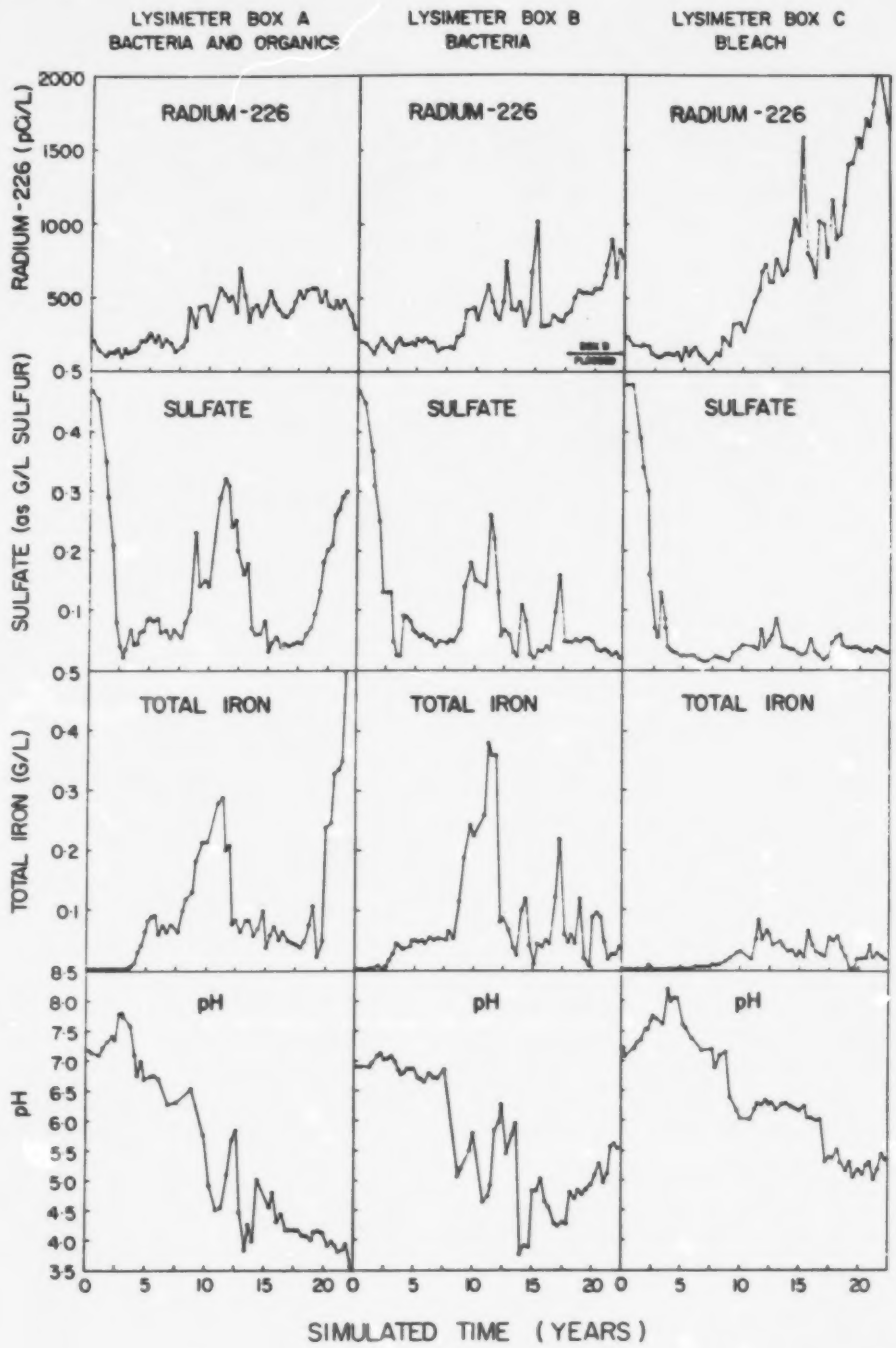

FIGURE 2. Solubilization of radium-226, sulphate and total iron and change in pH in the lysimeter box effluents with respect to simulated time.

TABLE 3. Solubilization of components from lysimeter boxes (simulated 22.5 years)

Component	Lysimeter box 'A' (bacteria and organics)		Lysimeter box 'B' (bacteria only)		Lysimeter box 'C' (bleach)	
	Amount	Proportion*	Amount	Proportion*	Amount	Proportion*
Uranium	9.34 g	12.74%	3.40 g	4.64%	1.43 g	2.18%
Radium 226	5.27 μCi	2.96%	5.70 μCi	3.20%	9.34 μCi	5.86%
Total sulphur	2.29 kg 71.58 moles	6.01%	1.45 kg 45.38 moles	3.80%	1.01 kg 31.55 moles	2.96%
Total iron	1.91 kg 34.16 moles	6.45%	1.15 kg 20.59 moles	3.89%	0.31 kg 5.64 moles	1.19%
Total iron to sulphate sulphur molar ratio	-	1:2.10	-	1:2.20	-	1:5.59

*as percentage of component initially present in the original tailings leached during the course of the experiment.

correction to these results is applied to compensate for evaporation of 9.3 ± 2.3%. The total amount and proportion of each constituent initially present in each of these three lysimeter boxes removed during the course of this experiment are summarized in Table 3.

Radium-226 is constantly being solubilized, the concentrations in the effluents from lysimeter boxes 'A' and 'B' being between 100 and 300 pCi/L for about the first 7.5 simulated years, increasing thereafter and remaining around 500 pCi/L. To demonstrate the effect of bacterial action on the tailings, box 'B' was flooded for a 200-day period after 17.5 simulated years, thus depriving the bacteria of one of their metabolic necessities, oxygen. The inhibition of the bacteria resulted in increases in pH and radium-226 concentration and decreases in total iron and sulphate sulphur concentrations in the effluents of box 'B' in comparison to box 'A', which was not flooded. The radium-226 content of the effluent of lysimeter box 'C' is between 85 and 240 pCi/L for the first 7.5 simulated years and increases thereafter to between 1000 and 2000 pCi/L. The decrease in the concentration of sulphate in the pore water would increase the solubility and thus mobilize the radium-226. The amounts and proportions of the radium-226 eluted from lysimeter boxes 'A', 'B' and 'C' are 5.77 μCi and 2.96%, 5.70 μCi and 3.20%, and 9.39 μCi and 5.86%, respectively.

Initially, the concentrations of sulphate and total iron of the effluents from each of the three lysimeters are similar. Subsequently, the concentrations of both sulphate and total iron in the effluents increase similarly in boxes 'A' and 'B', with the pH decrease correlating to the cumulative sulphate removal. The concentrations of these components are much less in the effluents of box 'C'. The total iron consists of both ferrous and ferric species; the ferric iron results from bacterial oxidation of pyrite and ferrous iron, whereas the ferrous iron results from the action of ferric iron and pyrite under the reduced conditions below the water table[16]. Sulphate is generated not only by the dissolution of gypsum, but also by bacterial oxidation of sulphide minerals, bacterial oxidation of elemental sulphur arising from the oxidation of sulphide minerals by ferric iron and the formation of secondary ferric iron minerals[16]. Thus, the presence of elevated concentrations of iron and sulphate in the tailings effluents is an indication of bacterial activity. The lower total iron to sulphate molar ratio of the effluents from box 'C' indicates less metabolic activity of the iron-oxidizing bacteria due to the presence of the bacteriostatic agent (NaOCl). This ratio also decreases during the course of the experiment[13] due to the incomplete bacterial and chemical oxidation of pyrite, which would occur according to the equation

$$2FeS_2 + 7O_2 + 2CaCO_3 + 2H_2O \rightarrow 2FeSO_4 + 2CaSO_4 \cdot 2H_2O + 2CO_2$$

yielding a theoretical iron to sulphate molar ratio of 1:1. In reality, this ratio would be greater than 1:1 due to the solubility of gypsum and the oxidation of other sulphide minerals in the tailings.

Thorium was not extracted from the tailings contained in any of the lysimeters, the concentrations in the effluents being consistently less than 0.1 mg/L. After an initial release, uranium was not found in the effluents of lysimeters 'A' and 'B' until after 7.5 simulated years and from lysimeter 'C' not until after 17.5 simulated years. Until 20 simulated years, when uranium was detected in the effluents, it was rarely found in concentrations greater than 1 mg/L. After 20 simulated years, the uranium concentration in the effluents of box 'A' increases to approximately 10 mg/L. In the effluents of box 'B', which was flooded between 17.5 and 22.5 simulated years, and of box 'C', which was treated with bleach, the uranium concentrations were always less than 1 mg/L.

The mixture of organic compounds originally introduced into lysimeter box 'A' was almost completely eliminated, either by voidage through the effluent or by evaporation within the first 11 simulated years. Kerosene, the largest component in the mixture of organic compounds, was quickly eliminated from the tailings, its concentration in the tailings decreasing almost by 80% in the first 4 simulated years and by more than 95% in the first 10.8 simulated years. Examination of the core samples from the centre and at the corners of lysimeter box 'A' indicated migration of the kerosene toward the effluent outlet. Isodecanol, which could be detected but not quantified due to the interference of the chromatographic spectrum by kerosene, was always found with the kerosene. The elution of Alamine 336 was observed to be much more rapid and was undetected after a 2-year simulation period.

Periodically, throughout the evaluation period, the boxes were photographed in order to compare the iron layering due to jarosite formation. There was a significant amount produced after 4 months of operation (approximately 3 years simulation) and acid production in the tailings was also noted. The presence of bacteria increased the acidity and dissolution of iron, but inhibited Ra^{226} release. Subsequently, the hydrolysis of iron would result in acid conditions. Continual application of water solubilized Ra^{226}.

Core sample profile analyses of the lysimeter contents for radium, sulphate and iron are shown in Figure 3 after a simulated 20-year period. The radium is being leached from the top layers downward, with no change or even enrichment of this radionuclide occurring toward the bottom of the lysimeter. Similar trends, but less pronounced, are shown for iron and sulphate. (The hash marks in Fig. 3 indicate a range of analysis.) The downward movement of these constituents is similar to some, but not all, sites of the Nordic tailings area at Elliot Lake[6].

A calculation, based on the rates of radium release over the simulated 25-year period, indicates that radium will pass through the tailings contained in the lysimeter boxes in about 300 simulated years. However, such calculations should not be directly extrapolated to actual tailings sites without obtaining specific site data.

Comparison of Lysimeter Size for Reliability

Concurrent with the studies on the large lysimeters, other measurements have been taken on various sizes of tailings tests to determine whether quick, small-scale tests could be useful

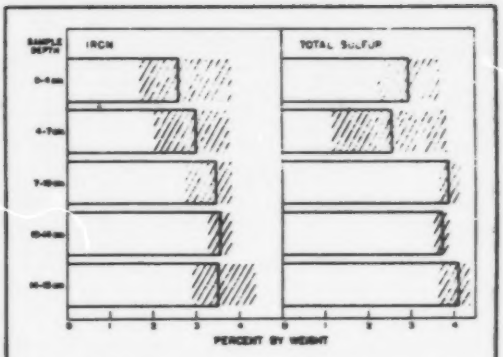

FIGURE 3A. Core sample profiles of lysimeter box—Fe and S.

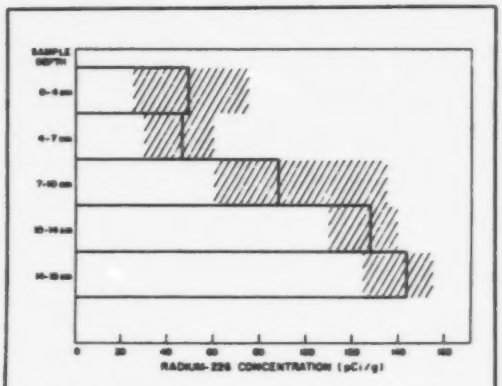

FIGURE 3B. Core sample profile of lysimeter box—Ra^{226}.

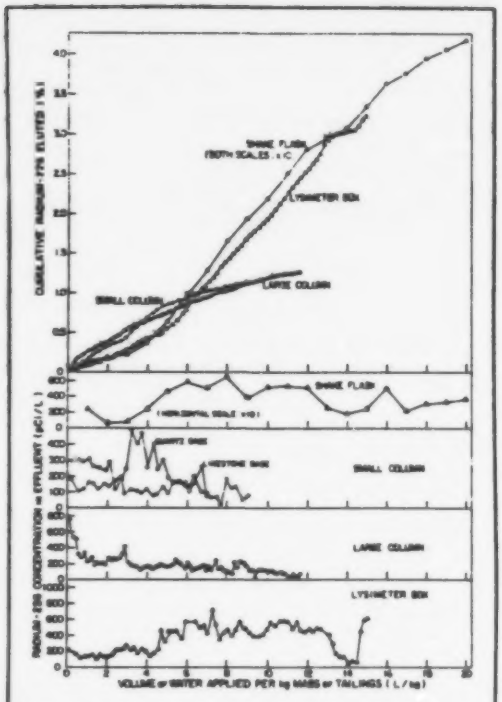

FIGURE 4. Comparison of lysimeter size based on volume of water applied per kg mass of tailings (Elliot Lake).

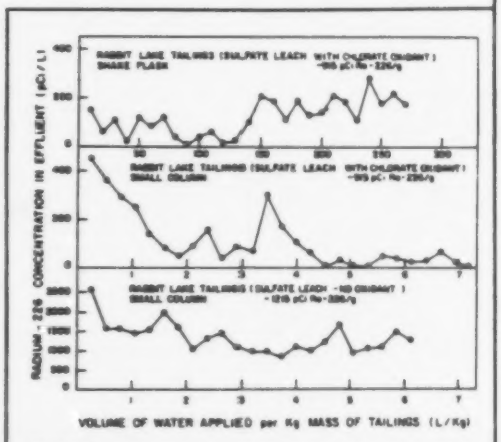

FIGURE 5. Effect of volume of water applied per kg mass of tailings (Rabbit Lake).

for predicting radium release. In these tests, two sizes of glass columns and shake flasks were used, and the data derived were compared to the box lysimeters, based on the amount of water applied per kg of tailings.

The small columns were 5.6 cm diameter by 25 cm long and filled with 0.75-kg tails. The large columns were 9.8 cm diameter by 90 cm long and filled with 12.5-kg tails. The water percolation rate was 200 mL weekly for the small columns and 1.75 L weekly for the large columns. The shake flask tests consisted of a 25-g quantity of the tails together with 250 mL H_2O at 30°C in a flask being agitated on a mechanical gyratory shaker. Each week the water was separated and analyzed; fresh water was then added to the solids and the shaking was continued. The results of these tests are given in Figure 4, based on the volume of water applied per kg mass of tailings. Lysimeter size does not seem to be important and the radium in the effluent appears to be related to its aqueous solubility. The results for the shake flasks and lysimeter boxes are similar due to the presence of bacteria. The column tests were similar to one another, but there were no bacteria in the columns. Note the difference in the two types of base present in the small columns. With a quartz base, the elution of radium is greater compared to the column with a limestone base. The presence of the limestone results in the radium being removed from solution by precipitation probably as the carbonate, thus resulting in a decrease in the concentration and the release of this radionuclide in the column effluent. A similar decrease in the concentration of radium occurs when a peat moss base is used.

Saskatchewan Ores

The work described above was on the Elliot Lake tailings. A comparison of the results obtained from tailings from H_2SO_4 leaching with or without chlorate as oxidant of the Rabbit Lake ore is shown in Figure 5. The concentrations of radium-226 in the leaching media from the shake flask and column tests on the tailings of the ore that had been leached with

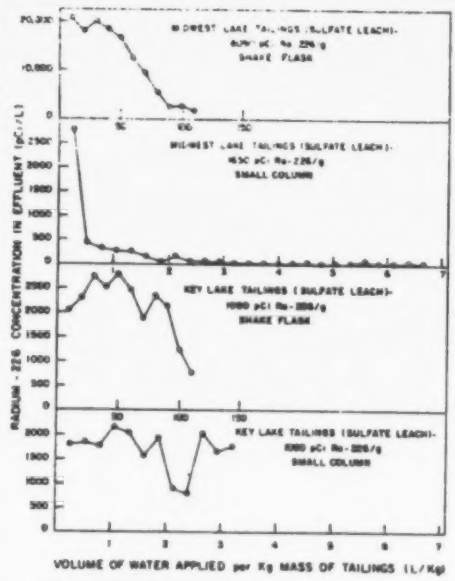

FIGURE 6. Effect of volume of water applied per kg mass of tailings (Midwest Lake and Key Lake).

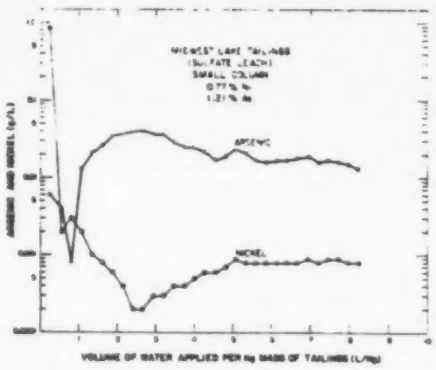

FIGURE 7. Arsenic and nickel solubilization by water from Midwest Lake tails.

sulphate in the presence of chlorate are in reasonably close agreement. However, radium is released more readily from the tailings of the ore that had been leached with sulphate in the absence of oxidant (about 1500 pCi/L) than that which had been leached in the presence of chlorate, indicating that the treatment of the original ore could be a critical factor in determining the solubilization characteristics of this radionuclide.

The high-grade complex uranium ores of Key Lake and Midwest Lake, containing nickel and arsenic, were similarly examined and these results are given in Figure 6. Because neither company has a mill yet in operation, the tailings were obtained from uranium extraction experiments. These high-grade ores, depending on the original blend of ores in the leach, will result in a difference in the radium content in the tails. A level of about 6000 pCi Ra^{226}/g would probably be expected for tails from such ore. In the tests shown, the levels range considerably lower because of the original blend. Nevertheless, there appears to be reasonable agreement of radium leaching patterns with the shake flask tests and the small column lysimeters for the Midwest tests when sufficient water is applied. The Key Lake data did not show such close agreement. Figure 7 shows that there is very little dissolution of nickel, but that there is a significant and continuous dissolution of arsenic with continued application of water of 0.01-0.04 g/L.

Shake flask tests on the Midwest tails were carried out to determine the effect of bacteria on release of constituents. These results (Fig. 8 and 9) indicate that in the presence of bacteria there is an increased acidity and therefore increased uranium solubility. There is also an initial increase in the solubility of nickel and iron. The presence of bacteria slowed the arsenic and radium dissolution rate. By the 7th week all the bacteria had died, due possibly to the arsenic and/or free acid concentrations.

Lysimeter Test Pit System

During the small-scale lysimeter test program, large-scale lysimeter tests were conducted for 5 years at the Rio Algom Quirke Mine, Elliot Lake[10]. The purpose of the large installation was to evaluate the effect of the different surface treatments of tailings on the oxidation of the sulphides and on the quality and quantity of the effluent. The initial tests indicated discrepancies between the amount of rainfall measured and the amount measured in the underflow from the pits. Subsequent tests in the laboratory were carried out to determine the various parameters affecting drainage, evaporation and transpiration, and the measurements were compared to measurements in the pits[17]. The test pits were 30 by 30 by 5 ft deep (with sides sloped at 45°), containing a single 10-cm-diameter drainage pipe. (If subsequent pits were to be constructed, the authors recommended a 3-pipe drainage system.) The tests were conducted in pits, each containing approximately 200 tonnes of tailings. Wood chips, gravel and also vegetation (grasses) were used as cover. The hydrology was studied by measuring density, porosity, water permeability, water retention, storage capacity of the wood chips and air migration through the wood chip cover, and capillary action. It was recognized that the shallow pit could not duplicate the effect of the capillary forces acting on an actual tailings pond.

The effect of climate on the pits, with extremes of cold winters and dry summers, created cracks in the tailings. Because of the scale of the experiment, difficulties were encountered in the control of the percolation and the maintenance of a water table. Some of the drainage tiles became obstructed by chemical precipitates, and some of the effluents were modified by the active iron-oxidizing bacteria during the sampling procedure.

The test pit measurements indicated that none of the treatments prevented pyrite oxidation and that it took 2.5 years for signs of oxidation (acidic effluents) to occur[10]. The behaviour of the lysimeter pit system was evaluated and no explanation for its behaviour could be given. It appeared that control of an experiment of this size exposed to natural conditions is extremely difficult.

In order to solve the problem, simple lysimeter models were recommended for study, measuring the following parameters:[17]

porosity	storage capacity
permeability	distribution of water
water saturation	penetration depth of rainfall
retention capacity	relationship between rain intensity and underflow

Pore Water Measurements

External contract studies were conducted on the chemical composition and movement of pore water in inactive tailings (Nordic) in the Elliot Lake district during 1979-1980[17]. These inactive tailings, 20-25 years old, had been vegetated.

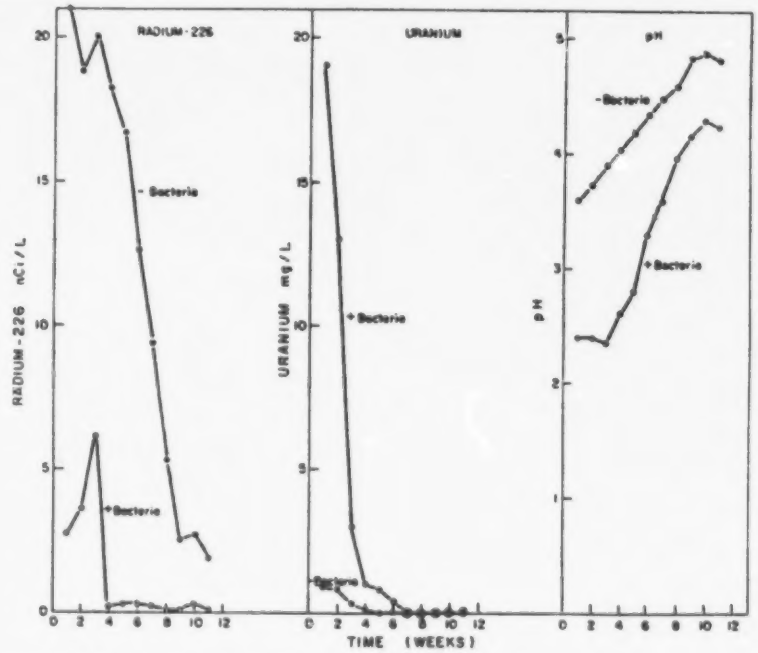

FIGURE 8. Effect of bacteria on pH and release of Ra^{226} and U from Midwest Lake tails.

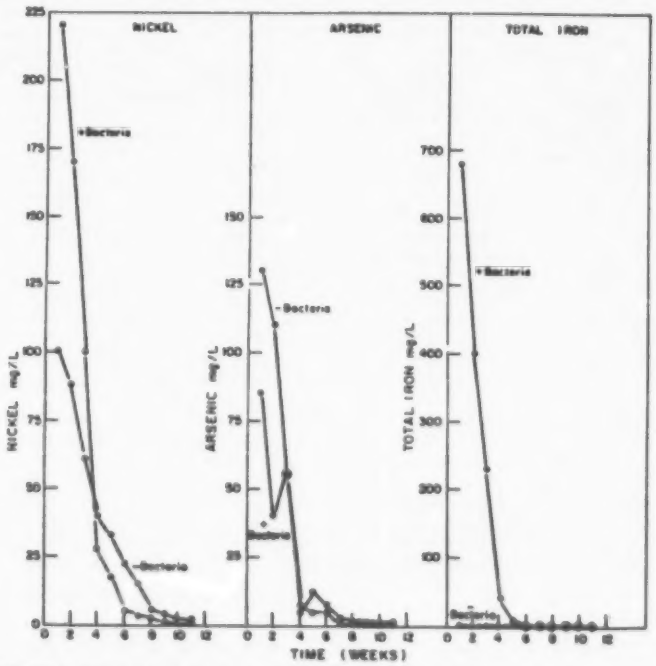

FIGURE 9. Effect of bacteria on release of Ni, As and Fe from Midwest tails.

Piezometer tests have indicated acidic water occurring in these vegetated areas due to the oxidation of pyrite (pH 3-7). The plume measurements indicated sulphate in the seepage water extending greater than 300 metres from the dam compared to only 15 metres for the radium. That is, the radium appears to be sorbed and desorbed, by an ion exchange mechanism, or by precipitation followed by solubilization, thus slowing its movement through the tailings. There is a continual build-up of organic soil in the uppermost layers, and together with the depletion of pyrite there is a possibility that the acid generation will decrease with time.

Future Considerations

Although we intend to continue the on-going large lysimeter tests for a prolonged period to obtain additional data, other lysimeter tests should be carried out.

Tests are in the initial stages on a new set of lysimeter experiments to further the knowledge already obtained. In the four test boxes recently started, we are studying the relationship between a compost or fertilizer cover together with vegetation on the seepage efforts, with and without the presence of bacteria. The presence of the humus-compost material (made from municipal garbage, as part of CANMET's tailings program) may result in a decrease in oxidation of the pyrite and therefore a decrease in rate of generation of acid and an increase in the release of radionuclides. Subsequent tests will include the results of chemically fixing the tailings as well as radionuclide sorption from the seepage effluent.

In addition to the lysimeter tests in progress and those planned for the future—all tests primarily to obtain a better understanding as to tailings predictability—work at CANMET will continue on removal of radionuclides from the ores prior to leaching by high-intensity magnetic separation and flotation. Preliminary work on salt washing of the tails to remove radium[13,18] should be pursued. With that in mind, we have recently installed a lysimeter box under test to determine whether the rate of radionuclides leaching can be significantly accelerated by a brine percolation leach so that long-term disposal problems of continued maintenance can be minimized. Because all previous reported work has been on a laboratory scale, a larger-scale test in the lysimeter boxes could be more meaningful. Also, the brine solution would be collected for radium removal and isolation.

Conclusions

1. With respect to the large lysimeter boxes, the following can be concluded:

(a) The presence of organic solvent extraction reagents (kerosene, isodecanol and Alamine 336) has little effect on the solubilization of Fe, SO_4, Th and Ra from fresh tailings in the presence of bacteria. The Alamine is voided during the first 2-3 simulated years and the kerosene during the first 11 simulated years.

(b) In the absence of bacteria, the concentration of Fe, SO_4 and Th decreased and less acid generation was noted. Also, the $Fe_{sol}/SO_4^{=}$ ratio is greatly decreased and the rate of radium release was increased.

(c) Bacterial action increases the dissolution rate of uranium and the $SO_4^{=}$ generated by the bacteria appears to limit the solubility of radium.

(d) With the continued application of water, and the removal of $SO_4^{=}$, the radium is rendered mobile and is solubilized.

(e) Assuming a steady state of 500 pCi/L Ra^{226} in the effluent from the lysimeter, and that all the radium present in the tailings is leachable, removal of radium-226 from the tailings in the lysimeter would be complete in about 300 simulated years. Actual tailings piles would require extensive tests at depth to verify such a calculation.

2. Small-scale lysimeter and shake flask tests agree with the large lysimeter test with respect to radium release and water application rate.

3. Much of the data that have been obtained on the large lysimeter boxes have been substantiated in field tests on existing tailings dams with respect to the movement of tailings constituents. The migration of radium in the lysimeter boxes is downward.

4. Comparison of the lysimeter tests with large test pits showed that the rate of acid production was similar in both, occurring after approximately 3 years.

5. In the complex tailings, arsenic continues to be solubilized with the continued application of water.

6. Radium is removed more rapidly by water percolation from tailings that had been leached with H_2SO_4 in the absence of oxidant than from those which had been leached with H_2SO_4 in the presence of chlorate.

The major function of a lysimeter test unit is to provide for controlled physical conditions during a predetermined testing period. Therefore, the design of the lysimeter and its operation are of importance if the data derived from the tests are to be meaningful. The data should then be useful in predicting chemical reaction and mobility throughout abandoned and new tailings areas.

The tests to date at CANMET have proved to be useful and give us sufficient assurance to continue further testing. Shake flask tests represent a quick, easy test and columns also prove useful. More reliable data on permeability and other parameters, and on the effects of different surface treatments, can be achieved using the larger lysimeter under controlled conditions.

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LEAK DETECTION IN IMPOUNDMENTS

Leaks can be detected by monitor wells as discussed in Chapter 60. An innovative new method for early warning of leaks is described by BOND and ROUSE (1985) whose paper is inserted in Chapter 60. They describe the use of Lysimeters placed beneath the tailings impoundment.

A useful geophysical technique employing remote sensing to locate leaks in water impoundments has been described by ARTHUR LANGE (1984) of Albireo Corp., Wheat Ridge, Colorado, whose paper is inserted in Chapter 59 on water impoundments and evaporation ponds. Since then, he has developed further innovations in this field which appear even more useful.

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Arthur L. Lange

Two further review papers on the subject by WALLER and DAVIS (1984) and DAVIS, et al. (1984) are inserted below as additional sources of information.

It is important to realize, however, that repairing leaks in tailings ponds may not be an easy matter. The leaks are likely to be located under millions of tons of tailings material, and retrofitting a lining is unlikely to be possible. Grout curtains and seepage interceptor trenches may prove partly effective with treatment or return of the collected solutions--both relatively expensive. Leak detection may provide a way of identifying where to place the grout curtain or the seepage interceptor trenches.

At Quivira Mining Company's Ambrosia Lake operations, evaporation pond lings were not feasible at ponds adjacent to an acid tailings dam because reaction with carbonate rocks caused so much CO_2 to evolve. Could this possibly lead to a means of detecting leaks and migration of acid seepage by perhaps monitoring for CO_2 content of soil gas in surface soils or shallow boreholes around the tailings site?

United States
Environmental Protection
Agency

Municipal Environmental Research
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Research and Development

EPA-600/S2-84-041 Mar 1984

EPA

Project Summary

Assessment of Innovative Techniques to Detect Waste Impoundment Liner Failures

M. J. Waller and J. L. Davis

Recommendations were developed for monitoring systems that will detect leaks in both new and existing landfill liner systems. Both solid and liquid impoundment sites were considered, but liquid waste impoundments were emphasized. The study was conducted in two phases. First a literature review was performed to establish the state-of-the-art in the leak detection field and to identify candidate methods. Second, a multiple-objective ranking matrix was designed and used to rank candidate techniques according to a predefined set of parameters covering pertinent technical, economic, and operational objectives.

Results indicate that no single technique or group of techniques can detect liner failure or leachate leaks with absolute certainty in either existing or planned sites. Several techniques used in combination will improve conventional water quality monitoring techniques at existing sites. In planned lined landfills, several techniques hold promise for future development.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Despite the many lined impoundment and disposal sites in use throughout the country, methods to monitor the performance of liners have not been adequately developed. When liner failures occur at a site, a monitoring system should provide warning before significant environmental damage can occur. Furthermore, such a system must be capable of locating a leak precisely so that repairs can be made. Finally, the monitoring system must be nondestructive to the liner. Efforts to determine the precise locations of liner leaks may be repaid many times in terms of reduced environmental damage, and resulting costly litigation, and by reduced costs for subsequent repairs.

During the course of this program, recommendations were developed for monitoring systems that will permit effective in situ detection of leaks in both new and existing landfill liner systems. Both solid and liquid impoundment sites were considered, but emphasis was placed on liquid waste impoundments.

Because assessing liner performance and detecting leaks varies in approach and complexity between existing and planned sites, each situation was considered separately. At existing sites, any leak detection program is almost totally site-dependent because of considerations such as site area, depth of impoundment, and the presence of waste already in the landfill. Sites still in the planning stage can be tailored to a monitoring program. Thus it may be possible to emplace a leak detection system directly under a planned site before construction, or even to select a configuration for site layout that will

readily lend itself to a routine monitoring program.

At the outset of this program, the primary objective for each candidate detection technique was the ability to pinpoint a landfill liner failure within a maximum area of 0.1 m^2 (1 ft^2). But because of restrictions placed on detection systems at existing sites (which in most cases will limit them to surface use), this goal was broadened to encompass any system that could feasibly improve current conventional monitoring techniques. Thus any system with the potential to detect a leachate plume before it contacts the groundwater was reviewed and evaluated. In the case of detection techniques applied to planned disposal sites, the 0.1 m^2 (1 ft^2) goal was retained. Thus plume detection at existing sites is distinguished from actual leak detection at planned sites.

Program objectives were met in two study phases. First, a literature review established a state-of-the-art in the leak detection field and then identified a list of possible candidate methods. Second, a multiple objective ranking matrix was designed and executed. This tool was used to rank candidates according to a predefined set of parameters covering pertinent technical, economic, and operational objectives. The program results in the information needed to set priorities for research and development and to allocate resources for future development of promising leak detection techniques.

Technical Considerations

To help define potential leak detection systems, the study identified certain phenomena that were expected to be associated with liner leaks. Various leak detection techniques for locating or identifying these phenomena were then selected. A review was also made of techniques that had been applied in various environments for a variety of purposes, as well as those that seemed to have conceptual application to the leak detection problem. Phenomena that might yield to leak detection techniques include the following:

- Leachate conductivity,
- Subgrade and landfill materials,
- Groundwater flow fields, and
- Liner and soil distress.

Various geophysical techniques might be applied to detecting these phenomena under favorable site conditions. Some of these techniques were selected for review and evaluation here based on the following criteria:

1. The ability to "sense" beyond their point of application to a depth greater than 30 m (33 yd),
2. The ability to be applied in situ without harming the liner,
3. The ability to improve conventional groundwater monitoring techniques at existing sites, and
4. The ability to detect a leak within 0.1 m^2 (1 ft^2) at planned sites.

Some geophysical techniques apply to both existing and planned sites, whereas others may be used in either one or the other.

The performance of a leak detection system depends on the site environment and the landfill contents. Any particular site may be subject to natural or cultural interferences that can degrade performance of the monitoring system.

Geophysical sensing techniques have inherent limitations on their ability to detect leaks, particularly at existing waste sites. Many of the geophysical methods are limited by the waste and background materials, which render surface measurements far from ideal. In many cases, geophysical methods may not be at all useful for detecting leaks under a site and may only be able to detect changed conditions over time in the unsaturated zone before a contaminant reaches the groundwater. Borehole methods improve the probability of detecting leaks because potentially they can reveal conditions under the site and do not have to sense through it. Borehole geophysical techniques are most useful when the distance between boreholes is not greater than about 30 m (33 yd), though this distance varies depending on soil type and conductivity of the host material. Most techniques fail to penetrate at greater distances.

Detecting leaks at sites that might undergo construction at some future date is not simple, but it is much less complex than for existing sites. A variety of sensing systems can be placed near the liner to detect the presence of leachate or its effects, or to evaluate the mechanical integrity of the liner itself. Ultimately, it may be advantageous to design a system combining several geophysical techniques for monitoring conditions such as the presence of leachate and the occurrence of mechanical failures.

At planned sites, the goal of detecting leaks within a 0.1-m^2 (1 ft^2) range becomes a very real possibility. Eventually it may be possible to design an inbuilt system to meet the needs of any site in terms of cost and technical precision. Thus a small site or a municipal landfill with nonhazarous wastes could use a relatively inexpensive system monitored quarterly or twice a year. For vast impoundments of hazardous liquid wastes, where the cost of liner failure would be great, it will eventually be possible to build in a continuous monitoring system with equipment and procedures designed for cell-by-cell monitoring and daily retrieval, processing, interpreting, analyzing, recording, and storing of liner performance data.

State-of-the-Art Review

Based on these technical considerations, a literature search was conducted to identify possible candidate methods being investigated in the laboratory or applied in the field. Five data bases were searched, including GeoRef, EnviroLine, Pollution Abstracts, NTIS, and DOD Documentation Center, followed by a manual search.

The literature review provided little information on actual leak detection techniques in existing or planned lined landfills. Considerably more information was available regarding the problem of leachate plume detection at existing sites. But in no case was successful leachate leak detection reported before it was detected by groundwater quality monitoring, which assumes fairly widespread contamination. This finding does not so much reflect the limitation of current geophysical leak detection techniques as it indicates the state-of-the-practice in groundwater quality monitoring. During the review, no cases were found in which techniques were actually being applied in the field to evaluate liner integrity.

All possible leak detection techniques reviewed in the course of the survey are summarized in Table 1. Techniques that have seen application in the field to detect a leachate plume include HF Pulse Techniques, electromagnetics, resitivity, and seismic techniques. Resistivity techniques appear to have had the greatest field application; these are followed by electromagnetic techniques, which are beginning to see wide application both for

: 1 ·mary of Candidate Methods

·nique	What is Measured in the Ground	Used from	Range Meters	Areal Extent of Anomaly	Leachate Properties in Contrast to Host Medium Properties	Estimated Cost for Leak Detection
·ric						
·sistivity	Resistance over a length versus horizontal and vertical position	Surface borehole	≤100's	Depth	≥2:1	Low
·	Voltage generated by electrochemical actions	Surface borehole	≤1	Meters	≥10:1	Low
·tromagnetic:						
w Frequency ·ectromagnetic	Conductivity versus horizontal and vertical position	Surface	≤100	Depth	≥2:1	Low
·gh Frequency ·ectromagnetic	Dielectric properties versus horizontal and vertical position	Surface borehole	≤10's	≈0.1 Depth	≥2:1	High
·stic						
·ismic	Elastic properties versus horizontal and vertical properties	Surface borehole	≤1000's	≈0.5 Depth	≥2:1	Moderate
·pus ·ission	Sounds emitted from fluid flow in soils	Borehole	?	--	Rapid flow in large pores	Moderate
·Planned Sites						
·DR Grid	Dielectric properties versus position on transmission line	Parallel wires in one direction	≤100's along line	≈Spacing of the line	≥2:1	High
·C Grid	Change of resistance of a wire due to corrosion caused by leak	Parallel wires in two directions	≤1000's	≈Size of grid spacing	--	High

·chate plume identification and areal ·: surveys. A number of other tech- ·ues were identified that are either ·ceptually applicable or have seen field ·a in related applications such as ·troleum exploration or extensive site ·aluations.

·Multiple Objective Ranking ·Matrix

Finally, a multiple objective ranking ·atrix was structured to compare the ·andidate methodologies with regard to a ·efined set of criteria. The criteria defined ·arlier for geophysical techniques were ·clude·d. Techniques were eliminated ·om trix if they were not identified ·n the ·ure survey as having at least the potential for producing satisfactory results. Also, only techniques that posed no significant risk factors to the operators or to the environment were considered. Thus any technique that could not possibly work without substantial penetration of the dumpsite and the liner was rejected from further consideration. This limitation severely reduces the number of techniques that can be used at existing sites and also the probability of success in detecting leaks under the waste site.

The completed matrix evaluates each techniqun on the following parameters:

- Technical factors (such as range, resolution, lateral extent, flow direction, etc.)
- Sensitivity (soil type, waste type, and cultural noise)
- Data reduction (data acquisition time, interpretation time, etc.)
- Impacts (safety, site disruption, and site safety and liability)
- Economic factors (capital cost, installation cost, etc.)
- System capabilities (operator skill, portability, survivability, and availability)

Since some of the parameters are more vital for success than others, a weighted scale was devised. The weighted curve applied to the matrix parameters appears in Figure 1. All the values are given on a relative scale of 1 to 10.

Matrix Results

Matrix results are summarized and displayed in Tables 2 and 3. The average values for all parameters tend to group around 6.7, except for the two grid techniques, which are about 7.8. Clearly, no significant variation exists among the techniques. Considering the conditions under which methodologies were included in the matrix, this consistency is neither surprising nor unreasonable.

All of the techniques are very sensitive to the soil and waste type, with an average sensitivity value of about 4. This value indicates that probably none of the techniques will work in certain situations found in a typical waste dumpsite. The two grid techniques are less sensitive to the site conditions because they are only feasible for planned sites where optimum conditions can be selected.

All the values in the impacts group have very high ratings because the only techniques that were considered were those that had no significant risk factors for the operators or the waste dumpsite. Lower values were given if the technique required the use of holes for short rods on the site or if boreholes near it were necessary. Obviously, if any risk exists for the operator or the site, the technique is impractical. This limitation severely reduces the number of techniques that can be used, and with it the probability of success for detecting leaks under the waste site.

All of the values in the technical factors group for existing sites tend to be about 6.7. This result appears to be discouraging at first, and it certainly indicates the difficulty of using any of the geophysical or other techniques for monitoring or detecting leaks from an existing waste dumpsite. Clearly no single technique stands out as superior for detecting leaks in existing sites. This matrix makes it abundantly clear that a composite of techniques must be used to solve this complex problem, particularly in existing sites. Nearly all the techniques are sensitive to the various electrical properties of a leachate in the host medium. The exceptions are the seismic and acoustic mission techniques, which are sensitive to the elastic properties and density changes caused by a leak or the acoustic emission from the fluid flow from a leak. A composite geophysical survey can be designed to monitor a complex of material properties, thus enhancing confidence in the survey results.

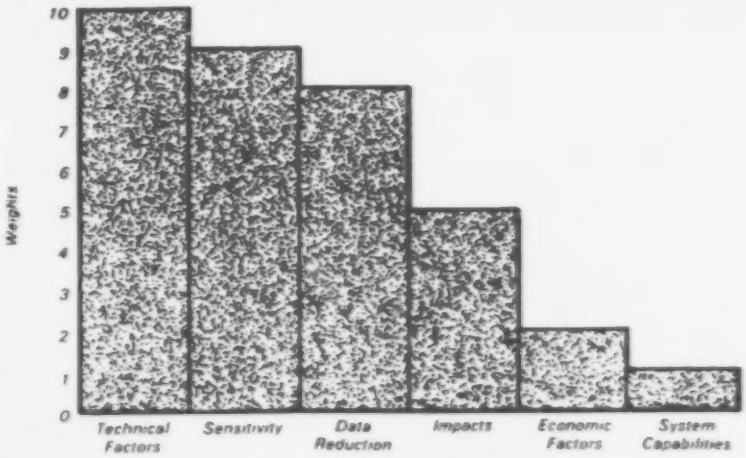

Figure 1. Weighting curve applied to matrix parameters.

Note that techniques evaluated for planned sites received overall higher scores. This result reflects the reality of the problem described in both the literature survey and the matrix results. Landfill liner integrity and performance monitoring programs will be easier to design when they are included and planned for at the conception of a total waste disposal program. Note that despite the problems associated with geophysical techniques, they still hold greater promise of success under optimum site conditions than do the conventional monitoring methods. Leak detection at existing lined sites is and will continue to be more problematic. But skillful use of the techniques described here should often lead to leak detection before extensive groundwater contamination occurs.

Table 2. Applied Methods Summary of Ranking Matrix

Technique	Technical Factors	Sensitivity	Data Reduction	Impacts	Economic Factors	System Capabilities	Average of All Parameters
Significance of Values	±1	±1.7	±1.7	±1.7	±1.7	±1.7	±1.5
Mutual Inductance	6.2	4.3	8.4	10.0	10.0	10.0	7.1
VHF Wave Tilt	6.1	3.7	7.4	10.0	10.0	10.0	6.7
HF Pulse Surface	7.2	4.7	7.5	10.0	7.6	6.8	7.1
Resistivity Schlumberger/Wenner	6.9	4.0	6.3	9.4	8.5	8.6	6.6
Resistivity Pole-Dipole	7.1	4.0	6.3	9.4	8.2	7.9	6.5
SP Surface	5.3	3.5	8.4	10.0	10.0	9.2	6.6
Seismic Surface	7.5	4.0	6.7	10.0	8.6	9.9	6.9

'e 3. R&D Methods Summary of Ranking Matrix

Technique	Technical Factors	Sensitivity	Data Reduction	Impacts	Economic Factors	System Capabilities	Average of All Parameters
Significance of Values	±1	±1.7	±1.7	±1.7	±1.7	±1.7	±1.5
Seismic Surface to Borehole	7.4	4.0	6.7	9.2	7.7	9.9	6.7
Seismic Borehole to Borehole	7.3	4.7	6.7	9.2	7.7	9.9	6.8
HF Pulse Borehole to Borehole	7.2	4.7	7.5	10.0	7.2	7.7	7.1
Resistivity Borehole to Borehole	6.5	4.4	6.8	10.0	8.7	8.0	6.8
Resistivity Borehole	5.6	4.3	8.1	9.8	8.8	8.6	6.7
Induced Polarization	6.6	4.0	6.7	9.4	7.4	8.3	6.4
CW HF Borehole to Borehole	6.8	4.0	5.0	10.0	6.1	5.9	6.1
CW HF Surface	6.2	4.0	5.1	10.0	6.6	7.2	6.0
SP Borehole	4.8	3.8	8.4	9.5	9.5	9.2	6.4
			Planned Sites				
,R Grid	8.5	6.7	6.8	10.0	7.9	8.0	7.8
DC Grid	7.2	6.7	8.1	10.0	8.6	8.3	7.8
Acoustic Emission	6.1	4.5	9.8	6.8	9.7	8.7	6.8

Conclusions and Recommendations

Results of the survey and the ranking matrix indicate that no single technique currently exists that is applicable in all or even many situations, particularly in existing sites. Each geophysical technique has both theoretical and site-specific limitations. Further research is needed to demonstrate the advantages and limitations of a number of the candidate methods in various dumpsite configurations. Such investigations should include both solid and liquid sites in various soil types, and they should include an array of techniques used in a composite mode. The optimum configuration for planned sites that are to be monitored may be long trenches up to 30 m (33 yd) wide. This shape should reduce the range limitations that exist with geophysical monitoring techniques.

Though no single technique or group of techniques has been identified as a solution to the leak detection problem, the group of techniques reviewed and evaluated here can be applied systematically and synergistically to existing lined sites with the eventual hope of detecting leachate contamination before damage occurs to the groundwater. Cetainly such techniques should be applied routinely in conjunction with water quality sampling at any site identified as a potential problem. In the case of planned sites, several solutions hold promise for future development.

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Carlton C. Wiles is the EPA Project Officer (see below).
The complete report, entitled "Assessment of Innovative Techniques to Detect Waste Impoundment Liner Failures," (Order No. PB 84-157 858, Cost: $14.50, subject to change) will be available only from:
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Agency

Research and Development

Municipal Environmental
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EPA-600/S2-84-058 Apr. 1984

EPA

Project Summary

Innovative Concepts for Detecting and Locating Leaks in Waste Impoundment Liner Systems: Acoustic Emission Monitoring and Time Domain Reflectometry

J. L. Davis, R. Singh, B. G. Stegman, and M. J. Waller are with EarthTech Research Corporation, Baltimore, MD 21227.

***Carlton Wiles** is the EPA Project Officer (see below).*

The complete report, entitled "Innovative Concepts for Detecting and Locating Leaks in Waste Impoundment Liner Systems: Acoustic Emission Monitoring and Time Domain Reflectometry," (Order No. PB 84-161 819; Cost: $13.00, subject to change) will be available only from:

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A project was conducted to develop reliable, nondestructive methods for detecting leaks in lined waste impoundments before the leachate can seriously damage the ground water. A second goal was to find a technique to locate the precise area where a known leak is occurring. After a preliminary study involving a literature review, a state-of-the-art survey, and a ranking matrix exercise, two techniques were recommended for immediate further study — acoustic emission monitoring (AEM) and time domain reflectometry (TDR). AEM determines the amplitude and frequency responses of sounds emitted when water flows at different rates through soils. TDR is a high-frequency electromagnetic technique that measures the electrical properties of materials in and around the conductors of a transmission line.

Laboratory and field studies were undertaken to evaluate the potential of these two techniques. Results indicated that AEM potentially offers a practical and inexpensive technique for leak detection and monitoring in both existing and planned liquid waste impoundments.

TDR appears to be a practical method for detecting and determining the position and extent of a leak under a small waste impoundment liner. Further testing is needed to determine the usefulness of both techniques in the field, however.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Each year about 35 million metric tons of hazardous wastes are disposed of in impoundments lined with natural or manmade materials. The liners act as barriers to impede the flow of the hazardous wastes to the underlying ground water. But presently, little information exists on the effectiveness of the different liner materials, and monitoring methods are unsatisfactory. Ground water is presently monitored through wells placed hydrologically down stream. Thus wastes must actually be present in the ground water before they are detected, and significant damage may already have occurred. No methods currently exist that can detect the source of a leak in a liner before the leachate reaches the ground water.

The purpose of this project was to develop reliable, nondestructive methods for detecting significant leaks in lined waste impoundments before the leachate can seriously

damage the ground water. A second goal was to find an economical technique that could locate the precise area where a known leak occurring in the liner.

The first step in the project was to identify and evaluate a wide range of techniques for liner leak detection. A preliminary study was conducted for this purpose (M.J. Waller, J.L. Davis, and William Kean, 1981. "Assessment of Innovative Techniques to Detect Waste Impoundment Liner Failures," EPA-600/2-84-041, U.S. Environmental Protection Agency, Cincinnati, OH). After a thorough literature review, state-of-the-art survey, and ranking matrix exercise, this earlier study recommended two techniques for immediate further study — AEM and TDR. AEM determines the amplitude and frequency responses of sounds emitted when water flows at different rates through soils. TDR is a high-frequency electromagnetic technique that measures the electrical properties of materials in and around the conductors of a transmission line.

The present study was undertaken to perform laboratory and field studies to evaluate the potential of these two techniques for detecting leaks under waste impoundment liners.

Acoustic Emission Monitoring

AEM techniques have been used for at least 50 years to evaluate stresses in rocks and metals, but their application to soil structures is more recent. Acoustic emission (AE) techniques have shown potential use in earth stability monitoring, settlement and deformation monitoring, and water flow monitoring through earthen dams. To determine the potential application of AEM for detecting leaks from lined waste impoundments, experiments were conducted to measure the amplitude and frequency responses of sounds emitted when water flows at different rates through different soils and rips in a liner material.

Methods and Equipment

Experiments were carried out with three objectives: (1) to determine whether sounds are emitted when water flows through soils and rips in liners, (2) to characterize the sounds emitted when water flows through soils and rips in liners, and (3) to determine the attenuation of these sounds in water. Laboratory studies were conducted to fulfill the first two objectives, and field studies were carried out to achieve the third.

Soil Columns

The laboratory experiments for determining and characterizing sounds produced from water flowing through soils and rips in liners were conducted in soil columns held by a polyvinylchloride (PVC) duct 4 m long and 30 cm in diameter (Figure 1). Different heights of soils could be placed in the column and water could be passed through the soils at different known rates. Some soil column experiments were conducted using 30-mil PVC sheets with either 5- or 15-cm rips. A microphone was placed in the soil of the columns and the sounds were amplified, processed, and displayed. Special care was taken to reduce unwanted background noise. A spectrum analyzer capable of capturing transient events was used to process the data. The amplitude and frequency response of the output signal was displayed on an oscilloscope, recorded on a digital tape recorder, and plotted on an X-Y plotter.

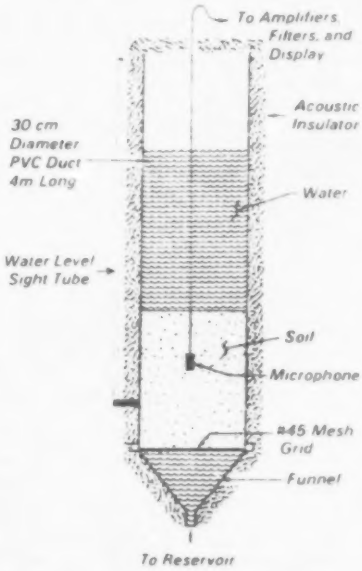

Figure 1. Schematic diagram of the experimental acoustic emission test arrangement

Electronic Equipment

The electronic equipment used to detect, amplify, process, and display the acoustic data included an acoustic receiver (Figure 2), a Weston Acoustic Emission Monitor* with variable gain amplifier of 1 to 5000, a Weston AEM filter unit modified to cover a frequency range of 20 Hz to 5 KHz, a Nicolet 446B mini ubiquitous spectrum analyzer, an analogue X-Y plotter, a sweep oscillator, and a loudspeaker.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Measurement Procedure

The method generally used for laboratory measurements was to place the microphone in the soil being tested (as shown in Figure 1) and let the water flow through the soil. The height of the soil in the column varied from 70 to 150 cm. The microphone was placed 15 cm above the bottom of the soil column (i.e., above the 45-mesh screen). The flow rate and the acoustic spectra were measured, and the spectral data were plotted on the X-Y recorder. The water level was recorded on an X-time recorder. After about every 30- to 40-cm drop in water level, the flow was stopped and a spectrum of the background noise spectra was obtained and subtracted from the response obtained when the water was flowing through the soil.

Soils Tested

The soils used in these experiments were 20/30 Ottawa sand and a pea gravel, with an average grain size of 0.7 mm. The grain size of more than 90 percent of the pea gravel sample fell between 25 and 5 mm, with the remaining portion between 5 and 1 mm.

Water Levels

The water level varied from about 3 m above the soil to just above the soil in each of the experiments; thus falling water head levels occurred during the experiments. The flow rates typically were varied from 0.3 to 1 cm/sec.

Attenuation of Sound in Water

An audio frequency sweep oscillator working over a frequency range from 20 to 500 Hz was used to drive a loudspeaker specially designed to operate underwater. The standard AEM system used throughout these studies was used as the receiver. The AE sensor was moved away continuously from the loudspeaker at a depth of 1 m in a lake whose depth was 2 meters. The sound amplitude over the frequency spectrum was measured as the distance between the source and receiver was varied from 0.2 to 5 meters. The attenuation was measured at 10 dB/m over the frequency range of 100 to 500 Hz in the lake. It was observed that the attenuation of the sounds decreased significantly as the frequency was increased into the kilohertz range.

Results and Conclusions

1. Acoustic signals are emitted when water flows in a turbulent mode through soils. Acoustic signals at frequencies up to 500 Hz are emitted when water flows at rates of 0.3 to 1 cm/sec through a sand and a pea gravel.

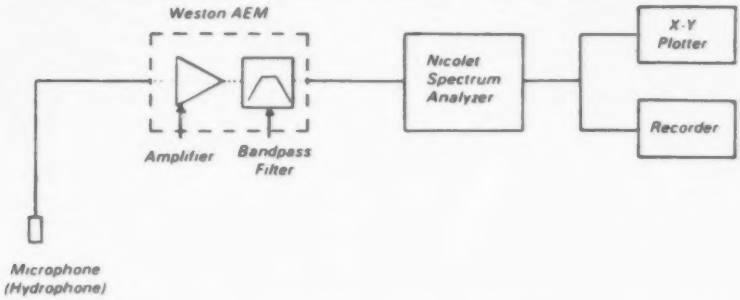

Figure 2. A block diagram of the electronic equipment used to detect acoustic signals emitted when water flows through soils.

2. The flow must be turbulent for acoustic signals to be emitted. Turbulent flow occurs at rates down to 0.1 cm/sec (1 gpm in the 30-cm-diameter test column) with the sands tested.
3. The amplitude of the sounds increases as the turbulent flow rate increases. For example, at a flow rate of 0.3 cm/sec (4 gpm through the 30-cm-diameter test column), the amplitude of acoustic signals through coarse-grained soils is about equal to the background noise likely to exist at liquid impoundment sites. But at an increased flow rate of 1 cm/sec (10 gpm in the 30-cm column), the amplitude is 100 times greater.
4. At a flow rate of 0.3 cm/sec, the sound amplitude increases with increasing variation in soil grain size.
5. At a flow rate of 0.3 cm/sec, the sound amplitude decreases with increasing soil density.
6. The sounds emitted when water flows through soils have significant amplitude at frequencies up to 500 Hz, and they have a peak amplitude between 100 and 200 Hz.
7. The attenuation of sounds between 100 and 500 Hz is 10 dB/m near the surface of a lake.
8. No significant sounds were detected when water flowed at rates up to 1 cm/sec through either a 5- or 15-cm rip in a 1-mm-thick PVC liner material.

Recommendations

1. Determine the spectral response for background sounds emitted at existing waste impoundment sites at frequencies up to 500 Hz.
2. Determine the attenuation of sounds at frequencies from 20 to 500 Hz in a typical waste impoundment site environment.
3. Determine the advantage of different arrays of acoustic sensors for detecting leaks at waste disposal sites.
4. Determine the spectral characteristics for acoustic signals emitted from leaks with known flow rates at a field model of a liquid impoundment site.
5. Determine the spectral response of sounds emitted when plastic liner materials creep.
6. Determine whether AE occurs when water flows through a silt or clay soil.

Time Domain Reflectometry

TDR is a wide-frequency bandwidth, short-pulse-length measurement technique that is sensitive to the high-frequency electrical properties of the material in and around conductors of a transmission line. The high-frequency (10^8 to 10^9 Hz) dielectric properties of water in its liquid state are about 20 times greater than the high-frequency dielectric properties of dry geologic materials: thus TDR is primarily sensitive to changes of water content in geologic materials and relatively insensitive to changes in soil type and density, temperature, and pore liquid salt content.* In materials with a relatively uniform water content, TDR is sensitive to changes of soil and rock type. This method is also sensitive to changes in the phase of the water molecule, and thus frozen or unfrozen wet soils. In addition, TDR can detect either water- or air-filled fractures and voids in the materials along the transmission line.

Leaks from liners of waste impoundments into the soil below are likely to have different electrical properties from those of the host material: thus TDR can measure leachates in the soil material along a transmission line. The TDR technique, using transmission lines placed under a liner offers the significant potential of being a practical method for detecting small leaks from waste dump sites.

*Topp, G.C., J.L. Davis, and A.P. Annan, "Electromagnetic Determination of Soil Water Content: Measurements in Coaxial Transmission Lines," Water Resources Research, Vol. 16, No. 3, June 1980.

The electrical measurements in soils are carried out by placing a transmission line consisting of two electrical conductors in the soils to be tested. Commercial high-frequency transmission line conductors are usually up to 1 cm apart, but it is intended to design and use transmission lines whose conductors are as far apart as possible — on the order of meters. Before a practical TDR system can be developed for detecting leaks under waste impoundment liners, tests are needed to determine the practical problems of increasing the spacing between the conductors.

The objective of this study was to determine the size of an anomaly (simulating a leachate) that could be detected as the spacing for the transmission line conductor was varied.

Background

TDR has been applied to measurements of geologic materials for fewer than 10 years, and therefore much of the work to date has been carried out to determine the practical applications and limitations of the technique. The main application of TDR for more than 30 years has been for testing transmission line cables such as those used in radio and telephone communications and in high-voltage transmission lines.

The electrical properties of geologic materials, especially soils, are very complicated at first glance. But over the frequency range we are interested in (10^8 to 10^9 Hz), the dielectric constant is primarily sensitive to changes in water content and has a relatively weak sensitivity to changes in soil type and density, temperature, and soluble salt content. TDR has shown excellent potential for carrying out useful electrical property measurements of geologic materials.

The TDR equipment is coupled to the geologic medium by a transmission line. A transverse electromagnetic (TEM) wave propagates along the transmission line in the dielectric material between and around the conductors, which act as guides for the waves. The propagation velocity and attenuation characteristics of the TDR signal in the transmission line are dependent on the electrical properties of the material in the transmission line.

Methods and Equipment

Experiments were first conducted in the laboratory to determine how the TDR signal pulse rise time response varied as the conductor spacing of the transmission line increased. Next, experiments were carried out to determine the physical size of the anomaly in the transmission line that could be detected by the TDR system as the conductor spacing was varied. Finally, tests were con-

ducted to determine the change of TDR response as the position of the anomaly was moved in the transmission line.

The equipment consisted of a TDR unit, an X-Y plotter, a parallel transmission line, an electrical connector to connect the TDR unit to the transmission line, and boxes filled with dry sand to simulate an anomaly. The TDR instrument used for these experiments was a Tektronics Model 1502 cable tester, a portable field unit with pulser, receiver, and display units in one package. The transmission line was a parallel wire transmission line. The two conductors of the line were made of 6-m-long aluminum tubes with a 5-cm outside diameter. These tubes were supported on a wooden frame so that the spacings between the tubes could be varied (10, 20, 40, 60, 80, 100, 120, 150, and 200 cm). A special electrical connector was designed and built to connect the TDR unit to the conductors at the different spacings. The connector consisted of a 50- to 200-ohm Balun transformer and two sheets of metal to connect the transformer to the aluminum tubes. Figure 3 is a schematic diagram of the TDR unit, the connector, and the parallel transmission line.

The anomalies that might be found in the field were simulated in the laboratory by boxes (15 cm^3) filled with dry sand and placed side by side and on top of each other when the size of the overall anomaly needed to be increased. The sand had a dielectric constant of 3.5. The boxes of sand were the equivalent of a water-saturated soil in a soil host material with a volumetric water content of about 20 percent. The electrical losses in the air and sand were negligible to the TDR pulse used. This arrangement provided a satisfactory initial model of an actual field setup under a waste impoundment liner.

Results and Conclusions

Findings of the project were as follows:

1. The TDR pulse signal rise time increases with the spacing between the conductors of a transmission line. The attenuation to the higher frequencies in the pulse increases with the frequency, and thus the TDR system resolution decreases as the spacing increases. In other words, the size of the anomaly in the transmission line must increase with the transmission line spacing to produce the same TDR-reflected signal amplitude.
2. The TDR signal amplitude does not vary when the TDR signal travel time in the anomaly is less than or equal to the total travel time necessary for the signal to propagate through the anomaly. As the electrical length of the anomaly decreases below the pulse travel time in the anomaly, the signal amplitude decreases.
3. The TDR signal amplitude varies slightly with the height of the anomaly (i.e., the dimension whose axis is perpendicular to the plane of the conductors in the transmission line varies as long as the height of the anomaly is at least three times greater than the diameter of the conductors).
4. The amplitude of the TDR signal is greatest when the anomaly touches both conductors of the transmission line. The signal amplitude decreases significantly as the width of the anomaly decreases relative to the spacing of the conductors. The signal amplitude decreases less rapidly if the anomaly is in contact with either of the conductors.

These findings lead to the conclusion that a cube-shaped anomaly whose sides are equal to at least half the spacing between the conductors will have a TDR signal amplitude of about one-fifth the maximum signal amplitude that would occur if the transmission line penetrated an anomaly that was very large relative to the spacing of the transmission line conductors. This generalization will be affected by a number of factors not included in the studies. The electrical loss properties of the materials likely to be found in the field will reduce the TDR signal amplitude. Thus the size of the anomaly will have to be increased to increase the reflected TDR signal amplitude. The electrical property contrast of the leachate-saturated soil relative to that of the host soil under the waste impoundment may not be as great as the electrical property contrast used in the model. Thus the reflected signal amplitude may not be as large in the waste site environment.

The model used in these experiments only tested the TDR response in transmission lines whose maximum spacing between the conductors was 2 m. Larger spacings between the conductors are practical using the same TDR unit, but experiments to determine the maximum spacing of the conductors still need to be carried out.

The TDR technique appears to be a practical method for detecting and determining the position and extent of a leachate under a small waste impoundment liner. A cube-shaped leak with dimensions on the order of one-half the space between the conductors of the transmission line is about the minimum practical size that can be detected using the TDR technique.

Recommendations

The following recommendations should be followed before a TDR system is placed in the field under a waste impoundment liner:

1. Carry out experiments using simulated leaks over transmission lines at different conductor spacings placed in a sandy soil about 1 m thick.
2. Based on the results of the above experiments, design a series of transmission lines with different spacings between the conductors and placed in a sandy soil under a lined pond filled with water. Vary the lengths of the transmission lines up to about 30 m. Use controlled leaks in the liner to test the ability of the TDR system to detect leaks of different sizes and positions around the transmission lines.
3. Carry out a TDR system field design configuration and cost analysis after the above tests have been made.
4. Design TDR equipment specifically for detecting leaks at actual waste impoundment sites. Possibly a higher-power pulse of longer duration would make the TDR system more economical for detecting leaks at large waste impoundment sites.
5. Determine the best materials for transmission line conductors to minimize corrosion in a waste dump environment.
6. Determine the high-frequency (1 to 1000 MHz) electrical properties of some leachate-saturated soils and of soils typically found under waste sites.

The results of the recommended research will help define the usefulness of the TDR technique for detecting leaks and for determining the extent of leaks from a waste impoundment liner. Such studies will also aid in the design of a practical TDR system for monitoring leaks from waste dump sites.

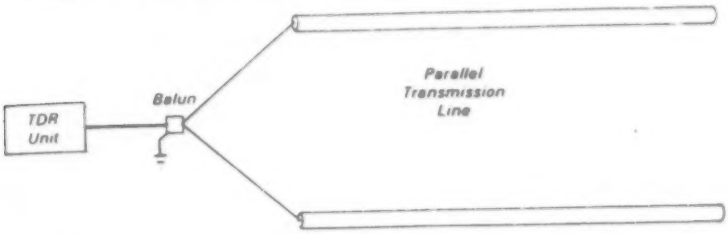

Figure 3. Schematic diagram of the TDR system

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CHAPTER 59

WATER IMPOUNDMENTS AND EVAPORATION PONDS

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INTRODUCTION AND FRAME OF REFERENCE

Impoundments or ponds are installed to store potable water as well as process water, e.g., pregnant solutions and barren solutions for recycle and as evaporation ponds to dispose of excess or contaminated water. Water impoundments can also be used to "age" recycled tailings water before it returns to the mill.

In very cold climates with snow and ice cover during winter, an interesting problem arises in controlling water inventories in ponds below the ice cover since the surface level is not visible from above. A public outcry arose when treated effluent from a pond at KEY LAKE MINING overflowed the impoundment under an ice cap about a year ago in Saskatchewan. Where the pond is covered in ice or snow in winter and where it contains solution that is not designed for discharge as an effluent, it is important to install a

remote level sensor in the pond so that inadvertent overflow can be avoided. Details of how this is now done at KEY LAKE can be requested from:

KEY LAKE MINING CORP.
229 4th Avenue South
Saskatoon, Saskatchewan
Canada 57K 4K3
(306) 665-7000
Bernard Rosner
Engineering Manager

When water is scarce or expensive, it becomes necessary to conserve it. Interestingly, at RÖSSING URANIUM LTD. in South West Africa/Namibia, the tailings pond itself is used to store process water for recycling. In the exceptionally hot, dry, and windy climate in the Namib Desert, RÖSSING water losses through evaporation are enormous. As part of their water conservation drive, many kinds of liquid films and other measures have been tested as a way to reduce evaporation from the tailings pond. After testing various alternatives to reduce evaporation, it was concluded that the most effective and only practical way is to reduce the surface area of the pond in the tailings impoundment. This was done by withdrawing water from the tailings pond and letting the waterline recede. Not only are evaporation losses cut in this way but undoubtably, by reducing the hydrostatic head on the porous pond, rate of seepage will have declined too.

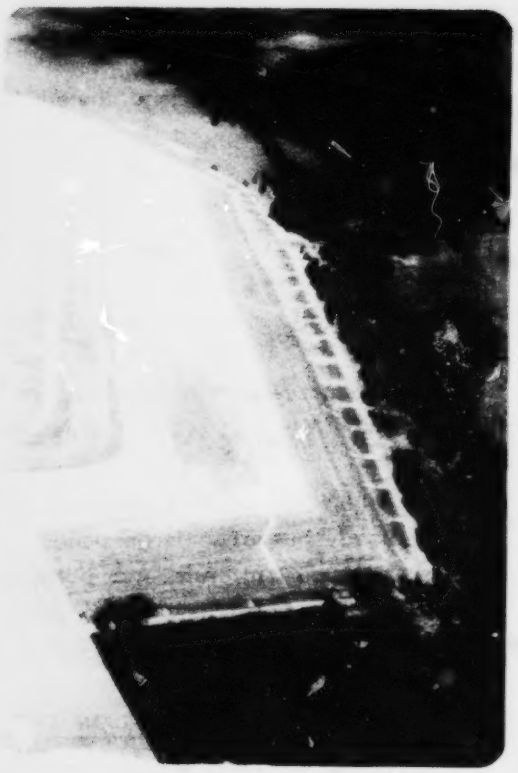
COTTER CORPORATION at Canon City has constructed a large lined tailings pond which also serves as an evaporation pond. In their case, no tailings water is recycled to the mill.

The above are two cases where different types of tailings impoundments are used as evaporation ponds or for water storage. Quite often, however, separate impoundments are installed as can be observed in the photograph of a modern Witwatersrand tailings impoundment where runoff and seepage is collected and evaporated in the ponds along their base.

Seepage from ponds can be considerable and, increasingly, impermeable linings are required to reduce water losses or to prevent environmental damage. With the recently increased awareness and emerging regulatory requirement to protect ground water quality, impermeable lining of water impoundments will increasingly be installed to meet permit requirements. Linings used include clay, bentonite stabilized soil, or plastic membranes.

Care should be taken in selection the type and grade of liner material as well as in applying the membrane, and attention should also be given to controlling the quality of the membrane delivered to the site to be sure that it is the same as that selected.

RUNOFF IMPOUNDMENTS ALONGSIDE WITWATERSRAND TAILINGS



CONCLUSIONS ABOUT POND LININGS

1) There have been many failures in synthetic impoundment linings. These have been due to improper selection of materials, improper installation, or improperly designed earth work support base for the membrane. To be able to function, the complete lining and support system must be correctly selected, designed, and installed.

2) Liner and lining installation suppliers are the major source of information on linings. They can recount prolific cases where their competitors' product failed, and their own is always the best and failure-proof.

3) Adequate means of detecting leaks early can be installed or used to survey impoundments early to find and repair leaks before serious damage is done.

4) When properly selected and installed, plastic liners can do a good job in storing liquids.

5) Investigation and discussion lead to the conclusion that there may be no such thing as a perfect lining. No matter how good the quality control during its application when hydrostatic pressure is applied, plastic liners invariably leak to some extent. The key is to keeping the extent of the leaks "negligible."

6) If seepage prevention is to be prevented, it is wise to apply the plastic membrane over a substrate that is itself impermeable, e.g., bentonite stabilized soil.

7) Small ponds, say 2,000-3,000 m^2 (20,000-30,000 ft^2) in surface area can be readily easily lined, but when large ponds of tens of acres and up are lined, wave action plays an important role and berm design must take this into account to avoid problems.

IMPACT OF EVAPORATION PONDS ON THE ENVIRONMENT

Evaporation ponds are used to dispose of excess contaminated or high TDS solutions from mine-mill operations. For example, where bleed streams from uranium leaching operations cannot be discharged because of permit restrictions and where metallurgical recovery problems or corrosion problems would result if a salt bleed is not achieved, the logical alternative is to dispose of it by evaporation in a shallow impermeable pond. In the U.S.A., usually these ponds are lined with plastic membranes. Many of the Witwatersrand gold milling operations collect runoff water from their tailings impoundments and dispose of it in evaporation ponds at the base of the impoundments.

As water evaporates from these ponds, the remaining solution of course becomes correspondingly more concentrated and the greater the need is to keep it contained. There are two potential problems with evaporation ponds. Firstly, they can spring a leak, the consequences of which are more serious the more concentrated their content has become. The second problem is how to dispose of the salts that accumulate and how to prepare an evaporation pond for abandonment, say at the closing of a milling operation. Covering over an evaporation pond and revegetation of the site, possibly after applying an impermeable cap to prevent water from seeping in, may be satisfactory for awhile, but will it be so after several decades or after a century or two?

If an abandoned evaporation pond is not capped with an impermeable liner but is merely covered over with soil, the real possibility exists for seepage from the surface to become

perched on the top of the liner where the salt contents will redissolve and migrate upwards by capillary action to the surface where it would likely destroy vegetation, result in surface erosion, and contaminate surface runoff. Similarly, if the pond is constructed over a porous base, the question could be asked as to how long the membrane will remain intact before becoming ruptured through natural forces and allowing a now highly concentrated solution to seep to groundwater below.

In some parts of the world, the term "evaporation pond" may be loosely used as the rate at which water is lost from the pond seems sometimes to exceed the rate of evaporation which indicates possible solution losses through seepage. Some sites where the natural base material is already highly impermeable in any case are ideal for evaporation ponds.

When an evaporation pond is to be used, the ultimate disposition of the concentrated salts and final closure of the site should be carefully considered in advance, as well as the consequences of a leak developing.

LINING MATERIALS FOR PONDS AND WATER IMPOUNDMENTS

GIROUD and FROBEL (1984) reviewed geomembrane products providing some insight into what a geomembrane is. Also provided is a list of liner suppliers, fabricators, and installers. Finally, a report by GUNDLE LINING SYSTEMS, INC. provides further insight into liner materials. The list of lining materials suitable for evaporation ponds is growing steadily. Lining materials may consist of:

- Plastic Geomembranes
- Fibre Reinforced Polymer Membranes
- Clay Linings with Membranes
- Clay Linings
- Bentonite Stabilized Soil
- Sprayon Polymer Liners

HYDROSEAL-PROCESSED BENTONITE

In addition to the liner materials and suppliers listed below, mention should be made of an activated bentonite lining material that has become popular in South Africa recently. The vendors claim to have installed 2 million m^3 (20 million ft^2) of pond linings over just a few years of operation. The vendor also applies the material and installs the lining:

AQUASAVE PTY LTD.
Post Office Box 68288
Bryanston 2017
(011) 789-1206
Chris Lee

The bentonite is spread out manually at 10 Kg/m². The hydroseal-processed bentonite is usually not mixed into the soil but is spread in an undiluted layer. The bentonite costs R290/t, and the complete lining can be installed for R5.00 (U.S. $2.50/m²) of which R2.90 ($1.45/m²) is for the bentonite. This is claimed to be much less than the cost of synthetic membranes.

Two laborers can spread 5,000 m³/d. The bentonite layer swells to about 12 times its original volume. The lining has the advantage of being flexible and self-sealing.

In the U.S.A., bentonite for pond linings would be supplied by:

AMERICAN COLLOID COMPANY
5100 Suffield Court
Skokie, IL 60077
(312) 966-5720
Telex: 724-413
Brigitte Mattison

AMERICAN COLLOID COMPANY suggests the application of their product as a soil-bentonite mixture, which is quite different to the way that it is applied by AQUASAVE. AQUASAVE claims that sand-bentonite mixtures work particularly well only if the soil consists of very clean sand.

SELECTION AND INSTALLATION OF LININGS

RANDOL INTERNATIONAL attended a geomembrane and geotextile conference and visited several mine-mill complexes where membrane linings are used. It was found that of the small number of membrane users in the mining industry for water impoundments or evaporation ponds that were visited, several had experienced problems.

It is essential that lining applications be regarded as lining systems consisting of the earth or clay base, the lining material with appropriate seams, and the way it is anchored into the ground around the pond, etc.

Membrane linings are routinely used on heap leaching operations as both pregnant solution and barren solution ponds. It is critical that appropriate membrane material be selected for the parts that are exposed to sunlight. For example, PVC linings work well as long as they are kept underwater. If they are exposed to the sun and air, PVC deteriorates very fast, becomming brittle. For this reason, Hypalon or high density Polyethylene lining are usually installed for the sides and exposed parts of impoundments.

In heap leaching applications, linings of the usually small ponds do not appear to present problems, except when occasionally an engineer drives across the membrane on an

Volclay
Landfill Sealants provide effective environmental protection from leachate pollution

American Colloid Company has been in the business of producing bentonite clay sealants since 1924. The company is the world's largest privately-owned bentonite mining company and operates processing plants in five states and several overseas locations. It has supplied bentonite sealant materials for almost one thousand landfill, lagoon and tank farm installations throughout the world.

Through its years of service to municipalities and other waste-containment operations, American Colloid has developed sealants specifically designed to be resistant to highly contaminated leachates commonly found in community waste or industrial landfills. Natural bentonite clays completely lose their sealing properties in the presence of landfill leachate through various contamination mechanisms. There are now four major types of Volclay landfill sealants:

SG-40 for capping landfills

SLS-71 for capping and lining municipal waste landfills

SLS-70 for industrial and hazardous waste landfills

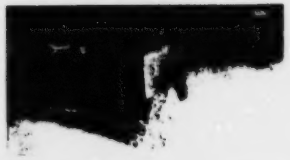
SS-100 for extremely hazardous industrial landfills or lagoons

3581

What is Volclay?

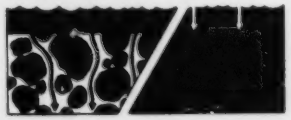
Volclay is produced from a special type of high swelling sodium montmorillonite (sodium bentonite). It has a unique molecular structure that captures water molecules, with the result that the bentonite expands up to 13 times its dry volume when wetted. The molecular structure is similar in several respects to ordinary clay, but the presence of sodium ions accounts for its ability to swell to a much greater volume than natural clay or other types of bentonite when saturated with water.

These unique swelling properties play a critical role in Volclay's effectiveness as a soil sealant.



How Volclay works

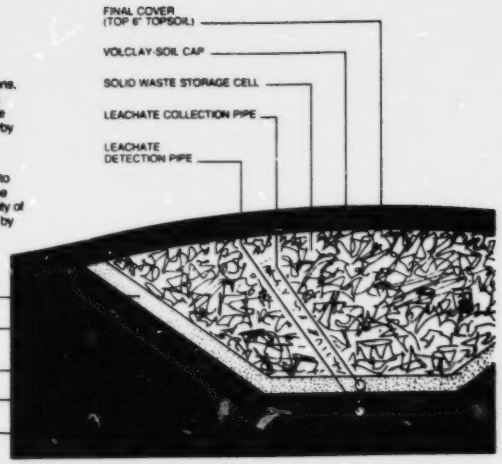
When a comparatively small amount of Volclay is mixed with soil and wetted, the Volclay particles swell and fill the voids between the soil particles. This creates a barrier that effectively stops further seepage through the soil. The swollen Volclay becomes a tough, highly flexible mastic that naturally expands and moves to self-seal any cracks that develop in the supporting soil. Thus, earth settlement and small ground movements which may damage membrane liners, native clay liners, or rigid liner systems, will not damage a Volclay-soil liner.



Volclay liner and cap for new landfills

With today's stringent construction regulations, both municipal and industrial waste landfills must be properly sealed to prevent leachate pollution of ground water supplies and nearby streams and rivers.

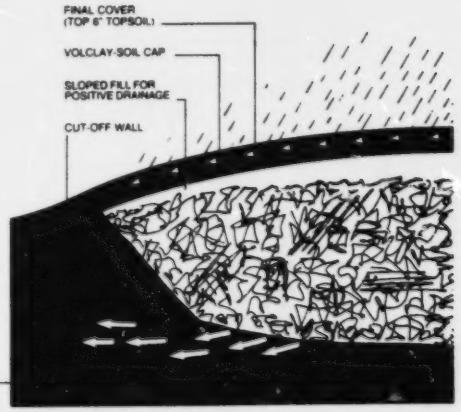
American Colloid's Volclay landfill sealants provide a positive and economical method to prevent leachate seepage from landfills. The method illustrated below provides the security of complete encapsulation of waste materials by Volclay barriers.

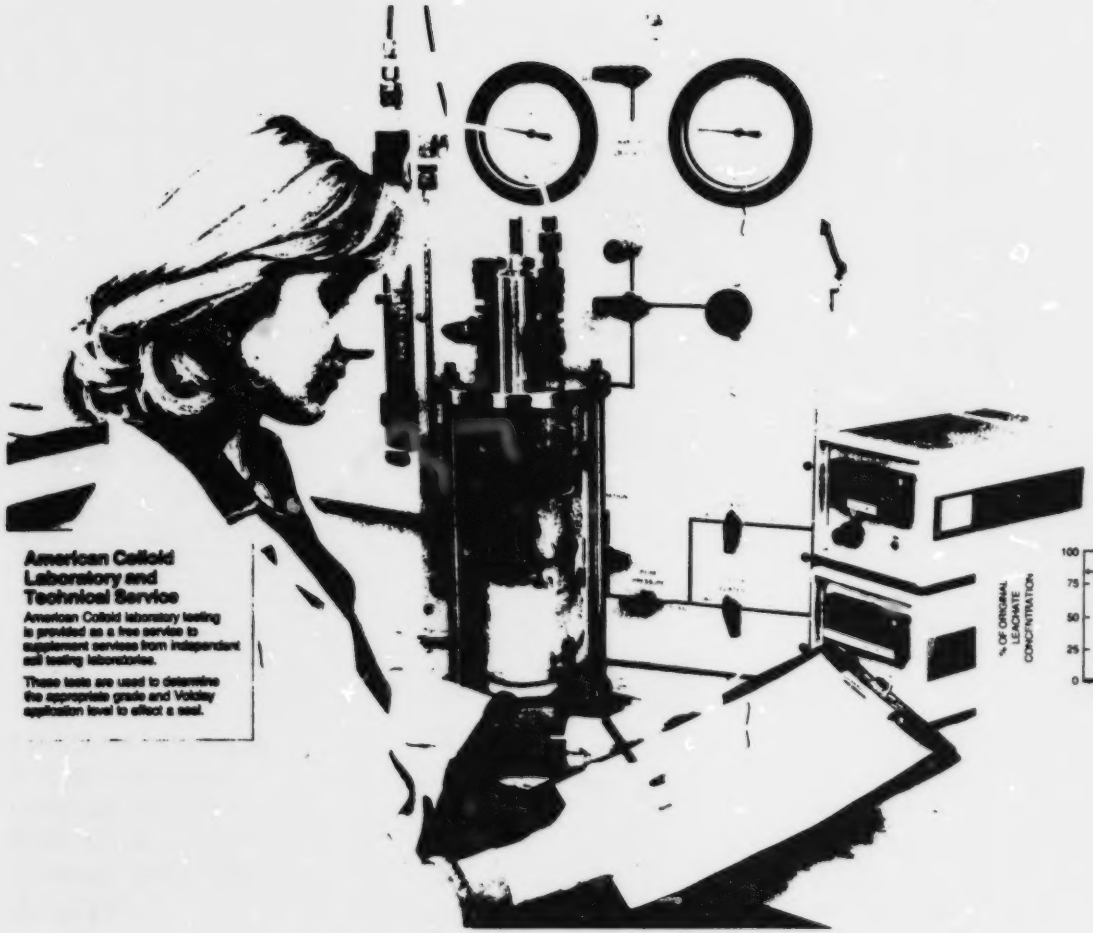


Volclay slurry wall and cap for existing landfills

Many existing landfills are being closed down every year because of leachate pollution of ground water supplies, streams and rivers. However, merely closing them down does not control the long-term problem of leachate spreading through permeable soil and rock strata adjacent to such landfills.

Encapsulation, using the double barrier approach illustrated below, provides the answer to leachate migration. A slurry cut-off wall, constructed with contaminant-resistant soil sealants from American Colloid, prevents leachate migration by forming an impervious barrier around the source of pollution. The Volclay-soil cap prevents rainwater percolation.





American Colloid Laboratory and Technical Service

American Colloid laboratory testing is provided as a free service to supplement services from independent soil testing laboratories.

These tests are used to determine the appropriate grade and Volclay application level to effect a seal.

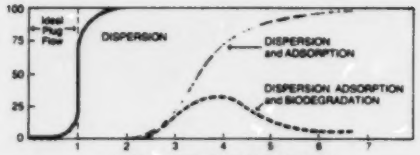
Volclay Product Compatibility Testing

American Colloid Company's contaminant-resistant products (SLS-70, SLS-71 and Saline Seal 100) have been extensively tested at American Colloid's laboratory and at independent laboratories against numerous organic and inorganic leachates that are known to either stop or reverse the swelling of untreated bentonite. Compatibility testing has repeatedly shown that specially-treated contaminant-resistant Volclay products outperform other untreated bentonite products. In addition to laboratory testing, these contaminant-resistant products have been used in hundreds of different projects and applications throughout the world with excellent success.

Our on-going testing program has resulted in a broad data base from which product recommendations are made for landfill applications.

Pore Volume Displacement Method

The sealing efficiency of a contaminant-resistant Volclay product with a specific leachate is determined by means of a permeability test. To conduct a permeability test properly, sufficient quantity of a leachate must contact and pass through a Volclay-soil specimen in a permeter unit until such time that steady state permeability conditions exist. This generally requires two to six pore volume displacements, depending on the leachate constituents. Reliable testing for contaminant-resistance over the life of a project commonly requires upwards of 20 pore volume displacements.



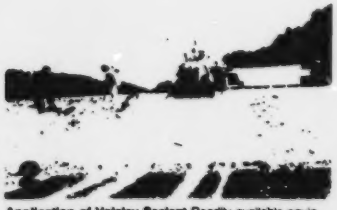
(Curve per Geraghty & Miller Groundwater Consultants)

The diagram above shows what typically occurs during the early stages of a permeability test prior to attaining steady state conditions. Accelerating the permeability test by means of unrealistic hydraulic gradients or unrealistic contaminant concentrations will not provide useful information about the long term effectiveness of such products in actual field conditions. Thus, permeameter test columns at American Colloid's laboratory are run at hydraulic gradients of 5 to 20, which is the range in which Darcy's Law is valid. In addition, contaminant-resistant Volclay products are exposed to actual leachate concentrations for whatever duration is necessary to achieve steady-state conditions.

Applying is easy, can be accomplished with readily-available mechanized equipment

Volclay mixed blanket application method

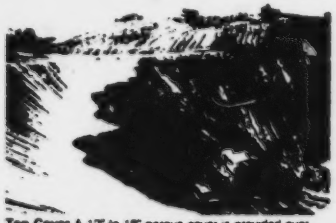
Soil Conditioning After finish grading has been achieved and excessively large rocks (larger than ⅓ the thickness of the Volclay-Soil liner) have been removed, a water truck is used to adjust the soil to optimum moisture content (8%-16% for most soils)



Application of Volclay Sealant Readily available equipment such as a bulk lime spreader or seed spreader may be used to apply the required amount of Volclay sealant. Manual application is also practical. Bags of Volclay weighing 100 lbs. are placed in a marked grid pattern on the surface of the area to be sealed. Bags are broken open and spread manually over the grid according to the specified application rate per square foot of area.

Blending Volclay with Soil A rotary tiller or roto tiller, with an adjustable depth control provides vigorous mixing which is necessary to achieve a homogeneous Volclay-soil blanket. An agricultural disc is sometimes used initially to loosen the soil prior to rototilling

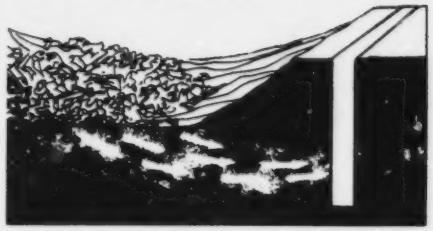
Compaction The Volclay-soil mixture is compacted to a minimum of 85% Modified Proctor with a wobble wheel or steel wheel vibratory roller. A sheepe foot roller should not be used.



Top Cover A 12" to 18" porous cover is provided over Volclay-soil bottom liners to facilitate drainage to collection pipes. An 18" layer of native soil is applied over a Volclay-soil landfill cap to provide a protective cover

An effective barrier to leachate pollution from existing landfills

Preventing leachate migration from existing landfills is possible with the slurry trenching construction technique and American Colloid's contaminant-resistant sealants. In the illustration, note that the trench is keyed into a natural impervious layer which prevents further migration of the leachate. The trench is composed of a well-graded backfill and contaminant resistant SLS-70 or Saline Seal 100



SPECIAL VOLCLAY FOR SLURRY TRENCHES

DESCRIPTION	TYPICAL MIX RATIO
A 90 barrel yield* 200 mesh bentonite	1 part Volclay to 15 parts water
A 125 barrel yield* bentonite	1 part Volclay to 22 parts water
A 70 barrel yield* Wyoming bentonite to be used specifically to resist contamination in excess of 100 000 PPM TDS	1 part Volclay to 12 parts water

*Based — API

Constructing the slurry trench

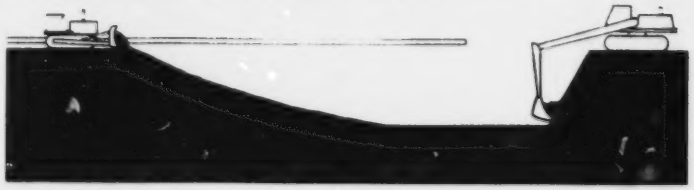
The first step in slurry trench construction is to excavate a trench from grade to approximately three feet into an aquaclude such as bed rock or an impervious clay strata, while keeping the trench filled with a Volclay-and-water slurry. In the illustration below, the hydraulic excavator has "keyed" the trench into an impervious clay layer under a full head of bentonite slurry

Because the Volclay bentonite slurry has a slightly higher specific gravity than water, it creates a positive hydrostatic head that stabilizes the sides of the trench to prevent collapse. The Volclay bentonite slurry also interacts with the sides of the trench to create a seal that tends to hold soil particles together. Because of this, it is possible to excavate a trench 3 feet wide and over 250 feet deep (although 20 to 50 feet is more common) with minimal danger of sidewall collapse.

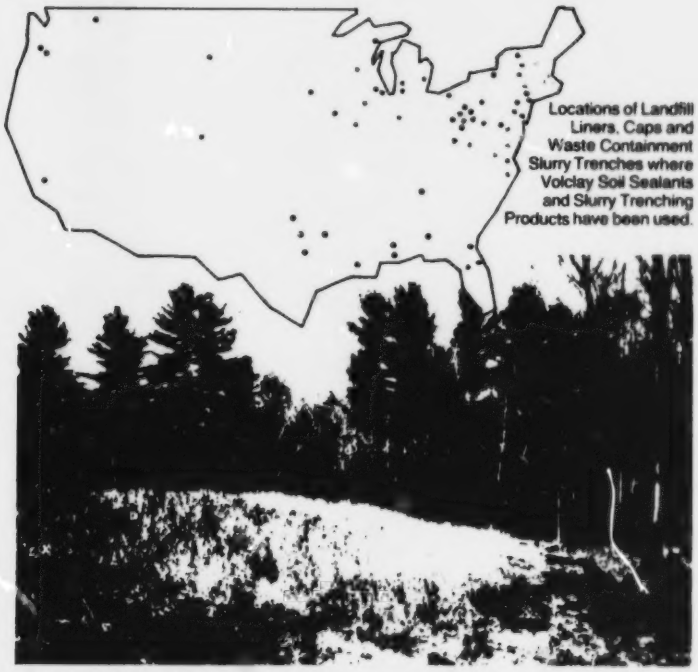
As trench excavation continues, additional slurry is added to compensate for each bucket of spoil removed.

After the trench has been keyed, the final step, of backfilling can begin. The backfill consists of additional Volclay and soil which have been mixed in the proper ratio to provide an impervious barrier. In the illustration, controlled back-filling has begun where the trench starts. The addition of backfill displaces spent slurry which is then pumped out and either returned to the trench or disposed of as excavation proceeds

Proper backfill is the key to long-term barrier effectiveness. American Colloid laboratory analysis can make an advance determination as to whether the spoil from the trench is suitable for backfill. If not, they will recommend a backfill, the right Volclay product, and the proper mix for an optimum barrier wall



Volclay Sealants are protecting communities all over the country from leachate pollution



This beautiful setting could be a park or just a green field. In actuality, it is a landfill of leather scrap over 30 feet deep. The fill is encapsulated by a Volclay liner and protected from rainwater intrusion by a Volclay Cap. Because the leather scrap produces a very springy fill, only Volclay with its flexible membrane and its ability to self-seal after flexure was able to meet the stringent requirements for this landfill.

Volclay also minimizes the escape of gases from the landfill and provides a beneficial substrate for grass-type foliage. It requires only annual mowing to inhibit the growth of woody plants whose roots might penetrate the Volclay membrane.

For additional information on product specifications, test data and test reports contact:

AMERICAN COLLOID COMPANY

Environmental Products Division

5100 Suffield Court • Skokie, Illinois 60077 • 312/966-5720

NOTICE: The information presented herein is believed to be correct. However, since it is provided without charge and without specific knowledge of the intended use or application of its products, American Colloid Company assumes no obligation or liability with respect to such use or application, and makes no warranty, either express or implied, as to the application or use of such product, or to the use or infringement of any patent or other proprietary rights of American Colloid Company or others with respect to such application or use.

Printed in U.S.A.

Form No. 5M684

Partial List of Volclay Installations

Municipal

City of Jacksonville, FL
Municipal/ Hazardous Landfill

Ellis & Gross
Kingland, GA
Municipal Waste Landfill

Lombardi & Son, Inc.
Fishkill, NY
Municipal Waste Landfill

City of Gainesville, TX
Municipal Waste Landfill

M & B Contracting
Pontiac, MI
Municipal Waste Landfill

Westmoreland County, VA
Municipal Waste Landfill

Oswego County, NY
Municipal Waste Landfill

Industrial

Suffolk Downs
Boston, MA
Hazardous Waste Landfill & Cap

Mill Services, Inc.
Bulger, PA
Industrial Waste Landfill

Speedway Landfill
Speedway, IN
Municipal/Industrial Waste Landfill

Attleboro Municipal Incinerator
Attleboro, MA
Incinerator Ash Landfill

Ciba Geigy Chemical Co.
Queensbury, NY
Hazardous Waste Landfill

WWTP Sludge Landfill
City of Wareham, MA
Waste Water Treatment Plant

Olin Chemical
Charlestown, TN
Industrial Waste Landfill

General Electric
Gainesville, FL
Industrial Waste Landfill

Caps

Schmul Park
Staten Island, NY
Landfill Cap

Sales Creek Drainage System
East Boston, MA
Landfill Cap

Veterans Avenue
Leachate Control Project
Staten Island, NY
Landfill Cap

Slurry Trench

Stroudsburg, PA
Saline Seal 100 Slurry Trench
Coal Tar Containment

Nekoosa Paper, Inc.
Port Edwards, WI
Saline Seal 100 Slurry Trench

Evansburg, PA
Saline Seal 100 Slurry Trench
Acid Mine Waste Containment

inspection, forgetting that his pickup truck is fitted with studded snow tires. Often these ponds are smaller than one acre, which seem to be easier to design.

QUIVIRA MINING COMPANY

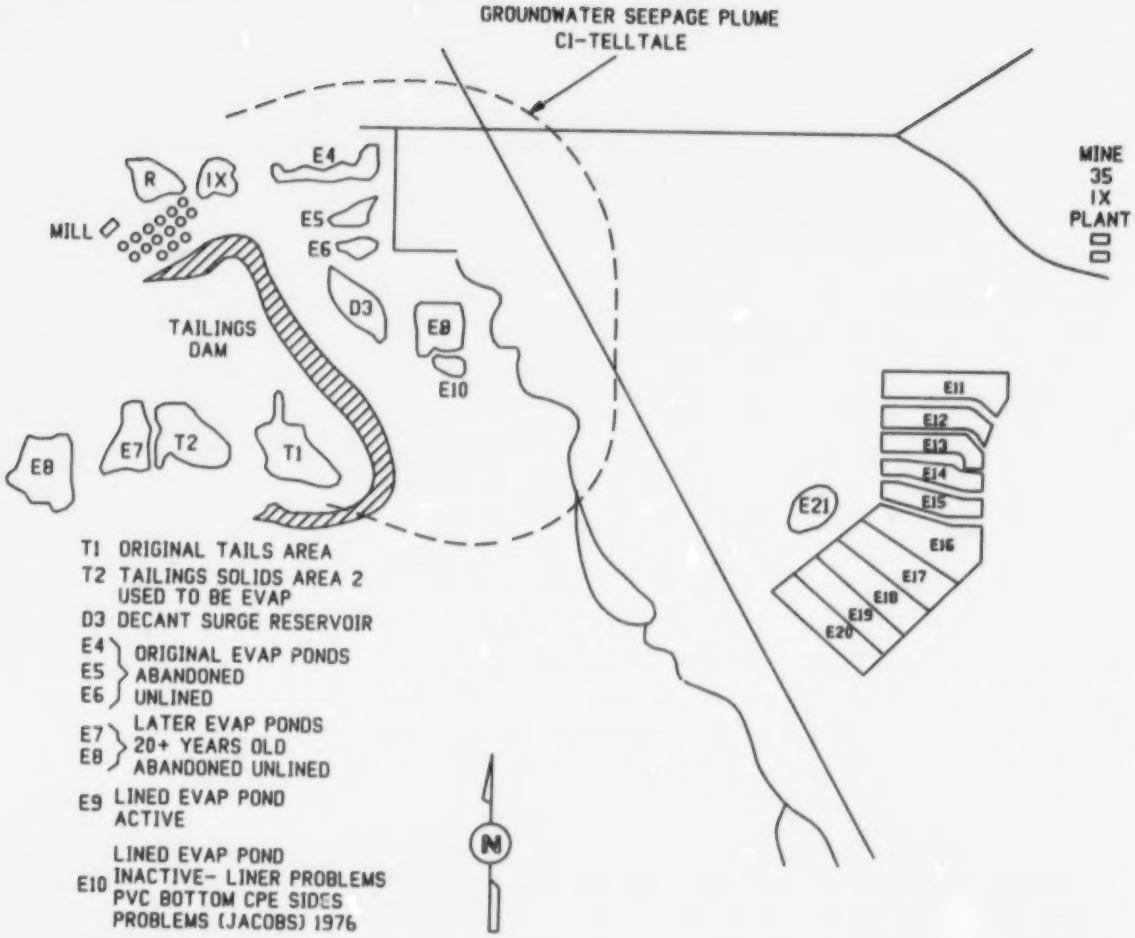
QUIVIRA MINING COMPANY disposes of a high TDS bleed from their acid leach uranium circuit. The bleed would consist mainly of raffinate at a very low pH with a high TDS level, including sulfate and chloride ions.

QUIVIRA MINING COMPANY is not the only uranium milling company in New Mexico that experienced similar lining problems in their evaporation ponds. Similar problems were reputedly experienced by municipalities until more was learned about building large impoundments. The experiences of QUIVIRA MINING CO. are worth recounting as they provide an insight into several of the pitfalls which an operator is likely to encounter which are not obvious in advance, yet can render ponds unworkable or result in the need for major repairs.

Many years ago, before the U.S.A. became "ground water quality conscious," QUIVIRA used to discharge their bleed solutions to three unlined ponds (E4, E5, and E6 in the diagram). These were unlined and resulted in seepage losses. Later, ground water monitoring defined a seepage plume radiating out from the tailings pond and indicated by chloride levels which would have originated in tailings solution or seepage from ponds E4, E5, and E6. It became clear that evaporation ponds would have to be lined.

QUIVIRA next installed a lined pond (No. 8) at the toe of the tailings dam. PVC lining was for the floor and chlorinated polyethylene (CPE) for the sides. When bleed solution flowed into this pond, an unexpected problem arose. Large gas bubbles formed under the membrane forcing it to "float" to the pond surface in places in such a way that the gas could not be removed. The gas was found to be CO_2 evolving from a reaction between acid seepage from the dam and carbonates in the alluvia beneath the pond. At the time, it was thought that the CO_2 was generated by the acid bleed solution which had been discharged to the pond before the lining was installed. Several "burpvalves" were installed by the WATERSAVER COMPANY as a means to get rid of the gas, but these failed to solve the problem.

A soil covering was applied to try and weigh the liner down, but this did not work either. A switchblade artist could have released the gas, but this would have left a leak. Eventually, Pond E8 was abandoned. Inspection today shows that where the PVC floor lining is covered by sediment, it appears to still be plastic and "in good shape." However, where exposed to the sun and heat, plasticiser has evaporated, and the PVC has decrepitated.



T1 ORIGINAL TAILS AREA

T2 TAILINGS SOLIDS AREA 2
USED TO BE EVAP

D3 DECANT SURGE RESERVOIR

E4, E5, E6 — ORIGINAL EVAP PONDS
ABANDONED
UNLINED

E7, E8 — LATER EVAP PONDS
20+ YEARS OLD
ABANDONED UNLINED

E9 LINED EVAP POND
ACTIVE

E10 LINED EVAP POND
INACTIVE- LINER PROBLEMS
PVC BOTTOM CPE SIDES
PROBLEMS (JACOBS) 1976

E11 ↓ E15 — LINED EVAP PONDS
1977,1978
PVC AND CPE SIDES
HEAVER GUAGE WATERSAVER

E16 ↓ E21 — LINED EVAP PONDS
1979,1980
PVC AND HYPALON SIDES

R MINEWATER- PROCESSWATER RESERVOIR
ALSO USED FOR FIRE PROTECTION

35 SETTLING $BaSO_4$ PONDS

Pond 10 was designed and installed by JACOBS ENGINEERING in 1976, also at the toe of the dam. Even though no effluent had been discharged to this pond before the lining was installed, the same gas bubbles plagued this pond until it too had to be abandoned. It was then established that the gas was CO_2 generated by a reaction between the carbonate alluvia and seepage from the main tailings dam a couple of hundred yards away.

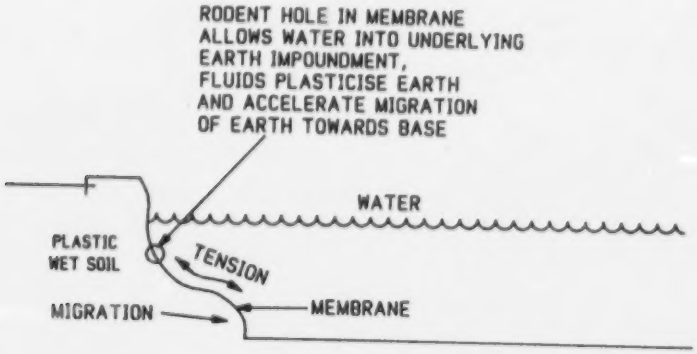
Ponds 11-15 were installed also with PVC floors and 20 mil. CPE on the sloping walls in 1977-1978, again by JACOBS ENGINEERING, with membranes supplied by PANASALL. This time, the ponds were located far enough away from the tailings pond to avoid gas bubbles. The membrane panels were installed from rolls with their seams parallel with the long sides of ponds. The walls were sloped at a gradient of 2.5:1 against sandy material that had been banked up. These ponds are large. The five ponds total 110 acres and cost $2 million in 1978.

Several problems have been experienced:

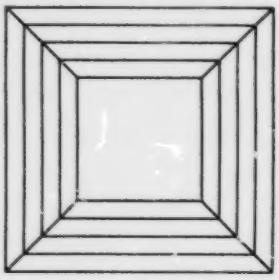
- The steep sides are vulnerable to wave action. Slope stability of the earth walls was inadequate, and the soil support beneath the membrane sloughed inward putting the liner under tension.

- The membrane panels were factory joined with seams parallel to the wall of the dam. These seams have failed in places due to the tension from the sloughed banks.

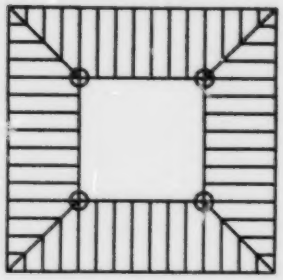
- Rodents have tunnelled to the membrane from below and gnawed holes through the plastic. The holes allow water to reach the underside of the membrane, allowing the earthen wall to become wet and plastic.



EXISTING DESIGN



HINDSIGHT RECOMMENDATION



Engineers on the site find that the 2.5:1 slope of the embankments combined with wave action has been the main cause of liner failure. The failures were exaggerated by improper panel orientation, rodent holes, membrane embrittlement, and seam failure on the 20 mil. CPE membranes used for the sides. The basic design of these ponds appears to be failure prone regardless of the membrane type selected.

Ponds 16-21

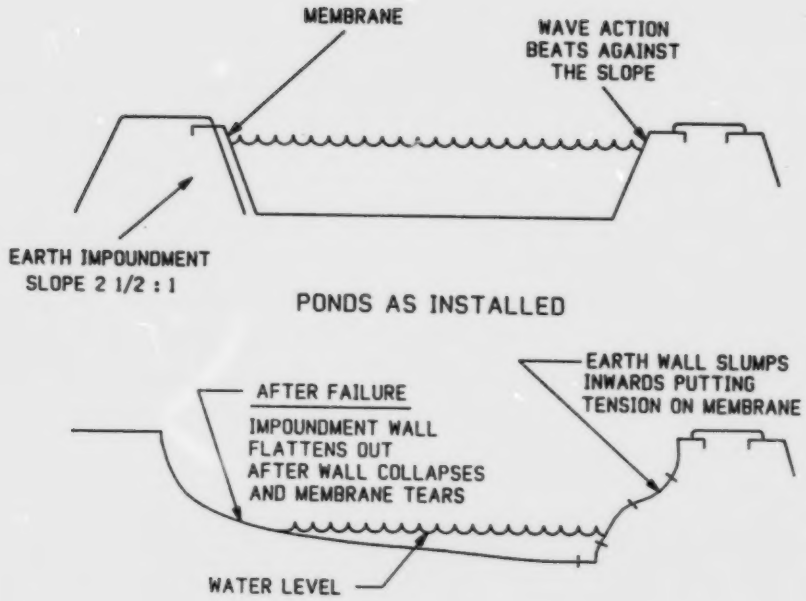
Ponds 16-21 were designed and installed by KERR McGEE CORP. along the lines of Ponds 11-15. These ponds, covering 160 acres, were installed in 1979-80 at a cost of $3.2 million. These ponds also have PVC floor panels but with hypalon sides. The basic configuration of the ponds is similar to that of the earlier ponds installed by JACOBS ENGINEERING with 2.5:1 slopes.

Once again, wave action against the unstable slopes of the earth pond walls has caused the wall material to slump behind the hypalon membranes. This has caused tension in the membrane and has resulted in failure. Again, the membrane panels are oriented parallel to the walls making them more susceptible to seam failure than if the panels were oriented across the slope.

Again, rodents have gnawed holes in the membranes on the exposed sides, allowing moisture to get behind them which, in conjunction with wave action, fluidizes the supporting pond walls.

MEMBRANE REPAIR

Membrane damage, apart from the rodent holes which are easily patched, usually takes the form of seam failure where the earth embankment walls have slumped and put stress across the seam.



The cost of retro-changing the slope profile of the impoundment walls would be exorbitant. To date, the repairs that have been made involve replacement of parts of the membrane panels. Several alternatives have been tested:

1. CHEVRON industrial membrane (CIM) painted over fiberglass reinforcement to make a new membrane to span the rips in the hypalon liner has been applied on the side of pond No. 16.

   Five gallons of CIM were required to cover an area 15' long x 2' wide at a cost of $15/gallon plus the fiberglass. Roller application of CIM was found to be messy and time consuming, although QUIVIRA MINING described CIM as a "very good product."

2. Hypalon patches on Hypalon. These proved difficult to glue.

3. CPE patches adhered to hypalon using STAFF INDUSTRIES' CC801 adhesive works very well. Expansion flaps are left in the inserted CPE panels. Liberal amounts of adhesive are applied to both membrane surfaces before pressing the two together. The glue works best if applied in warm weather. It is supplied by:

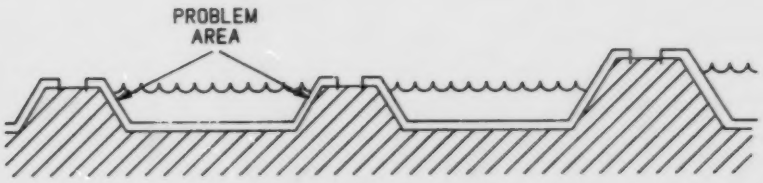
STAFF INDUSTRIES, INC.
240 Chene Street
Detroit, MI 48201

SUGGESTED ALTERNATIVE EVAPORATION POND DESIGN

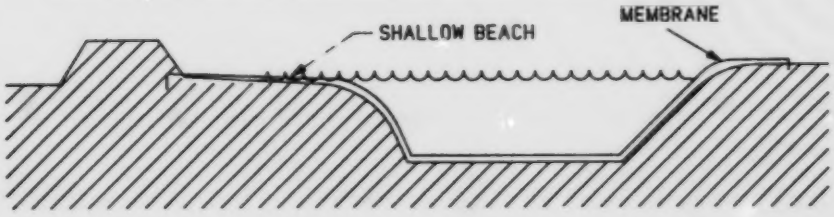
Since wave action appears to cause a steep wall to seek an equilibrium low angle beach, QUIVIRA MINING believes that the beaches of evaporation ponds should be constructed that way in the first place.

At QUIVIRA MINING, it has been observed that when the water level drops so that waves can run up a shallow beach, then there are no slopes to become unstable. The shallow beach areas also seem to become protected by a layer of silt. In order to get the volume required in the ponds, it is necessary to have an adequate depth. To achieve this, an "inverted tophat" profile design has been suggested. Such a design would require more real estate but, hopefully, would avoid the expensive maintenance and potential for leaks. The profile for this design is illustrated below.

OLD "FARM-TYPE" POND PROFILE



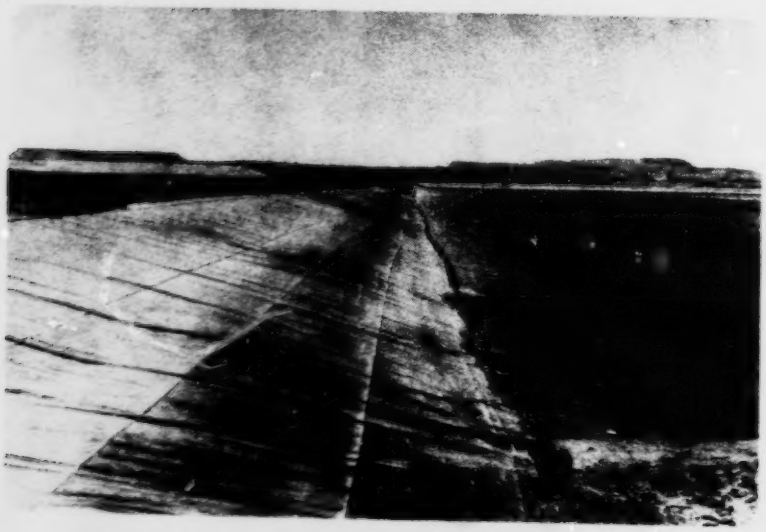
PROPOSED IMPROVED "INVERTED TOP HAT" PROFILE



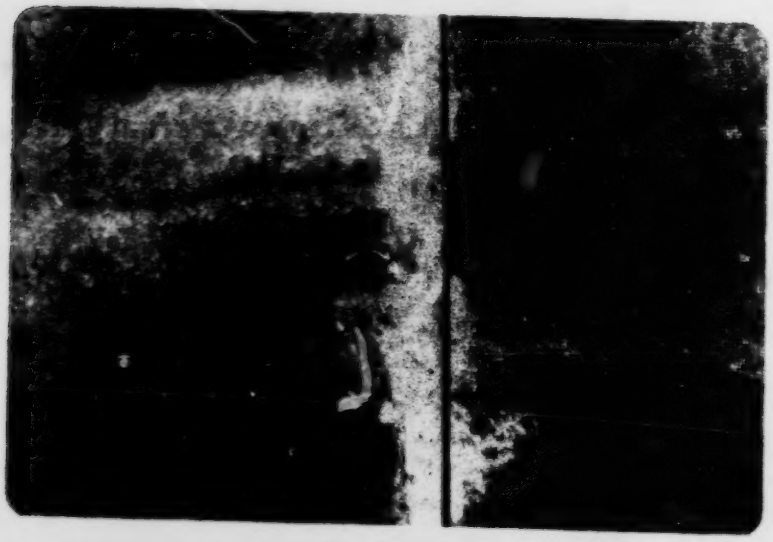
QUIVIRA MINING COMPANY was one of the pioneers in applying lined evaporation ponds, and they have considerable experience with pitfalls and problems in this area. A QUIVIRA engineer who has been directly involved in solving these problems and who has also conceptualized improvements may now be available for consultation since QUIVIRA operations have shut down due to weak uranium prices:

QUIVIRA MINING COMPANY
Ambrosia Lake Operations
Post Office Box 218
Grants, NM 87020
(505) 287-8851
Ralph Yetter
Mill Engineer

RALPH YETTER
Home: (505) 287-2457



HYPALON SIDES 2.5:1 SLOPE EARTH SUPPORT

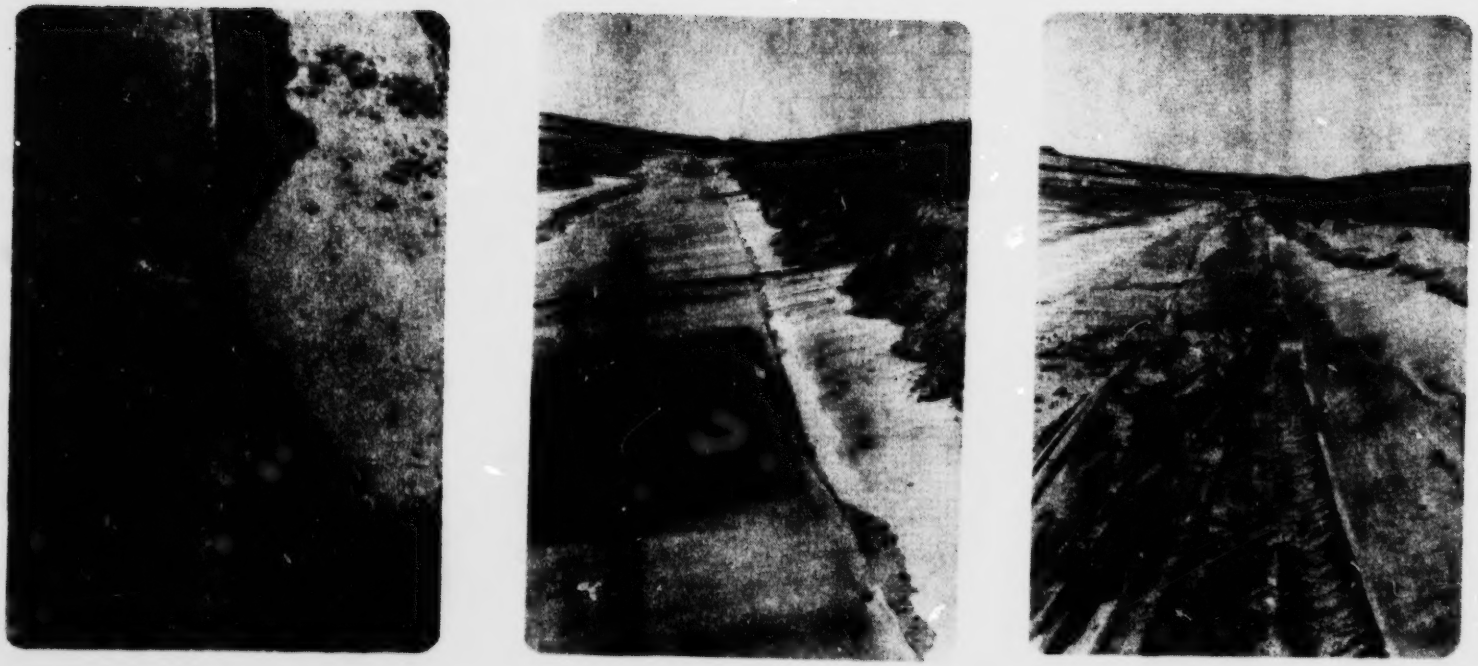


RODENT HOLE ALLOWS MOISTURE BEHIND MEMBRANE

UNSTABLE BANKS SLOUGH IN - TENSION ON LINER
(Note Gas Bubble in Pond)

ULTIMATE FAILURE DUE TO UNSTABLE STEEP BANKS

'INVERTED TOPHAT' PROFILE - STABLE BEACHES

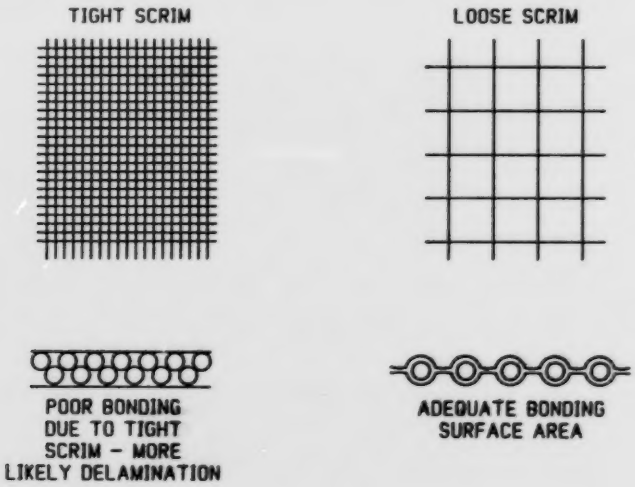


PROGRESSIVE SEAM FAILURE - TENSION CAUSED BY BANK SLOUGHING

KEY LAKE MINING

KEY LAKE MINING CORPORATION installed Hypalon linings in two reservoirs and five monitoring ponds at their Saskatchewan operation. These linings were installed some months in advance of the impoundments being filled. In this case, the linings failed even before the impoundments were used. Apparently, delamination of the membrane occurred.

Industry observers point out that if the individual strands of nylon reinforcement are too close together, i.e, if the scrim is too tight, then the bonding area in the spaces between fibers is too small for a good bond between the two layers of membrane. This observation seems plausible and is an aspect of thermobonded reinforced membranes that is worth being congnisant of.



Possibly more information would be available from:

KEY LAKE MINING
229 4th Avenue South
Saskatoon Saskatchewan
Canada S7K 4K3
(306) 665-7000

IN·SITE

Schlegel

A PUBLICATION FOR LINING SYSTEM USERS FROM SCHLEGEL LINING TECHNOLOGY. VOL. 1, 1984

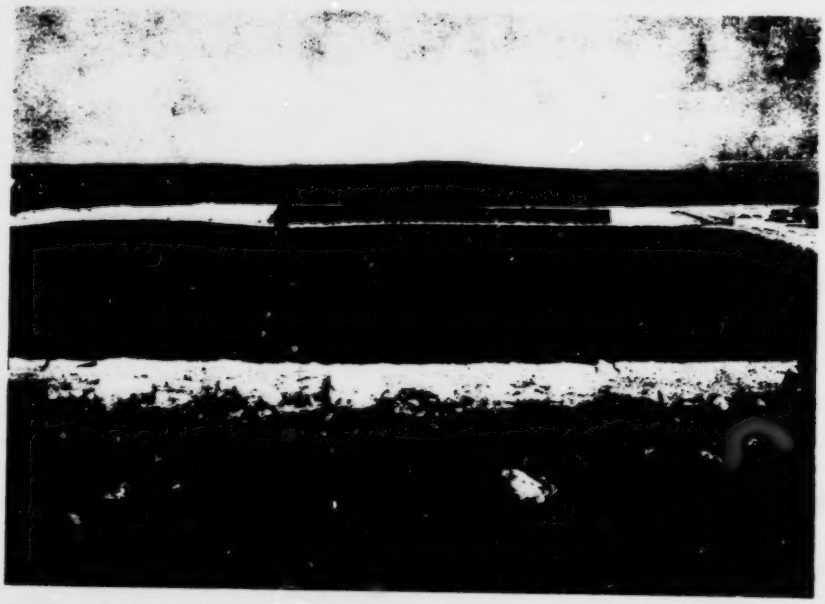
ARE GEOTEXTILES NECESSARY WITH THICK LINERS?

Puncture and Tear Resistance Not Necessarily Improved

POLLUTION ENGINEERING magazine in its November 1983 issue reported the results of a study made by a geotextile manufacturer in which various geomembranes were evaluated for their puncture and tear resistance, alone and then with the addition of three different grades of geotextile. A laboratory procedure was developed to simulate the effects of equipment moving over the geomembrane. According to the magazine article, "Although there were major differences in the resistance of various membranes, the geotextile fabric offered significant protection from aggregate cutting, puncture and abrasion . . . "[1]

Is a geotextile always necessary for cushioning and protection against puncture and tear? The incorporation of a geotextile with a geomembrane may serve many important purposes, including filtration, soil stability, overburden stabilization, drainage, gas ventilation and so forth. But an appropriately thick liner, which Schlegel Lining Technology defines as 2.0 mm (80 mil) or more, is usually thick enough to resist both high and low speed puncture and resultant tear without the expense of

Continued on page 2.



World's largest uranium mine lines reservoirs with 100 mil HDPE

In the summer of 1983, officials of Key Lake Mining Corporation (KLMC) were faced with the task of having to reline two reservoirs and five monitoring ponds. These are sited adjacent to the mill and tailings deposition area on surficial materials of glacial till, sand and gravel.

Key Lake Mine will eventually be the largest uranium mining/milling complex in the world. Ore is extracted from two discrete deposits by open pit mining methods. The mill is designed to process 780 tons of ore per day using conventional separation and extraction techniques.

The Key Lake Mine site is located 400 miles north of Saskatoon, in Saskatchewan, Canada. Severe winters, featuring temperatures as low as −40°F, are the norm.

The purpose of the reservoirs is to store contaminated water from the open pit and ore stockpile areas. The first reservoir, with a capacity of 240,000 m³, holds mine water and site and stockpile runoff. All runoff from the ore stockpiles, the open pits and the mill is considered contaminated, and is collected and stored in this reservoir. This reservoir also serves as a source of process water for the mill, as no free water is ordinarily introduced into the milling process, other than what is collected by dewatering. This reservoir was lined with 37,000 m² (400,000 ft²) of HDPE material.

The second reservoir holds supernatant water from the tailings area, as well as any other water requiring treatment before it is recycled or discharged to the environment through the monitoring ponds. The capacity of this reservoir is 120,000 m³; it was lined with 20,800 m² (224,000 ft²) of HDPE liner.

The five monitoring ponds with individual capacities of 5,000 m³, hold treated supernatant water from the process plant and are used to test treated water before it is

Continued on page 5.

resistance. As with puncture, however, the right side of the Table gives an evaluation of each system's tear resistance as a whole.

The thickness dependence of both puncture and tear resistance was found to be satisfactorily approximated by a linear function in both cases. The testing also showed that material selection has a significant effect in resisting these failure mechanisms, with HDPE giving the highest values among the materials tested.

Design Option: Dimension Liner Thickness For Earth Settlement

This discussion has not touched on the critical aspect of dimensioning liner thickness to accommodate the almost-inevitable subsoil settlement that can be expected under most impoundments. The puncture and tear resistance of a geomembrane in this situation must certainly be provided for, but far more importantly, the design engineer must ensure that the geomembrane is sufficiently strong and thick to withstand the increase in biaxial tensile loading beyond the design loads, and to alleviate localized stress points. Interestingly enough, a geotextile underlying a geomembrane in these circumstances may be a handicap. This subject will be discussed in the next issue of IN-SITE.

So should the design engineer incorporate a geotextile with a geomembrane for puncture and tear resistance? If a high strength, thick material like SCHLEGEL® sheet is specified, the use of a geotextile for this purpose alone is unnecssary.

References

1. Collins, Thomas G., "Geotextiles Plus Geomembranes Make Containment Better," *Pollution Engineering* (November, 1983), pgs. 33-35.
2. Collins, T. G. and Newkirk, D. D., "The Use of Geotextile Fabrics in Pond Construction Beneath an Impermeable Membrane (Geomembrane)," *Volume I: Proceedings of the Second International Conference on Geotextiles*, (August 1-6, 1982).
3. *Ibid.*

FAILED BRINE POND LINER REPLACED WITH SCHLEGEL® SHEET

When a brine pond liner at Warren Petroleum's Mont Belvieu, Texas, petroleum terminal failed, Schlegel Lining Technology was chosen to handle the relining work. Schlegel used 85,500 square meters of 2.5 mm (100 mil) SCHLEGEL sheet, a thick, high density polyethylene (HDPE) liner to complete the project.

Until recently it was common to line the ponds that hold the salt-saturated solution with 1.5m of clay or with thin (less than 2.0 mm/80 mil) membrane liners. But recent studies, showing that clay liners have a tendency to shrink and crack, allowing rapid transport of fluids through them, are moving the industry away from automatic reliance on clay. And the thin liners have shown a susceptibility to puncture and tear, both during their installation and during operation of a facility. Seepage of the saturated salt solution from a brine pond will not only kill vegetation, but can pollute groundwater as well.

The Texas Project.

At the Warren terminal, a variety of petroleum fractions are handled, stored and, ultimately, transported by tank, truck or pipeline to end users.

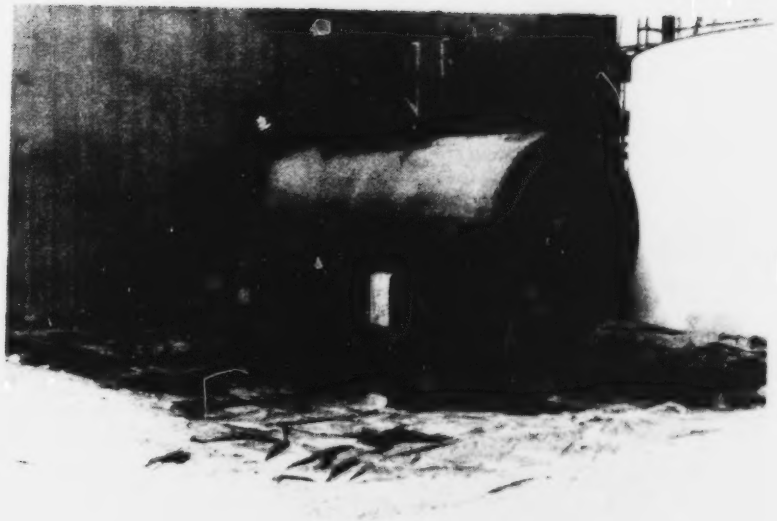
Salt dome formations are utilized for product storage. The construction of the underground storage caverns is accomplished by injecting fresh water under high pressure into the salt strata. The water dissolves the salt to create a cavity of the required capacity. When the cavern has been hollowed, it is pumped dry, filled with LPG and capped. The salt-laden brine is pumped into holding ponds; as product is required, the brine is forced back into the cavern to displace the petroleum.

SCHLEGEL sheet is highly resistant to both salts and hydrocarbons.

As is true in the United States, HDPE is being used with increasing frequency in Canada for similar applications. New LPG storage beds that underlie Alberta and other parts of western Canada, for example, are creating a demand for brine ponds that are more secure than those constructed in the past. Brine ponds lined with SCHLEGEL sheet are in use for Chevron Canada Resources Limited and Procor Limited, with other installations now in the planning stage.

DENISON MINES $BaRaSO_4$ SETTLING POND

LININGS MUST BE MOOSE- AND PEOPLE-PROOF



DENISON MINES LTD.

DENISON MINES LTD. at Elliot Lake uses a lined pond to settle out $BaRASO_4$ after treatment of tailings decant water before it is discharged to Quirke Lake. This impoundment with plastic dikes to provide a longer residence time is illustrated. Of interest are the moose prints shown on the membrane illustrating that liners should be able to withstand large animal hooves and also not be so slippery that once an animal gets to the water's edge, it cannot climb back up the embankment again.

Details of the DENISON settling pond liner would be available from:

DENISON MINES LTD.
Post Office Box B2600
Elliot Lake, Ontario
Canada P5A 2K2
(705) 848-9111
Dr. J. L. Chakravatti

Of interest here are the steep sides of the banks around the pond and the absence of any sign of the problems experienced by QUIVIRA MINING COMPANY with sloughing embankments and torn membranes. Possible reasons for that are firstly, the more sheltered setting, lower wind velocities (and hence less wave energy), more stable embankments, and absence of the type of rodents that burrow under membranes and gnaw holes though it. In addition, panel seams are down dip rather than along the strike of the walls.

IMPOUNDMENTS AROUND REAGENT TANKS

Increasingly, impoundments are required to be installed around hazardous reagent tanks in case there is a spill or in case the tank develops a leak or fails.

The illustration below shows a berm constructed around a sulfuric acid tank installed at a effluent treatment plant at a Canadian gold mine for pH adjustment. The impoundment has been lined (expensively) with hypalon. The second illustration shows the condition of this liner only 2 years after it was installed--the cement holding the hypalon membrane panels in place is already failing even though no acid has ever spilled.

This example is shown without even mentioning the installation. The important point to stress is that failure of membrane liner systems is all too frequent. In this case, the liner fails because a glue was used that is not compatable with the northern climate or was applied incorrectly. Great care must be taken in selecting both the liner material, the installer, and the impoundment designer. This is an area where failures seem to match successes in number.

LEAK DETECTION BENEATH LINED IMPOUNDMENTS

If a leak occurs in a lined impoundment, by the time it is picked up in the ground water monitoring program, so much water or solution will already have leaked that a major problem may have already been caused requiring an expensive ground water cleanup program.

Early leak detection devices would be a safeguard against this. Two such approaches were identified. One is the use of pressure-vacuum lysimeters that sample fluids in the vadose or unsaturated zone beneath an impoundment. This new system is described by BOND and ROUSE (1985), whose paper is inserted in Chapter 60 on monitoring.

The second is the following paper by Art Lange describing a geophysical leak detection method. More information can be obtained from him at:

ALBIREO LTD.
3798 Marshall Street
Wheat Ridge, CO 80033
(303) 431-0432
Art Lange

Albireo Ltd. is also developing a simple system for leak detection under lined ponds allowing periodic leak surveys. Preliminary tests have proven very effective and by the time this report is distributed, Albireo's patent protection should allow them to demonstrate the new method.

GEOMEMBRANE PRODUCTS

By

J. P. Giroud and R. K. Frobel

Geomembranes are very low permeability membrane liners and barriers used with any geotechnical engineering related material so as to control fluid migrations in a man-made project, structure or system. The term liner applies when a geomembrane is used as an interface or a surface revetment. The term barrier is usually reserved for the cases where the geomembrane is used inside an earth mass. Geomembrane is a generic term which has been proposed to replace many terms such as: synthetic membranes, polymeric membranes, plastic liners, flexible membrane liners, impermeable membranes and impervious sheets. These terms are not appropriate because: (i) synthetic, polymeric and plastic are too restrictive; (ii) geomembranes are not always used as liners; (iii) flexible membrane is redundant; and (iv) no material is absolutely impermeable or impervious. In addition, many users of these materials habitually designate them with trade names, which adds to the terminology confusion. Geomembranes should not be confused with other similar membranes used for such applications as single-ply roofing, floating covers and air supported roofs. Also, geomembranes should not be confused with geotextiles as explained in the foreword.

The types of geomembranes that adhere to the above definition include those composed of polymeric or asphaltic materials,non-reinforced or reinforced with a fabric, made in a factory or applied in situ (ie, at the construction site). Compacted earth linings, incorporating various types of manufactured or natural additives, and hard surface linings such as steel, concrete, gunite, asphaltic concrete and soil cement are not considered as geomembranes.

Geomembranes are used in the construction of potable water reservoirs, distribution canals, municipal and hazardous solid waste landfills, liquid waste lagoons (also called liquid impoundments or surface impoundments), cutoff walls, dam facings, final closure landfill cover, spill containment systems, etc. In these structures, geomembranes serve the primary function of controlling the migration of fluids.

This paper will discuss composition, production, classification and identification of geomembranes.

Composition of Geomembranes

Geomembranes are composed of a very low permeability material, reinforced or not with a fabric.

Very low permeability materials are materials having a very low hydraulic conductivity (also called coefficient of permeability), typically 10^{-14} to 10^{-13} m/s (10^{-12} to 10^{-11} cm/s). (Although, as explained in the foreword, the mechanism by which fluids pass through geomembranes is different from the mechanism by which fluids pass through soils, it is convenient to evaluate permeability of geomembranes using coefficients originally defined for soils.) Among materials having a very low permeability are compounds of which the base product is asphalt and/or a polymer.

Asphalt is obtained either from natural deposits or as a by-product of oil distillation. Blown asphalt, often used to make geomembranes, has been hardened by blowing air through the molten asphalt to raise its softening temperature and decrease its tendency to flow.

Polymers are chemical compounds of high molecular weight. Only synthetic polymers are used to make geomembranes. The most common types of polymers presently used as base products in the manufacture of geomembranes can be classified as follows (symbols in parenthesis are adopted from symbols used by the National Sanitation Foundation (NSF) Joint Committee on Flexible Membrane Liners (FML)):

1. Thermoplastics: Polyvinyl Chloride (PVC); Oil Resistant PVC (PVC-OR); Thermoplastic Nitrile-PVC (TN-PVC); Ethylene Interpolymer Alloy (EIA);

2. Cristalline Thermoplastics: Low Density Polyethylene (LDPE); High Density Polyethylene (HDPE); High Density Polyethylene-Alloy (HDPE-A); Polypropylene; Elasticized Polyolefin;

3. Thermoplastic Elastomers: Chlorinated Polyethylene (CPE); Chlorinated Polyethylene-Alloy (CPE-A); Chlorosulfonated Polyethylene (CSPE), also commonly referred to as "Hypalon"; Thermoplastic Ethylene-Propylene Diene Monomer (T-EPDM);

4. Elastomers: Isoprene - Isobutylene Rubber (IIR), also commonly referred to as Butyl Rubber; Ethylene-Propylene Diene Monomer (EPDM); Polychloroprene (CR), also commonly referred to as "Neoprene"; Epichlorohydrin Rubber (CO).

In addition to the base product, compounds used in geomembranes generally include various additives.

Additives typically compounded with asphalt are fillers, fibers, and elastomers. Fillers are small mineral particles (typically 1 to 200 microns) used to reduce the cost of the asphaltic compound and increase its stiffness, without altering its very low permeability. Examples of particles used as fillers are: limestone, ground calcium carbonate, slate flour, kaolin clay, talc, mica, fly ash, barite, graphite. The weight ratio filler/(filler + asphalt) is usually between 0 and 60%, typically 30%. Fibers, such as asbestos or glass fibers, are sometimes added to asphalt to reinforce it. Elastomers, such as thermoplastic butadiene-styrene-butadiene copolymer, or reclaimed rubber from tires, are sometimes included in asphaltic compounds to improve their mechanical behavior and their resistance to weathering. Typical proportion of elastomer added is between 5 and 15%.

Additives typically compounded with polymers are fillers, fibers, processing aids, plasticizers, carbon black, stabilizers, antioxidants and fungicides. Fillers used with polymers are mineral particles (such as the fillers used with asphalt discussed above), metallic oxides (such as alumina, magnesia, zinc oxide, antimony oxide), ground polymers, saw dust, etc. The weight ratio filler/(filler + polymeric compound) is usually between 0 and 20% for thermoplastics and cristalline thermoplastics, and between 10% and 50% for elastomers and thermoplastic elastomers. Fibers (typically chopped glass, polyester or nylon fibers) are sometimes included in the compound. Inclusion of chopped fibers is delicate and may trigger the formation of pinholes in the geomembrane. Processing aids are used to reinforce or soften the compound during the manufacturing process. Plasticizers are used to impart flexibility to the compound to produce membranes from otherwise stiff compounds such as PVC. Plasticizers may also facilitate the manufacturing process. The weight ratio plasticizer/base product typically varies from 0 to 2% in elastomeric compounds (mostly to facilitate the manufacturing process) to 55% in PVC compounds. Carbon black (typically 1 to 2% of the base product in the case of

thermoplastics and cristalline thermoplastics, and 10% to 45% in the case of elastomers and thermoplastic elastomers) imparts a black color to the compound which retards aging by ultraviolet light from the sun and increases the stiffness of elastomeric compounds. In hot climates, light color geomembranes with a low carbon black content are sometimes used to decrease the risk of degradation of the geomembrane by sun generated heat. Light color geomembranes made with some polymers such as Hypalon may be protected from ultraviolet light by addition of titanium dioxide. Various stabilizers and antioxidants reduce the effect of outdoor aging (by ultraviolet light, ozone, etc) as well as provide compound stability during the manufacturing process. Fungicides prevent fungi and bacteria from attacking the polymer.

Fabric reinforcement is used for one or several of the following reasons: (i) to impart stability to the compound (eg, asphalt, Hypalon) during the manufacturing process; (ii) to provide dimensional stability to compounds that would excessively shrink or expand as a result of change in physical conditions such as temperature; (iii) to increase the strength (tensile, tear, burst, puncture) of the geomembrane to prevent it from being damaged during handling and installation, and to allow it to withstand the design stresses; and (iv) to increase the modulus of the geomembrane in order to decrease its elongation when subjected to stresses. Fabric reinforcement can be of various types depending on the manufacturing process of the geomembrane as discussed below.

In the recent years, knitted fabrics have been introduced to reinforce geomembranes, especially the geomembranes made in a factory by spread coating. However, the most widely used reinforcement fabrics are the nonwovens and the wovens, especially the scrims, as discussed below.

Nonwoven fabrics are used to reinforce geomembranes made in situ and some geomembranes made in a factory by spread coating. Nonwoven fabrics can also be bonded to geomembranes by the calendering method. The nonwoven fabrics used to manufacture geomembranes are usually needlepunched, with a mass per unit area typically ranging between 200 and 600 g/m^2 (6 to 18 oz./sq. yd.) (see the article entitled "Geotextile Products", by J. P. Giroud and R. G. Carroll, Jr, published in the first issue of the Geotechnical Fabrics Report, Summer 1983).

Woven fabrics are used to reinforce some spread coated and some calendered geomembranes. The type of woven fabric generally used to reinforce calendered geo-

membranes is a scrim. A scrim is a type of open weave fabric with a low mass per unit area (ie, a "lightweight" fabric). A plain weave scrim is one in which each filling (cross-machine direction) yarn passes successively over and under each warp (machine direction) yarn, alternating each row. A leno weave scrim is one in which warp yarns are arranged in pairs and twisted around each other between picks of filling yarn (each warp yarn passing successively over and under each filling yarn). This type of weave imparts strength and prevents slippage in an open weave fabric. In some scrims, one half of the filling yarns are over the warp yarns, the other half being under the warp yarns (ie, yarns in one direction do not pass successively over and under yarns in the other direction). These scrims have no stability. They must be dipped into a liquid that bonds yarns together. Sometimes scrims are made thinner by calendering them prior to calendering the compound. A scrim is characterized by its count and the linear density of its yarns. The count is the number of yarns per unit width (in meter, centimeter, or inch) in each direction (warp and filling). The linear density of a yarn is its mass per unit length. Units for linear density are kg/m or, more conveniently, tex which is 10^{-6} kg/m (ie, g/km or mg/m). The traditional unit for linear density is the denier (one tex = 9 deniers, ie 1000 deniers = 111 tex). Examples of scrims available in the United States are:

- 630 x 315/m (16 x 8/inch), 14 tex warp/28 tex filling (125 deniers warp/250 deniers filling), leno weave, often referred to as 8 x 8, 250;
- 480 x 240/m (12 x 6/inch), 55 tex warp/111 tex filling (500 deniers warp/1000 deniers filling), leno weave, often referred to as 6 x 6, 1000;
- 4 x 4/cm (10 x 10/inch), 111 tex (1000 deniers), plain weave, often referred to as 10 x 10, 1000.

Examples of scrims available in Europe are:

- 4 x 4/cm (10 x 10/inch), 28 tex (250 deniers);
- 2 x 2/cm (5 x 5/inch), 111 tex (1000 deniers);
- 3 x 3/cm (7.5 x 7.5/inch), 111 tex (1000 deniers).

The mass per unit area of a scrim is derived by multiplying the count by the linear density in both directions and adding. Example: the mass per unit area of a 480 x 240/m, 55 tex warp/111 tex filling is $480 \times 55 \times 10^{-6} + 240 \times 111 \times 10^{-6} = 0.053$ kg/m^2 = 53 g/m^2 (1.6 oz./sq. yd.)

Although all reinforced geomembranes presently available are, to the best of our knowledge, reinforced with fabrics, it is possible that, in the future, other forms of reinforcement will be available.

Production of Geomembranes

Most geomembranes are made in a plant using one of the following manufacturing processes: (i) extrusion, (ii) spread coating, or (iii) calendering.

Extrusion process is a method whereby a molten polymer, usually of the polyolefin family (such as polyethylene, polypropylene), is extruded into a non-reinforced sheet. Immediately after extrusion, when the sheet is still warm, it can be laminated with a fabric, through light calendering; the geomembrane thus produced is reinforced.

Spread coating process usually consists in coating a fabric (woven, nonwoven, knit) by spreading a polymer or asphalt compound on it. The geomembranes thus produced are therefore reinforced. Non-reinforced geomembranes can be made by spreading a polymer on a sheet of paper which is removed and discarded at the end of the manufacturing process.

Calendering is the most frequently used manufacturing process. A calendered non-reinforced geomembrane is usually a single sheet of compound made by passing a heated polymeric compound through a series of heated rollers (calender). Some calendered non-reinforced geomembranes are produced by simultaneously running two sheets of compound through heated rollers. The purpose of this process is to minimize the risk of having a pinhole through the entire thickness of the geomembrane. Pinholes are small holes that can exist in a sheet of compound as a result of grit or other cause during the manufacturing process. Calendered reinforced geomembranes are produced by simultaneously running sheets of compound and scrims through heated rollers. A three-ply calendered reinforced geomembrane is made of the following layers: compound/scrim/compound. A five-ply calendered reinforced geomembrane is made of the following layers: compound/scrim/compound/scrim/compound. The polymeric compound, when heated and pressed by the rollers, tends to flow through the openings of the scrim, thus providing adhesion between the sheets of compound located on both sides of the scrim. This adhesive mechanism is commonly known as "strike-through".

the resulting membrane is reinforced (however, at fabric overlaps, the reinforcement is continuous only if the reinforcing fabric is sewn). The sprayed material must penetrate the fabric and thus adhere to it after curing to provide a consistent reinforced spray-applied geomembrane.

Classification of Geomembranes

Based on the information discussed above, geomembranes can be classified according to production process and reinforcement:

1. Made in situ, non-reinforced geomembranes are made by spraying or otherwise placing a hot or cold viscous material directly onto the surface to be lined (earth, concrete, etc). The non-reinforced geomembranes made by spraying are called "sprayed-on (or spray-applied, or sprayed in situ) non-reinforced geomembranes". Typical materials used are based on asphalt, asphalt-elastomer compound, or polymers such as polyurethane. Due to the spray application, the final thickness of such geomembranes is not easy to control and may vary significantly from one location to another. Typically, required thicknesses range between 3 and 7.5 mm (120 and 300 mils).

2. Made in situ, reinforced geomembranes are made by spraying or otherwise placing a hot or cold viscous material onto a fabric. The reinforced geomembranes made by spraying are called "sprayed-on (or spray-applied, or sprayed in situ) reinforced geomembranes". Typical materials used are the same as for the made in situ non-reinforced geomembranes described above. Typical fabrics used are the needlepunched nonwoven geotextiles because they can absorb viscous materials. As discussed above, the final thickness of such geomembranes is not easy to control. Typically, required thicknesses range between 3 and 7.5 mm (120 and 300 mils).

3. Manufactured, non-reinforced geomembranes are made in a plant by extrusion or calendering of a polymeric compound, without any fabric reinforcement, or by spreading a polymer on a sheet of paper removed at the end of the manufacturing process. Typical thicknesses range from 0.25 to 4 mm (10 to 160 mils) for geomembranes made by extrusion and 0.25 to 2 mm (10 to 80 mils) for geomembranes made by calendering. Typical roll width for geomembranes made by extru-

sion is 5 to 10 m (16 to 33 ft), although some are narrower. Typical roll width for geomembranes made by calendering is 1.5 m (5 ft), with some manufacturers producing 1.8 to 2.4 m (6 to 8 ft) wide rolls.

4. Manufactured, reinforced geomembranes are made in a plant, usually by spread coating or calendering. In spread-coated geomembranes, the reinforcing fabric (woven or nonwoven) is impregnated and coated on one or both sides with the compound, either polymeric or asphaltic. In calendered reinforced geomembranes, the reinforcing fabric is usually a scrim. Calendered geomembranes are always made with polymeric compounds and are usually made up of three plies: compound/scrim/compound. Sometimes they are made of five plies: compound/scrim/compound/scrim/compound. Geomembranes with additional plies can be made on a custom basis. Typical thicknesses of asphaltic spread-coated geomembranes are 3 to 10 mm (1/8 to 3/8 inch). Typical thicknesses for polymeric spread-coated and three-ply calendered geomembranes are 0.75 to 1.5 mm (30 to 60 mils). Typical thicknesses for five-ply calendered geomembranes are 1 to 1.5 mm (40 to 60 mils). Some two-ply reinforced geomembranes are manufactured by extrusion of a non-reinforced sheet, followed by light calendering with a fabric.

5. Manufactured, reinforced geomembranes laminated with a fabric are made by calendering a manufactured geomembrane (usually a non-reinforced geomembrane previously made by calendering) with a fabric (usually a nonwoven) which remains apparent on one face of the final product.

Identification of Geomembranes

An abbreviated system for identifying geomembranes consists of providing the generic name (or initials) of the base product, followed by the letter R if the geomembrane is reinforced. Examples: a PVC geomembrane; a CPE-R geomembrane. (Note: the term "supported", sometimes used for "reinforced", is not recommended because it may create a confusion with the "supporting" soil or geotextile on which the geomembrane is resting.)

A comprehensive system for identifying geomembranes consists of listing: (i) the production process, only if the geomembrane is made in situ (if the geomembrane is made

in a plant, this does not need to be mentioned); (ii) generic name of the base product (ie, asphalt or type of polymer); (iii) thickness (since the significant thickness is the thickness of the low permeability compound, the thickness to be indicated is the total thickness of geomembranes types 1 through 4 (except the case of fabrics coated one side only), while it is the thickness excluding the associated fabric in the case of geomembranes type 5); (iv) reinforcing fabric, if any (the type of fabric and the type of polymer, such as polyester or nylon, should be given; if the fabric is a woven (including scrim) or a knit, count and linear density of yarns, and the type of weave or knit should be given; if the fabric is a nonwoven, the mass per unit area should be given). (Note: for fabric types see the article entitled "Geotextile Products", by J. P. Giroud and R. G. Carroll, Jr, published in the first issue of the Geotechnical Fabrics Report, Summer 1983.)

Examples of geomembrane identification are as follows:

- sprayed in situ, asphalt-neoprene compound, 3 mm (120 mils) in thickness, non-reinforced;
- sprayed in situ, asphalt, 2.5 mm (100 mils) in thickness, reinforced with a polypropylene spunbonded needlepunched nonwoven, 370 g/m^2 (11 oz./sq. yd.);
- polyvinyl chloride (PVC), 0.75 mm (30 mils) in thickness, non-reinforced;
- asphalt-elastomer compound, 3.5 mm (140 mils) in thickness, reinforced with a polyester staple fiber needlepunched nonwoven, 230 g/m^2 (7 oz./sq. yd.);
- chlorinated polyethylene (CPE), 0.75 mm (30 mils) in thickness, reinforced with 4 x 4/cm (10 x 10/inch), 111 tex (1000 deniers) plain weave polyester scrim;
- chlorosulfonated polyethylene (CSPE), 0.9 mm (36 mils) in thickness, reinforced with 480 x 240/m (12 x 6/inch), 55 tex warp/111 tex filling (500 deniers warp/1000 deniers filling) leno weave polyester scrim (Note: The scrim can more simply be described by: 240 x 240/m (6 x 6/inch), 111 tex (1000 deniers) leno weave);
- chlorosulfonated polyethylene (CSPE), 1.15 mm (45 mils) in thickness, five-ply, reinforced with two plies of 315 x 315/m (8 x 8/inch), 28 tex (250 deniers) leno weave polyester scrims;
- butyl rubber, 1.5 mm (60 mils) in thickness, laminated with a polypropylene spunbonded heatbonded nonwoven fabric, 270 g/m^2 (8 oz./sq. yd.).

The above identifying characteristics are only minimum descriptors. Detailed information on physical and mechanical properties as well as chemical resistance and compatibility with hot, cold or wet environments is needed before a geomembrane is determined to be suitable for a specified application. All pertinent characteristics and properties must be considered before final selection of a geomembrane is made.

Conclusion

The information presented herein should provide the reader with a basic knowledge of the types of geomembranes in use today. This article has purposely avoided such subjects as geomembrane polymer technology, physical and mechanical test procedures, design methodology, and installation technology. These are separate topics that are addressed in numerous technical journal articles and books available through libraries throughout the world. A wealth of information is also available from geomembrane manufacturers and marketing groups. Those readers who wish to gain first hand knowledge on geomembranes should attend the International Conference on Geomembranes to be held in Denver, Colorado, 20-24 June 1984. For further information and a bulletin, please contact:

International Conference on Geomembranes
IFAI
Suite 450
345 Cedar Street
St. Paul, Minnesota 55101 USA

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APPENDIX II

REPRESENTATIVE LIST OF ORGANIZATIONS IN LINER INDUSTRY

A. POLYMERIC MEMBRANE LINERS

1. Polymer producers
2. Manufacturers of polymeric membrane sheeting
3. Fabricators of liners
4. Installing contractors

B. BENTONITE PRODUCERS AND SUPPLIERS

C. OTHER LINER MATERIALS

D. MISCELLANEOUS ORGANIZATIONS IN THE LINER INDUSTRY

A. POLYMERIC MEMBRANE LINERS

1. Polymer Producers

DOW CHEMICAL COMPANY
2040 Dow Center
P.O. Box 1847
Midland, MI 48640

Product Sales Manager,
Chlorinated Polyethylene Designed Products Department
Phone: 517-636-1000

E.I. du PONT de NEMOURS AND CO., INC.
Elastomer Chemicals Dept.
Wilmington, DE 19898

Contact: Bernard F. Anderson
Phone: 302-774-1000
Contact: Gerald E. Fisher
3707 Chevy Chase Road
Louisville, KY 40218
Phone: 502-459-8752

EXXON CHEMICAL CO.
Elastomer Technology Division
P.O. Box 45
Linden, NJ 07036

Contact:
Phone: 201-474-0100

HERCULES INCORPORATED
910 Market St.
Wilmington, DE 19899

Contact: Norman C. MacArthur
Phone: 302-575-6293

MONSANTO INDUSTRIAL CHEMICALS CO.
260 Springside Drive
Akron, OH 44313

Contact: Gary E. O'Connor,
Project Manager
Commercial Development Department
Rubber Chemicals Division
Phone: 216-666-4111

PANTASOTE, INC.
26 Jefferson St.
Passaic, NJ 07055

Contact: Dr. R. Brookman
Phone: 201-777-8500

POLYSAR, LTD.
Technical Development Division
Vidal Street
Sarnia, Ontario
Canada N7T 7M2

Contact: John Redland
Phone: 519-337-8251

SHELL CHEMICAL COMPANY
605 N. Main Street
Altamont, IL 62411

Contact: Larry Watkins
Phone: 618-483-6517

UNIROYAL CHEMICAL COMPANY
Spencer Street
Naugatuck, CT 06488

Contact: Allen Crepeau
Phone: 203-723-3825

2. Manufacturers of Polymeric Membrane Sheetings

BURKE RUBBER COMPANY
2250 South Tenth St.
San Jose, CA 95112

Contact: D. Kutnewsky
Manager, Flexible Membranes
Phone: 408-297-3300

CARLISLE TIRE AND RUBBER CO.
Construction Materials Department
P.O. Box 99
Carlisle, PA 17013

Contact: Hugh Kenney
Phone: 717-249-1000

COLUMBUS COATED FABRICS
1280 N. Grant St.
Columbus, OH 43216

Contact: Lee Fishbein
Phone: 614-225-6069

COOLEY, INC.
50 Esten Ave.
Pawtucket, RI 02862

Contact: Paul Eagleston
Vice President
Phone: 401-724-9000

DUNLINE LIMITED
(A Dunlop Company)
160 Eglinton Ave. E.
Toronto, Ontario
Canada M4P 1G3

Contact:
Phone: 416-487-1114

GACO
P.O. Box 88698
Seattle, WA 98188

Contact: Earle Johnson
San Jose, CA
Phone: 415-341-5661

B. F. GOODRICH COMPANY
Engineered Rubber Products Division
500 S. Main Street
Akron, OH 44318

Contact: R. D. Cunningham,
Sales Manager,
Environmental Products
Phone: 216-379-2226

GUNDLE PLASTICS, INC.
5340 Alpha Road Suite 101
Dallas, TX 57520

Contact: Richard K. Schmidt
Phone:

HART & COMPANY
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KOKOKHU, USA, INC.
P.O. Box 2287
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Contact: Ms. Miki Nakamura
Phone: 806-353-7000

MAINLINE, INC.
3292 South Highway 97
Redmond, OR 97756

Contact: DeWitt Maine
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PANTASOTE, INC.
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PLYMOUTH RUBBER COMPANY
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Contact: Charles Neese
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REEVES BROS., INC.
Vulcan Coated Fabrics Division
P.O. Box 431
Rutherford, NC 28139

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SCHLEGEL LINING TECHNOLOGY, INC.
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Contact: James M. Price, President
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713-350-1813 (Houston)

SEAMAN CORP.
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Charlotte, NC 28209

Contact: Jack Watson
Phone:

SHELTER-RITE, INC.
P.O. Box 331
Millersburg, OH 44654

Contact: Dr. Bala Venkataraman,
Vice President,
Research and Development
Phone: 216-674-2015

STAUFFER CHEMICAL CO.
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Yardville, NJ 08620

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Technical Manager
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STEVENS ELASTOMERIC & PLASTICS
PRODUCTS, INC.
27 Payson Ave.
Easthampton, MA 01073

Contact: Arnold G. Peterson
Phone: 413-527-0700

TENNECO CHEMICALS, INC.
P.O. Box 189
Piscataway, NJ 08805

Contact: Bob Hayes/Kent Turner
Phone: 201-356-2550

UNIROYAL, INC.
312 N. Hill St.
Mishawaka, IN 46544

Contact: D. L. Zimmerman
Phone: 219-256-8181

3. Fabricators of Liners

BROWN AND BROWN
P.O. Drawer 269
Mobile, AL 36601

Contact: Sam Brown, President
Phone: 205-479-6581

ELECTRA TARP, INC.
Park Centre
7241 Whipple Ave., N.W.
North Canton, OH 44720

Contact: Bob Fulmer, President
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ENVIRONETICS, INC.
9824 Industrial Drive
Bridgeview, IL 60455

Contact: Ray Winters, President
Phone: 312-585-6000

FABRICO MANUFACTURING CORP.
1300 West Exchange Avenue
Chicago, IL 60609

Contact: Jay Sabath, Sales Manager
Phone: 312-254-4211

MCKITTRICK MUD CO.
P.O. Box 3343
Bakersfield, CA 93305

Contact: Bill Wheeler, President
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PALCO LININGS, INC.
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Contact: Richard Cain,
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POLY-PLASTICS
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PROTECTIVE COATING, INC.
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Phone: 219-422-7503

M. PUTTERMAN & CO.
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REVERE PLASTICS
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Little Ferry, NJ 07643

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SOUTHWEST CANVAS MFG. CO.
Oklahoma City, OK

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WATERSAVER COMPANY, INC
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Denver, CO 80216

Contact: Bill Slifer, Vice President
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MANUFACTURERS WHO ALSO FABRICATE

Burke Rubber Company
Carlisle Tire and Rubber Co.
B. F. Goodrich
Schlegel Area Sealing Systems, Inc.

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CRESTLINE SUPPLY CORP.
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ENVIROCLEAR, INC.
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Falls Village, CT 06031

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518-325-3332

AL GASTON CONSTRUCTION CO., INC
Gaston Containment Systems
P.O. Box 1157
El Dorado, KS 67042

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GLOBE LININGS, INC.
1901 East Wardlow Road
Long Beach, CA 90807

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GULF SEAL CORPORATION
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M&M CONTRACTING CORP.
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PACIFIC LININGS, INC.
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PLASTI-STEEL, INC.
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SCHLEGEL AREA SYSTEMS, INC
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Contact: James M. Price
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Phone: 408-224-0604

THE THURSTON WALLACE CO.
5470 East Evans Ave.
Denver, CO 80222

Contact: Hank Thurston, President
Phone: 303-758-2232

TRI STATE CONSTRUCTION
959 108th Avenue, N.E.
Belleview, WA 98004

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UNIT LINER CO
P. O. Box 789
Shawnee, OK 74884

Contact: J. A. Hendershot, President
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UNIVERSAL LININGS, INC.
P. O. Box 315
Haverford, PA 19041

Contact: David M. Small, President
Phone: 215-649-3600

FABRICATORS WHO ALSO INSTALL:

McKittrick Mud
Synflex Industries, Inc.

B. BENTONITE PRODUCERS AND SUPPLIERS

AMERICAN COLLOID COMPANY
5100 Suffield Court
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Commerce Station
Minneapolis, MN 55415

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ASHLAND CHEMICAL
9450 Midwest Avenue
Cleveland, OH 44125

Contact:
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DOWELL
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Tulsa, OK 74102

Contact: Chris Parks
Mining and Construction
Technical Services
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DRESSER MINERALS
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Phone: 713-972-2670

INTERNATIONAL MINERALS &
CHEMICAL CORP.
IMC FOUNDRY PRODUCTS
17350 Ryan Road
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CHARLES PFIZER & CO.
235 East 42nd Street
New York, NY 10017

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WILBUR ELLIS CO.
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Fresno, CA 93715

Contact:
Phone: 209-226-1934

WYO-BEN PRODUCTS, INC.
P.O. Box 1979
Billings, MT 59103

Contact:
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C. OTHER LINER MATERIALS

THE ASPHALT INSTITUTE
Asphalt Institute Building
College Park, MD 20740

Contact:
Phone: 301-277-2458

CHEVRON, USA, INC.
Asphalt Division
P. O. Box 7643
San Francisco, CA 94120

Contact: Kenneth Coleman
K. D. Coleman Co
P. O. Box 414
Santa Clara, CA 95052
Phone: 408-244-8948

I.U. MANAGEMENT SYSTEMS, INC.
1500 Walnut Street
Philadelphia, PA 19102

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MICHELLE CORPORATION
Division of Weychem Canada Limited
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Charleston Heights, SC 29405

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PHILLIPS PETROLEUM COMPANY
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Phone: 918-661-6428

PORTLAND CEMENT ASSOCIATION
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Skokie, IL 60076

Contact:
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D. MISCELLANEOUS ORGANIZATIONS IN LINER INDUSTRY

HOVATER-WAY ENGINEERS, INC.
23011 Moulton Parkway, Suite F-5
Laguna Hills, CA 92653

Contact: Louis R. Hovater
Phone:

Type of service: Design engineering, specializing in membrane liners.

LINING MATERIALS
23011 Moulton Parkway, Suite F-4
Laguna Hills, CA 92653

Contact: George J. Miller, General Manager
Phone: 714-581-9292

Type of service: Supplier of a variety of lining materials.

LIQUID CONTAINMENT SYSTEMS
P. O. Box 324
South Holland, IL 60473

Contact: Jack Moreland, President
Phone: 312-468-2500

Type of service: Design, planning, engineering, and installation of liners.

NATIONAL SANITATION FOUNDATION
NSF Building
Ann Arbor, MI 48105

Contact: Gary W. Sherlaw, Director Standard Development
Phone: 313-769-8010

Type of service: Developing national specifications for membrane liners.

SARNAFIL CANADA, LTD.
75 Horner Avenue
Toronto, Ontario, Canada

Contact: Ursala Schenck
Phone: 416-259-9203

Type of service: Developing, marketing, manufacturing, and selling membrane liners.

WATERPROOFING SYSTEMS, INC.
P.O. Box 2182
Santa Barbara, CA 91320

Contact: O.E. Hengsen
Phone: 805-963-6785

Type of service: Consulting, engineering, and contracting of various lining materials.

Guide to Polymers used in Flexible Membrane Liners		Butyl Rubber		Chlorinated Polyethylene		Reinforced Chlorinated Polyethylene		Chloro-sulfonated Polyethylene		Reinforced Chloro-sulfonated Polyethylene		Elasticized Polyvinyl		Epichlorohydrin Rubber		Ethylene Propylene Diene Monomer		Polychloroprene		Polyethylene		Polyvinyl Chloride	
Low Temperature Resistance - °F	−20																			•		X	
	−40	X		X		X		X		X								X					
	−60											X		X						X			
	−80															X							
High Temperature Resistance - °F	+150			X		X		X		X		X										X	
	+200	X												X		X		X		X			
Field Seaming Method		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives		Adhesives	
A = Adhesion E = Extrusion F = Fusion		A		A		A		A		A		A		A		A		A		E & F		A	
Good UV Resistance		X		X		X		X		X		X		X		X		X		X			
General Chemical Resistance X = General Good Resistance		100 °F	150 °F	100 °F	150 °F	100 °F	150 °F	100 °F	150 °F	100 °F	150 °F	100 °F	150 °F	100 °F	150 °F	150 °F	150 °F	100 °F	150 °F	100 °F	150 °F	100 °F	150 °F
	Aliphatic Hydrocarbons			X	X	X	X					X		X	X			X	X	X	X		
	Aromatic Hydrocarbons											X		X	X			X	X	X	X		
	Chlorinated Solvents	X	X									X		X	X	X		X		X	X		
	Oxygenated Solvents	X	X									X		X		X	X	X	X	X	X		
	Crude Petroleum Products			X	X	X	X					X		X	X			X	X	X	X		
	Alcohols	X	X	X	X	X	X					X		X	X	X	X	X	X	X	X	X	X
	Acids	X	X	X	X	X	X	X		X		X		X		X	X	X	X	X	X	X	X
	Bases	X	X	X	X	X	X	X		X		X		X	X	X	X	X	X	X	X	X	X
	Heavy Metals	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X
	Salts	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X

Gundle Lining Systems Inc 1340 East Richey Road
Houston Texas 77073 USA Phone (713) 443-8564
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Gundle

Technical Report No.101

SELECTION CRITERIA FOR THE USE OF SYNTHETIC MEMBRANE LINERS IN THE CONTAINMENT OF HAZARDOUS WASTES

BY

RICHARD K. SCHMIDT, Ph.D.
PAUL W. BARKER

PRESENTED TO:
54TH ANNUAL WATER POLLUTION CONTROL
FEDERATION CONFERENCE
OCTOBER, 1981

3623

INTRODUCTION

Recent studies have revealed the existence of over 70,000 water impoundments and landfill sites, many which contain hazardous and toxic material capable of contaminating ground water supplies. The majority of these sites fail to provide properly designed containment security of their contents. The passage of the Resources Recovery Act (RCRA) requires more stringent engineering design of the containment aspects of existing and future disposal sites.

There are numerous materials which can be considered for use as linings for hazardous waste impoundments. Among them are clay and bentonite, cement stabilized sand, and flexible membrane liners.

Clay layers, often 2' or 3' thick have been used extensively but recent work and study has shown that certain solutions, particularly alkaline solutions can seriously affect clay's use as a permanent lining material.[1]

The use of thinner layers of betonite which swells in contact with water to form a relatively impermeable layer can also be limited in certain chemical environments.

Cement stabilized sand is not suitable when acidic conditions are experienced.

As far as flexible membranes are concerned there is a wide range of materials available all of which can find application with greater or lesser success in hazardous waste environments. It should be realized that in civil engineering, a membrane is defined as a thin impermeable sheet which may be flexible or rigid and used to separate two environments. Such a membrane normally only has strength in two directions and requires support to resist load normal to its plane. One of its principal properties is impermeability - particularly important in the containment of hazardous waste.

Because of their cost effectiveness, synthetic membrane liners are gaining increasing engineering acceptance as the containment material of choice. The intent of this paper is to review the history of flexible membrane liners, discuss the physical and chemical characteristics of the more widely used materials and to present the design engineer with a step by step approach to be used in the application and selection of the correct liner.

HISTORY OF FLEXIBLE MEMBRANE LINERS

At this point it would be appropriate to review the history of the development of the use of flexible membranes over the years. Much of the early lining work was carried out at the U. S. Department of Agriculture's Research Station in Utah. Here in 1948 the first reinforced butyl rubber lining was installed in an irrigation canal.

Other materials such as PVC and low density polyethylene were also studied and in 1955 the first butyl rubber pond liner was installed. In the early sixties in Europe there was considerable interest by the rubber producing oil companies to develop the market for butyl rubber in particular and a method of vulcanizing relatively narrow - 4 feet wide - sheets of rubber was developed. At the same time wider widths of low density polyethylene became available although the jointing method remained relatively unsophisticated involving the use of soft, sticky tapes with relatively low shear strengths. Subsequently more sophisticated mechanical clamp systems for sealing low density polyethylene were developed.

Plasticised PVC in sheet form also began to be used in the early sixties. In this case 4' or 5' wide calendered sheets were welded together in a prefabricators factory usually by means of high frequency welding machines. The large panels were joined together on site using special adhesive.

Also in the U.S.A., chlorosulphonated polyethylene, commonly known as Hypalon, was developed in the early fifties and was first used in a reinforced form for a floating cover application in 1972. During the late seventies chlorinated polyethylene, CPE, sheeting was introduced and as with Hypalon, relatively narrow widths had to be prefabricated in a factory prior to site installation. Yet another lining material known as 3110, a polyolefin was available for a few years from 1975-79.

Blends of nitrile rubber and PVC in sheet form were developed in the late seventies for oil resistant lining applications whilst in the mid seventies, thick HDPE, pure high density polyethylene was used for the first time as a lining material.

The history is summarized in Figure 1.

FIGURE 1

HISTORY OF MEMBRANE DEVELOPMENT

```
1948            1950            1960            1970            1980
*-------------------------------BUTYL-------------------------------*
                                *----------------PVC----------------*
                                 *-------------LDPE---------------*
                                                *------HYPALON------*
                                                 *---------CPE------*
                                                   *-----HDPE------*
```

From this discussion, we can see that synthetic membrane liners have been in extensive use for over 30 years and that in time, better materials have been developed to meet the demands of the marketplace. It is believed that the most recent generation of lining materials offers the designer the type of product required for the permanent encapsulation of hazardous waste facilities.

MEMBRANE PROPERTIES

To be effective, flexible membrane liners should have a combination of the following properties:

1. Strength
2. Toughness and flexibility
3. Durability
4. Chemical resistance
5. Effective jointing system

Strength involves the tensile properties at various elongations - that is to say the stress strain characteristics of the material.

Toughness involves the tear and puncture resistance of the material while flexibility is a desirable feature both during installation and in service.

Durability involves resistance of the material to environmental factors and clearly long term durability is an important consideration in most lining applications.

Chemical resistance is primarily concerned with the membrane's ability to withstand exposure to a wide range of chemically aggressive environments without deterioration or loss of properties.

An effective jointing system is of course the "link in the chain". Ideally the jointing system should involve true welding that creates a perfectly homogeneous fusion of the two edges, achieved as necessary by the introduction of a material of identical nature to the lining membrane. Systems based on adhesives have characteristics that could produce variable results and are therefore not ideal for more critical applications.

Let us now focus in more detail on the physical properties which may be used as indicators in the evaluation of various membranes. Table 1 presents physical properties which are typically evaluated.

TABLE 1

PHYSICAL PROPERTIES

Tensile Strength - at yield and break	Water Absorption
Elongation - at yield and break	Volatiles
Tear Resistance	Low Temperature Impact
Puncture Resistance	Ozone Resistance
Dimensional Stability	Abrasion Resistance
Permeability	

The tensile strength of lining materials is normally measured at yield and at break. Standard samples are cut and pulled at a constant speed on sophisticated tensometers and readings taken, units being in lbs/inch. The same equipment is used to measure elongation at yield and break; units are given as a % of the original. Tear resistance involves pulling a standard tear sample and measuring the force in pounds required to tear the material. Puncture resistance measures the resistance of the material to the application of the standard pointed steel piece and units are measured in lbs. These tests measure the strength and toughness of various materials.

Dimensional Stability measures the % change in dimensions in a standard piece after heating the sample for 15 minutes at 212°F. Permeability of a membrane to moisture vapor is measured in $gm/m^2/24$ hrs.

A water absorption test is carried out which measures the % water absorbed after two weeks immersion at 50°C. The Volatile's test measures % of loss at 105°C - an important test to determine the amount of volatile constituent in the compound which could be affected by loss over the years.

Low temperature impact is a test carried out to determine the temperature at which the lining material becomes unable to resist impact and ozone resistance is measured to determine the material's resistance to this active gas present in the atmosphere. No cracks should be visible in the membrane after 7 days exposure at 20% elongation at 104°F and 100 pphm of ozone. Abrasion Resistance is often measured and this property can be important in the abrasive environments. These tests provide guides to a material's ability to withstand long term weathering.

At this point it would be interesting to carry out some comparisions of the physical properties of the most frequently used lining materials.

Figure 2 shows comparative data on 30 mil unsupported materials namely PVC, CPE, Hypalon, Butyl, and HDPE. The diagram illustrates the high tensile strength of HDPE when compared to other polymer materials.

Because some basic polymers have low tensile strengths, flexible membrane liners made from this material must be reinforced with a fabric scrim to obtain additional strength. Scrims are open weave mesh fabrics which are laminated between layers of sheeting to produce a single sheet. Materials containing a fabric are given the designation, reinforced, because of the scrim reinforcement they contain.

Figure 3 shows the effect of scrim addition to two common reinforced products, Hypalon and CPE. PVC, Butyl and HDPE are unreinforced products. Figure 3 also presents information on the elongation characteristics of these materials. An unreinforced material, such as HDPE will typically yield at 10% of its ultimate tensile strength but will continue to stretch, breaking at an ultimate elongation of 700%.

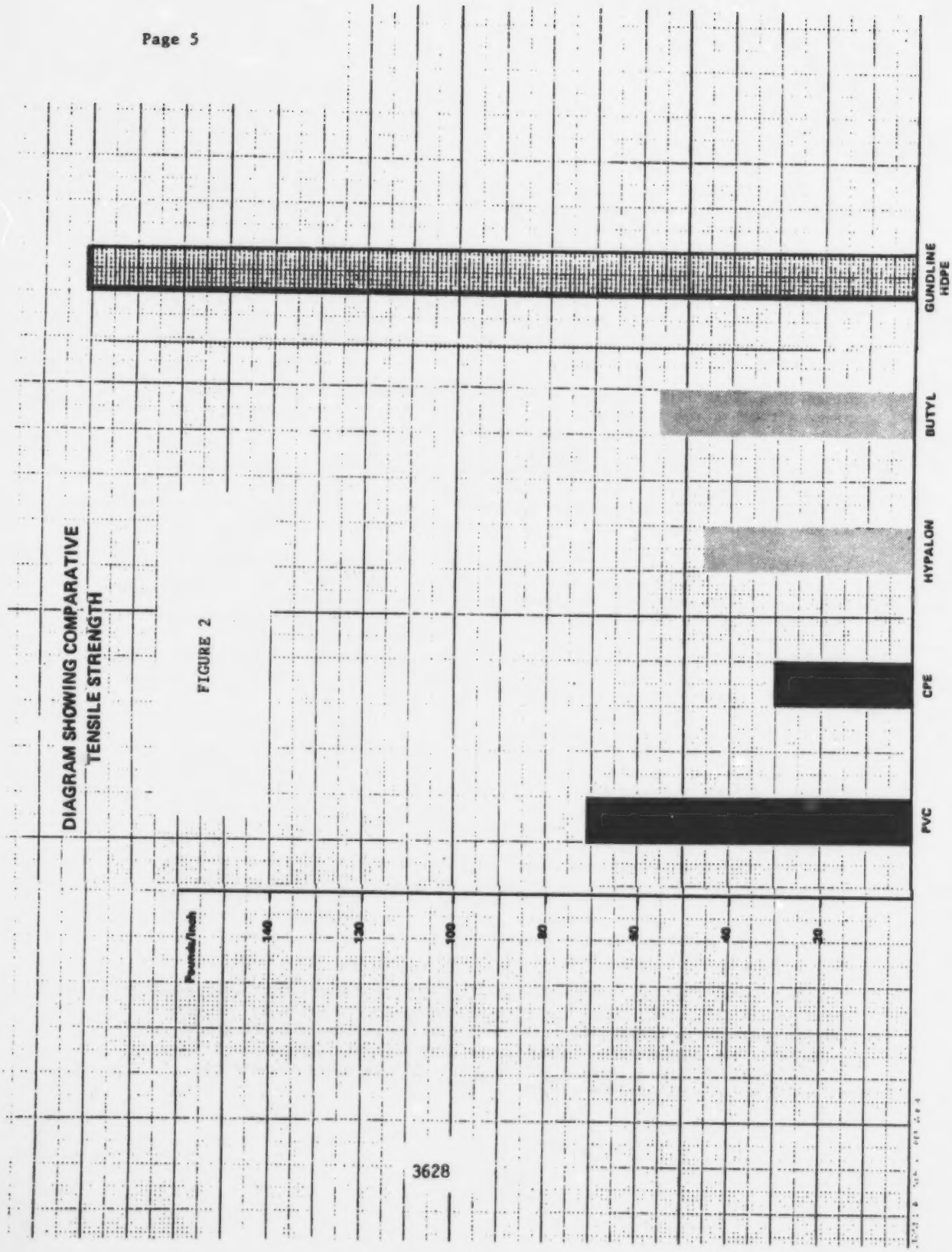


FIGURE 2

DIAGRAM SHOWING COMPARATIVE TENSILE STRENGTH

FIGURE 3

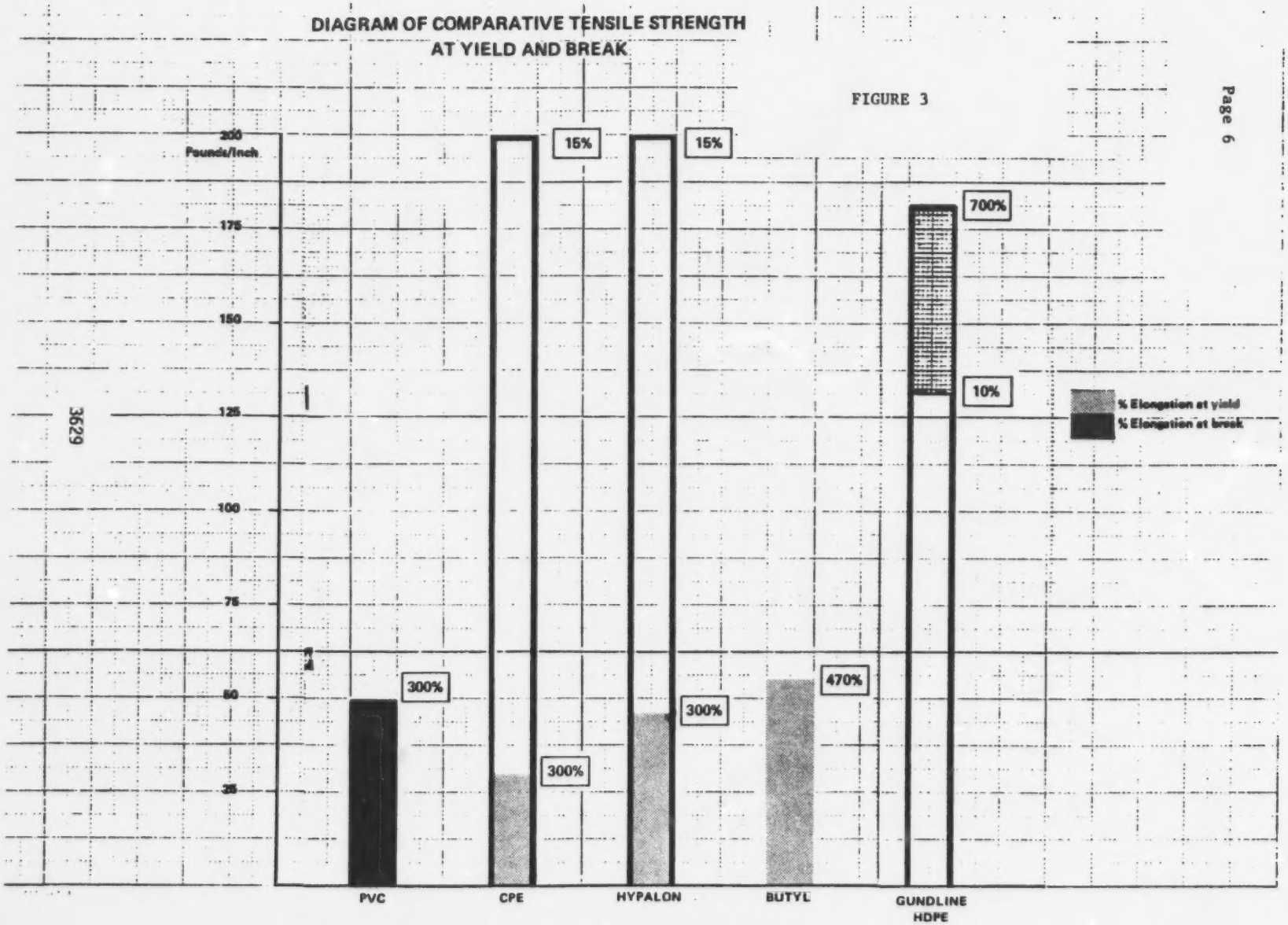


DIAGRAM OF COMPARATIVE TENSILE STRENGTH
AT YIELD AND BREAK
200
Pounds/Inch
175
150
125
100
75
50
25
15%
15%
700%
10%
300%
300%
300%
470%
% Elongation at yield
% Elongation at break
PVC
CPE
HYPALON
BUTYL
GUNDLINE
HDPE

The strength of reinforced materials comes from the scrim. Once the scrim fails, typically occurring at about 15% of the breaking strength, the strength properties revert back to the relatively low physical properties of the unreinforced polymers compound. These materials also tend to have lower elongation characteristics.

Figure 4 shows data on puncture resistance. The data is more closely correlated for all materials since this property is usually a function of thickness.

A study of all physical properties of lining materials is an important phase of the evaluation procedure. However, it is also important to be able to know how these properties change on exposure both to the weather and to particular environments. Accelerated heat aging tests have been carried out onmany lining materials and it is possible to extrapolate from this test data to determine an ultimate life, heat of course being one of the main factors causing deterioration of membranes in service. Ideally test data obtained from samples of lining material which has been exposed to certain environments for many years gives the best indication of longevity. Table 2 summarizes the desired properties of flexible membrane liners and the test which can be used to evaluate them.

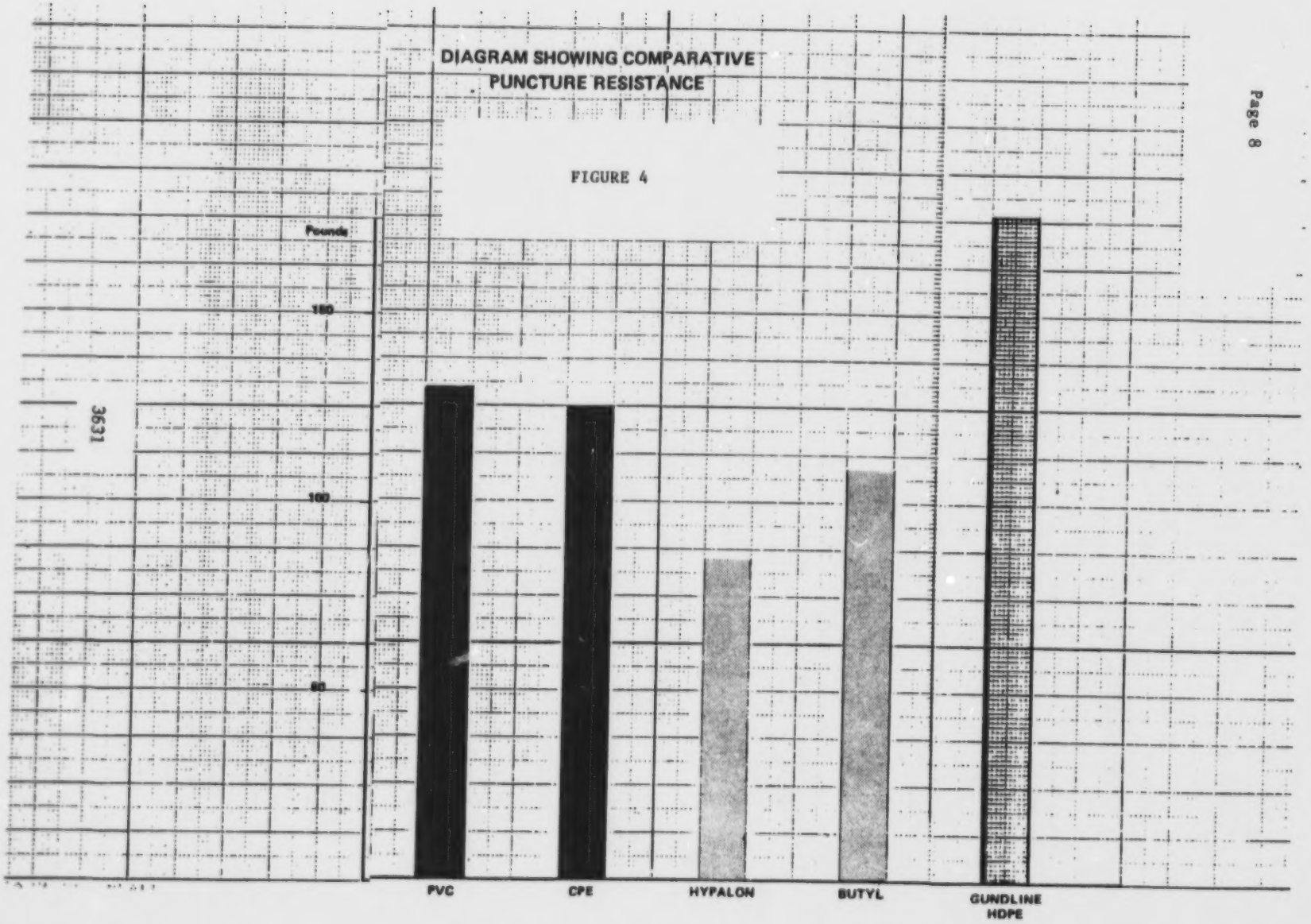
TABLE 2

DESIRED MEMBRANE PROPERTIES AND ASSOCIATED TEST PARAMETERS

DESIRED PROPERTY	TEST PARAMETER
Chemical Resistance	Chemical Immersion Testing Stress Crack Resistance
Low Permeability	Water Absorption Permeability
Durability	Ozone Resistance Temperature Range UV Resistance Heat Aging Long Term Weathering
Strength and Flexibility	Tensile Strength Elongation
Toughness	Puncture Resistance Tear Resistance Abrasion Resistance

DIAGRAM SHOWING COMPARATIVE PUNCTURE RESISTANCE

FIGURE 4



CHEMICAL COMPATIBILITY

Turning now from physical properties, we must now consider the question of chemical resistance. There are of course a wide range of chemicals to which the lining material can be exposed, particularly in hazardous waste applications. Therefore, the lining material chosen must have a degree of chemical resistance appropriate to the type of installation envisaged. The main types of chemical include acids, alkalis, aromatic solvents, and oils.

Most membranes currently available are able to withstand acids and alkalis but resistance to solvents and oils is limited, the most resistant lining materials being PVC Nitrile blends and HDPE. It must be realized of course, that any waste or effluent stream can contain a wide range of chemicals and different combinations can have different effects particularly in fluctuating temperature situations. If at all possible it is always better to carry out immersion tests in actual solutions of effluent in order to determine possible effects.

For most applications, immersing a sample of the material into the waste liquid for approximately 30 days will give a good indication of the material compatability. This test can be easily run in the laboratory and should as closely as possible, approximate field conditions. This is particularly true if temperature extremes are expected.

After 30 days, the samples are removed from the immersion tests, weighed to determine if the waste material has been absorbed, and then a series of physical tests are run to determine if there has been any change in the physical characteristics of the material. If deterioration has occurred, this may indicate that the material is not suitable for the intended application. In cases where an extreme hazard exists, the tests may be run for an extended period in time. Also, there are methods available to run accelerated aging tests on materials, however, these are quite expensive. For most applications the 30 day laboratory compatability test will suffice. Figure 5 presents tensile strength data for various materials after immersion in landfill leachate for 8 and 19 months. This is typical of data which can be obtained from immersion studies.

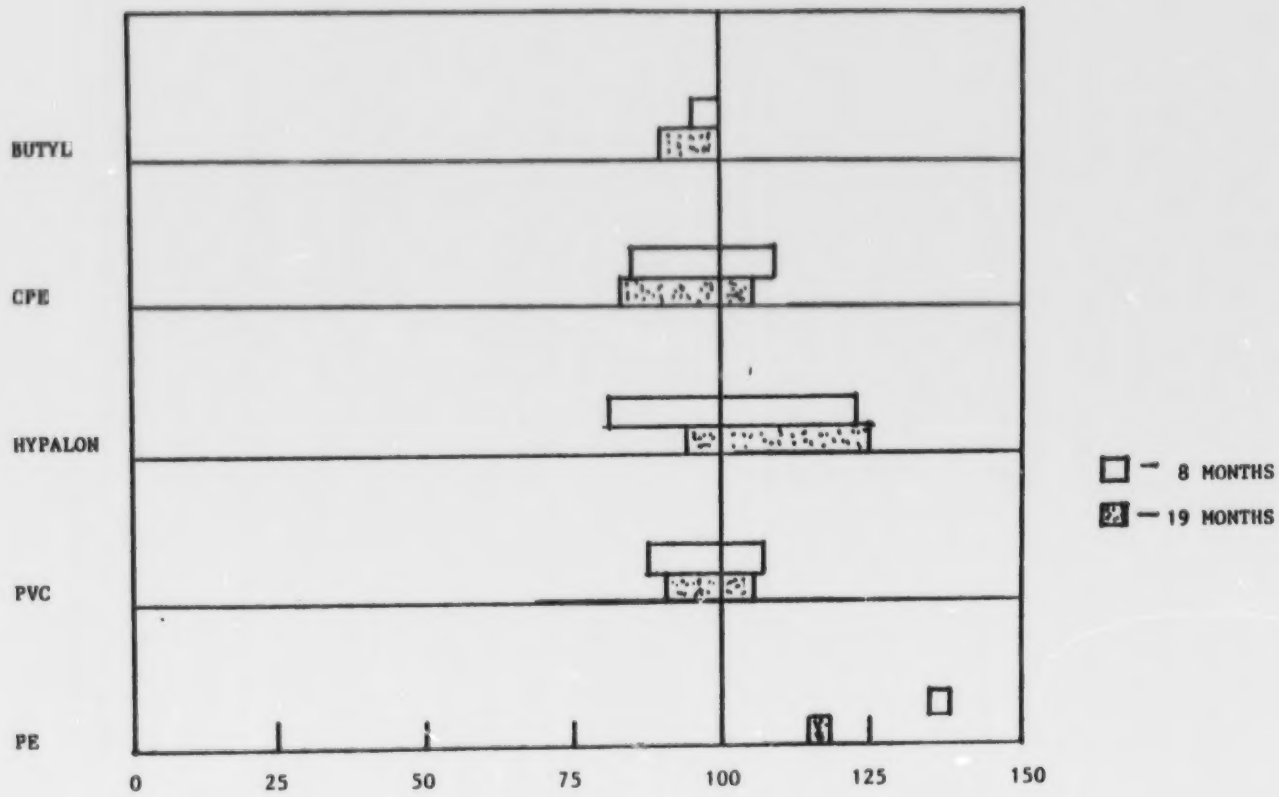
SEAMING

Potentially the weakest link in any liner system is the joining system. The type and number of joints influence the degree of safety achieved in a particular application.

Most lining materials are manufactured in roll goods whose width is only 4 - 5 ft. Since it is uneconomical to field seam such narrow widths, larger panels of material are fabricated in the factory to reduce field installation costs.

FIGURE 5

RETENTION OF TENSILE STRENGTH OF MEMBRANE LINERS AFTER IMMERSION IN LANDFILL LEACHATE FOR 8 AND 19 MONTHS.



REF: EPA REPORT
SW 870

Thus, there are two types of seams, factory and field. The only commercially available material which contains no factory seams is HDPE. Manufacturing techniques allow this material to be fabricated in widths exceeding 20 ft., thus, the sheets are taken directly to the field for installation.

The types of seaming methods currently in use are as follows:

1. Solvent/Adhesive
2. Thermal
3. Dielectric
4. Homogeneous Welding

These are listed in ascending order in terms of cost. Typically PVC, Butyl, Hypalon, and CPE can be bonded using solvent/adhesive, thermal or dielectric means. Of the three, the dielectric method provides the best seam but it is the most expensive and is also not conducive to field installation. As a result, many fabricators use dielectric methods for factory seams and use either solvent/adhesive or thermal means for field seaming.

HDPE uses the homogeneous welding technique for field seams. This involves the extrusion of a bead of parent material directly onto the lapped edges which if properly applied develop a bond as strong as the parent material. The technique is similar to the welding of steel.

For greatest security, the seaming method should be capable of producing a bond as strong as the base material. Seams should be tested in both shear and peel to ensure their integrity.

SELECTION CRITERIA

Up until now we have discussed various properties of available membranes. Since there are significant differences in chemical and physical properties, the engineer is faced with the task of applying the correct membrane to each application. To begin with, there are four basic criteria which should be evaluated, these are:

1. Site planning considerations
2. Degree of hazard
3. Service time
4. Membrane selection

By far the most important selection element is site planning considerations. Table 3 list various factors which should be considered when designing a containment facility.

TABLE 3

FACTORS TO BE CONSIDERED IN THE SITE PLANNING CONSTRUCTION PROCESS

1. Characteristics of the waste to be impounded
2. Characteristics (type and texture) of "in situ" soil materials
3. Subgrade characteristics - soil borings
4. Desired characteristics of bottom and side surfaces
5. Location of bedrock
6. Stability of materials
7. Drainage considerations
8. Impoundment dimensions
9. Wind direction and velocity
10. Ambient temperature
11. Gas venting
12. Local vegetation
13. Floor considerations
14. Berm width requirements
15. Inflow/outflow/overflow conveyances
16. Monitoring/leak detection systems
17. Cover material availability/characteristics
18. Proximity to major waste generators
19. Proximity to residential and commercial areas
20. Coupon testing and evaluation, if applicable
21. Weed control

The geotechnical aspects of site design are extremely critical. It should be emphasized that while flexible membrane liners offer a high strength/thickness ratio, they should not be considered structural members. Numerous failures have occurred as a result of poor engineering design of the containment system. The base and side slopes of the pond should be well stabilized to assure there will be no slope failure or significant differential settling. Movement of the underlying base can create inordinate stresses in the membrane which could result in ultimate failure. One of the important properties of membranes is that they will elongate and therefore, can accommodate some movement, however, the design engineer should try to minimize this. The subbase should also be properly graded with no rocks or penetrating objects which could puncture the material.

The subsurface conditions below the pond bottom should also be considered. A high or fluctuating water table could create undue pressure on the membrane. Additionally, if gas is present below the membrane it can be forced upward by the water table and if not properly vented can cause the membrane to float.

Environmental factors are also key to selection criteria. Such factors as light and ozone intensity, can affect the membrane if it is installed exposed. Exposed membranes normally contain carbon black to protect against the effect of exposure to weather.

Temperature both ambient as well as the temperature of the contained waste water also plays a critical factor. Most membranes lose strength with increasing temperature.

Degree of hazard will also influence selection criteria. Put simply, containment of a pure water supply does not present the same degree of hazard as containment of a toxic and hazardous waste, although the former may be as equally important due to water conservation requirements.

Service time should also be considered. There are many applications which only require service for one or two years. The membrane for this service could be of a lower quality than one required for twenty years service.

Having decided upon the type of liner, the engineer must still determine the design thickness. This will be affected by subgrade preparation, installation method, and future maintenance requirements. For example, for a properly prepared subgrade in a pond which will be completely full after installation a relatively thin film membrane could be selected in the order of magnitude of 30 to 35 mil. However, if the membrane is to be installed over a rougher subsurface or will be drained and cleaned by mechanical means at some later date the application may require a thicker membrane.

One of the most effective methods of analyzing the effects of thickness was recently developed by the U. S. Department of Interior.(2) It involves placement of the membrane in a pressurized vessel over a sample of the actual subbase. The vessel is then pressurized at various levels to determine the failure point of membranes over different subbases. This method is particularly valuable for deep ponds where large hydraulic heads are anticipated. It does not give a direct correlation to tire loads and or track loads which could be created during the installation process or subsequent cleaning process. The engineer can calculate these loads and relate them back to thickness.

FLEXIBLE MEMBRANE SUPPLIERS

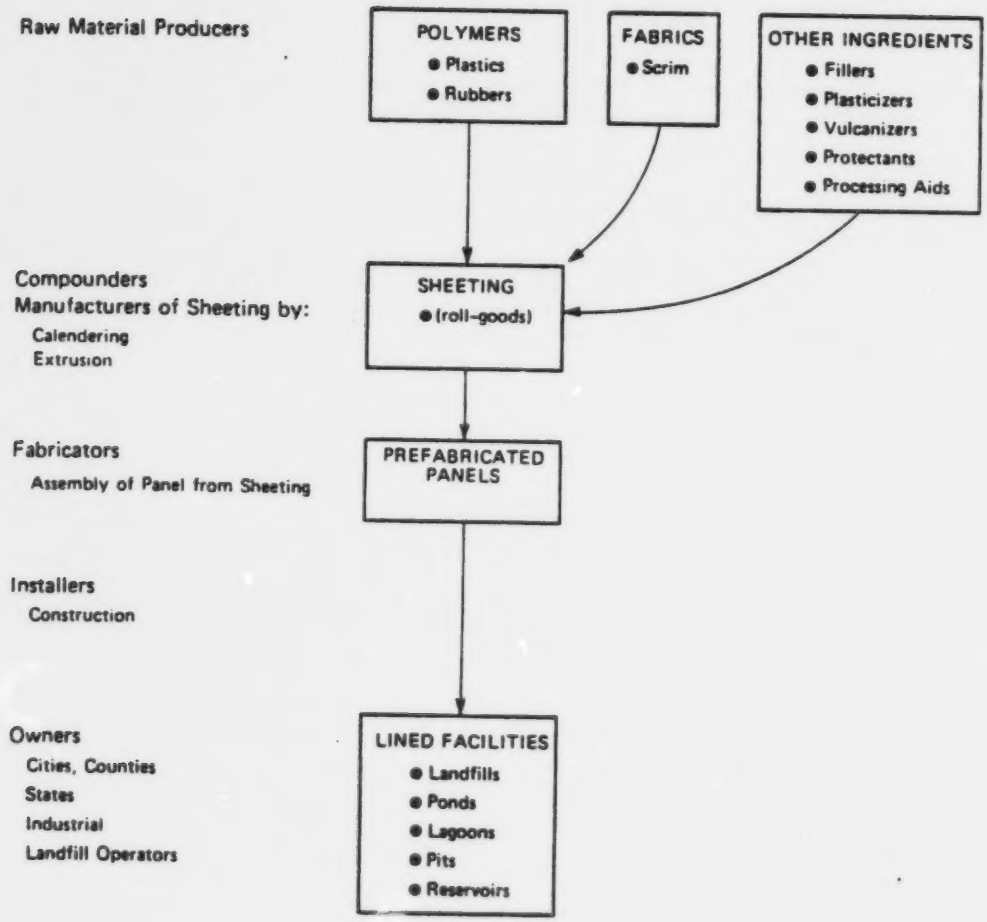
Once all of the economic and technical evaluations have been completed, a supplier will ultimately be selected to supply and install the material. Figure 6 diagramatically shows a breakdown of the flexible membrane liner industry.

The process begins with raw material production which is typically done by the major chemical companies. Using basic polymer components, the raw materials are then compounded into various chemical compounds. It is at this step that the formulations are "customized" for specific applications.

After compounding, the materials are manufactured into sheets by either calendering or extrusion. Sheet goods are then fabricated into larger panels which are then shipped to the field for installation.

FIGURE 6

FLEXIBLE MEMBRANE LINER INDUSTRY



There are some suppliers who are fully integrated from the compounding of the raw material through to installation. Others are merely installers of fabricated panels. If warranty and security are important, the integration of the supplier may become an important consideration.

ECONOMICS

Last but not least is the estimated cost of the material selected. Figure 7 gives budget estimate installed costs for the liner materials described in this paper as well as the range of thicknesses normally available. PVC is usually the most economical material although it must be covered due to its generally poor long term weatherability. HDPE, Hypalon and CPE are normally considered for most hazardous waste facilities with selection dependent on the specific nature of the application. HDPE offers the broadest range of thickness availability while Butyl is usually the most expensive.

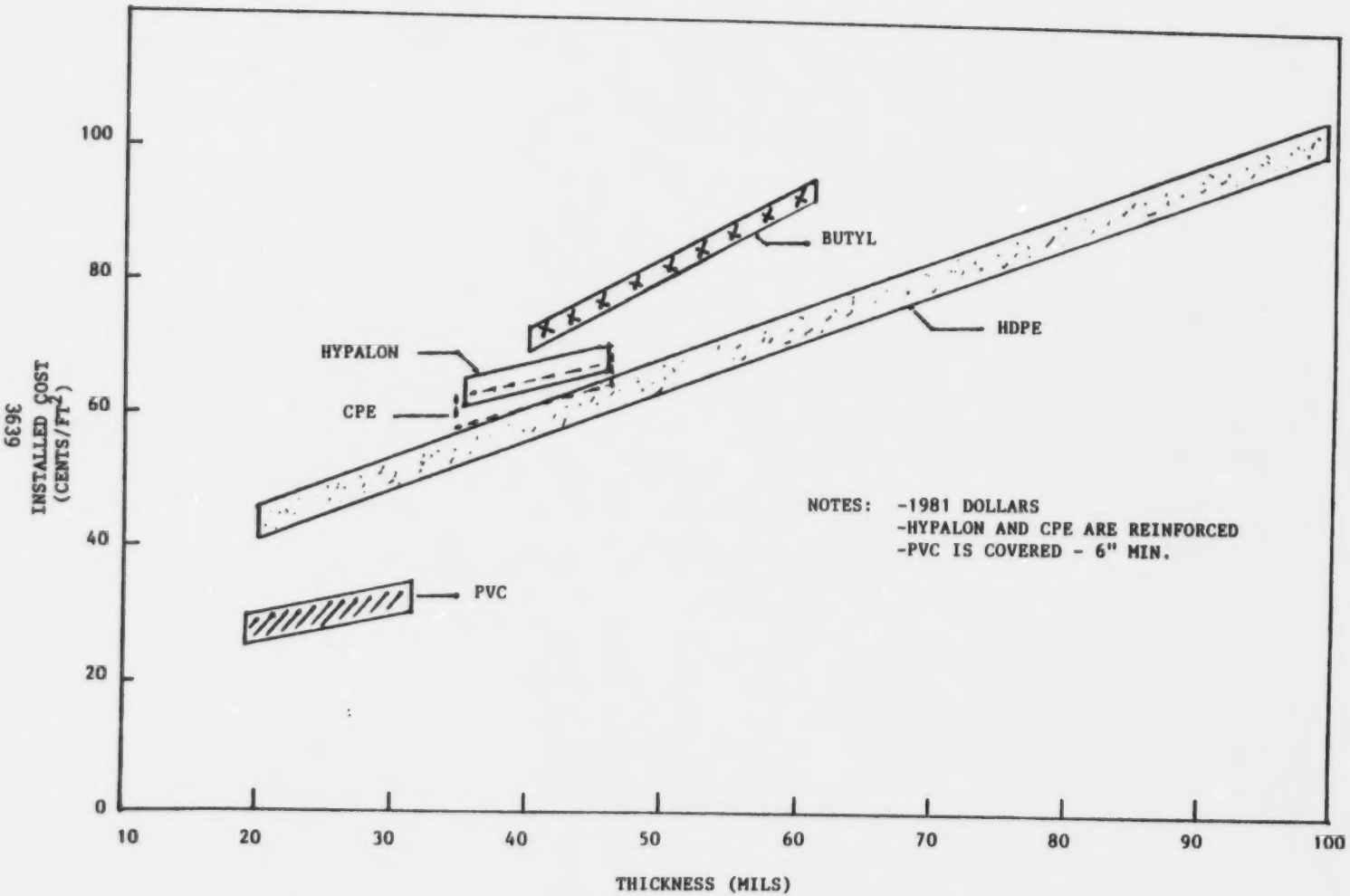
It should be emphasized that the overall cost/performance ratio of a particular liner material should be evaluated prior to final selection.

SUMMARY

The use of flexible membrane liners for the containment of hazardous wastes is very cost effective. However, careful engineering evaluations of a material's chemical and physical properties, joining techniques and careful supplier selections are required. By following the steps outlined in this paper, the engineer can assure himself of selecting and applying the correct membrane for each application.

FIGURE 7

BUDGET INSTALLED COSTS FOR A VARIETY
OF FLEXIBLE MEMBRANE LINERS



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1. Mansen, Allen, "Can Clay Liners Prevent Migration of Toxic Leachate?", Civil Engineering Magazine, July 1981, pp 60 - 63.

2. Frobel, Ronald K., "Design and Development of an Automated Hydrostatic Flexible Membrane Test Facility," U. S. Department of Interior, Water and Power Resources Service, Report No. REC-ERC-80-9.

3. Lining of Waste Impoundments and Disposal Facilities. U. S. EPA, Report No. SW-870, September, 1980.

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LEAK-DETECTION IN DAMS OF RESERVOIRS AND TAILINGS PONDS BY THE SELF-POTENTIAL METHOD

The problem of leaky dams and tailings ponds is one that is becoming of increasing concern these days. In the case of water reservoirs the danger lies in possible dam failure or water loss; in the case of tailings, we have a potential problem of contamination of streams or groundwater by waste water. There exists a powerful geophysical method for locating such leaks--a method that also happens to be quite economical. I am speaking of the self-potential method (Figure 1), devised during the 1800's for the purpose of mapping mineral deposits, and--more recently--applied to the solving of groundwater and engineering problems. It is the method commonly used to find leaks in pipelines. I employed the technique in the search for geothermal fluids for AMAX since 1977, and, with my present firm ALBIREO, have been applying SP to mineral, groundwater, and petroleum exploration, as well as to leakage problems in reservoirs. Self potential is a passive electrical technique that maps distortions of the natural d.c. electric field in the ground, arising from natural and artificial conductors, movement of fluids, and other causes. Here is an example of the SP response due to a cylinder of powdered pyrite as modeled in our (Figure 2). The presence of oxidation/reduction reactions going on above and below the groundwater level sets up a natural batteries that generate local electrical circuits in the surrounding medium. The net result is typically a sharp negative anomaly over the conductor. Here is a classic example of an SP negative anomaly over an auriferous sulfide deposit in Turkey (Figure 3).

Another laboratory experiment demonstrates the effect of moving groundwater on the surface potential (Figure 4). Streaming potentials arise from the stripping of ions across the Helmholtz double layer between the solid/liquid boundaries of a porous or fissured material. In this case we are dealing with a solution of potassium nitrate in quartz sand. The negative ions customarily adhere to the sand, while the positives move with the fluid: the end result is a potential gradient along the flowpath, with the more positive response around the point of discharge. In the natural environment this process gives rise to negative voltages over areas of recharge and positives in the discharge areas, such as valleys. Here is an example from Kansas, obtained during a petroleum SP survey, where a potential difference of about 35mV

correlated closely with the inverse of the terrain (Figure 5). Another example is from the Caucasus (Figure 6). Groundwater anomalies exceeding 2 volts can be found over volcanic craters in areas of high precipitation, such as Alaska and Hawaii.

At this point let's explain briefly how SP readings are taken. We employ non-polarizing electrodes--either copper/copper- sulfate or lead/lead-chloride types--inserted into shallow holes in the ground and connected by a long cable and high-impedance digital meter (Figure 7). One electrode serves as a base, while the other is a roving element, which we continually move outward along a line. Voltage readings are made at intervals, anywhere from 10 or 20ft (in the case of dam work) up to 100 or 200 meters for geothermal prospecting. Data are then subjected to a number of corrections (for electrode drift, etc.) and profiles and contour maps are plotted to depict local anomalies. The field procedure is carried out by two persons, and preliminary data processing can be done at the end of each day. Final analysis, plotting and interpretation are done later at our computer.

That positive SP responses come about over fluid discharges can be seen in these examples: 1) a karst rise of groundwater from carbonate solution conduits into overlying alluvium (Figure 8); a pair of convection cells driven by hot lava in a dike in Hawaii (Figure 9), and the discharge of Red Hills hot spring in Utah, correlated with the temperature profile (Figure 10). The Soviets have published numerous cases of SP response over dams and reservoirs, and I show several cases here. Monitoring is done across either face of an earth-fill dam, around the shoreline of the reservoir, as well as across the water surface. Here is an example of a reservoir that was elevated after a long period of sedimentation (Figure 11). SP measured along the water surface showed a relatively flat response over the stable former lake; however, as the lake level encroached on new ground, negative SP anomalies were seen. Flowmeter measurements confirmed that water was leaking into the underlying rock and producing eddies. Corresponding positive anomalies were observed around the base of the dam. Another case of a high dam in Armenia 180m wide shows the results of SP surveys across the dam face at two different water levels (Figure 12). The contours of SP response reveal a depression surface shifting in orientation from the east to the southwest as the water rose. The localized negative anomalies represent concentrated zones of downward infiltration later found to result from inhomogeneities within the fill. The result was considerable frontal and roundabout seepage, with consequent water losses. Measures were then taken to control the leakage.

I am permitted to show examples of SP profiles over two leaky reservoirs on a livestock ranch in Wyoming. In the first case the dam had a head of about 15 feet, and observed seepage varied from that of muddy ground to flowing water (up to 10gpm, estimated) (Figure 13). We devised a rough seepage index ranging from 0 for dry ground to 10 for fountains (Table 1). Five represents very muddy ground, and at a value of 6 or 7 water is discharging as a small stream. After sampling the ground and noting the seepage at 20ft intervals, SP measurements were made at the same sites along profiles at the dam base and 10ft upslope. Both showed a strong correlation between the apparent seepage and positive SP

response. One evident exception likely represents seepage that is not obvious at the surface. We had hoped to be able to run a profile along the waters edge of the reservoir to look for corresponding negative SP features indicating points of infiltration; however, excessive metal junk used to prevent wave erosion made the attempt futile. As I mentioned earlier, SP does respond strongly to the presence of conductors.

In a second dam--this one over 1500ft long--a similar correlation was found (Figure 14). In this case sharp negative anomalies appeared in the vicinity of metal pipes serving as drains. SP negative trends beyond the ends of the dam correspond to rising ground, and reflect normal groundwater movement beyond the influence of the dam itself. Again in this case we couldn't survey along the water's edge because of the abundance of automobiles parked in the water.

The SP techniques that I have illustrated can be applied to any kind of impondment, particularly that of tailings. While there can be a decline in SP response with lowered pH of the contained fluids, we can still expect to see substantial leakage, particularly within porous fill. Resistivity methods, on the other hand, which map only the presence of the fluid rather than its movement, would probably fail in the case where the fluid or the fill was very conductive. In any event, SP anomalies can be reinforced by other geophysical tools, such as thermal, seismic, flowmeter and electrical surveys;, however, these are more expensive and time-consuming. A typical SP survey over a dam such as I have shown might require one or two days in the field plus the subsequent data processing. Self potential should be considered as the primary tool to employ, to be followed up by another method directed at the leaks identified by the SP survey.

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Arthur L. Lange
Managing Partner, ALBIREO Ltd

FIGURES

Figure 1. Reading a self-potential station on a dam. The roving electrode is connected through the staff, meter, and a long cable to a reference electrode at the start of the line.

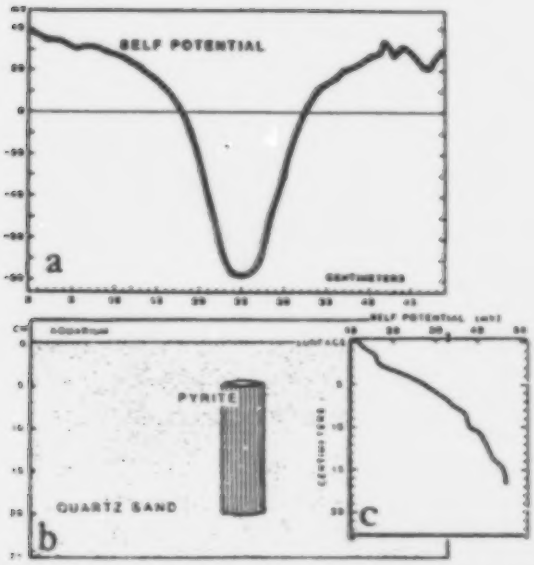

Figure 2. SP response over a 5 - 15cm cylinder of powdered pyrite and its corresponding downhole log, resulting from laboratory tests by Albireo.

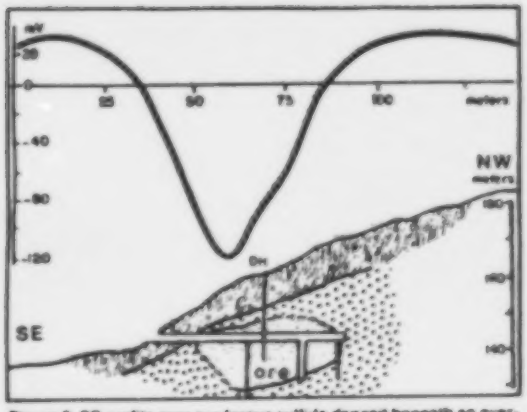

Figure 3. SP profile over auriferous sulfide deposit beneath an overthrust in Turkey (after Yüngül, 1954).

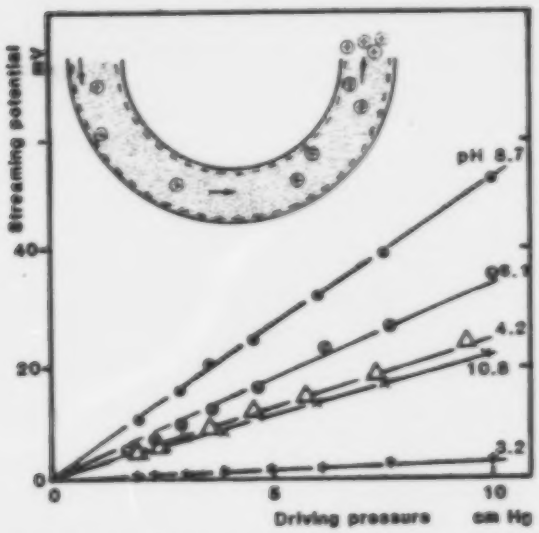

Figure 4. Streaming potential vs. driving pressure for a sand-filled tube plotted for various pH solutions. Negative ions adhere to the walls, while the positive ions move with the fluid (from Ishido & Mizutani, 1981).

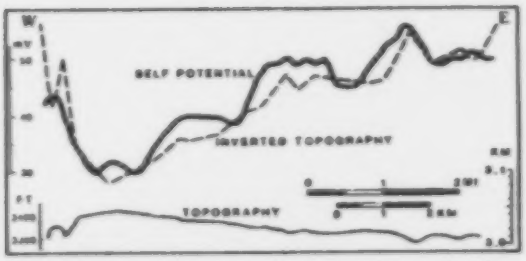

Figure 5. Inverse relationship of SP to topography resulting from groundwater movement in Kansas Ireas (Albireo survey)

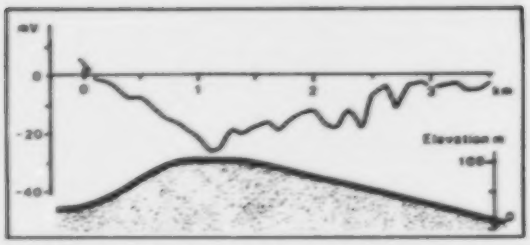

Figure 6. Inverse correlation of SP response with elevation (from Semenov, 1974).

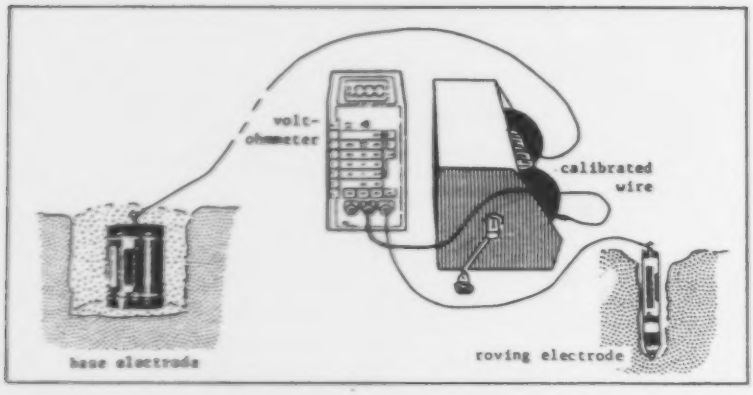

Figure 7. Basic SP field instrumentation.

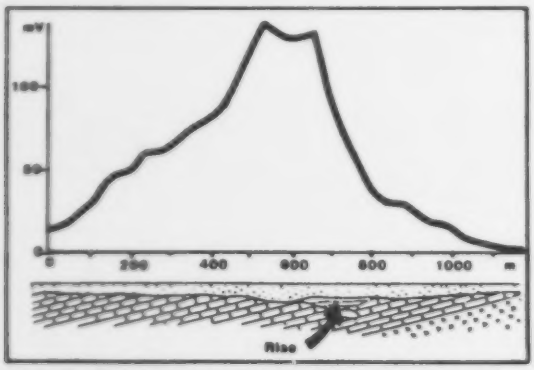

Figure 8. SP response over a groundwater discharge from karst solution channels into overlying alluvium (Semenov, 1974).

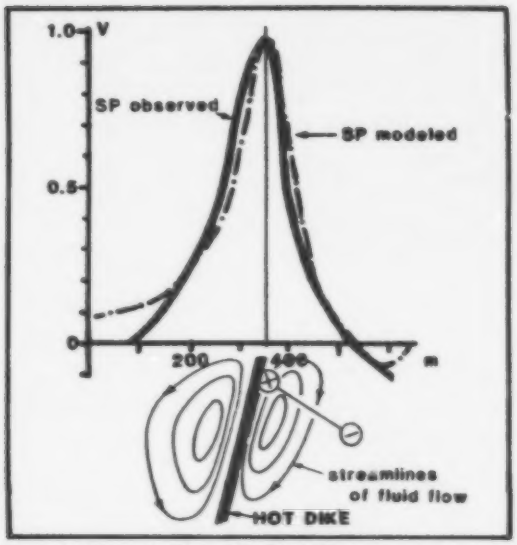

Figure 9. Observed and modeled SP responses over a hot dike near Kilauea volcano, Hawaii. The SP results from convecting groundwater, driven by heating (Zablocki, 1976).

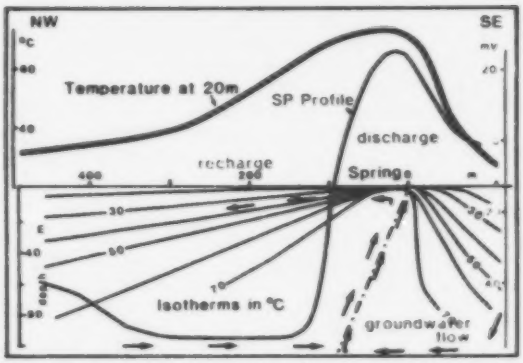

Figure 10. Self-potential response resulting from fluid movement at Red Hill Hot Springs, Utah (from Sill, 1983). The corresponding temperature profile and underground isotherms, as well as the groundwater pattern are taken from Kitty, et al., 1979)

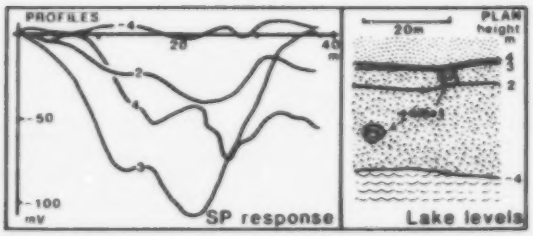

Figure 11. SP responses to leakage beneath a reservoir for successive water levels. No leakage was detected below the natural lake (Level -4m), where sedimentation had long before plugged any channels (Semenov

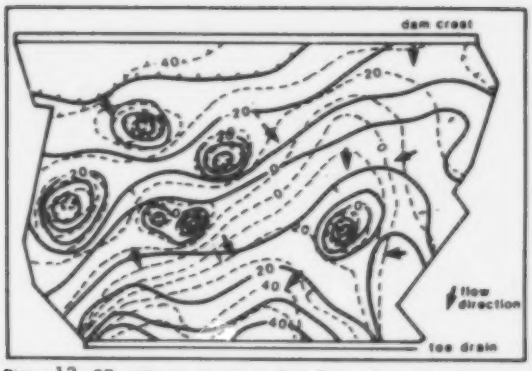

Figure 12. SP patterns across a dam face, where the negatives illuminate points of seepage. Contours corresponding to minimum water level are solid; maximum, dashed. Frontal and roundabout seepage shown by arrows (Bogoslovsky & Ogilvy, 1970).

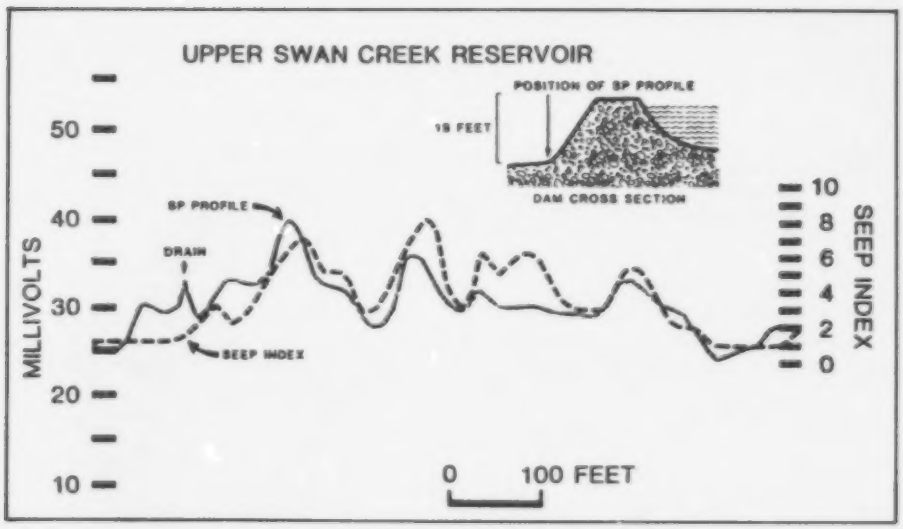

Figure 13. Self-potential profile along the base of a dam, compared to an estimated seepage profile (cf., Table 1).

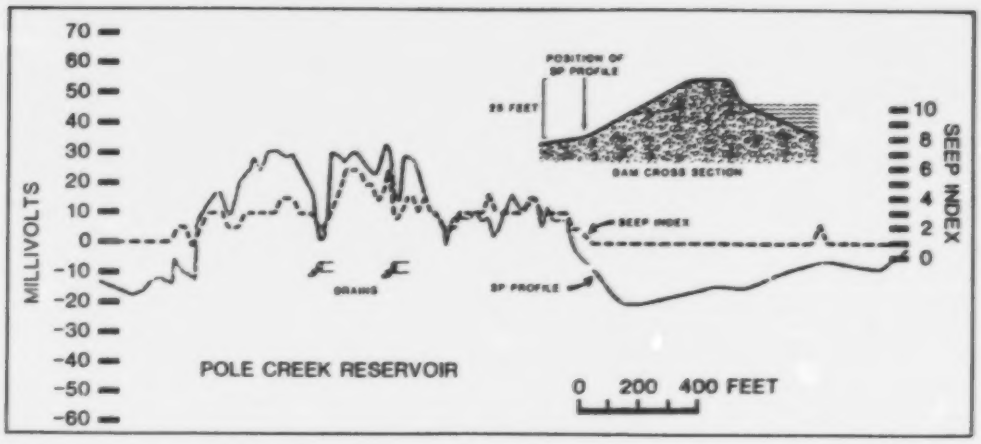

Figure 14. Self-potential profile along the base of a dam, compared with the seepage profile. Pull-downs of the SP towards the ends of the dam result from rising terrain.

Table 1. SEEPAGE SCALE

0 =	bone dry
1	less dry
2	less dry
3	moist, clayey
4	somewhat muddy
5	sink-in type mud
6	mud and evident trickeling
7	puddles and trickling
8	active flowing rivulet
9	evident upwelling and flowing
10	fountaining

CHAPTER 60

MONITORING AND SAMPLING

- Monitoring Ground Water 3651
- Environmental Monitoring for Regulatory Compliance and Operational Control, JIM V. ROUSE (1984) 3653
- Unsaturated Vadoz Zone Sampling 3662
- Ground Water Monitoring - Sources of Information 3663
- Ground Water Monitoring: Saturated Zone 3663
  - Grab Sampling 3664
  - Down-the-Hole Submersible Pumps 3665
  - Down-the-Hole Analyzers 3668
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- References 3672
  - Lysimeters Allow Quicker Monitoring of Heap Leaching and Tailings Sites, BOND and ROUSE (1985) 3673
  - Groundwater Monitoring Technology, ROBERY D. MORRISON (1984), Order Form for Book 3679
  - Variation in Water Quality During Initial Pumping of Monitoring Wells, WILSON and ROUSE (1983) 3681
  - Laboratory Evaluation of Ground Water Sampling Mechanisms, BARCELONA, HELFRICH, GARSKE, and GIBB (1984) 3685
  - Johnson Environmental Equipment Brochure 3695
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MONITORING GROUNDWATER

To determine whether impoundments are achieving what they were installed to do, namely to keep contaminants from escaping to the environment, it is necessary to monitor groundwater around many tailings and effluent ponds. Ground water quality protection is currently becoming one of the main focal points of the USEPA and also of some state regulatory agencies. Groundwater monitoring is required in most operator permits for new hydrometallurgical mineral processing installations in the U.S.A. and is likely to be required increasingly for non-U.S.A. operations in the near future. When RCRA regulations are finally formulated for solid waste disposal in the mining industry, the need for monitoring is expected to increase considerably, especially if the RCRA

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ENVIRONMENTAL MONITORING FOR REGULATORY COMPLIANCE AND OPERATIONAL CONTROL

INTRODUCTION

Environmental monitoring is currently required under a number of various environmental regulations. All too often, such environmental monitoring is regarded by the operational personnel as a necessary evil, to be conducted at the least possible cost, with little or no in-house use of the data or any significant effort at quality control of the data other than that required by the regulations.

Contrary to this common approach, environmental monitoring can be highly useful, not only as a protection against being blamed for natural environmental degradation resulting from mineralized ground or from past operations, but such environmental monitoring can also be highly useful in operational controls of milling and leaching operations. The following discussions will center on the types of environmental monitoring which must and should be conducted, and uses of such operational monitoring data in control of the facility.

APPLICABLE REGULATIONS

Environmental monitoring of various media (air, receiving water, effluent, ground water, etc.) is required by a number of Federal regulations and state counterparts. Some of the more critical regulatons are discussed below.

Waste water discharges are permitted under a National Pollutant Discharge Elimination System (NPDES) permit issued under the Clean Water Act. Such permits require effluent monitoring and frequently specify receiving water monitoring, to assure compliance with stream standards. Extensive ground water monitoring is required by the Resource Conservation and Recovery Act (RCRA), for solid waste or hazardous waste facilities. At present, mining operations are exempt from RCRA; however, this happy condition is likely of short-term duration. Many states have existing ground water regulations which mandate monitoring. Stack and ambient air sampling is required under the Clean Air Act. Preparation of an environmental impact statement will often require preoperational air, stream and ground-water sampling. Facilities operating under an NRC Source Materials License will similarly require air and water sampling.

TYPES OF MONITORING

Monitoring types can be subdivided under a number of categories, such as chronologic (time sequence) or media monitoring which centers on the type of material (air, effluent, or receiving water) being sampled.

Chronological Monitoring

Monitoring operations follow a logical chronological sequence, beginning with preoperational monitoring, going through monitoring conducted during the life of the operation, and culminating with monitoring during reclamation and post-closure periods.

The preoperational monitoring is required by a number of environmental regulations, to define baseline conditions which exist prior to the onset of project activities. Generally, such preoperational monitoring is considered to extend over at least a one-year period of time, to provide information of the seasonal variability of ground water levels and quality, surface stream flows and quality, and ambient air quality. This type of preoperational monitoring can be highly useful in that it can document both natural contamination and contamination resulting from past, historical mining activities.

It is important that preoperational monitoring truly reflect conditions which exist. This requires that the monitoring wells (for ground water) or surface stations be adequately located to provide coverage for the facility. In the case of ground water sampling it is vitally important that the monitoring wells be adequately purged to eliminate water which is standing within the bore hole. As is described by Wilson and Rouse (Winter 1983) there frequently are order of magnitude variations between the water standing in a bore hole and the true formation fluids. Pumping of the sample until stable values of pH and conductivity are achieved can do much to assure that the sample is truly representative.

Preoperational sampling should be done under chain of custody procedures such to allow the reconstruction of the "paper trail" of the sample from the time of sample collection until delivery to a qualified laboratory. Chain of custody merely means that

the sampler can document, by written records, the movement of the sample from one person to the other. The sample is considered to be within a person's custody when he has it either in sight or in a locked or sealed container. (Moran & Rouse, June 1981)

During preoperational monitoring, the list of parameters of analysis will generally be more extensive than during subsequent monitoring since it is important to address the potential presences of a number of parameters. As a minimum, Envirologic Services International would recommend the analysis of all major ions (calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, and sulfate together with total dissolved solids), to allow an analysis of the water mass by means of geochemical techniques. In addition, the samples should be collected and analyzed for relevant primary and secondary drinking water parameters such as arsenic, cadmium, chromium, lead, mercury, selenium, silver, iron, manganese, zinc, and copper. If radioactive minerals are associated with the project, radium 226 and 228 concentrations should also be determined.

Operational monitoring, conducted during the life of the project, will require a number of monitoring sites and parameters specified by the operational license. Many times, the regulatory agency can be persuaded to reduce the suite of parameters relative to preoperational monitoring, based on a geochemical analysis of the potential migration of contaminants and their demonstrated absence during preoperational monitoring. The approach would be to monitor for initial, conservative parameters

until they arrive at the monitoring site, and only then to inaugurate subsequent monitoring for less conservative parameters.

Post closure monitoring also will frequently be required by the regulatory bodies, which will specify the parameters of analysis. Post closure monitoring frequently can involve even fewer parameters.

Media Monitoring

The type of monitoring involved with various media will obviously vary greatly. For example, air monitoring can be of two types, stack sampling and ambient air monitoring. The former is conducted by means of carefully specified techniques which traverse facility smokestacks, and are required on a periodic basis by the regulatory agency. Such stack sampling can be highly useful in explaining losses of desired product and in adjusting the operation to achieve better recovery. Ambient air monitoring is specified by the regulatory agency, and probably does fall under the "necessary evil" category.

Liquid effluent sampling is required where there are direct discharges, under a NPDES permit, to receiving surface waters. As in the case of air stack sampling, effluent samples can be highly useful on an operation basis, to control dissolved or suspended losses of desired product.

In the case of liquid effluent sampling, the regulatory agencies frequently require the installation of flow-measurement devices such as Parshall flumes, or V notch weirs. Such flow measurement can be useful in an operational mode, to reduce excess water usage, together with allowing the collection of flow-weighted composite samples rather than time-weighted monitoring. Flow-weighted composite samples are those in which a volume of the sample is collected at a regular time period, with the volume depending on the flow at that time, while time-weighted samples utilize equal volumes of sample collected over each of a number of composite periods. A flow- weighted sample is generally more representative, especially under those conditions where effluent flow varies widely during the process stage. The collection of flow weighted effluent composite samples requires the presence of a calibrated flow measurement device, and the permission of the regulatory agency. (Moran & Rouse, June 1981)

The operational permit will likely specify whether effluent samples are to be reported on a "total" or "dissolved" basis. In the case of total samples, the sample should include suspended material contained in the flow, while "dissolved" samples should be field filtered through 0.45 micron filters prior to the addition of the preservative. Dissolved data are generally more informative, from an operational control standpoint.

Receiving water samples for surface streams are generally collected upstream and downstream of the point of discharge, to allow an evaluation of the impact the discharge has on the

receiving stream. Generally, such receiving water samples are collected on a "grab" basis at a selected location. Care should be taken to assure that the sampling site has adequate mixing across the surface stream. This can be ascertained in the field by a traverse of pH and conductivity readings across the width of the stream. If the stream is deep, consideration should also be given to vertical traversing, to assure that there is not vertical stratification of water quality. (Moran & Rouse, June 1981)

Probably the greatest waste of money in the environmental monitoring area occurs in the collection of inappropriate ground-water samples. Not only can such samples represent a waste of money in that they do not properly reflect true conditions, but the samples can lead to a false sense of security when there actually is a problem or conversely they can cause concern when there is actually no problem. Probably the greatest source of error in ground water sampling results from failure to adequately purge the well prior to sample collection. It has been the ESI experience (Wilson & Rouse, Winter 1983), supplemented by published literature, that there frequently is an order of magnitude variation in water quality between the water standing in a well bore and the true formation fluid. This can be overcome by a knowledge of the hydrologic regime and a careful withdrawal of water, with continuous or intermittent measurement of pH and conductivity until stable values are achieved in the pump discharge. The samples should then be collected, appropriately field filtered through a 0.45 micron filter to

remove suspended material and adequately preserved in accordance with standard procedures prior to shipment to the analytical laboratory. It is important the dissolved constituents in the sample remain dissolved, and not precipitate on the bottom bottle. Therefore, appropriate preservatives should be added to the bottle prior to placing the sample in the sample container.

Experience has shown that many times the results from analytical laboratories bear little or no relationship to the water within the sample. For this reason, ESI routinely collects 15% interlaboratory quality control samples, in which duplicate samples are sent to separate laboratories comparative assay. A blind duplicate intralaboratory quality control sample, intentionally mismarked with a ficticious name, should also be collected at the QC site and submitted to the primary analytical laboratory, along with the original, properly marked sample. A comparison of the three results from the same source is often highly informative and educational.

SUMMARY

Environmental monitoring can be useful as protection against blame for pre-existing contamination, assuming the samples are properly collected, documented, and analyzed. Such sampling can also provide operational personnel information on losses of product material via stack emissions, effluent discharge, or seepage losses from storage tanks or ponds. Environmental monitoring is dictated by environmental regulations, at a

significant cost, but should become an important part of the operational control of a facility.

Heap leaching operations represent a low capital cost approach for recovery of precious metals from tailings, waste rock, or ore, assuming that the loaded leach solution is properly recovered, and not lost by seepage from leach pads or pregnant solution ponds. Many such facilities are located in areas where the water table is far below the land surface. Conventional monitoring wells can be very expensive and do not adequately address such losses. A better approach is to monitor changes in moisture quality within the vadose (unsaturated) zone by means of pressure/vacuum lysimeters. Such units actually draw water from the soil below leach pads or pregnant storage ponds. They are inexpensive to purchase and install and have been accepted for monitoring, in lieu of monitor wells, by various agencies. Their installation is very critical and should be carefully supervised by experienced personnel with prior history of lysimeter installation.

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1. Moran, Robert E. and Jim V. Rouse, June 1981, "Procedures for collection of water-quality samples and data", Envirologic Systems, Inc., METF-3, prepared for Central Arizona Association of Governments, Florence, Arizona

2. Wilson, Lee C. and Jim V. Rouse, Winter 1983, "Variations in water quality during initial pumping of monitoring wells", Ground Water Monitoring Review, Vol. 3, No. 1

regulations adopt a site-specific approach to mining waste disposal as hoped for by the mining industry.

There are three aspects to determining whether contaminants are leaking to the environment. Firstly, monitoring obtains samples that are analyzed to measure whether ground water quality is being impacted and if so, by how much. Several ways of doing this are reviewed below. In each case, a monitoring grid is required because contamination moves through an underground aquifer in plumes and, unless the sampling pattern intercepts such a plume, a leak can go undetected for years. Monitoring can only detect a leak after a considerable volume of contaminated water has left the impoundment and has migrated at least as far as the monitoring well.

A second approach is to detect leaks early in the impoundment itself. This technique shows where the leak is located, and this can be helpful in planning a repair program. If a leak can be detected early enough, hopefully before contaminants reach the monitor well sampling points, then it may be possible to correct the problem before real damage is done. LANGE (1984) described a geophysical method of leak detection which appears to be useful. His paper is inserted in Chapter 59 on water impoundments and evaporation ponds, and he has subsequently developed another method to conveniently survey beneath impoundments for leaks which looks as though it will prove to be both simple and useful.

ARTHUR L. LANGE
Albireo Ltd.
3798 Marshall Street
Wheat Ridge, CO 80033
(303) 431-0432

UNSATURATED OR VADOSE ZONE SAMPLING

A third and new approach is described by BOND and ROUSE (1985), inserted at the end of this chapter, and mentioned by MORRISON (1984) which involves the installation of Lysimeters which allow very much quicker monitoring of heap leaching and tailings sites as well as storage reservoirs and evaporation ponds. As BOND and ROUSE point out, the conventional perimeter monitor well may take months or years to detect a leak that will be detected within several days or weeks using a properly placed and installed lysimeter.

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(303) 759-2611
Jim V. Rouse

For the time being, unsaturated or vadose zone monitoring with lysimeters is regarded as an extra safeguard rather than as a replacement of perimeter monitor wells.

GROUND WATER MONITORING - SOURCES OF INFORMATION

Numerous publications review the goals and techniques for ground water monitoring. One useful source is: "Ground Water Monitoring Technology" by Robert D. Morrison and available at $31.00 plus $2.00 shipping ($12.00 outside U.S.A.).

TIMCO MANUFACTURING, INC.
851 15th Street
Prairie du Sac, WI 53578
(608) 643-8534

BARCELONA, et al. (1984) evaluated a whole range of groundwater sampling mechanisms. These authors undertook this survey on behalf of the Illinois State Water Survey which is recognized as a leading authority on groundwater monitoring:

ILLINOIS STATE WATER SURVEY
Dept. of Energy and Natural Resources
Champaign, IL
Michael J. Barcelona
Robin A. Miller

Their paper is inserted below as it is an excellent review.

GROUND WATER SAMPLING - SATURATED ZONE

There are several important aspects to ground water monitoring, the ones that come to mind immediately being:

- Validity of the sample.
- The positioning of the Monitoring Well
- The depth in the well from which the sample is taken.
- The equipment used.

Validity of the sample is all important. Is the sample collected representative of water in the aquifer? Is there any possibility of contamination or dilution of the water in the well? Has standing well water been adequately flushed out for a representative sample to be taken? Understanding this latter question is made possible by WILSON and ROUSE (1983) whose paper is inserted below.

The positioning of the monitor wells is also vital. Contamination migrates in plumes, and monitor well positioning should be compatable with what can be learned about the hydrology of the site. BOND and ROUSE (1985) above mentioned the case where a "contaminant leak was detected on a stream bank before it was detected in monitor wells. There is little point in monitoring samples from groundwater at locations that will be missed by contaminant plumes. These days, where CERCLA or Superfund laws are being

enacted, monitoring programs serve to protect the operator--the sooner he finds out about a leak or contaminant excursion, the less costly it is likely to be to repair the "damage." Monitor well positioning to provide a timely warning which would allow corrective measures to be taken before damage has been done rather than after it is too late to avoid damage would, of course, be most useful.

Many monitoring systems are able to seal off the well at a selected level to make sure that ground water is being sampled at a prescribed depth. It is vital that the correct depth is used. Is the sample being drawn from the aquifer of interest or from the one below it?

There are several types of monitoring equipment, most of which are listed and discussed comparatively by BARCELONA, et al. (1984) whose paper is inserted below. They evaluated performance of various available ground water sampling mechanisms for purgeable and gas-sensitive parameters and found that positive displacement bladder pumps were the best of all kinds that they evaluated from that standpoint.

There are several approaches to the equipment used for ground water monitoring:

- Grab Sampling
- Down-the-Hole Pumps
- Dedicated Monitor Pumps
- Down-the-Hole Analysis

Grab Samples

Grab samples drawn with the use of a bailer are the simplest devices as far as equipment and cost of hardware are concerned. These may be useful for very shallow monitoring wells containing a very limited volume of water. This system becomes extremely time consuming and presents samples of questionable validity, especially from deeper wells. Total flushing out of standing well water using a bailer is often impractical. The bailer moving up and down in the casing will cause a fair degree of mixing. Because the bailer must move to the actual point at which the sample is to be drawn, it is not possible to plug off higher levels of the casing to gain control of where the sample is actually being drawn from. Because the same bailer is used from one monitor hole to another, there is a possibility of cross-contamination even if the bailer is rinsed between holes. For a large wellfield, the bailer approach is labor intensive.

A company that specializes in this type of monitor well which involves well casing with a screened end and an innovative bailer is:

GROUND WATER SAMPLING, INC.
West Union Business Park
1855 West Union, #35
Englewood, CO 80110
(303) 781-5589
Geoff Hunken

The entire down-hole assembly of GWSI systems is made of Bisphenol-A Epoxy with fiberglass reinforcement which provides very high strengths and has tested well to show zero priority pollutant leaching. The casing is suitable for all weather installations, unlike PVC which gets brittle in freezing weather.

GWSI claims cost savings resulting from the elimination of on-site casing preparation time and the rapid, simple installation procedures of GWS, Inc. casings compared with other casings available. Rig time for the entire casing installation in a 100-foot well of any diameter is claimed to be six minutes. This vendor claims that for a typical conventional 100-foot well with sand control screens, assembly of the casing, screens, crossovers, and bottom caps, steam cleaning inside and out, and installation down the hole, usually 3.5-4 hours of rig time is required. At 1983 costs, GWS, Inc. claims that their casing can save $500 per hole. The GWS, Inc. casing requires no couplings, adapters, crossovers, or bottom caps, and no field welding or adhesives.

Ground Water Sampling, Inc. offered 4.3" ID wells to 100' at $17.95/foot in 1983, and $11.50/foot for 2.2" ID casing installed to 38 feet.

A second wellknown supplier of bailer sampling equipment is:

TIMCO MANUFACTURING, INC.
Post Office Box 8
Prairie du Sac, WI 53578
(608) 643-8534

Envirologic Services International uses a bailer for some shallow well monitoring jobs in preference to lowering a submersible pump down the hole. The reason is that the bailer is easy and quick to clean between wells, and it is simple to cut off and discard the rope that was submerged in the previous well before lowering the bailer into the next hole. More time is needed to clean out submersible pumps, and the sampling tube as well as the cable, etc. when using the latter.

Down the Hole Submersible Pumps

If a wellfield is to be infrequently sampled--perhaps just once, for example, it would not be practical or economical to install dedicated pumps in each hole. In such cases, as well as in some others where monitoring is more frequent, down-the-hole submersible pumps are often used. There are several to choose from.

Down hole submersible centrifugal pumps such as are used in conventional water wells are used with success. These normally fit down 4"Ø casing which is larger and more expensive to install that some of the other alternatives. These pumps require a power supply--portable gasoline driven generators are used. Depending on the pump size, 4 to 5 kW generators are typically used. One disadvantage of down hole submersible pumps is that they must be raised and lowered which requires time and, in addition, equipment on which to wind the cable and sampling tube.

Down hole submersible pumps can pump at a high flow rate, e.g., 10 to 30 gpm, and are useful also in well drawdown tests. This type of pump is routinely used to depths of 300 feet and fits into schedule 40 PVC casing. By measuring pH, temperature, and conductance of the water while it is being pumped out of the hole, it is possible to tell when the water being samples is representative of the aquifer. Jack Lundberg of Envirologic Services International normally pumps 3 to 4 casing volumes from a well before the sample is taken.

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Denver, CO 80222
(303) 759-2611
Jim V. Rouse
Jack Lundberg

If the well is not a good producer, the well is pumped dry and allowed to stand. Sometimes it takes a day or longer to fill the well enough to draw a sample in which case, it is not possible to remove 3 casing volumes before taking the sample, and a sample is taken once the well has filled after having been emptied once.

Between wells the pump, cable, and tube must be thoroughly rinsed using tap or deionized water to avoid cross-contamination. If monitoring history shows that the analyses of all wells is very similar, then this is not so critical and by flushing out the standing water in the well, cross-contamination problems will be negligible. If, however, very low contaminant levels, e.g., in the sub-ppm level, are of concern and if the levels vary greatly from one hole to another, then the probability of cross-contamination is high, and great care must be taken. At very low levels of contaminant interest, it may not be feasible to avoid cross-contamination when using down-the-hole submersible systems without excessive care in washing all parts that will come into contact with the water and large volumes of flushing before the sample is taken.

Between jobs, the plastic tubing that comes in contact with the well water is replaced. If, in the course of a monitoring survey there is a chance of contamination because of highly variable levels from one hole to another or if sediment collects in the tube which is not easily washed out, then the tube may be replaced between holes as well.

Envirologic Services International employs four monitoring pumps:

1) Trailer-mounted 4"Ø submersible centrifugal pump capable of pumping from 300 feet and fitting into a schedule 40 PVC casing. This unit requires a 7-8 kW power source. This pump can deliver 30 gpm.

2) A 4"Ø submersible centrifugal pump capable of reaching 150 feet and delivering 10 gpm. It requires 4-5 kW.

3) A 1 3/4"Ø Johnson-Keck pump which fits down a 2"Ø well. This stainless steel constructed pump uses a screw mechanism and can deliver 1 gpm from 100 feet through a 1/2 inch discharge line.

The Johnson-Keck pump illustrated in the Johnson-UOP catalogue below is available from:

JOHNSON DIVISION
UOP, Inc.
Post Office Box 64118
St. Paul, MN 55164
(800) 328-9891
(612) 636-3900
Telex: 29-7451

4) A teflon bailer is used preferentially for sampling shallow aquifers for organics which are of less interest in the mining industry than in other industries.

Some monitoring companies employ an airlift powered by compressed air to draw samples from monitor wells. Where air comes in direct contact with the sample, these are considered unsuitable if contact with air can result in a change in composition of a sample--e.g., if air oxidizes ferric to ferrous ions, or introduces CO_2 which may precipitate carbonates from the water before it is sampled.

Peristaltic Pumps

Another innovative method for down-the-hole monitoring for very shallow lifts down to 26 feet are the light-weight, portable, battery operated peristaltic pumps which are very inexpensive and which can pump 2-3 liters per minute. Two suppliers of units were identified:

ISCO
Post Office Box 82531
Lincoln, NE 68501
(800) 228-4373
(402) 474-2233
Telex: 43-8028

GEOTECH ENVIRONMENTAL EQUIPMENT, INC.
1441 West 46th Avenue, Unit 17
Denver, CO 80211
(303) 433-7101

Down-the-Hole Analyzers

For macro water quality surveys, yet another approach is possible. Down-the-hole analysis avoids the need for sampling although once again, the question of whether standing water in wells is representative. An example of this type of equipment is the Digital Water Quality Analyzer produced by Martek.

MARTEK INSTRUMENTS, INC.
17302 Daimler Street
Irvine, CA 92713
(714) 540-4435
Telex: 692-317

DEDICATED MONITOR PUMPS

Dedicated monitor pumps can avoid many problems and, at the same time, save many dollars in labor costs. Dedicated monitor well pumps would be of particular interest where:

- Wells are relatively deep, say 100-150 feet.
- Low levels of conamination are of concern, so cross-contamination is a bigger problem.
- Multiple repetitive sampling programs are anticipated.

Dedicated monitor well pumps and tubing save the time not only of hauling and lowering the pumps, but also the time it would otherwise take to clean them between sampling.

When lowering a pump down a hole, there is always a risk of it sinking into the sediment at the bottom if it is lowered just a little to far--then the pump and tube and any filters get loaded with sediment that must be cleaned out and which can alter the water sample composition.

Very often, a sample is needed of a particular level only. Dedicated monitor wells are suspended at a very specific depth, and this does not constantly have to be changed going from one well to another. Also, by using an air bladder to isolate one section of the well, the amount of standing water that must be flushed from a well before a valid sample is taken can be greatly reduced.

Dedicated monitor well pumps avoid any questions of cross-contamination. They are available in inert material such as teflon and PVC that will not contaminate water either.

Because the tubing and pump remain in place dedicated to each well, the equipment required to sample wells using pumps is minimal. Usually, a battery-powered compressor and a controller are all that is required. These are highly portable and suitable for getting to wellsites that would be hard to reach by pickup truck.

Several dedicated monitor systems are available on the market. Of these, the best appears to be one offered by:

QED ENVIRONMENTAL SYSTEMS, INC.
Post Office Box 7209
Ann Arbor, MI 48107
(313) 995-2547
Fred Bernardin
President
Dave Kaminsky

The QED system is described in the following brochures. These are light weight and made of inert materials with no moving parts down in the down-the-hole system. Solution pumped from the wells does not come into contact with air.

Dedicated monitor wells are used increasingly in municipal landfill monitoring programs and around hazardous waste sites. They have only recently been introduced to the mining and milling industry, and it is expected that these will in due course become the most commonly used technique, primarly because of the man hours that they save and because they avoid any possibility of cross-contamination. As water quality standards increasingly specify parts per billion levels and the possibility of cross-contamination becomes increasingly important, so dedicated monitor wells will become more popular. It is very easy to contaminate a sample with a fraction of a ppm of a contaminant, and the consequence of high readings in monitored sample assays is so serious that this risk is not worth taking. A final advantage of these light weight sampling devices is that they are simple to use and virtually anyone can be shown how to operate them without the risk of things going wrong.

Suppliers of dedicated monitor well pumps include:

QED ENVIRONMENTAL SYSTEMS, INC.
Post Office Box 7209
Ann Arbor, MI 48107
(800) 624-2026
(313) 995-2547
Dave Kaminsky

MONITOR, INC.
912 East Briarwood Circle South
Littleton, CO 80122
(303) 798-2844
W. Uski

ISCO
Post Office Box 82531
Lincoln, NE 68501
(800) 228-4373
Telex: 43-8028

GEOTECK ENVIRONMENTAL EQUIPMENT, INC.
1441 West 46th Avenue, Unit 17
Denver, CO 80211
(303) 433-7101

SURFACE WATER SAMPLING

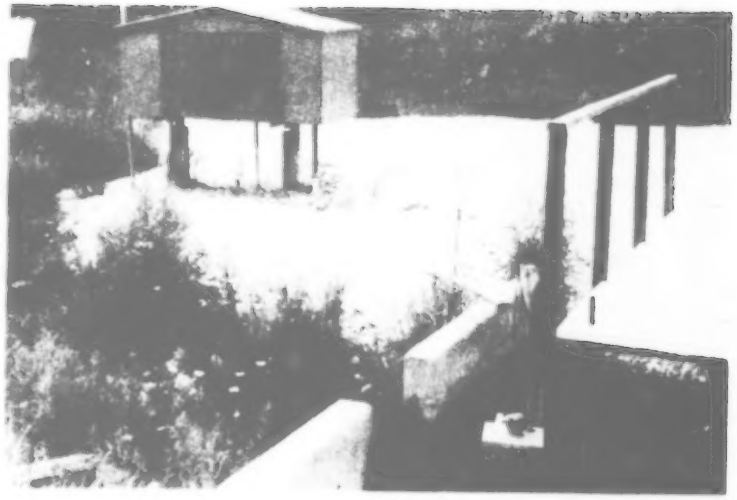
Water sampling techniques and sampling devices for surface water are critical in obtaining valid representative samples. The following brochure describing equipment supplied by one of the leaders in this field is helpful in showing some of the options available:

ISCO
Post Office Box 82531
Lincoln, Nebraska 68501
(800) 228-4373
(402) 474-2233
Telex: 48-8028

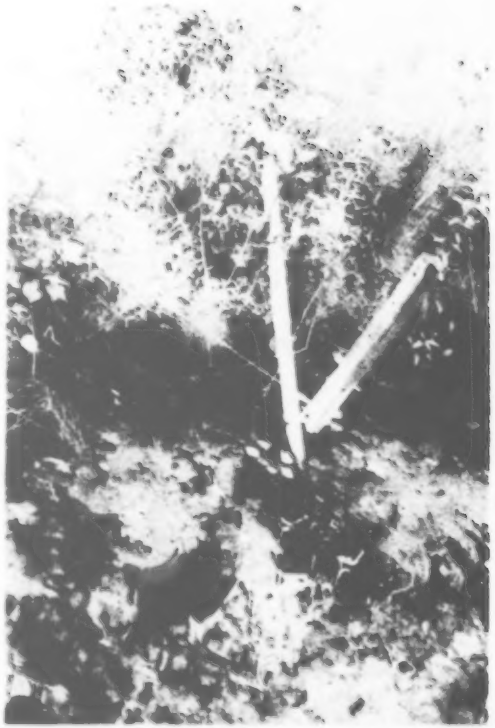
Environmental Control publications and directories list very many suppliers of samplers for all kinds of applications, and these are not reviewed here in detail. Sources of information on what is available in this market include:

POLLUTION EQUIPMENT NEWS
8650 Babcock Blvd.
Pittsburgh, PA 15237
(800) 245-3182
(412) 364-5366
K. Galante
Circulation Manager

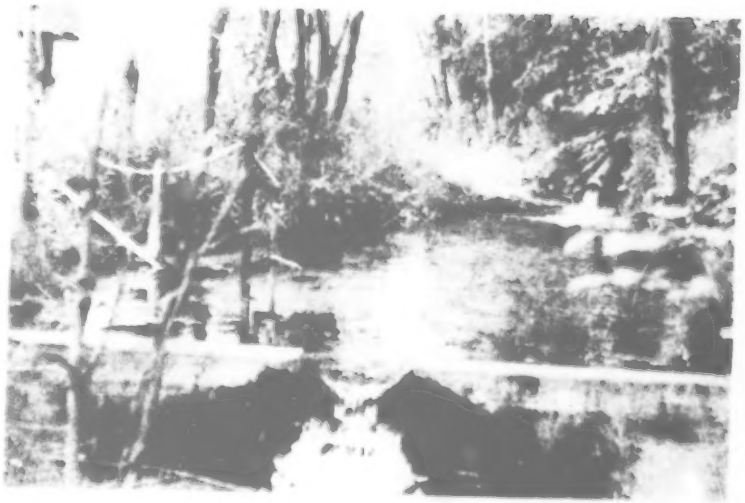
Attention is drawn to the photograph shown below of an automatic sampling device installed at the effluent discharge point of a mine-mill complex in New York state. This type of device works very well. However, possibly not very clear in the reproduction of the photograph is the algal matte suspended in the water. Algae frequently thrive in flotation mill effluents (apparently their growth is encouraged by species such as some flotation reagent degradation products, but this is not clearly understood). Algae take up metals from solution and if loose fragments of these algae were to get into the sample, this could give a bias to the analysis which could indicate a higher metal content than is really there. When drawing samples by hand, and particularly when relying on unattended automated effluent samples, this factor should be borne in mind.



AUTOMATIC SAMPLING STATION



NOTE ALGAL MAT AROUND SAMPLING POINT



NOTE ALGAL MAT IN EFFLUENT BEHIND V-NOTCH WEIR

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Lysimeters allow quicker monitoring of heap leaching and tailing sites

William R. Bond and Jim V. Rouse

Pressure/vacuum lysimeter use at mine sites has proven to be a valuable early warning system for detecting leakage of precious leachate fluids. Such a device can detect solution leaks in several days or weeks, whereas a conventional perimeter monitor well may take months or years.

Introduction

The pressure/vacuum (p/v) lysimeter or soil water sampler has become useful for monitoring vadose zone or unsaturated zone water conditions. The soil water sampler was first introduced around 1961. It was used as a monitoring and research device for studies in agriculture and soil contamination around landfills. Since then, it has been used for many purposes.

The use of p/v lysimeters at mining facilities to monitor for solution loss is a relatively new idea. The primary purpose of the lysimeter here is to function as an early warning system. It detects leakage through liners of tailings ponds, heap leach pads, and leachate holding ponds. Their use has proven valuable for collecting baseline data and detecting loss of precious leachate fluid.

Different lysimeter designs are capable of vadose moisture sampling from near the surface and down to 90 m (300 ft). They are also capable of sampling soil moisture or saturation plume contaminants from areas not accessible by conventional water well installations.

William R. Bond and **Jim V. Rouse**, member SME, are staff supervisor and principal, respectively, for Envirologic Services International, 2425 S. Colorado Blvd., Denver, CO 80222.

The most common installations are usually simple and cost-effective. In many cases, they can be installed without the use of heavy drilling equipment. A properly placed and installed lysimeter can detect solution leaks in several days or weeks. A conventional perimeter monitor well may take months or years to detect a leak of the same magnitude.

A discussion on the general design and installation of p/v lysimeters will give an understanding of its versatility. Three case studies of lysimeter installations at mining sites will be examined in detail.

Design, Installation, and Sampling

Design

The basic design of a p/v lysimeter chamber consists of a porous material through which the soil is drawn into a collection chamber. Access tubes run from the unit to the sample station at the ground surface. Most units currently available range from 25 to 76 mm-diam (1 to 3 in.-diam).

The sample collection chamber, or body, can vary from 0.6 to 1.8 m (2 to 6 ft) in length. The body can be constructed of PVC casing or Teflon, depending on the installation desired. The collection chamber functions as a holding reservoir for the collected soil moisture.

The intake, or porous material, on the lysimeter is the most complex and vulnerable portion of the unit. The pore size selection varies based on the needs of the installation, type of fluid to be sampled, and type of soil material surrounding the unit. Teflon (PTFE) and porous ceramic are used in fabrication of the porous inlet portion.

When using a Teflon material, which is hydrophobic, a larger pore size of 70 μm is needed to overcome surface tension and draw water into the collection chamber. It is typically used at sites involving organic contamination, because of its inert properties.

Ceramic material is generally hydrophilic, having less surface tension. Therefore, it has a smaller porosity range to conduct the moisture through the porous medium while under vacuum. Pore sizes may be selected from 0.16 to 6 μm, and can be manufactured for the specific needs of the installation.

The final major design component of the p/v lysimeter is the access or sampling tubes. The tubes are usually of 6.3-mm-outside-diam. (0.25-in.-outside-diam). They are made of rigid polyethylene or flexible Tygon with a wall thickness of 1.5 mm (0.06 in.). The con-

nection of the access tubes depends on the type of lysimeter being installed.

On the shallow lysimeter model, for use at less than 15 m (50 ft) of depth, the tubes are inserted through two holes in the neoprene rubber top of the shallow unit. They are individually designated as a p/v line or discharge line.

Deep installations involve high p/v lysimeters that use internal check valves. These lysimeters are equipped with brass tube fittings connected to the access portals on the top of the unit. The attachment procedure of the access tubes also depends on the manufacturer and specific design of the unit. In most cases, the outer surface of the tube connection is sealed with a silicon caulking.

Beyond the basic design of the p/v lysimeter, variations have been made in the intake medium position on the chamber, the access tube installations, the construction material used, and the use of vacuum gauges for readout of internal residual vacuums. But the standard design and function of the unit, drawing capillary or available moisture from the vadose zone and sample retrieval, remains the same.

Installation

Installation techniques for permanent placement of p/v lysimeters are varied. The high pressure unit can be installed at depths up to 91 m (300 ft) below grade or serviced by sample tubes up to 152 m (500 ft) in linear distance.

Several different installation procedures allow for placement of the units in subgrade soils before building a permanent leach pad, pond facility, or tailing disposal structure. The access or sample tubes are then buried in trenches. Their sample stations are located at a considerable distance from potential disturbances due to traffic and future construction. Before choosing the type of lysimeter and bedding medium for the final placement, several questions should be answered and several conditions must be satisfied.

First, what kind of mining facility is being considered, and are lysimeters the right tool for monitoring? Lysimeter monitoring has been found to be effective at heap leach facilities when placed under the heap leach pad areas and below the pregnant, barren, and overflow ponds. They are also being used successfully as leakage monitoring devices around old and new tailings pond disposal areas.

In the case of old, leaking tailings pond disposal areas, they are useful in detecting the concentration of contaminants and direction and size of existing leakage plumes. In newly constructed mining facilities, they are being readily accepted by regulatory agencies as a first-line warning system to detect leakage through synthetic liners.

Lysimeters are not designed to function as remedial action tools and should not be considered as such. They are designed to detect leakage problems early enough to allow adequate planning before the leak becomes a vadose and ground water pollution problem.

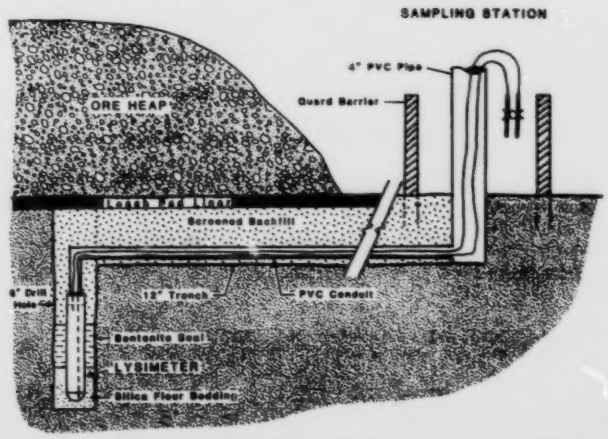
What is the geology of the area where the mining facility will be constructed and in which horizons will lysimeters be used? Lysimeters may not be an appropriate monitoring tool in areas of shallow water tables or dense rock formations. In shallow water areas, they will easily obtain samples. But monitor wells may be more efficient.

Lysimeters are not well adapted for sampling vadose moisture from dense, unsaturated, hard rock materials. They are more appropriately used in areas of unconsolidated materials. These include weathered bedrock, glacial till, unsorted alluvial material, and deep soil horizons. In general, the less consolidated and finer materials — such as silts, clays, fine sands, and mixtures thereof — yield vadose water more readily than fractured crystalline rock, cemented sandstone, or very coarse sand.

The chemical nature of the leachate fluid that may leak into the vadose zone should be considered. Highly acidic fluids or highly alkaline fluids may not be readily sampled by all lysimeter installations. Consult the lysimeter manufacturer before selecting the units.

It also should be determined which chemical components of the leachate solution will be most mobile in the geochemical regime of the local vadose zone. These el-

TYPICAL LYSIMETER INSTALLATION AT A HEAP LEACH MINING OPERATION



ements or compounds are then used as indicator parameters to determine possible leachate solution losses or migrations.

Site access is an important consideration for installation of lysimeters. Preferably, they should be installed before or during construction of the facility. With difficulty and less efficiency, they can be installed after construction is completed. In the case of heap leach pads and solution ponds, it is imperative that the units be installed before completing the subgrade and liner emplacement.

When installing lysimeters around ponds, angle drill holes can be used to place units around the pond bottom perimeter. It is also imperative that the sample tubes be safely buried. And they must terminate in a location that is out of danger for long-term sample station establishment.

The earthmoving contractor should know the installation procedures and equipment needed when building a lysimeter installation. Trenching machines, road graders, bulldozers, and other machines have been known to damage and cut lysimeter sample lines after they have already been buried.

The length of the sample lines under pads and ponds, and their relative gradient from the lysimeter should be considered for final location of sample stations. In several instances, up to 152 m (500 ft) of sample line has been used in conjunction with high p/v lysimeters.

It is important to consider the head differential from the lysimeter unit to the sample station and the friction involved with forcing the water sample through a small tube over a long distance. Lysimeter units without check valves may be appropriate for installations of up to 15 m (50 ft) of head differential. But they may not be suited for several hundred meters of sample delivery line that may be necessary for their final installation.

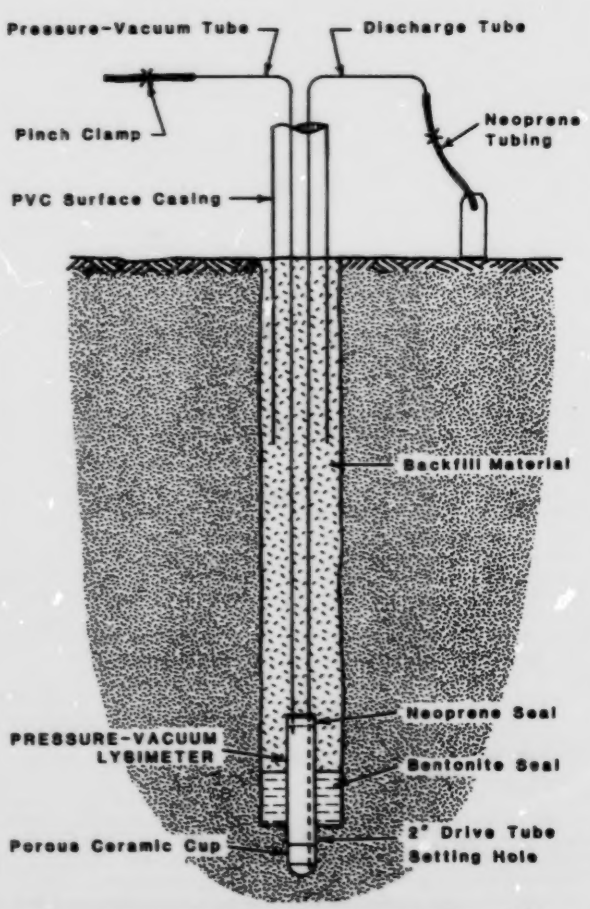
In general, if an installation involves more than 15 m (50 ft) of head differential or more than 30 m (100 ft) of sample line distance, high p/v lysimeters with check valves to control sample retrieval pressures should be used.

The most desirable emplacement of the porous ceramic cup lysimeter is usually in an in situ setting. The small pore size and hard surface area of the porous ceramic enables a direct contact between soil particles and the cup with little effect of soil clogging the ceramic. This type of installation has been quite successful in finer grained materials.

The in situ setting of the lysimeter can be accomplished using a drive tube or split spoon soil sampler of the same diameter as the lysimeter. When the drill hole depth is just above the desired sample horizon, the soil sampler is driven to form the final setting in the material to be monitored.

The lysimeter is then fed down the drill hole by a placement pipe. It is pushed into the drive tube sampler hole fitting firmly into the soil. The placement pipe can then be removed by sections or it can be left in place as protection for the sampling lines. The unit can then be backfilled with ben-

DIAGRAM OF PRESSURE-VACUUM LYSIMETER INSTALLATION



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tonite material or screened drill cuttings as the installation dictates.

In coarse sand, alluvium, and loose fill material, a bedding material, such as crystalline or flour silica is needed. The silica flour bedding material acts as an artificial soil to surround the porous intake medium of the lysimeter when the natural soil conditions or contaminant type does not allow for an in situ setting. This type of backfill bedding is used exclusively when installing Teflon type lysimeters.

When the drill hole has reached the desired depth, the lysimeter is inserted down the hole. The hole is then backfilled with crystalline silica flour that has been mixed in a distilled water slurry. After placement of the silica bedding, the hole can be completed with a bentonite seal and backfilled.

One drawback of this method is that the first several samples obtained from the lysimeter will be diluted with distilled water. But, after an average of three sample collections, distilled water should no longer be a factor.

Drilling equipment needed for lysimeter installation includes hollow stem auger drill rigs (preferably) or hand-dug post hole augers for shallow settings. It is recommended that in firm material or depths greater than 3 m (10 ft), an auger drill be used. The hollow stem of the 152-or 203-mm (6-or 8-in.) auger is ideal for access to the bottom of the drill hole for emplacement of the lysimeters. Trimmy lines can be used to emplace the silica flour slurry and bentonite seal at the desired depths. Other drilling methods have the potential for collapse of loose material in the drill hole. This greatly jeopardizes proper installation of the unit.

A final item to consider for the installation is a permanent sampling station. Typically, this involves using a length of PVC or steel pipe buried vertically, 1 m (3.3 ft) into the ground as a surface casing.

The sample lines should be set through the surface casing before setting and should extend 0.9 to 1.5 m (3 to 5 ft) from the top of the casing. This allows for easy sampling of the unit while placing sample equipment on the ground. After sampling, the access tubes can be coiled up and placed inside the protective casing. In areas subject to possible tampering or vandalism, a more secure steel surface casing with a locking cap should be used.

Sampling

Several different sample collection procedures have been developed to contain the often limited amount of soil water. After the unit has been installed and the sample tubes buried in trenches to the designated sample station, a vacuum is drawn on the unit. A handheld vacuum pump is attached to the designated p/v line. A vacuum is then drawn on the unit that is compatible to the type of soil material where it has been installed. Vacuums will range between 254 to 457 mm (10 to 18 in.) of mercury vacuum. In general, higher vacuums are applied to tighter, finer materials, and lower vacuums to more coarse, sandy materials.

After the desired vacuum has been applied, the clamps on the neoprene tubing are closed tightly to secure the vacuum. Several days or even a few weeks must pass before attempting to retrieve a water sample from the lysimeter. During this time, the handheld vacuum can easily be attached to the p/v line. The clamp can then be released to allow reading of the residual vacuum in the unit. In many cases, it is desirable to have a permanent vacuum gauge attached in-line for constant readout on lysimeter vacuum. When the residual vacuum has dropped substantially within the unit, or sufficient time has passed to allow collection of soil water, a sample may then be retrieved. Before a sample collection is attempted, the residual vacuum on the lysimeter should be recorded. An ongoing record such as this will provide valuable information to indicate the time needed to absorb a sample, the volume expected to be recovered, and the drop in vacuum attributed to the sample volume recovered.

The vacuum is then released from the lysimeter. An air pressure source is attached to the same p/v line. The air pressure source may be a hand-operated pump or a compressed air tank.

In cases where atmospheric oxygen may alter the water sample parameters being analyzed, a nitrogen gas tank source should be used. In this way, atmospheric oxygen contact with the sample is limited. And the lysimeter unit itself is purged with the nitrogen gas, leaving an inert atmosphere within it.

The discharge line should be cleaned and placed in an appropriate sample collection container. A clean sample container should be obtained from the laboratory that will perform the analyses. It should also be properly preserved before emplacement of the collected water sample.

Usually, a glass or polyethylene lab bottle is supplied for collection of samples. The bottle should have volume gradation markings to allow the sampler to record the volume of soil water. In those cases involving sampling that must eliminate contact with atmospheric oxygen, a method has been developed using a 50-cm³ (1.7-oz) syringe to collect the sample for shipment to the lab.

This method involved inserting the tip of the syringe, without the needle, into the discharge opening. Pressure is fed into the lysimeter and a water sample is forced out. The syringe plunger is withdrawn and the container fills with the sample, thus avoiding direct contact with atmospheric oxygen.

Patience must be used when applying pressure to the lysimeter sample line. In many cases, sample lines are long enough that the

Where atmospheric oxygen may alter the water sample parameters being analyzed, a nitrogen gas tank should be used as a pressure source. In this way, atmospheric oxygen contact with the sample is limited and the lysimeter unit is purged with the nitrogen gas.

travel time for the sample may be several minutes. It must be remembered that in the regular p/v lysimeters, check valves are not used to eliminate the possibility of forcing the sample back through the porous material. Usually, if the unit has collected a sample, it will discharge within a minute. If the unit is dry or only a small sample has been collected, a gurgling noise or escaping air can be heard coming from the discharge line. After the sample has been recovered, the discharge line clamp should be secured and the desired vacuum reapplied to the unit.

Examples of P/V Lysimeter Installations

Uranium Tailings Pond

This installation involved placing 15 high p/v lysimeters around the base perimeter of a newly constructed, membrane-lined, uranium tailings disposal pond. It is located in glacial outwash deposits in Washington. The pond received tailings from an acid leach circuit. Before building the pond, the old tailings were discharged to adjacent, unlined ponds.

The need for an early warning leak detection system became apparent when a seepage plume from the old ponds was detected in a streambank seep and nearby monitor well. The site topography and stratigraphy allowed the seepage plume to discharge on a nearby streambank before its detection in the monitor well.

As a follow-up to the plume investigation, it was suggested that p/v lysimeters be used as a leak detection device around the new pond. The mining company personnel agreed with concept. The idea was forwarded to the Nuclear Regulatory Commission (NRC).

After lengthy negotiations between Envirologic Services (ESI) and NRC, a location plan was developed for the installation of the 15 p/v lysimeters. At the time of installation, May 1981, the use of the p/v lysimeter as a tailings pond leak detection device was, to the authors' knowledge, the first of its kind.

In defining the depths and locations of the lysimeters, consideration was given to the nature of the glacial till material and the potential configuration of a leakage plume. Prior investigation by ESI on the earlier leakage from the old pond was done by resistivity and monitor wells. This gave a good indication of the dimension and character of movement of a possible contaminant plume.

The final specifications for emplacement of the lysimeters involved auger drill holes about 11 m (35 ft) deep from a midpoint construction bench on the side slope of the pond. The holes are located about 61 m (200 ft) apart. They terminate at about the same 11-m (35-ft) depth, except where shallow bedrock prevented further drilling. The pond volume is about 1.5 hm^3 (1200 acre-ft). Its average depth is 21 m (70 ft). The construction bench is about 9 m (30 ft) above the base level of the pond. Therefore, most lysimeters are located about 1.5 m (5 ft) below the pond bottom.

The emplacement of the lysimeters involved the previously discussed in situ setting technique where the porous ceramic cup tip is fitted into a 50-mm (2-in.) drive tube hole for tight soil contact. The hole was then backfilled with a bentonite plug and screened glacial till. The upper backfill surface material was tamped with a shovel handle. This avoids additional settling and conduit of precipitation during completion of construction.

Timing of the lysimeter installations into the contractor's overall schedule was very important. The most critical aspect was the completion of all rough grade work for the pond base. The drill rig was then mobilized and installation began without concern for disturbing the finished grade.

Before installing the lysimeters, it was emphasized that all rough grade work be completed to avoid disturbing the units and sample lines. After installing the lysimeters and backfilling the boreholes, a small trenching machine was used to dig a trench from the top of the borehole to the rim of the pond. A final sample station for each lysimeter was constructed on the pond rim. Care was taken in backfilling the trenches to avoid crushing the lines.

The sampling of the lysimeters began within one week of their installation. This was an effort to secure baseline vadose moisture samples before completion of the pond liner and disposal of tailings. The average volume recovery from the lysimeters is 0.15 to 0.2 L (0.04 to 0.05 gal) of water.

At the time of sample collection, the samples are checked for field pH and conductivity. An ongoing record is kept of these parameters to note variations from the established baseline data. These two parameters are indicators of the possible migration of acid mill wastes through any leaks in the liner. Collected samples are then appropriately bottled and preserved as necessary for lab assay.

A sufficient volume of water cannot be obtained with any regularity. Therefore, radiochemical analysis is not possible on all samples collected. Existing studies document that radiochemical contaminants are retarded by ion-exchange reactions in soil, in comparison to other more conservative parameters. For this reason, samples are analyzed for other, more mobile parameters such as pH, specific conductance, TDS, sulfate, U_3O_8, NO_3, manganese, chloride, NH_4, COD, and iron. These also require less sample volume for detection.

The parameter list was agreed on through negotiations with NRC. The parameter selections were de-

Timing of lysimeter installations into the contractor's overall schedule was very important. The most critical aspect was the completion of all rough grade work for the pond base. The drill rig was then mobilized and installation began without concern for disturbing the finished grade.

termined using information from the prior investigation of seepage at the disposal site.

Gold Heap Leach Facility

The gold mine facility studied lies in a hilly, mountainous area of the North Black Hills of South Dakota. The selection of p/v lysimeters was decided in part to satisfy concerns of state regulatory personnel. It was also to assure the mining personnel that precious pregnant solution was not being lost to the subsurface.

Lysimeter units were used under both pad liners and solution holding ponds. The site is underlain primarily by weathered and fractured limestone. The heap leach pad construction removed all overburden organic materials, leaving as much clay veneer as possible over the limestone.

In most instances, the lysimeter installations are at or below the clay-limestone interface. The installation depths varied from 0.6 to 2.4 m (2 to 8 ft). Drilling was easily conducted with a Mobile auger rig using 100-mm (4-in.) auger sections. Shallow installation depths allowed for several holes to be drilled and logged in succession.

The lysimeters were then easily installed without using the drill rig. Specifications for the emplacement of the units involved a dry bedding of silica flour around the porous ceramic tip of the lysimeter. The silica flour bedding was then capped with a bentonite seal 0.5-m (1.5-ft) thick.

The main difficulty with installation was associated with trenching through the weathered limestone material and clays for safe burial of sample lines. The original specifications called for a 0.5-m (1.5-ft) trench with the lines buried in clean bedding sand in the bottom one-third of the trench. The presence of the cobble-sized limestone material made trenching difficult. It also jeopardized the integrity of the sample lines. To remedy this, the sample lines were fed through 25-mm (1-in.) PVC casings and laid in the trench.

The trench was then backfilled with bedding sand to minimize the risk of line damage during subsequent backfilling and compaction. This trench backfill technique was used under the heap leach pad area and under the pregnant, barren, and overflow ponds. In several cases, sample lines were buried that were up to 122 m (400 ft) long from sample station to lysimeter unit. Coordination and timing with the earthmoving contractor was essential.

> There is growing interest in heap leach techniques to recover precious metals from low grade ores. So the monitoring of leach solution flow balance is a primary concern for production efficiency.

Samples were first collected one month after installation to establish baseline information. All lysimeters are now being sampled on a regular basis. Negotiations with state regulatory personnel were required to determine a suitable lysimeter array and priority list of parameter analysis.

Old Tailings Deposits

Pressure/vacuum lysimeters were very useful in determining the migration of arsenic and other contaminants within old tailings deposits on a river floodplain. Lysimeters were used to recover soil water samples from the tailings in the vadose zone. Saturated zone sampling suggested a complete understanding of arsenic migration in the tailings could not be determined solely by ground water and soil sampling. Data collected from lysimeters in this study proved valuable in formulating the movement of arsenic and other contaminants within the tailings.

A total of 24 lysimeters were installed at 11 different sites over a 14.5-km (9-mile) stretch of the study area. At each site, an array of ground water wells and lysimeters were installed. These obtained water samples from the various horizons of native material and tailings.

All sites included one deep monitor well installed in the local bedrock, one or more monitor wells in the stream alluvium and overlying tailings, and lysimeters at various horizons within the unsaturated portion of the tailings. Some areas involved nests of three wells and up to five lysimeters. With this array, it was possible to correlate the analytical data to determine the relative-vertical movement of the elements of concern.

All lysimeters in this study were installed using the in situ method. The drill rig was a CME 55, using 152-mm (6-in.) hollow stem augers. In installations less than 1.8 m (6 ft) deep, hand augering was done. Drive tubes were then used to form the setting hole for the lysimeter tip. All holes were then backfilled with a bentonite seal and screened tailings material.

The tailings material was tamped to prevent excessive downward percolation of rain water. Sample stations were established directly above the lysimeters in this case by using 76-mm (3-in.) PVC casings supported with standard steel fence posts.

All lysimeter units installed in this study were purged with nitrogen gas before applying the first vacuum. Nitrogen gas pressure tanks were used in subsequent sampling.

Sampling of the lysimeters involved both the sample bottle method and syringe container method. The latter method was developed during the study when it became apparent that samples had been altered by atmospheric oxygen during collection and subsequent transport to the lab. After collecting water samples in the syringes, they were quickly frozen in dry ice-alcohol bath and maintained in a frozen state for shipment. This supplied confidence to the values of arsenic and iron speciation that were determined during the analyses.

Final results indicated that, in contrast to previous assumptions on the vadose water movement in the tailings, there was actually a net upward migration of the contaminants due to capillary attraction. ■

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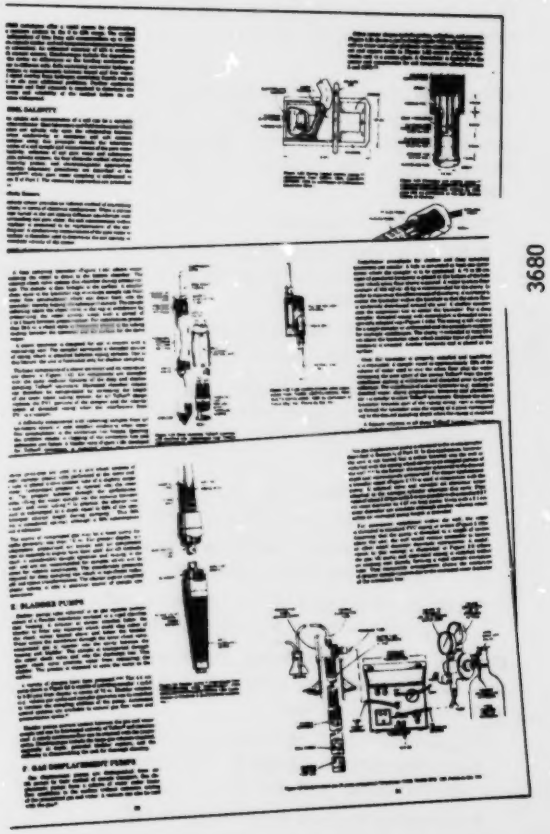

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Two years in preparation

VARIATIONS IN WATER QUALITY DURING INITIAL PUMPING OF MONITORING WELLS

Because standing well water may differ significantly from formation water, pumping and sample methods must be designed to minimize sample contact with atmospheric gas. The authors illustrate water variations over time.

by Lee C. Wilson and
Jim V. Rouse

The objective of most ground-water monitoring programs is the determination of ambient water quality in a particular aquifer or aquifers. The details, and thus requirements, of each program are site specific; however, the need to obtain the most representative and undisturbed water sample possible is usually of primary importance in any study.

Water lifting, filtration and preservation methods have all shown an effect on measured parameters in water samples. Filtration, preservation and other sample handling factors have been studied in connection with surface, as well as ground-water sampling. However, methods of sample lifting and adequate well purging are unique features associated with ground-water sampling. Our experience, as well as that of others (Schmidt 1977; Schuller et al. 1981; Humenick et al. 1980) indicates that pumping a well is necessary to obtain a representative aquifer sample. Bailers will deliver an unaltered sample of well water to the surface, but water stored in a well bore often has significant chemical differences from the water in the aquifer. If an aquifer sample is desired, water must be drawn from the aquifer rather than merely the column of water standing in a well. Then, the water must be transported to the surface, filtered, preserved and shipped to the analytical laboratory with as little alteration as possible. This article discusses relationships between field parameters and laboratory analyses of water samples collected as well pumping progresses.

Previous Work

As a result of improved analytical sensitivity and monitoring requirements, numerous workers have recognized the need for additional investigations related to the adequacy of ground-water sampling procedures. Pump equipment, bailers, filtration apparatus, preservation technique and effects of pumping time have been studied and compared (Summers and Brandvold 1967, Schmidt 1977, Summers 1972, Kelly 1982, Schmidt 1982).

Schuller, Gibb and Griffin (1981) offer criteria for selection of pumping apparatus, procedures for determining the necessary extent of well flushing and procedures for sample preparation, preservation and storage. They indicate the site-specific nature of sampling protocol, point on the desirability of pumps vs. air or nitrogen lift mechanisms or bailers and indicate a desirable range of well volumes (4 to 6) to be removed prior to sample collection. In addition, they indicate the need for pH, Eh and specific conductance measurements to determine adequacy of well purging. Humenik, Turk and Colchin (1980) discuss sampling near in situ uranium leach operations in which field and laboratory parameters are compared in relation to pumping rate, duration and installation depth. Completion and pump rate were shown to be particularly important; again, field parameters were instrumental in determining adequacy of purging.

Many authors point out the necessity of well purging prior to sample collection, as well as the utility of using field parameters to determine adequacy of purging.

Experimental

The data comparing field parameter trends to dissolved constituent variations were collected in conjunction with water sampling in areas affected by mining and milling activities in the western U.S. The data from wells WC were obtained from flood plain deposits downstream of an historic gold district in which cyanide mill tailings were transported and deposited. Most of the other comparison samples were collected during extended pump tests in an area affected by open pit copper mines, leach facilities and mills. In addition to these specific comparison analyses, similar field data trends have been documented in sampling studies located throughout the western U.S. in areas surrounding uranium, silver, coal, copper and gold mining and milling operations, as well as hazardous waste disposal sites.

This article concentrates on the collection of multiple samples and the simultaneous measurement of field parameters as monitor well pumping progresses. The first sample was usually collected immediately after water began flowing from the pump discharge line. Thereafter, samples were collected at intervals designed to correspond to progressively larger numbers of bore volumes removed from the well. The wells WC sampling was performed using a small, battery-operated pump at the surface. In our experience with western sampling, shallow water levels allowing the use of surface pumps are the exception rather than the rule. Well A-1 was pumped with a permanently installed turbine pump. The other comparison data were gathered in conjunction with extended pump tests using a trailer-mounted submersible pump unit. This unit consists of a self contained generator that powers a 10cm (4-inch) diameter stainless steel submersible pump and a powered reel with 91m (300 feet) of discharge hose. This pumping unit allows sampling of monitor wells without the permanent installation of a pump. Other advantages include immediate and relatively easy adjustment of pumping depth during sample collection and the pumping of samples where no power facilities are easily accessible.

The discharge hose from the sampling trailer has a sample bleed that allows a portion of the discharge to flow through a chamber containing pH, specific conductance and temperature probes. This arrangement assures that there will be a minimum mixing of sample water with atmospheric gases prior to the measurement of field parameters. The flow-through chamber also maintains all probes in a stabilized temperature bath as pumping progresses. In some instances continuously recording pH and specific conductance meters were installed in the flow-through chamber. A continuous record of field parameters can be a significant advantage if extended pumping is expected to produce break-through of contaminants from a nearby source.

All field parameters were taken using techniques specified in a sampling protocol document (Moran and Rouse 1981) which is based on U.S. EPA and USGS procedures. Sample filtration and preservation were also performed on-site as prescribed in this protocol document. Samples were transported to EPA-approved laboratories within holding time limits outlined in the sampling protocol document.

Because many investigators routinely use bailed samples and there are times when sampling is limited to this technique, a comparison was done in which both bailed and pumped samples were collected from a well. The bailed sample was collected shortly after well completion and development by means of air-lifting. The pumped sample was later collected using a submersible pump and monitoring of field parameters until stable conditions were achieved. Multiple samples were not collected during well purging.

Throughout the multiple sampling study, a great amount of care was taken to maintain uniform sampling technique and high sampling accuracy; however, a certain amount of site-specific variability is always present. Knowledge of the hydrologic regime into which the monitor well is installed can be very important for the correct interpretation of field parameters and sample collection timing. The other major site-specific variable that goes hand in hand with an understanding of the subsurface environment is detailed, accurate information concerning well completion. The data presented comparing field parameters to analytical results were obtained from wells in which drilling and completion had been supervised by the authors or where good geologic and completion records were available.

Site-specific geohydrologic or well-completion details were considered in the selection of pump intake depths. The hydrogeology and position of slotted sections in the wells can be very important factors when deciding pump-setting depth and rate of pumping. When pumping from wells with sealed, piezometer-style completions, the pump is normally set just above the screened section. This allows water from the entire (usually short) screened section to flow upward to the pump intake while reducing the need to pump out the entire column of water above the pump. Humenick et al. (1980) studied pump-setting depths and found a deep setting (near the zone to be monitored) and low pump rate to be advantageous.

Well Completions

In the case of the WC sampling, the wells are relatively shallow. The other monitor wells are completed in more complex regimes with two or more aquifers. Wells WC-1, WC-2 and A-1 are designed to monitor the entire saturated section, while wells A-2, A-3, A-4 and A-5 are completed as piezometers to monitor only the lowest aquifer.

Well WC-1 has a total depth of 9m (29 feet) through interlayered alluvial sand, gravel and silt. The sand and silt fractions contain a high percentage of stream-transported gold mill sands and slimes. Casing is 5cm (2-in.-h) diameter PVC with annular gravel pack and saw cut slots in the bottom 3m (10-foot) section. Depth to static water level was 0.8m (3 feet) below land surface and the suction hose was set at approximately 6m (20 feet).

Well WC-2 is completed through similar alluvial material to a total depth of 5.4m (18 feet). It is also cased with 5cm (2-inch) PVC with gravel-packed annulus. Static water level was 2.2m (7.4 feet) with the suction hose set at approximately 5m (16.5 feet).

Well A-1 is 76m (250 feet) total depth with static water level at 15m (50 feet). This well is completed through an alluvial conglomerate containing variable lenses of coarse sandstone and clay-rich sandstone interbedded with sandy and clay-rich conglomerate. Casing is 40cm (16-inch) steel perforated from surface to total depth. A 760 liter/min (200 gpm) turbine pump is installed in A-1.

Well A-2 has a total depth of 47m (154 feet) with static water at 1.4m (34 feet) and is cased with 10cm (4-inch) PVC casing. Well A-2 is completed through mixed gravel, sand and silt alluvium to 30m (98 feet), clay-rich sand from 30 to 31m (98 to 102 feet) and bottoms in sandy, silty conglomerate from 31 to 47m (102 to 157 feet). The casing has commercial saw-cut perforations from 41 to 47m (135.3 to 157 feet) with a bentonite seal at 40m (132 feet). This well was pumped at 18.5 liters/min (4.8 gpm) with the pump set at 40m (132 feet).

Well A-3 is completed to a total depth of 48m (157 feet) through 22m (72 feet) of clayey sand and gravel alluvium, sandy clay from 22 to 24m (72 to 80 feet) and sandstone and sandy conglomerate from 24m (80 feet) to total depth of 48m (157 feet). The well is cased with 10cm (4-inch) PVC casing with commercial saw-cut slots from 42 to 48m (137 to 157 feet) and a bentonite seal at 40m (130 feet). Depth to static water level was 3.7m (12 feet). A-3 was pumped at 26 liters/min (6.8 gpm) from a depth of 38m (125 feet). The last two samples of the sequence on figures A-3.1 through A-3.3 were collected after extended pumping at a rate of 10 liters/min (2.75 gpm).

Well A-4 is completed to a depth of 48m (158 feet) through 20m (67 feet) of clayey sand and gravel allu-

vium, 20 to 42m (67 to 137 feet) of clay-rich sandstone and conglomerate and 42 to 48m (137 to 158 feet) conglomerate and coarse sandstone. Casing is 19cm (4-inch) PVC, with commercial saw-cut perforations from 42 to 48m (138 to 157 feet) and a bentonite annular seal at 41m (135 feet). Well A-4, with static water at 16m (52 feet), was pumped at 13 liters/min (3.5 gpm).

Well A-5 was sampled by bailer and later a pumped sample was collected. This well is 107m (351 feet) in total depth, is cased with 10cm (4-inch) PVC with perforation cuts between 98 and 107m (321 to 351 feet) and has an annular bentonite seal at approximately 66m (200 feet). Static water level was 96m (315 feet). This well monitors alluvial conglomerate beneath a tailings pile.

Geochemical Factors

Although the water standing in well casing may have originally come from the formation, various chemical reactions can take place in the casing that will substantially alter the nature of the water. The most important factor that affects the water chemistry is contact with atmospheric gases, most notably oxygen and carbon dioxide. Dissolution of these gases at a greater concentration than found in the formation environment changes the pH and oxidation conditions of the water.

Carbon dioxide dissolution or outgassing and pH readjustment can occur very rapidly in water. Some sampling procedures recommend pH field readings be performed in close chambers, before pumped water has had any chance to contact the atmosphere. The pH of water that has been standing in a well for weeks or months must certainly be suspect when a few minutes exposure at the surface can cause a pH change.

In general, metals are more soluble in acidic water, so a rise in the pH can cause some dissolved metal species to precipitate; or a decrease in pH can cause metals near the casing to be mobilized. In either case, water that has had time to establish equilibrium with atmospheric gases is not likely to be representative of the water chemistry in the formation.

Another important chemical change that standing well water can undergo is related to its oxidation potential. Usually, ground water in its subsurface environment comes into contact with only limited sources of free oxygen or other oxidizing agents. The resultant reduced ion species are likely to be oxidized when exposed to atmospheric oxygen. The most notable example of this behavior is ferrous iron. The green color of ferrous iron is common in well drilling when the reduced zone is reached. Formerly rusty sections of drill stem are often removed with a green/black coating. At a given pH, ferrous iron is more soluble than ferric, so oxidation often causes iron precipitation. The most common precipitation mechanism is the formation of ferric hydroxide.

As shown in reaction 1:

$$Fe^{2+} + 1/4\,O_2 + 2\text{-}1/2\,H_2O \rightarrow Fe(OH)_3 + 2\,H^+$$

the iron not only comes out of solution, but the pH of the solution is also affected. As Cherry et al. (1982) point out, this mechanism can have a very important effect in determining contaminant migration rates if sufficient oxidizing agent is available in the subsurface environment. They point out that sufficient free oxygen is rarely available in most aquifers to invoke the ferrous to ferric mechanism to a major extent. However, unlike native aquifer conditions, oxygen is usually available in monitoring well bores.

In addition to the acid contribution of the iron hydroxide precipitation reaction, the behavior of iron species has often been indicated as a very important factor related to heavy metal mobility. Coprecipitation of trace metals with the iron and adsorption mechanisms on iron hydroxide surface coatings have both been suggested to explain the iron-heavy metal interaction. Of course, any trace metals associated with the iron hydroxides would also be susceptible to remobilization because of Eh or pH changes affecting the hydroxide solubilities.

Results of Multiple Sampling

Figures 1 through 5 and Table 1 show field and laboratory results of the multiple samples collected for the various wells.

Prior to detailed descriptions and highlighting of notable trends found in the data, it is important to understand some complicating variations which are superimposed on the significant data. The most obvious source of parameter variability is normal laboratory precision limits, or in the case of the field data, variation due to equipment and operator precision. For example, field pH values, which can be read to 0.01 pH units, are reported only to the nearest 0.1 unit, a normally reliable field precision. Unfortunately, resources did not permit an extensive quality assurance program with multiple duplicates for strict statistical analysis of accuracy and confidence limits. In addition to the normal precision limits, minor variations in temperature have been noticed in response to ambient air temperatures or direct sun on hose rolled on the sampling trailer. A large amount of hose on the reel and a low pumping rate can cause a significant residence time in the hose at the surface. When this is the case, it appears that heat transfer in the hose can vary the temperature measured at the flow-through chamber by one-half to one degree C.

One of the most obvious characteristics of the sampling results is the lack of consistency of trends between wells. Note the difference between wells WC-1 and A-1 in relation to pH vs. specific conductance. As well WC-1 was pumped, both pH and specific conductance showed a marked decrease and then stabilized. In contrast, A-1 showed pH values that appear stable and then dropped to a new stable value after approximately five well-bore volumes were pumped. Conductivity values increased steadily. However, in each case, the laboratory parameters follow the field analysis trends quite closely. In well WC-1, iron concentration increased threefold and manganese twofold as the pH and specific conductance stabilized. In A-1, magnesium, sodium, chloride and sulfate followed the A-1 specific conductance increase. Zinc, the only heavy metal above detection limits in A-1, showed unpredictable variations; however, small variations this near the detection limits may be insignificant. Although trend directions are not the same in both wells, relatively stable field parameters appear to indicate stability of laboratory parameters. This is of particular interest because well WC-1 is a 2-inch well with a low pumping rate and A-1 is a 16-inch well pumped at 200 gpm.

Sampling in well WC-2 shows a well that stabilized relatively quickly, but produced some ambiguous field parameters. This is the sort of well that can cause sampler difficulty because one of the field parameters continued to drift as the well was pumped. The specific conductance gave a reasonable, or possibly slightly early, indication of the point at which the constituents had stabil-

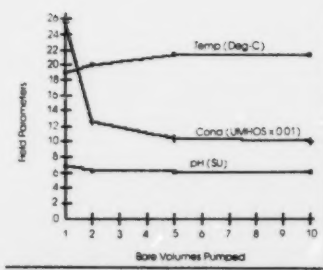

Figure 1A. Well WC-1 field parameters

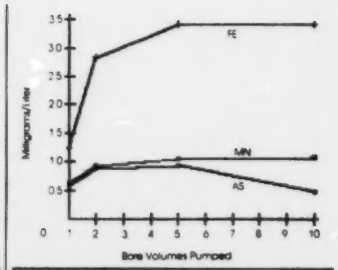

Figure 1B. Well WC-1 laboratory parameters

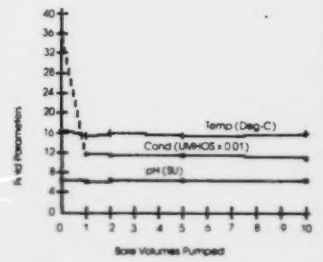

Figure 2A. Well WC-2 field parameters

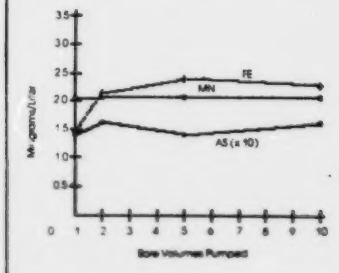

Figure 2B. Well WC-2 laboratory parameters

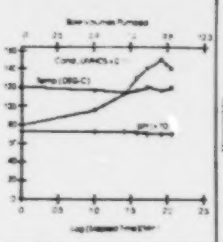

Figure 3A. Well A-1 field parameters

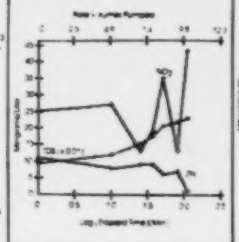

Figure 3B. Well A-1 laboratory parameters

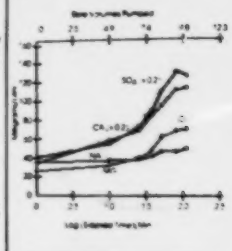

Figure 3C. Well A-1 Laboratory Parameters

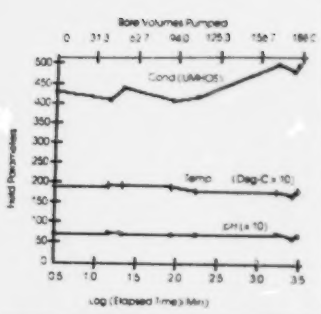

Figure 4A. Well A-2 field parameters

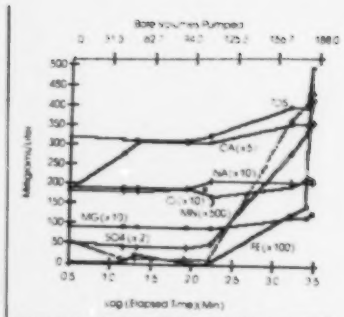

Figure 4B. Well A-2 laboratory parameters

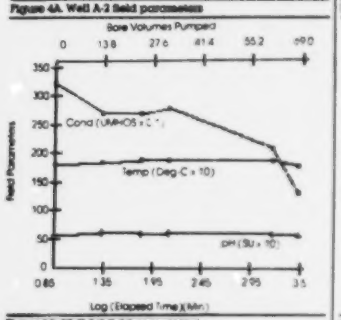

Figure 5A. Well A-3 field parameters

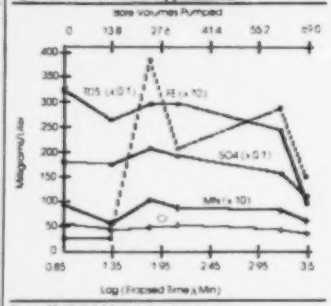

Figure 5B. Well A-3 laboratory parameters

ised, but the pH drift continued even after laboratory parameters had stabilized.

Well A-2 is an example of a well that required purging, but was subsequently over-pumped sufficiently to mix in water of the much different quality. The field parameters were ambiguous in the early pumping; samples most representative of the aquifer were probably collected between five and 10 bore volumes. Most of the laboratory parameters had stabilized by that time (note calcium and aluminum), however heavy metals values were below detection limits. In contrast, notice the increase in specific conductance and variability of pH that marks later sampling, when mixing was occurring. Values of almost all parameters were affected by the new water that was being pulled into the well by extended pumping.

The effects of over-pumping can also be seen in the data from well A-3. In addition, A-3 data indicates water-quality zonation or stratification near the casing. A slug of water with low chloride, copper, magnesium, manganese, zinc and TDS values was drawn in at approximately two bore volumes and then followed by a slug of water with higher iron and copper concentrations. A complex interaction of two or more aquifers is likely in this case. Well log, completion and pump test data indicate that there may be a leaky aquiclude between the aquifer through which the well is screened and the overlying water-table aquifer. Also a zone surrounding the casing may have been altered by or mixed with drilling fluids. A large amount of water was injected when this well was rotary drilled. The last sample of the well indicates that a water with higher copper and aluminum, and lower pH sodium and sulfate was being mixed into the sample after extended pumping.

Table 1 (well A-5) shows the field and laboratory data from the well which was both bailed and pumped. The sampling personnel were aware of the need to purge wells when sampling with the bailer and the bailer was tripped into the well at least four times, after developing the well by air-lifting. The difference in laboratory and field data point out an extreme example of the misinformation possible when a well is not purged sufficiently before a sample is collected. Although the contamination of this aquifer under the tailings was hinted in the bailed sample, the pumped sample shows the true extent of the problem with pH 2.5 and contaminant concentrations of 35,112 mg/l TDS, 383 mg/l copper and 6,832 mg/l iron. Note that this water sample consists of 3.5 percent dissolved solids.

Discussion

The comparative sampling data presented here shows the need to understand the hydrologic regime into which a monitoring well has been installed.

Although it is important to purge water from wells before collecting a sample, over-pumping of complex regimes can cause mixing of water of different quality and, in the extreme case, contamination of non-contaminated aquifers by previously localized or stratified pollutants. The results indicate the importance of monitoring field parameters as pumping progresses. The number of bore volumes pumped provide an estimate of the amount to be purged before sampling, but is no substitute for real-time monitoring of field parameters to determine when samples are likely to be representative of the formation near the monitor well. Bailed samples or over-pumping are likely to result in grossly inaccurate monitoring data.

Rate of pumping can also be an important factor when related to the overall hydrologic regime. Mixing of aquifer water or induced leakage is much more likely if a large cone of depression is created by either a high rate of pumping or extended pumping. Well A-1 is an example of a well where a high pumping rate of 76.0 liter/min (200 gpm) was reasonable, because of a high well capacity. Again, the importance of understanding the hydrologic regime and well completion is apparent. A moderate pumping rate (8 parts/dash) important if multiple zone sampling is to be done in a well. The natural tendency for higher horizontal than vertical permeabilities will usually reduce the amount of interzonal mixing if a low pumping rate is utilized. A large amount of pumped water can also be a hazard if highly toxic contaminants are present. Excessive pumping can create a large volume of hazardous waste for disposal with no attendant increase in sampling accuracy.

Table 1
Well Data Analysis/Well A-5

Elevation M.P.	3,750 ft.
Total depth	351 ft.
Perforated zone	321-351 ft.
Aquifer	Gila
Diam. & type casing	4-inch schd. 40 pvc

Remarks: 1st round sample was obtained in the first round by compositing four (approx.) 1 gal. bails. Pump was installed for second round sample.

Field data		
Date	3/25/82	5/19/82
Time	1,105	1,030
Depth to water, ft.	313.86	315.12
Water elev., ft.	3,436	3,435
Conduct. Umhos/cm	1,720	18,000
Temp., deg. C.	17	16
pH, std. units	6.3	2.5

Analysis results, dissolved basis, mg/l unless noted		
Arsenic	<0.02	<0.02
Cadmium	<0.005	.03
Nitrate	.2	.1
Selenium	<0.01	<0.1
Alkalinity	616	<1
Calcium	227	409
Chloride	43	92
Copper	.09	383
Hardness	801	4,009
Iron	.95	6,832
Magnesium	57	726
Manganese	8	143
Sodium	46	220
Sulfate	591	19,981
TDS	1,770	35,112
Zinc	1.8	45
Potassium	11.9	2
Silicon dioxide	25.3	100
Aluminum	1.4	765

It would be convenient if stabilized field parameters would always indicate an accurate, representative monitoring well sample. However, as is apparent from the presented data, there are many factors which make sampling more complex. The results do indicate that the first water to be removed from the well is very unlikely to represent formation water quality. Variations in field parameters as pumping progresses will usually detect other parameter variations that must be interpreted in light of hydrogeologic and well completion information.

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Biographical Sketches

Jim Rouse has an M.S. degree in hydrology from Stanford University and a Professional Degree in geological engineering from the Colorado School of Mines. He is president and general manager of Envirologic Systems Inc., serving the mining and waste disposal industries with baseline data collection, disposal impact mitigation, regulation advice, compliance monitoring and environmental permitting services. Previously, Rouse has had more than 16 years of experience with federal water pollution control agencies, the last seven years as the Environmental Protection Agency Mining and Milling Specialist.

Lee Wilson has an M.S. degree in geology from the University of Colorado and a B.A. in chemistry from Grinnell College. He is a geochemist and branch manager with Envirologic Systems Inc., consultant to mining, milling and waste disposal industries, providing hydrologic and geochemical services related to baseline monitoring, environmental permitting, compliance monitoring and environmental report preparation. Previously, Wilson has been a geology instructor at Angelo State University in San Angelo, Texas, and field geologist mapping oil shale in the Piceance Basin of Colorado.

A Laboratory Evaluation of Ground Water Sampling Mechanisms

by M.J. Barcelona, J.A. Helfrich, E.E. Garske and J.P. Gibb

Abstract

The reliability of ground water monitoring information can be assured by careful selection of sample handling and analytical procedures. Sampling mechanism selection has been studied far less than analytical methodologies (Scalf et al. 1981, Nacht 1983). This study has as its primary goal the identification of reliable sampling mechanisms for purgeable organic compounds and gas-sensitive chemical parameters in ground water. Carefully controlled sampling experiments were run to investigate the error contributed to chemical results due to sampling mechanism alone. Fourteen commercial sampling devices in five mechanistic categories were evaluated for their performance in sample collection for solution parameters, dissolved gases and purgeable organic compounds. Systematic errors related to sampling mechanism can reduce the accuracy of monitoring data by factors of two to three times that involved in analytical procedures.

Introduction

One of the principal obstacles to the reasoned management of ground water regulatory programs is the assurance of high quality reliable monitoring results. Research studies of subsurface processes share many of the same difficulties in sample collection and analysis. The ultimate utility of analytical results from monitoring or research efforts and the conclusions drawn from them depend heavily on the collection of representative samples.

Sampling procedures have been neglected over the years as sources of error in ground water work. Far more emphasis has been placed on analytical methodology, well design and construction. Since there now exist many sensitive, reliable protocols for the analysis of natural water samples for most chemical constituents, we are in a position to improve sampling methods based on known analytical benchmarks.

The reduction of systematic or determinate errors arising from biased sample handling procedures can be achieved when analytical interferences and materials' effects are known. These errors may yield both inaccurate, as well as imprecise results when unproven sampling protocols are used under field conditions. Systematic errors in sample handling stem from the physical and chemical disturbance of ground water solution composition during sample collection, preservation and storage prior to analysis. Field standards, spiked samples and blanks can be used to correct for errors that occur after the sample is brought to the surface. Only carefully controlled laboratory or field experiments can account for bias or imprecision due to sampling mechanism effects.

The need to sample ground water for specific chemical constituents under widely varying conditions demands that exhaustive testing of sampling mechanisms be conducted under carefully simulated or controlled conditions. The present study is an attempt to achieve this control for testing commercially available sampling devices. Operational performance characteristics of the sampling devices, master variables for ground water solution chemistry (e.g. pH, Eh, temperature and specific conductance) and dissolved volatile constituents are the main parameters of concern. Even if volative organic compounds or gases (O_2, N_2, CO_2, CH_4) are not of analytical interest, their loss from or introduction to a ground water sample can significantly affect solution chemistry and the speciation of other analytes. If sample collection causes the loss of soluble gases at the parts-per-million (ppm) level, the effect on trace constituents could be far more drastic. Since ground water samples are rarely in equilibrium with atmospheric gases, the disturbance of the sample matrix or background electrolyte must be minimized to collect analytical data that is representative of in situ conditions.

Experimental Design

The objective of this work was to identify faithful sampling mechanisms. We were primarily interested in comparing the relative magnitudes and causes of sampling bias or imprecision and those introduced in analytical methodologies.

Preliminary work in ground water sampling (Gibb et al. 1981, Schuller and Griffin 1981) has served to identify the general characteristics of a faithful sampling mechanism. They are detailed below:

1. The device should be simple to operate in order to minimize the possibility of operator error.

2. The device should be rugged, portable, cleanable and repairable in the field.

3. It should have good flow controllability to permit low flow rates ($\leq$100 mL·min^{-1}) for sampling volatile chemical constituents, as well as high flow rates (~1 L·min^{-1}) for large-volume samples and purging stored water from monitoring wells.

The mechanism should minimize the physical and chemical disturbance of ground water solution composition in order to avoid bias or imprecision in analytical results.

With these general characteristics in mind, a testing program was developed to permit the evaluation of commercially available sampling mechanisms. Fourteen commercial devices chosen for preliminary evaluation are shown in Table 1. They are representative of sampling devices in five mechanistic categories. Gas-lift devices employing rapid gas/water mixing and [illegible]ing and bubbling of water up and out of the well bore were not evaluated, as they have been documented as biased sampling mechanisms (Gibb et al. 1981, Schuller and Griffin 1981). Gas-lift mechanisms are clearly different from the gas-drive devices (e.g. Barcad®), which operate by a positive displacement mechanism with limited gas/water contact.

The evaluation was designed on a three-tiered structure shown schematically in Figure 1. The first level of testing consisted of a comparison of operational characteristics. The second level consisted of evaluating the performance of each operable device, both for the determination of the parameters indicative of well purging (pH, Eh, temperature and specific conductance) and the recovery of dissolved gases, e.g. CO_2, O_2, N_2, and CH_4.

Level 3 testing included the evaluation of sampling mechanism performance for the collection and analysis of specific compounds in the purgeable category of priority pollutants. Those devices that showed acceptable levels of performance in both Levels 1 and 2 entered Level 3 testing.

Level 1: Evaluation of Sampling Mechanism Operational Characteristics

The evaluation of sample collection mechanisms began with a critical comparison of the existing commercial designs using 14 criteria. These criteria and relative performance levels are shown in Table 2.

Each device was rated according to the criteria and the sum of all ratings was taken. Then the mean score

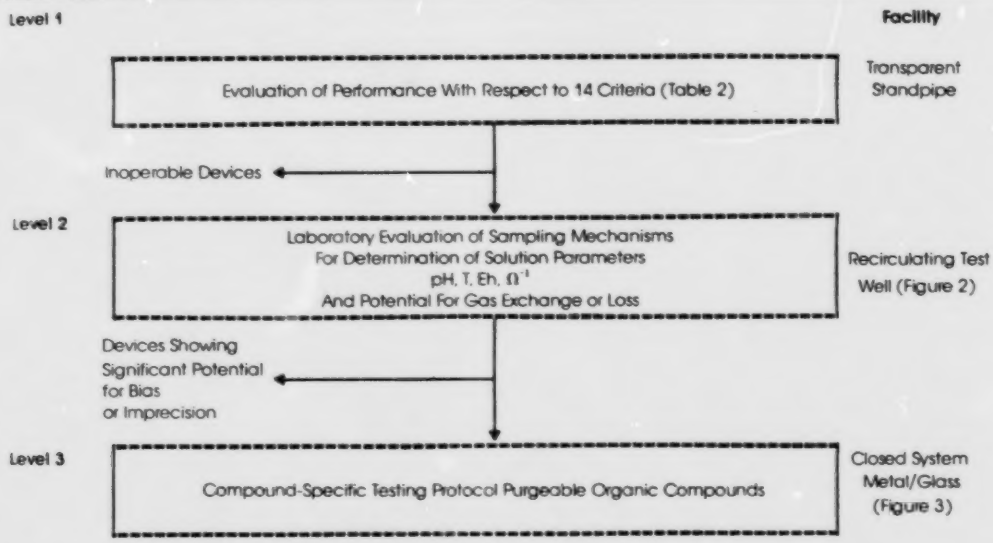

Figure 1. The three-tiered structure of the evaluation is shown here schematically

Table 1.
Sampling Mechanisms and Commercial Examples of Ground Water Monitoring Sampling Devices

Mechanism	Type	Commercial examples
Grab	Bailer	Homemade, TIMCO® (dual check-valve; bottom draw)
	Syringe	IEA Inc.
Positive displacement (bladder, non-gas contact)	"Middleburg" squeeze	IEA Inc. (Aquarius); QED Corp. (Well Wizard), Timco (GFP-TRV-2558)
	Bladder inflation	ISCO® (#2600)
Positive displacement (mechanical)	Helical rotor reciprocating diaphragm	Johnson Div. (UOP) — Keck, #SP-81 Bennett® (#180)
Gas displacement (gas contact)	Dedicated or pressure lysimeter type	Barcad® TIMCO® (GFP-TTVPLS-2474)
Other	Venturi suction (peristaltic)	ECO® (Samplifier) Masterflex® (#7570)

for all devices was calculated and the categories were rated as above-average or average-to-below-average on the basis of the score being either one standard deviation higher or within one standard deviation from the overall mean, respectively.

Determinations of flow rate output from the device over a range of head and lift conditions were the only actual measurements that went into this level of testing.

Level 2: Evaluation of Sampling Mechanism Effects on Solution Parameters and Gases

This level was designed to evaluate the range of utility of various sampling mechanisms. A reliable measure of the efficiency of well purging prior to sampling and the capability to collect unbiased samples for volatile constituents are important considerations for routine ground water monitoring.

Level 2 testing was conducted in a hydrologic test well facility, which allowed the circulation of a suitable background solution under controlled conditions (Figure 2). The testing system was designed to simulate conditions of 9.2m (30 feet) of lift at 5.0m (16 feet) of head above the sampler, conditions that are similar to many shallow ground water monitoring installations. The recirculating system incorporated a floating, lid-covered vat through which solution composition could be checked and adjusted. The background solution was dechlorinated Champaign, Illinois, municipal tap

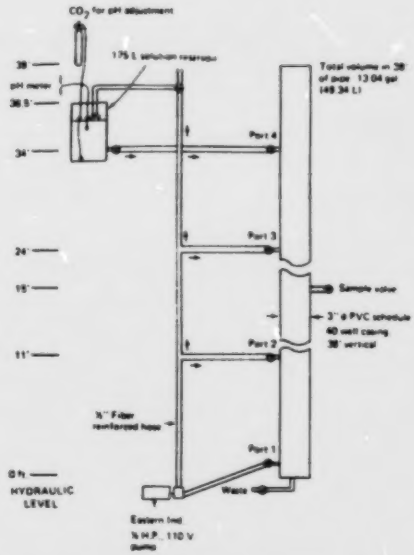

Figure 2. Level-two testing was conducted in a hydrologic test well facility

Table 2.
Sampling Mechanisms: Operational Evaluation Criteria

Criteria	Score 1	Score 2	Score 3
1. Availability	Limited	Adequate	Facile
2. Portability	Limited	Adequate	Facile
3. Simplicity of operation	Demanding	Moderate	Facile
Flow controllability (without modification)			
4. Sampling ($\leq$100 mL·min^{-1})	Poor	Good	Excellent
5. Purging (1−10 L·min^{-1})	Poor	Good	Excellemt
6. Range of operation	0-20 ft. Suction lift capacity	0-150 ft. Moderate	0-$\gg$150 ft. Unlimited
7. Compatibility with in-line sampling methods	May be difficult	Good	Excellent
Potential for disturbance of sample chemistry			
8. Volatile compounds (relative to bailer)	Poorer	Similar	Superior
9. Non-volatile compounds	Likely	Possible	None
10. Cleanability, Sterilizable	Poor	Good	Excellent
11. Ability to cope with turbid samples	Poor	Good	Excellent
12. Ease of recognition of malfunction in use	Poor	Good	Excellent
13. Overall reliability and field repairability	Poor (may involve considerable time and effort)	Good	Excellent
14. Adequacy of manufacturer's instructions for operation	Poor	Good	Excellent

Table 3.
Average Background Solution Chemistry for Level 2 Testing

Parameter	Mean*	Number of biweekly determinations*	Relative standard deviations** (%)
TDS	164	21	8
TOC	2.80	9	64
pH	8.72	21	4.0
Alkalinity ∇	109	19	4.3
Hardness Δ	74.5	21	7.1
Ionic strength	0.0041		

Ranges of Specific Chemical Constituents

					Trace elements ($\mu g \cdot L^{-1}$)
K^+	1.9– 2.4	$SO_4^=$	18.5–37.6	Cd	0.01–0.32
Na^+	25.6–32.0	Cl^-	4.0–14.6	Cu	4.5–238
Ca^{++}	9.6–14.4	Si (as SiO_2)	6.4– 8.9	Fe	<50–70
Mg^{++}	14.6–17.0			Mn	<3–5
				Pb	0.5–8.3
				Zn	16–100

* All values are in $mg \cdot L^{-1}$ except where noted.
∇ Reported as $mg \cdot L^{-1}$ $CaCO_3$.
Δ Calculated from average TDS, alkalinity and hardness, expressed in molar units.
** The relative standard deviation is the sample standard deviation from the mean expressed as a percent of the mean.

water amended by the introduction of O_2, CO_2 or CH_4, depending on the objectives of the specific experiment. The average background solution composition is detailed in Table 3.

The Level 2 test runs began by gentle sparging of an appropriate gas into the vat for a period of 30 to 45 minutes with the circulating pump in operation. (Carbon dioxide was used for pH adjustment (~7.5) in the runs for the indicator parameters, O_2, N_2 and alkalinity, while methane was used in supplemental testing for gas exchange and loss of volatiles). When in-line pH, Eh, temperature and specific conductance measurements stabilized (Garvis and Stuermer 1980), circulation was continued while water sampling was conducted.

The output of each operable device was sampled in triplicate during a minimum 15-minute period of operation. At the appropriate time, triplicate water samples were collected for O_2, N_2, CH_4 and alkalinity determinations, and a reading was taken for each of the solution parameters. Calibration standards and blanks for the gas determinations were prepared in triplicate at the beginning of the experimental period. Control samples were collected simultaneously with those from the devices via a sampling port in the well, which was at the same depth as the device under testing. Selected control samples were also taken from the vat to ensure that the recirculating solution was homogeneous.

Water samples for gases were collected by gently flowing the output from the device, well-sampling port or vat through the tip and out the top of a 20 mL polyethylene syringe. After the passage of several syringe volumes, the syringe plunger was replaced and all but 10.0 mL of the sample was forced out the tip through a three-way valve. This three-way valve permitted the introduction of 10.0 mL of helium headspace via a second syringe at atmospheric pressure. Once the sample and headspace had been vigorously agitated and allowed to equilibrate, the headspace was drawn back into the second syringe and the headspace sample was ready for analysis by gas chromatography (GC). Dissolved oxygen and nitrogen determinations were done by Winkler titrations (Carpenter 1965) and thermal conductivity GC, respectively; methane was determined by flame ionization GC (McAuliffe 1971).

Level 3: Recovery and Precision of Purgeable Organic Compound Sampling

Level 3 testing consisted of the analysis of water samples discharged from the sampling devices while they were operated in a closed system. Essentially the same lift and hydraulic head characteristics as in the Level 2 testing were maintained in this effort.

A schematic diagram of the closed-system test cell is shown in Figure 3. The sampling device was installed inside the 22-liter cell, which was constructed entirely of glass, aluminum and Teflon®. The background solution was spiked with four trihalomethane (THM) compounds (chloroform, bromodichloromethane, chlorodibromomethane and bromoform) and added to the test cell at a pressure of ~1.3 atm. The compounds were added in equal mixtures to give total THM's at levels from 80 to 8,000 ppb. The cell temperature was maintained at 15 C. Each device and associated tubing was flushed for at least five minutes. Sequential samples from the device under test were taken from the pumped flow at a height of approximately 40 feet (12.2m) above the cell while parallel control samples were taken from the cell. As in prior testing, triplicate samples were collected and each sample was analyzed in duplicate along with control samples, standards and system blanks according to EPA Method 601 (U.S. EPA 1982). Grab samplers that could not be operated in a totally closed system were tested through a larger opening in the test cell. Additional control samples were taken

before and after each of three grab samples for each device.

Results and Discussion

Level 1 Results: Operational Characteristics

The criteria used in the Level 1 testing (Table 2) are the essential attributes of an ideal sampling device. Accordingly, none of the existing designs was expected to merit a perfect score. This is indicative of the fact that no single type of device could be expected to provide representative samples under all conditions for a wide range of chemical constituents.

In this study, the conventional bottom check valve bailer received an average score. The remaining mechanisms were rated above-average or average-to-below-average, depending on whether the score fell at least one standard deviation above or within one standard deviation of the overall average, respectively. These results are shown in Table 4. The positive displacement bladder pumps, syringe sampler (grab mechanism) and gas displacement devices were rated above-average in probable performance. The other mechanisms were rated equal to or slightly below the bailer, since they were all within one standard deviation of the average. The order of the devices in the latter grouping has no particular significance.

The evaluation of the operational performance of the commercial samplers was instructive from two standpoints. First, very few of the devices have easily controllable flow rates for both volatile sampling and high rate well purging. In fact, several devices have a single high operational flow rate ($>2\ L \cdot min^{-1}$), roughly independent of lift or hydraulic head. Second, the operating instructions and general documentation of system operation, control and troubleshooting were inadequate in most cases. Given that there are a large number of monitoring installations that are serviced by relatively inexperienced technicians, the documentation could be improved substantially.

It is also noteworthy that at least half of the 14 devices evaluated failed to operate properly on delivery to the laboratory. In several cases, malfunctions (e.g. poor seals, leaky check valves) were observed when devices were operated in the transparent stand pipe.

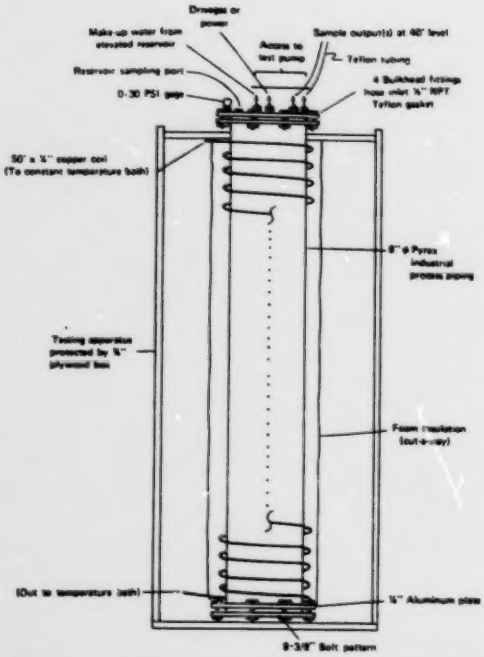

Figure 3. A schematic diagram of the closed-system test cell

Since such problems may be difficult to diagnose and repair in field operations, it is important that all sampling gear be carefully checked out prior to use or installation. Minor repairs were conducted on several devices when possible in order to conduct further testing. At this point, 11 operationally reliable devices were considered for Level 2 testing.

Level 2 Results: Solution Parameters, Gas Exchange/Loss

In Level 2 testing, all devices were operated accord-

Table 4.
Sample Collection Mechanisms: Probable Operational Performance Characteristics as Measured by the Evaluation Criteria

Pump/device mechanism	Number evaluated	Category
Positive displacement (bladder, no-gas contact)	(5)	Above average performance
Syringe sampler (vacuum-assisted fill)	(1)	Above average performance
Gas displacement devices	(2)	Above average performance
Positive displacement (reciprocating diaphragm, no-gas contact)	(1)	Average to below average
Bailer (dual-check valve/bottom draw)	(1)	Average performance * *
Bailer (conventional)	(1)	* *
Positive displacement (helical rotor)	(1)	* *
Venturi	(1)	* *
Peristaltic pump (suction)	(1)	* *

* Categorization based upon performance that may be expected under "normal" field conditions and without extraordinary modification of commercial devices as represented by the preliminary performance evaluation criteria.

ing to manufacturers' specifications under the same conditions of head and lift.

Laboratory testing of ground water sampling mechanisms began with measurements of solution parameters indicative of the progress of well purging or flushing prior to sampling. The hydrologic test well was charged with background water (Table 3) and CO_2 gas was added to adjust the pH to 7.5-8.0. The water was then circulated through the test well to obtain initial readings of pH, alkalinity, specific conductance and temperature before the sampling device under examination was lowered into the well. Deviations from the background solution readings were observable to: ±0.01 (pH units), ±2 mv(Eh), ±5 μS (specific conductance) and ±0.1 C (temperature). A significant deviation from background levels was determined to be five times these observable differences.

The most sensitive parameters to the pumping mechanisms were pH and Eh. No significant deviations in specific conductance or temperature as a consequence of pumping were noted, although some heating did occur in long tubing bundles. This may be a problem in hot, sunny situations where transfer tubing is exposed to direct sunlight. Significant pH and Eh changes were observed for the peristaltic (suction) mechanism. Average changes of +0.05 pH units and -20 mv in Eh were noted for samples taken with this device. These are exactly the coincident changes one would expect if the mechanism encouraged degassing of CO_2 and O_2 in the pumped solution.

These results demonstrate the usefulness of most commercial sampling mechanisms for purging stagnant water from monitoring wells. This is true to the extent that our testing conditions simulate actual field conditions. With the exception of the peristaltic pump, adequate flow rates and the use of a less than ±10 percent change in the indicator parameters for complete purging are reasonable expectations from the pumping mechanisms.

Investigation of the potential for gas exchange with the atmosphere was conducted initially using high precision determinations of O_2 and CH_4. Oxygen runs were conducted in the 2 to 6 mg-$O_2 \cdot L^{-1}$ range, while methane levels varied from 0.1 to 18 mg-$CH_4 \cdot L^{-1}$.

Since the detection of significant mechanism-related error was made relative to the errors involved in both sample handling and analysis, it was important to establish the performance attainable for control samples (precision) and calibration standards (accuracy and precision). The accuracy (percent bias) and precision (percent relative standard deviation-RSD) for the controls are shown in Table 5. The average accuracy and precision for the calibration standards for both the oxygen and methane determinations were better than 10 percent. The fact that the control samples showed better precision than the calibration standards (made up by sequential dilution of saturated solutions) established that the test conditions were optimal to investigate the contribution of sampling mechanism to overall error.

The performance of 11 commercial devices in five mechanistic categories is shown in Tables 6 and 7. The accuracy of analytical results on water samples collected by the various mechanisms was uniformly poorer than that observed for the control samples. In most cases, the bias introduced into the analytical results fell in a range from -1 to 24 from the mean control values. This means that exchange or loss of gaseous solutes can be expected to cause false low values even in carefully collected ground water samples. The use of the positive displacement (no-gas contact) pumps (operated with air or N_2)and the grab mechanisms tended to minimize losses of oxygen and methane when carefully operated under controlled conditions. The gas displacement devices provided reasonably accurate results except with oxygen-sensitive constituents when air was used as the drive gas. Only the bladder pumps and the dual check valve, bottom-draw bailer sample results were not significantly different from the control mean values. This was a direct consequence of sampling precision (Table 7), which limited direct statistical tests (e.g. Student's "t" test) of mechanism-related errors. The data in Table 7 clearly show that the precision of samples collected by most of the devices was poorer by a factor of two or more than that of the control samples.

The Level 2 evaluation illustrated two major points. Inaccurate results (negative bias) can occur from sampling mechanism effects alone, which are two to three times higher than analytical bias. Poor precision arises from the actual operating conditions during sample collection. In this respect, the sampling mechanism and the expertise of the sampling technician are the major sources of imprecision. Critical variables are: time, temperature, reproducibility of flow rates and the technique of storage vessel filling.

On the basis of these results, two bladder pumps, both bailers, the peristaltic pump and the gas displacement devices were selected to undergo Level 3 testing.

Level 3 Results

Level 3 evaluations were conducted under closed-system conditions where the operation of the mechanism permitted. The bailers and syringe sampler were operated through the top of the system (Figure 3), while the peristaltic pump was operated at 12 feet (3.7m) of lift. All of the other pumping mechanisms were operated in the enclosed system pumping to a

Table 5.
Average Accuracy and Precision of Controls

	Oxygen			Methane		
	Recovery/addition	RSD*	(N)	Recovery	RSD*	(N)
Type of control	% Bias	%		% Bias	%	
Samples	**	2		**	8	
Standards	−1	7	(4)	−8	10	(9)

* Relative standard deviation is the standard deviation from the mean expressed as a percentage of the mean.

** Control samples were taken as the true values for comparison purposes.

Table 6.
Average Accuracy of Results from Device-Collected Samples Relative to Control Samples

	Oxygen Recovery/addition		Methane recovery		Overall accuracy	
	% Bias*	(N)**	% Bias	(N)	% Bias	(N)
Positive displacement (bladder, no-gas contact, 3 designs)	− 3	(3)	−15	(4)	−10	(7)
Grab sampling						
conventional bailer	**− 8.5∇**	(3)	**−35**	(1)	**−12**	(4)
dual-check valve bailer	**−13.5**	(3)	**− 6.8**	(1)	**−12**	(4)
syringe sampler	**− 7.0**	(3)	**−20**	(1)	**−10**	(4)
Gas displacement (2 designs)	**+ 9**	(3)	**−18**	(4)	**−12Δ**	(6)
Suction (1 design)	**− 8**	(1)	**−23**	(2)	**−18**	(3)
Positive displacement (mechanical, 2 designs)	**−13**	(4)	**−36**	(4)	**−24**	(8)
Control samples	− 1	(4)	− 8	(9)	− 7	(13)

* % Bias — Average percent bias for the category.
** (N) — Number of individual experimental runs. Each device was run with triplicate samples, control samples and calibration standards.
∇ Bold entries denote significant differences were observed in more than half the experimental runs at the 95% confidence interval from Students "t" test.
Δ Overall accuracy cannot be reasonably assessed, since gross oxygen addition was observed in one run due to a check valve malfunction that resulted in a high positive average bias. Discounting this value, the overall accuracy was statistically identical to the conventional bailer results.

height of 40 feet (12.5m). Teflon transfer tubing was used to minimize materials' effects (Ho 1983; Barcelona, Gibb and Miller 1983).

Similar to the Level 2 testing, control samples were taken directly from the cell at intervals of five minutes, simultaneous with the pumped/collected samples. Calibration standards were made to ensure the integrity of sample handling and analytical steps throughout the study. The analytical performance data in Table 8 demonstrate that method performance for the four purgeable trihalomethane (THM) analyses was more than adequate to evaluate the effects of sampling mechanism-related errors. The accuracy and precision of both the calibration standards and control samples were better than 85 percent and five percent, respectively. THM compounds were used in equal concentration mixtures and the data analysis was conducted on each compound as well as total THM levels. Either mode of interpretation led to the same conclusions on sampling recovery and precision. Since analytical procedures and sample handling methods were identical for each mechanism and parallel control samples, mechanism-related error alone was isolated.

The accuracy and precision of the sampling runs for each mechanism at three levels of THM mixture concentration are shown in Table 9. Relative to the control samples, the positive displacement bladder pumps and the bailers showed no significant difference in accuracy or precision. Negative biases due to degassing and loss of volatiles in these results supported the conclusions of prior testing for O_2 and CH_4 recovery. With reference to the bailers, it should be noted that grab samples were taken directly from the reservoir and the samples were not subjected to the typical disturbance involved in retrieving the bailer from depth in a well bore. The results are indicative, therefore, of optimum sampling conditions and should not be considered typical of field performance. In general, the observed precision of the devices and control samples was sufficient to permit the treatment of the data by Student's "t" statistic. This was not the case in the Level 2 results where the variances were judged statistically different by the variance ratio (F) test.

Table 7.
Average Precision of Results From Device-Collected Samples Relative to Control Samples.

	Oxygen	Methane
	RSD_s / RSD_c	RSD_s / RSD_c
Positive displacement (bladder)	1	1
Grab samplers		
conventional bailer	1	1
dual-check valve bailer	4	2
syringe sampler	3	3
Positive displacement (mechanical)	3	1
Gas displacement	4	3
Suction	4	1

Ratio of the relative standard deviation (RSD) of the samples from the devices to the RSD of the control samples.

The gas displacement and the peristaltic pump results clearly show that statistically significant losses of purgeable organic compounds can occur due to mechanism effects even under controlled sampling conditions. In most cases the bias worsened as the total concentration of THM's increased. The effects observed for the peristaltic (suction) mechanism are

Table 8.
Average Accuracy and Precision of Controls

Compound		$CHCl_3$		$CHBrCl_2$		$CHClBr_2$		$CHBr_3$		Total THMS	
		Percent									
N	Type of Control	Bias	RSD	Bias	RSD	Bias	RSD	Bias	RSD	Bias	RSD
(611)	Samples* (20–2,000 ppb)	*	4.0	*	3.5	*	2.6	*	2.1	*	2.7
(80)	Calibration standards** (10–2,000 ppb)	NA	4.7	NA	3.8	NA	3.9	NA	3.6	−9.9	4.4
(5)	Procedural standards*** (4.5–68.3 ppb)	−9.5	5.4	−15	5.8	−9.7	9.9	+13.5	15.5	−6.8	11.6

* Control samples were taken as the true values for comparison purposes.
** Standards used daily to establish relative response factors (RRF) for each compound relative to dichlorobutane internal standard; criterion for acceptance was ±10% from the RRF range established by procedural standards.
*** Method procedural standards run at intervals during the four-month study to evaluate the stability of the methodology.
N Denotes the number of samples run in duplicate.
NA Not applicable.

Table 9.
Average Accuracy and Precision of Results From Sampling Devices Relative to Control Samples*

	Total THM levels (ppb)					
	80–150		700–1000		2,000–8,000	
		RSD sample		RSD sample		RSD sample
Sampling device	% Bias	RSD control	% Bias	RSD control	% Bias	RSD control
Positive displacement (bladder)	−0.9	0.6	−1.3	0.1	<0.1	0.8
Grab samplers						
conventional bailer	−2.2	0.8	−0.4	0.7	−0.9	2.5
dual-check valve bottom draw bailer	+0.8	1.5	+0.8	1.2	+1.7	0.6
Gas displacement	**−7.7****	1.6	−3.2	1.4	−5.5	0.4
Suction	**−4.1**	0.8	**−14.8**	0.7	**−16.1**	0.3

* At least 18 samples and control samples were run at each concentration level for each device.
** Bold entries denote statistically significant differences from controls at the 99% level.

further supported by the recent work of Ho (1983), who evaluated the effects of lift, concentration and materials on purgeable compound recoveries. He observed strongly negative biased recoveries ranging from 5 to 8 percent for THM compounds at lifts of 8 to 16 feet. These values are in excellent agreement with the value of 4.1 percent at 12 feet of lift observed in this study in the low concentration range. He further observed losses from 8 to 10 percent due to the use of silicone rubber transfer tubing as compared to Teflon®. It may be expected that ground water sampling for volative organic compounds with either gas displacement or suction mechanisms will introduce significant error into monitoring results. Figure 4 graphically depicts the relative magnitude of analytical and sampling bias observed in this study. Sampling mechanisms' effects under field conditions may be much greater, particularly for the conventional single check valve bailer, gas displacement and peristaltic devices. These devices demand very careful control of operating variables: agitation, pressurization/depressurization cycles, and pump speed, which complicate sample retrieval. Because this study was conducted at or below 25 C with low total dissolved solids (<200 $mg \cdot L^{-1}$) background solution, the results minimize the effects of temperature or the "salting-out" of volatile constituents (Friant and Suffet 1979). These observations underscore the need for careful selection of sampling mechanisms and methods in ground water monitoring efforts in order to ensure the reliable collection of representative samples.

In summary, the overall performance ranking of commercial sampling mechanisms is shown in Table 10 with recommendations for use. It is presented as a guide for planning comprehensive ground water data collection efforts. It should be reiterated that a careful evaluation of the information needs of the ground water monitoring program must be conducted prior to deciding on sampling mechanisms and protocols.

Conclusions

The task of obtaining representative samples of ground water in both research and compliance moni-

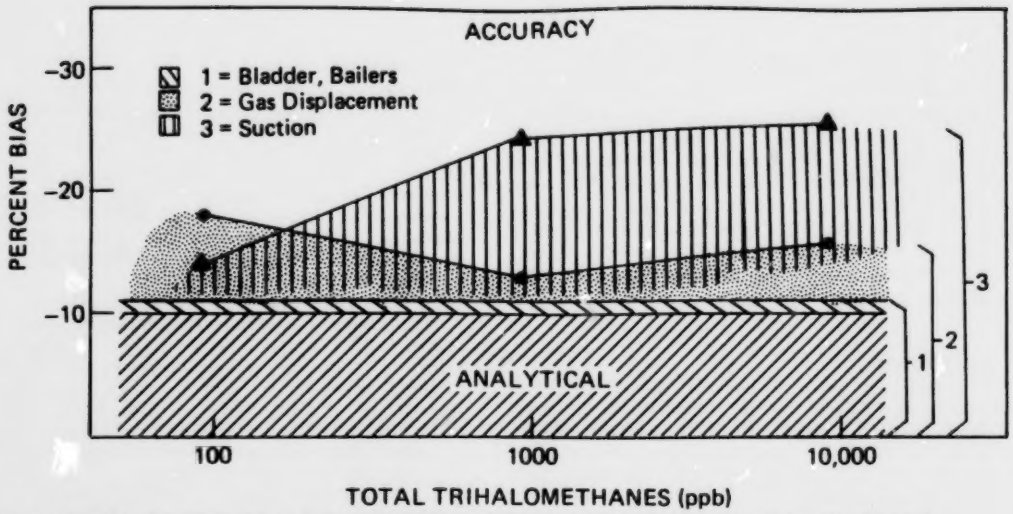

Figure 4. Graphic depiction of the relative magnitude of analytical and sampling bias observed in this study.

Table 10.
Performance Evaluation of Ground Water Sampling Mechanisms for Purgeable and Gas-Sensitive Parameters

Mechanism category	Overall performance ranking	Remarks
Positive displacement (bladder)	Above average	Expected to provide both efficient well purging and representative samples over a range of conditions with minimal difficulty in field operations.
Grab samplers		
conventional bailer	Average	Unsuitable for well purging; require very careful operation and sample handling precautions under field conditions; field performance open to question.
dual-check valve bailer	Average	
syringe pump	Average—below average	
Positive displacement (mechanical)	Average—below average	Suitable for well purging; sampling performance very dependent on specific design and operational details.
Gas displacement (gas drive; not gas lift)	Average—below average	May be suitable for well purging if used in conventional installations; malfunctions are difficult to assess or repair; significantly lower recoveries of purgeable organic compounds and gases may occur depending on field conditions and operator experience.
Suction	Below average	Suitable for well purging at depths to approximately 20 feet; significantly lower recoveries of purgeable organic compounds and gases will result from sampling with this mechanism.

toring programs must be carefully approached. Most pumping mechanisms may be expected to perform satisfactorily for well purging and the measurement of solution parameters. However, sampling for gas-sensitive and volatile chemical constituents can be significantly biased by degassing and loss of volatiles during sample collection.

Significant bias and poor precision may be expected in shallow ground water sampling with gas displacement, positive displacement mechanical, and suction mechanisms, unless extraordinary care is taken in sample retrieval, transfer and collection. Bladder (no-gas contact) pumps are superior for most applications. The performance of grab samplers, particularly bailers, is heavily dependent on both the expertise of sampling personnel and field conditions. The ideal controlled conditions under which these performance data were collected represent an optimum situation for the observance of minimal sampling error. Field conditions and solution composition are complicating factors that must be evaluated on a case by case basis.

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James P. Gibb is the head of the Ground Water Section of the Survey. He has more than 20 years experience in both ground water research and resource assessment investigations and has authored many scientific publications on these topics. He received a B.S. degree in civil engineering from the University of Illinois in 1966.

References

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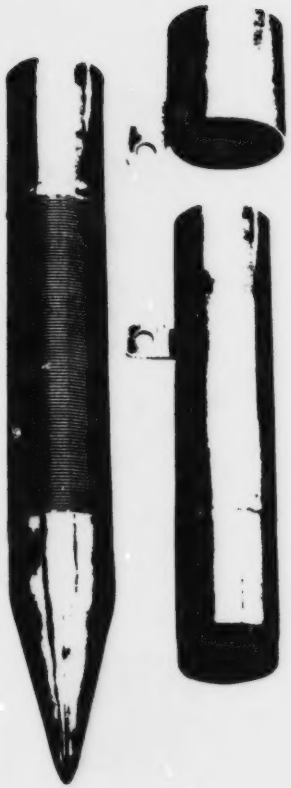
Stainless Steel Pipe and Screens

- Stainless steel provides strength, long life and minimum interference with sample analyses.
- Continuous slot construction produces high open area. Higher volume of water can be drawn in a shorter length of screen which allows more representative sampling.
- Flush joints between screen and pipe lengths mean sampling devices won't hang up inside. Gravel pack and backfill won't bridge outside.
- Screens and pipe available in various lengths and 6 diameters.
- Locking cap available for protection of the well.



Stainless Steel Pipe

PIPE SIZE	PIPE DIAMETER		SHIP WT (lb/ft)	PRICE (INCLUDES END FITTINGS)				ADDITIONAL PIPE (per ft)
	O.D. (IN.)	I.D. (IN.)		3 FT	5 FT	10 FT	20 FT	
1¼ inch	1.660	1.380	1.2	$ 35.35	$ 44.15	$ 66.15	$110.15	$ 4.40
2 inch	2.375	2.067	1.7	44.60	56.60	86.60	146.60	6.00
3 inch	3.500	3.068	3.1	61.40	82.90	136.65	244.15	10.75
4 inch	4.500	4.026	4.0	79.55	108.75	181.75	327.75	14.60
5 inch	5.563	5.047	6.5	130.50	171.30	273.30	477.30	20.40
6 inch	6.625	6.065	7.7	168.00	225.00	367.50	652.50	28.50

Stainless Steel Screen

SCREEN SIZE	SCREEN DIAMETER		SHIP WT (lb/ft)	PRICE (INCLUDES END FITTINGS)					ADDITIONAL SCREEN (per ft)
	O.D. (IN.)	I.D. (IN.)		2FT	3 FT	4 FT	5 FT	10 FT	
1¼ inch	1.660	1.130	3.0	$ 59.35	$ 77.95	$ 96.55	$115.15	$208.15	$18.60
2 inch	2.370	1.800	4.0	78.80	104.90	131.00	157.10	287.60	26.10
3 inch	3.500	2.970	5.0	87.75	117.05	146.35	175.65	322.15	29.30
4 inch	4.500	3.985	6.0	117.95	159.05	200.15	241.25	446.75	41.10
5 inch	5.563	5.000	7.5	165.10	213.00	260.90	308.80	548.30	47.90
6 inch	6.625	6.065	9.0	189.60	243.15	296.70	350.25	618.00	53.55

IMPORTANT NOTE: Pipe and screen lengths shown do not include length of fittings. Pipe fittings are Johnson flush thread female top and male bottom. Screens have female flush thread top and stainless steel point bottom on 1¼" and 2" size; stainless steel flat plate bottom on 3-6" sizes.
TO PRICE UNLISTED LENGTHS: Add appropriate "per foot" price to nearest listed length. For example, an 8-ft length of 2-inch diameter pipe is $56.60 plus 3 x $6.00 = $74.60 total.

Stainless Steel Locking Cap (U.S. PAT. NO. 4376619)

PART NUMBER	CAP SIZE	PRICE
6200351	1¼"	$22.50
6200352	2"	27.50
6200353	3"	32.50
6200354	4"	37.50
6200355	5"	43.00
6200356	6"	49.00

These prices are for the locking cap with the locking lug welded to that cap. The compatible locking lug is welded to the top section of stainless steel pipe in each well. On the pipe we substitute the female threaded end fitting with the locking lug with no change in pricing. If customers wish to adapt their own pipe, the locking lug is available separately for $4.50.

Johnson screens by UOP

ALL PRICES ARE F.O.B. ST. PAUL, MN AND ARE CONTRACTOR NET

3695

PVC Plastic Pipe and Screens

- Sonic welded PVC produces high strength screen.
- Sonic welded PVC wire-wrapped screen has high strength and more open area per given slot size than any other non-metallic screen available.
- Resists corrosion from salts and gases commonly found in either fresh or salt waters.
- Precision slot openings available in sizes from 0.006 inches on up.
- The only continuous slot non-metallic screen available without a restricting pipe base.
- Thermally attached fittings eliminate need for joining solvents.
- Screens and pipe are available in 6 diameters and various lengths.
- PVC thread is compatible with SS thread.
- SS locking cap assembly can be used with PVC.

PVC Pipe

PIPE SIZE	PIPE DIAMETER		SHIP WT (lb/ft)	PRICE (INCLUDES END FITTINGS)				ADDITIONAL PIPE (per ft)
	O.D. (IN.)	I.D. (IN.)		3 FT	5 FT	10 FT	20 FT	
1¼ inch	1.660	1.380	0.5	$11.15	$13.45	$ 19.20	$ 30.70	$1.15
2 inch	2.375	2.067	0.7	13.60	16.80	24.80	40.80	1.60
3 inch	3.500	3.068	1.4	20.60	27.00	43.00	75.00	3.20
4 inch	4.500	4.026	2.0	25.95	34.45	55.70	98.20	4.25
5 inch	5.563	5.033	2.7	35.25	46.75	75.50	133.00	5.75
6 inch	6.625	5.993	3.5	46.45	62.75	103.50	185.00	8.15

PVC Screen

SCREEN SIZE	SCREEN DIAMETER		SHIP WT (lb/ft)	PRICE (INCLUDES END FITTINGS)					ADDITIONAL SCREEN (per ft)
	O.D. (IN.)	I.D. (IN.)		2FT	3 FT	4 FT	5 FT	10 FT	
1¼ inch	1.660	1.125	0.5	$ 25.10	$ 33.80	$ 42.50	$ 51.20	$ 94.70	$ 8.70
2 inch	2.375	1.875	0.8	30.60	41.50	52.40	63.30	117.80	10.90
3 inch	3.500	2.890	1.5	41.50	56.75	72.00	87.25	163.50	15.25
4 inch	4.500	3.890	1.7	48.90	66.75	84.60	102.45	191.70	17.85
5 inch	5.563	4.810	2.5	59.10	79.65	100.20	120.75	223.50	20.55
6 inch	6.625	5.690	3.2	72.80	98.20	123.60	149.00	276.00	25.40

IMPORTANT NOTE: 1¼" through 4" size pipe are Schedule 40; 5" and 6" sizes are SDR-21. Length shown for pipe does not include fitting lengths which are Johnson flush thread female top and male bottom. All pipe meets ASTM F480-81 specifications.
Screen length is acutal length of effective screen area. Price includes Johnson male and female flush threads or male iron pipe threads or flat plate bottom.
TO PRICE UNLISTED LENGTHS: Add appropriate "per foot" price to nearest listed length. For example, a 7-ft length of 4-inch diameter screen is $102.45 plus 2 x $17.85 or $138.15 total.

PVC End Cap (with female flush thread)

PART NUMBER	CAP SIZE	PRICE
6600209	1¼"	$ 7.00
6212320	2"	8.00
6600235	3"	10.00
6600244	4"	12.00
6600255	5"	16.00
6600265	6"	20.00

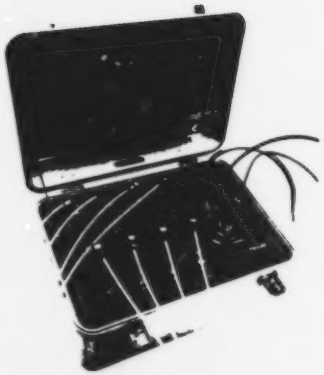
ALL PRICES ARE F.O.B. ST. PAUL, MN AND ARE CONTRACTOR NET

Johnson screens by UOP

Johnson-Petur™ Water Level Monitoring Systems

Designed for accurate water well pumping tests and for aquifer testing with observation wells.

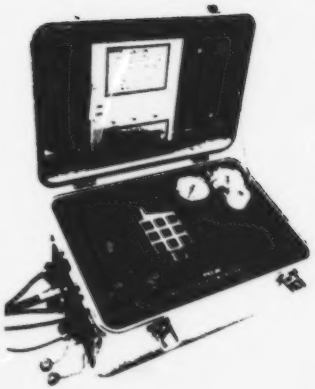
- Senses water level from pneumatic piezometer or bubbler tube.
- Two sensing channels in readout instrument.
- Eight additional sensing channels with pneumatic multiplexer.
- Programmable for metric or English units.
- Pre-programmed, automatic sequential readouts for time and water level changes.
- Reprogrammable for other time and water level changes.
- Standard pressure range is 0-100 psi (231 ft)—other ranges available on request.
- Strip chart data recording.
- RS232 serial data port to interface with other outside recording devices.
- Power supply is rechargeable Ni-Cad battery and/or external 12v DC source such as vehicle battery.
- Self-contained gas supply tank plus external connections for CO_2 or N_2.
- LCD data display independent of strip chart printer.
- Time data is in minutes and tenths of minutes.
- Pressure data is in psi, ft of H_2O or meters of H_2O.
- Optimum temperature range -4F to 176F (-20C to 80C).
- Accuracy at 0 - 115 ft is 0.1% (0.12 ft)
  0 - 231 ft is 0.35% (0.80 ft)
- Sensitivity at 0 - 115 ft is 0.0022% (0.003 ft)
  0 - 231 ft is 0.0112% (0.03 ft)



C-300-2 MULTIPLEXER

Standard 8-channel pneumatic multiplexer connects to the C-108 Controller. Unit includes airlines and electrical wire to make connection.

$2,655.00



C-108 CONTROLLER-READOUT

Gives readout of water levels measured by pneumatic sensors. Programmable for either metric or English units, timing of automatic sequential readouts and given waterlevel changes. Standard pressure range of 0-100 psi. Unit includes rechargeable Ni-Cad battery and recharger, and tank connectors and supply airlines for CO_2 or N supply. Also included is 1,000 ft of 3/16-inch O.D. nylon surface airline tubing and instruction book.

$5,820.00

Extra tubing for surface airline, 1,000 ft roll

$80.00

C-28 PRINTER

Electrostatic printer connects to the C-108 Controller. Electrical connecting wire and paper included.

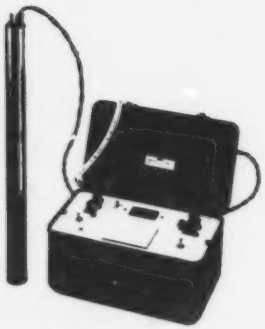
$1,830.00

Shipping Box holds one, two or all three Johnson-Petur™ components. Price is $150.00. On return of the shipping box, freight paid, $100 will be refunded.

ALL UNITS SHIPPED FOB ST. PAUL, MN.
SHIP WEIGHT: 100 LBS.

Johnson-Keck® Model SP-81 Submersible Sampling Pump

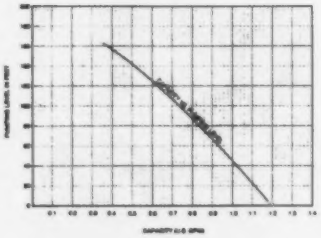
Designed for use in 2-inch diameter monitoring wells, the SP-81 is made of essentially chemically inert materials. Easily cleaned and reused, it operates by rechargeable battery at remote sites. Produces uniform, continuous flow. No special tools needed for on-site cleaning or repair.



Specifications

Pump outside diameter: 1.75 inches
Pump length: 25.0 inches
Pump weight*: 8 lbs.
Power: 12 volts DC at 10 amps
Capacity: 0.6 gpm at 125 ft head
1.2 gpm at 10 ft head
Operating temperature: -20C to 38C
Pressure: 120 psi (Refer to the pumping curve for other minimal operating ranges.)
RPM: 500

*Weight does not include power cable, discharge tubing or battery pack.



Standard Equipment

PUMP:
- Positive displacement
- 304 stainless steel pump housing
- EPDM synthetic rubber stator
- 316 stainless steel rotor
- DC motor housing is 304 stainless steel
- Electrical terminations are Teflon† and 304 stainless steel
- 3/8-inch 304 stainless steel barb discharge tubing connector

BATTERY PACK:
- Weight 25 lbs.
- 12-volt DC rechargeable by AC or DC
- Forward/off/reverse switch
- Voltage and current monitoring display
- Thermal auto-off circuit breaker
- DC power cable
- AC power cable

POWER CABLE:
- 125 feet long
- Teflon sheathed
- 10-gauge, 2-connector serves as pump lowering wire
- 750 lb. breaking strength

DISCHARGE TUBING:
- 125 feet long
- Bev-A-Line Type X polypropylene

Optional Equipment
Viton stator
Teflon discharge tubing
Cable tubing storage reel
Inflatable packers (2-in. or 4-in.)
Cable clamp to suspend pump
Auto battery monitor

†Teflon is a registered trademark of Du Pont Inc

STANDARD UNIT	Includes complete pump with EPDM stator, battery back, power cable, Bev-A-Line X discharge tubing, cable clamp and shipping crate	$3,900.00
OPTIONAL UNIT	Includes complete pump with Viton stator, battery pack, power cable, Teflon discharge tubing, cable clamp and shipping crate	$4,330.00

- All units & accessories shipped FOB St. Paul, MN or East Lansing, Mich.
- Standard unit in shipping crate is approximately 100 lbs.

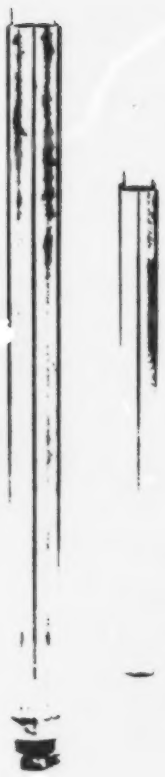
Stainless Steel Bailer Water Sampler

Designed especially for obtaining water samples from small diameter monitoring wells, these samplers are made of type 304 stainless steel. Check valve is all Teflon material. All sizes shown are in stock for immediate shipment.

Teflon Bailer Water Sampler

Made completely of Teflon† to assure integrity of water samples, the bailer has removable molded ends for thorough, easy cleaning. The sampler has a built-in check valve and lifting hook. Not illustrated.

†Teflon is a reg. TM of DuPont Corp



STAINLESS STEEL

1¼" SIZE (1.060 in. or 2.667 cm. O.D.)

PART NUMBER	SAMPLER BOTTOM TYPE	TUBE LENGTH		SAMPLE VOLUME		PRICE
		INCHES	CM	CU INCHES	CC	
9420001	CLOSED	9	22.9	6.0	100	$41.00
9420002	CLOSED	18	45.8	12.0	200	45.00
9420021	THREADED PLUG	9	22.9	6.0	100	59.00
9420022	THREADED PLUG	18	45.8	12.0	200	63.00

2" SIZE (1.660 in. or 4.216 cm. O.D.)

PART NUMBER	SAMPLER BOTTOM TYPE	TUBE LENGTH		SAMPLE VOLUME		PRICE
		INCHES	CM	CU INCHES	CC	
9420005	CLOSED	20	50.8	36.6	600	$ 72.00
9420006	CLOSED	27	68.6	48.4	800	78.00
9420007	CLOSED	34	86.4	61.0	1000	84.00
9420025	THREADED PLUG	20	50.8	36.6	600	90.00
9420026	THREADED PLUG	27	68.6	48.4	800	96.00
9420027	THREADED PLUG	34	86.4	61.0	1000	102.00
9420045	THREADED W CHECK VALVE	20	50.8	36.6	600	90.00
9420046	THREADED W CHECK VALVE	27	68.6	48.4	800	96.00
9420047	THREADED W CHECK VALVE	34	86.4	61.0	1000	102.00

TEFLON

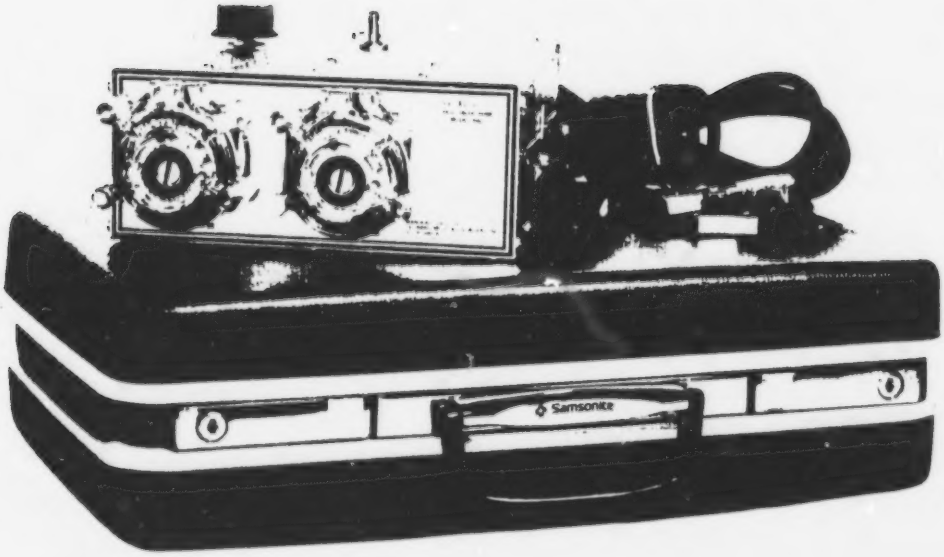
2" SIZE (1.660 in. or 4.216 cm O.D.)

PART NUMBER	SAMPLER BOTTOM TYPE	TUBE LENGTH		SAMPLE VOLUME		PRICE
		INCHES	CM	CU INCHES	CC	
2300097	MOLDED WITH CHECK VALVE	36	91.4	61.0	1000	$139.00

ALL PRICES F.O.B. ST. PAUL, MN AND ARE CONTRACTOR NET

geotech

SERIES II PERISTALTIC PUMP

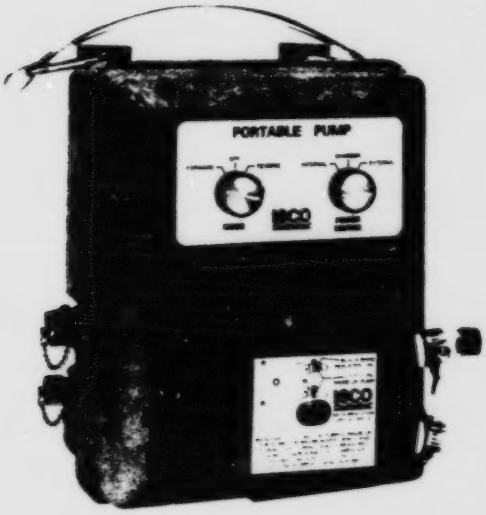


3699

The GeoFilter Series II Peristaltic Pump was designed for multistation pressure or vacuum pumping for liquids or gases in or out of the laboratory. This unit is ideally suited for sample removal from shallow wells. They are compact, measuring 3½" X 8½" X 8, and are constructed from heavy gauge anodized aluminum which provides durability and corrosion resistance without excess weight. The unit operates at 300 and 600 RPM individually and simultaneously, and is capable of pumping 500 milliliters per minute from the 300 station, and 1000 milliliters per minute from the 600 station. The complete unit comes with the GeoFilter Peristaltic pump, one Masterflex 7015 pump head, Samsonite carrying case, and 5' of silicon tubing.

ORDERING INFORMATION	ORDER NUMBER
12 Volt DC, 300 and 600 RPM variable speed pump with pump head, carrying case, silicon tubing, and 10' power cord with battery terminal clips, or cigarette lighter adaptor.	0710
115 Volt AC, 300 and 600 RMP variable speed pump with carrying case, silicon tubing, and 6' power cord with grounded AC plug.	0730
12 Volt DC and 115 Volt AC, 300 and 600 RPM variable spped pump with pump head, carrying case, silicon tubing, and two power cords, a 10' with battery terminal clips or cigarette lighter adaptor, and a 6' with grounded AC plug.	0760
Add-on Pump head, mounts directly to the face of existing pump head.	5701
Additional 7015 pump head, standard with unit.	5702
F.D.A. approved silicon tubing.	5703

Masterflex-Registered TM of Cole-Parmer Instrument Co.



ISCO's new battery-operated Portable Pump for shallow lift liquid sampling

Specifications

PHYSICAL SIZE:	Height: 11 in. (28cm) Width: 9 in. (23cm) Depth: 9 in. (23cm)
WEIGHT:	8 lbs. (3.6kg)
POWER REQUIREMENTS:	12 VDC
CURRENT CONSUMPTION:	2.5 amps, typical
OVERCURRENT PROTECTION:	5 amp slow blow fuse
SUCTION LIFT:	26 ft. (7.9m) maximum
PUMP RATE (3' of head):	1/4" I.D. suction tube: 2400 ml/min 3/8" I.D. suction tube: 3000 ml/min
LINE TRANSPORT VELOCITY: (3' of head)	1/4" I.D. suction tube: 4.1 ft/sec 3/8" I.D. suction tube. 2.1 ft/sec
AMBIENT TEMPERATURE RANGE:	32° to 120°F (0° to 49°C)

ISCO's new Portable Pump is specifically designed to sample shallow test wells with up to 26 feet of lift. The pump is also suitable for collecting samples from a variety of other sources, such as sewers, streams, lakes, etc.

Field-proven reliable

The rugged unit utilizes the same proven peristaltic pump system found in ISCO's wastewater samplers. All controls and the pump drive mechanism are housed in a water-tight, structural foam plastic case.

Non-contaminating

Pumped straight from source to bottle, the sample contacts only the Teflon* or vinyl suction line, the polypropylene and stainless steel inlet strainer (use optional), the medical-grade silicone rubber pump tubing, and a glass or plastic sample container. Samples do not contact any part of the pump mechanism. Cleaning the system is easily accomplished by reversing the pump, purging with distilled water or the next sample, or replacing relatively inexpensive lengths of tubing.

Easy to use

The compact Portable Pump can be powered by a rechargeable Nicad battery (may be mounted internally), a 12 VDC automotive battery, or a 117 VAC power converter. Pump action is controlled simply by setting a three-position manual switch to "FORWARD," "OFF," or "REVERSE." Ambient operating temperatures range from 32° to 120° in weather conditions including rain or dust.

* DuPont

Ordering information

For each complete Portable Pump, you must specify the pump, a power source, suction line, and sample container.

Portable Pump, without power source 60-3004-060

POWER SOURCES

Nicad Battery, without charger. Installs inside the control unit 60-1684-040
Battery charger only. To recharge internally mounted Nicad Battery 60-3004-070
AC Power Converter/Battery Charger, 117 VAC, 50/60 HZ to operate pump from 117 VAC. May also be used with connect cable below to recharge internally mounted Nicad Battery, or without cable below, may be used to recharge external Nicad Battery 60-1684-088
Same, except 234 VAC, 50/60 HZ 60-1684-093
Connect Cable, Portable Pump to power converter, for recharging internally mounted Nicad Battery 60-3004-068
Connect Cable, Portable Pump to external automotive type battery 60-1394-023

SUCTION LINES, STRAINERS

1/4" I.D. x 22' vinyl suction line with weighted polypropylene bodied strainer 60-1394-054
3/8" I.D. x 20' vinyl suction line with weighted polypropylene bodied strainer 60-1684-035
3/8" I.D. x 10' Teflon® suction line, Neoprene® rubber protective coating, without strainer 60-1683-146
Same, except 20' length 60-1683-144
Weighted strainer only, 3/8", all stainless steel 60-1684-110
Teflon® suction line flaring tool, to allow insertion of above strainer 60-2103-093
Bulk 1/4" I.D. vinyl tubing, 100', without strainer 68-1680-055
Same, except 500' 68-1680-056
Same, except 1000' 68-1680-057
Bulk 3/8" I.D. vinyl tubing, 100', without strainer 68-1680-058
Same, except 500' 68-1680-059
Weighted strainer only, 1/4" polypropylene body 60-1394-070
Weighted strainer only, 3/8" polypropylene body 60-1394-071
Extra silicone rubber pump tubing, 33" length 60-2104-054
Bulk silicone rubber pump tubing, 15' length 68-1680-061

SAMPLE CONTAINERS

1/2 gallon polyethylene bottle with cap 68-2600-002
1/2 gallon glass bottle with cap 68-2600-003
2 1/2 gallon polyethylene sample container with cap 299-0013-04
2 1/2 gallon glass bottle with cap 291-0000-00
3 gallon polyethylene sample container with cap 299-0013-02
5 gallon polyethylene sample container with cap 299-0013-01

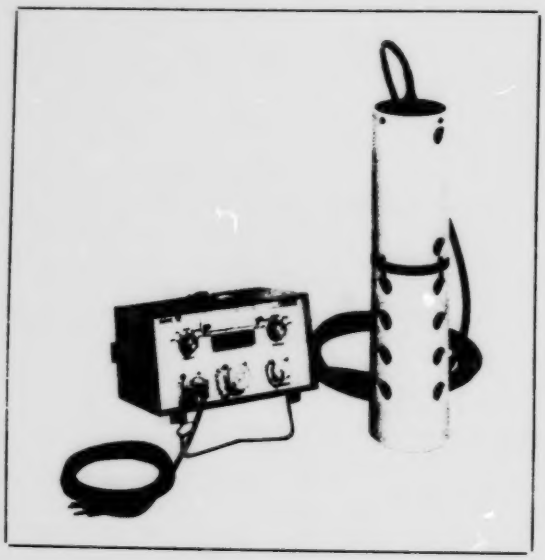
ISCO

P.O. Box 82531 • Lincoln, Nebraska 68501 • Telex 43-8028
Phone toll free (800) 228-4373 • In Nebraska (402) 474-2233

MARTEK® MARK V DIGITAL WATER QUALITY ANALYZER

MARTEK INSTRUMENTS, INC. MANUFACTURERS OF ENVIRONMENTAL INSTRUMENTATION

. . . low cost multi-parameter field or laboratory water quality analyzer



DESIGN AND PERFORMANCE FEATURES

- Direct in situ measurements of temperature, conductivity, dissolved oxygen, and pH to depths of 300 meters.
- Automatic temperature compensation for dissolved oxygen and pH.
- Digital display with simultaneous four parameter recorder output signals.
- AC or DC power operation with internal rechargeable batteries.
- Operates in very low temperature (−30°C or −22°F) and rugged environment.
- Better than ±1.0% overall measuring accuracy.
- Simple to operate and calibrate.

DESCRIPTION

The Mark V Water Quality Analyzer is a four parameter digital analyzer that provides optimum efficiency for accurately measuring the basic physical and chemical properties of coastal, inland, and ocean waters. The unit is designed to measure in situ temperature, conductivity, dissolved oxygen, and pH to depths of 300 meters (1000 feet) with automatic temperature compensation for pH and dissolved oxygen. A regulated AC/DC power supply unit contained in the instrument case offers optional operation from internal rechargeable batteries, AC, or external +12 volts DC power sources. Simultaneous recorder output signals are provided for all four parameters for telemetering or on-site recording of data. Individual parameter signals may be directly read out on digital display through a selector switch.

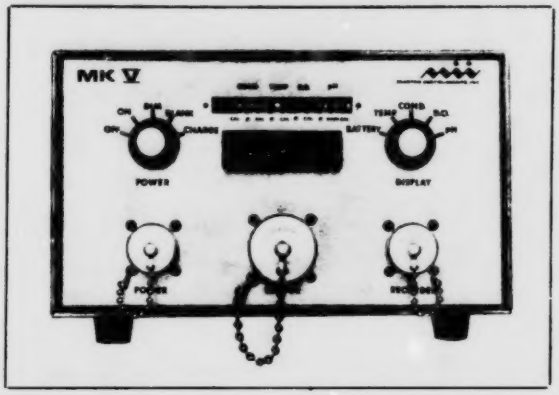
The Mark V Digital Water Quality Analyzer System is a general-purpose, multi-parameter measuring instrument suitable for intermittent or permanent use when making in-situ, vertical-profile, and remote unattended long term surveys at selected sites. It is specifically adaptable to projects requiring continuous, stationary operation from fixed shore stations, or for profiling surveys in shallow water depths to 300 meters (1000 feet). Moreover, through the utilization of MIL SPEC components, the instrument can operate in extremely low temperature environments (−30°C or −22°F) without affecting the quality of measurement. Standard measuring ranges offered for the various parameters meet most fresh and salt water conditions. The operation, maintenance, and calibration of the instrument are designed for use by personnel with a minimum of instrumentation experience, yet yield laboratory accurate data of better than ±1.0%.

APPLICATIONS

The Mark V is designed to provide easy-to-read digital parameter data for laboratory and field applications. Its unique circuitry permits digital operation under remote rugged field environments where AC power may not be available. It is ideal for sophisticated measurements of water samples of either fresh or salt water bodies. It is an efficient and reliable instrument for providing portable spot-tests, and long term measurement of water samples aboard floating laboratories, in water treatment and waste water facilities; and for in situ measurements of water bodies such as rivers, reservoirs, ponds, lakes, coastal and inland waters, and sewage and industrial plant effluents.

MARK V SPECIFICATIONS

MEASUREMENT PARAMETERS	RANGE	ACCURACY	RESOLUTION	SENSOR TYPE
Temperature	−5 to 45°C	±0.1°C	0.01°C	Thermolinear array
Conductivity	0-1000 micromhos/cm or	±10.0 micromhos/cm	1.0 micromhos/cm	Platinized nickel Electrodes
	0-100 millimhos/cm	±1.0 millimhos/cm	0.1 millimhos/cm	
Dissolved Oxygen	0-20 ppm (mg/liter)	±0.1 ppm	0.01 ppm	Polargraphic gold/silver electrode system; automatic temperature compensation and in situ stirrer.
pH	0-14 pH	±0.1 pH	0.01pH	Combination pH electrode with silver-silver chloride reference internals mounted in plastic housing; automatic temperature compensation.



SYSTEM PERFORMANCE

SENSOR ASSEMBLY

Housing: Hard-anodized aluminum and PVC plastic.

Dimension: Overall 4.5 inches (11.5 cm) diameter by 19 inches (48.3 cm) length

Weight: 8.0 pounds (3.6 Kg)

Cable: 0.32 inches (0.81 cm) diameter and (0.1 lb per foot) (0.15 kilograms per meter).

DATA READOUT:

Controls:

A. Power Switch
1. OFF
2. ON – Turns power ON to digital display DPM.
3. DIM – DPM digital display flashes seven times per second to conserve battery power; recorder signal output available for four parameter simultaneous recording.
4. BLANK – DPM digital display meter is off, but instrument is still on permitting continuous recorder monitoring. This setting provides maximum battery conservation.
5. CHARGE – Connects charging circuit to internal rechargeable batteries.

B. Function Switch
1. BATTERY – Measures battery voltage to determine if the batteries require recharging.
2. TEMP., COND., DO., pH – Selected parameter id displayed on DPM digital display.

Dimension: 6.4 inches (16.3 cm) high x 11.1 inches (28.2 cm) wide by 11.3 inches (28.7 cm) deep.

Weight: 15 pounds (7.0 kg) net weight
16 pounds (7.5kg) shipping weight

POWER SUPPLY:

Regulated self-contained internal rechargeable battery pack with built-in charging circuit external + 10-14 volts DC, or 105-125 VAC (210-250 VAC), 50/60 Hz.

RECORDER OUTPUT:

0-1 volts DC analog full scale for each of the four parameters.

ENVIRONMENTAL CONDITIONS

Temperature Effects: −30°C to 38°C (−22°F to 100°F) operation and storage (accurate performance of sensors and batteries are affected below 0°C temperature operation).

Moisture: Gasketed, splashproof construction throughout.

Corrosion: Aluminum control panel and carrying case prepared and coated to MIL specs for maximum corrosion resistance in the marine environment.

ORDERING INFORMATION

PART NUMBER DESCRIPTION

166 Model Mark V Water Quality Analyzer, includes:
a) 166-10 Data Readout Module
b) 166-20 Sensor assembly for temperature, conductivity, dissolved oxygen with stirrer and pH probes.
c) Cable Assembly
d) 166-50 Detachable lids with storage compartments for power cable, two solution bottles for pH buffers, DO membrane and electrolyte kit, and screwdriver.

Note: Specify 115 volts or 230 volts, 50/60 Hz

NOTE: All pricing F.O.B. Irvine, California including 12-month product warranty against defects in material and workmanship. Prices and specifications subject to change without notice.

MARTEK INSTRUMENTS, INC.

17302 DAIMLER STREET, IRVINE, CALIFORNIA 92713 PHONE (714) 540-4435 TELEX 692 317

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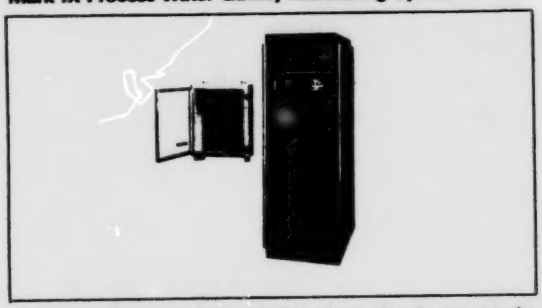
Martek®
Product Digest

MARTEK INSTRUMENTS, INC. MANUFACTURERS OF ENVIRONMENTAL INSTRUMENTATION

MEASUREMENT SYSTEMS

Mark IX Process Water Quality Monitoring System

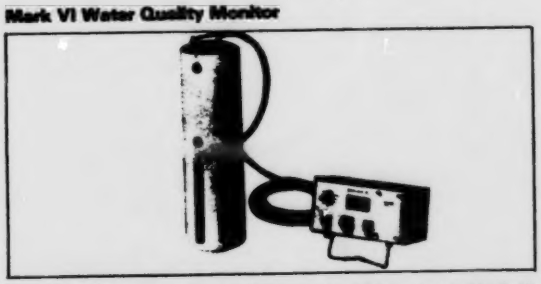


The Mark IX Process Water Quality Monitoring System may be operated in conjunction with other members of the Martek instrumentation family to produce a fully automated monitoring and control system with features such as video display of sensor data; formatted hard copy printouts; micro-programmed data acquisition; and recording and control of desired parameters. The Mark IX offers a combination of practicality and economy for large scale monitoring or control situations. A 64-channel signal conditioning unit utilizes a built-in multiplexer; provision for up to eight multi-sensor plug-in signal conditioning printed circuit boards; on-board drivers for up to 12 flow sensors; and easy sensor hook-up terminal strip. The unit has a flexible motherboard design which permits a wide variety of sensor configurations featuring all of Martek's popular sensors. As many as four 64-channel signal conditioning units may be utilized in a system completely controlled by the Martek Model DMP Data Microprocessor/Controller.

Mark VII Digital Water Quality Analyzer/Controller

The Mark VII Digital Water Quality Analyzer/Controller is designed to provide flexibility and efficiency for accurate measurement of the basic physical and chemical properties of coastal, inland, and ocean waters to depths of 300 meters. Specific parameter sensors and their related signal-conditioning plug-in printed circuit boards can be omitted or added depending on the user's field requirements. The user can select up to four parameters including multiple single parameters from the following available measurements: temperature, conductivity, salinity or temperature-corrected conductivity, depth, dissolved oxygen, pH specific ions, and turbidity. A regulated AC/DC power supply unit contained in the instrument case offers optional operation from internal rechargeable batteries, AC, or external 12-volt DC power sources. Simultaneous recorder output signals are provided for all four parameters as well as battery voltage for telemetering or onsite recording of data. Individual parameter signals may be directly read out on the digital display through a selector switch. Through the optional use of plug-in printed circuit boards, the Mark VII can also serve as a controller for any given two parameters monitored by the analyzer.

Mark VI Water Quality Monitor



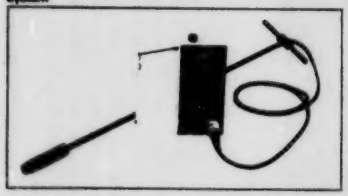
The Mark VI Water Quality Monitor is similar to the Mark V configuration, but it represents a more sophisticated and expanded instrument. The Mark VI monitors seven parameters: temperature, conductivity, salinity or temperature-corrected conductivity, dissolved oxygen, pH, depth, and optional ion selective electrode to depths of 300 meters. It features a five-element conductivity sensor which permits operation in fresh or sea water bodies without changing the sensor. The unit can operate on internal rechargeable batteries, AC or external DC power. All calibration adjustments, including reference voltage adjustments, are easily made and accessible through the front panel. Like the Mark V, the Mark VI features a single digital panel meter for readout of individual parameters via a selector switch while providing simultaneous recorder output signals for all parameters regardless of the selector switch position.

Mark X Water Quality Monitor

The Mark X is an in situ self-contained system for measuring tempurature, pH, conductivity, and temperature corrected conductivity or salinity in the field or in the laboratory. The standard configuration, including the readout module, weighs less than 6 pounds (2.7 kg); thus facilitating field monitoring under rugged environmental conditions. It can operate throughout the standard conductivity range of fresh to sea water samples without altering the conductivity sensor.

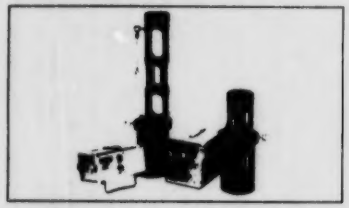
MEASUREMENT SYSTEMS

Model SCT Soil Conductivity And Temperature Monitoring System



The Model SCT is an in situ system for measuring soil conductivity and temperature, which are utilized for calculating soil salinity. The unit provides an accurate method of determining the changes in salinity caused by seepage, irrigation or other influences. For convenience, the conductivity is corrected to 25°C which provides the soil scientist with a useful number without conversion. The Model SCT readout module incorporates a four digit liquid crystal display, a battery power supply, switch controls, and front panel access to calibration controls. The battery power supply is rechargeable with the charger provided for the system.

Model XMS In Situ Transmissometer



The Model XMS In Situ Transmissometer is a portable, research-quality instrument specifically designed for optimum underwater measurements of turbidity by determining the percent transmission of a light beam through a known pathlength in the water. It provides high accuracy, ± 1.0% over a wide alpha measurement range (0.1 to 4.6 meter for one meter pathlength). Readout of the light transmittance measurement is obtained instantaneously on a high resolution digital panel meter. A recorder output permits onsite or telemetry recording. Continuous records of percent transmission versus temperature and/or depth may be obtained by using optional plug-in signal conditioning printed circuit boards and sensors. The Model XMS separate power supply permits operation from either internal rechargeable batteries, external 12 volts DC, or 105-125, 210-250 VAC, 50/60 Hz. The one meter cell path underwater sensor can be used in either turbid or clear water without altering the cell path of the sensor to depths of 300 meters. For very turbid measurements, a 25 cm cell path sensor is available.

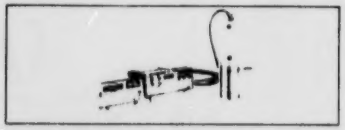
Mark V Water Quality Analyzer

The Mark V Water Quality Analyzer is a low cost four parameter digital analyzer designed to provide economical field measurement of temperature, conductivity, dissolved oxygen, and pH in fresh and salt water bodies to depths of 300 meters. A regulated AC/DC power supply unit contained in the instrument case offers optional operation from internal rechargeable batteries, AC, or external DC power sources. Individual parameter signals may be directly read out on the digital display through a selector switch, while simultaneous recorder output signals are provided for all four parameters.

Mark XI Digital Process Monitor/Controller

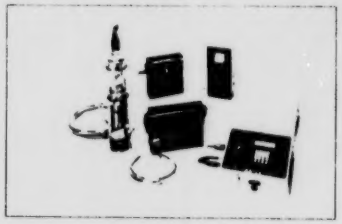
The Mark XI Digital Process Monitor/Controller is designed to monitor and control either pH or conductivity. Temperature circuitry is standard and may be monitored by simply adding the sensor. The Mark XI contains a display selector switch which permits the user to view the pH or conductivity value, temperature, plus low and high set-points values from the optional controller board. Both 0-1 volt DC and 4-20 ma milliamp outputs are available. The optional controller is plug-in compatible and offers two single pole, double throw relays for peripheral control. The relays may be operated in either a simple "ON-OFF" mode or a "TIMED RESET" mode. The "TIMED RESET" period is adjustable from one to five minutes.

Mark VIII Water Quality Data Logger



The Mark VIII Water Quality Data Logger is a combination analyzer and data logger packaged in a single case. It provides direct field *in situ* measurements of temperature, conductivity, salinity, dissolved oxygen, pH and depth; or multiple single parameter sensors to depths of 300 meters. Specific parameter sensors and their related signal conditioning plug-in circuit boards can be omitted or added depending on the user's field requirements. While the parameters are being read out on the digital display, the signals are recorded on a magnetic tape cassette. The logger accepts up to 14 data channels with day and time recorded with each scan of data. The ID switch may be used to identify 1000 locations. The Mark VIII can operate in manual, continuous, or program mode, thus providing flexibility as well as facilitating the accumulation and processing of field data.

Mark XV Water Quality Microprocessor

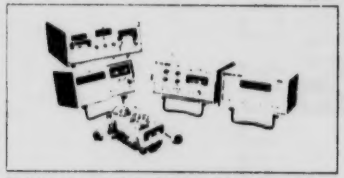


The Mark XV Water Quality Microprocessor is designed to measure *in situ* seven parameters of temperature, salinity or temperature corrected conductivity, depth, dissolved oxygen, pH and optional selective ions as a function of depth with automatic temperature compensation for all parameters. System calibration for all sensors is controlled by the low power, CMOS, microprocessor. All screw-driver adjustments have been eliminated. Calibration is performed digitally with calculated factors being stored in non-volatile RAM. The alphanumeric display allows any two parameters to be displayed simultaneously. For data recording purposes, the Mark XV is equipped with a serial ASCII, RS232 port for compatibility with computer peripheral equipment. Sensor data along with date and time of day may be transmitted to this port at anytime under operator control. This serial data may be used to drive external telemetry equipment or to provide a local print-out. The conductivity measurement is unique by providing auto ranging for the solution being monitored. Two ranges, 0-9.999 millimho/cm or 0-99.99 millimhos/cm are automatically selected according to the value of the sample. The displayed conductivity reading is temperature corrected between 0 to 50°C and in certain instances may be calibrated in salinity units.

Model PEW Portable Environmental Winch

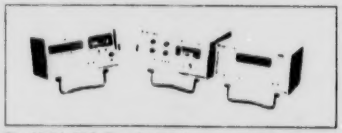
The Model PEW Portable Environmental Winch has been designed to facilitate cable handling and to record multi-parameter water quality data during descent and ascent for any type of profiling or monitoring requirements. The winch is a compact, rugged unit capable of operation in the marine environment. It is supplied with 25 slip rings which permit operation with the Martek Water Quality Analyzers, or the Model XMS *in situ* Transmissometer. The Model PEW can handle cable capacity up to 300 meters (1,000 feet). The unit is available with an electric motor drive.

DAS Series Data Acquisition System



The DAS Series Data Acquisition System is an economical and extremely flexible data system designed to meet a wide range of applications, from stand-alone environmental data loggers to industrial monitors. The system is comprised of a multitude of independent modules that can be arranged in various configurations to meet each specific application. All data acquisition parts of the system are built from advanced logic circuitry (COS/MOS) having high reliability and noise immunity, and extremely low power consumption. Hence, data logging in remote areas can be accomplished easily, since a small battery pack can operate a data logger for a full year. All data retrieval modules are TTL compatible, which simplifies interfacing with external data handlers and processors such as multi-track digital recorders and digital computers.

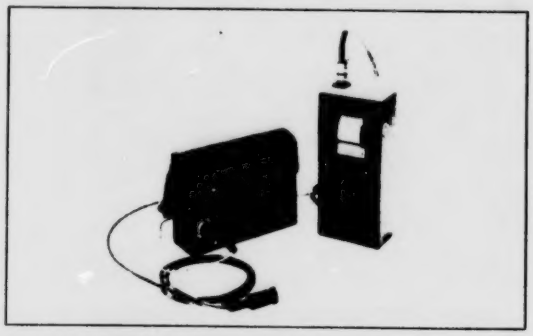
Model DLS Data Logger / Model DRS Data Reader



The Model DLS Data Logger is an economical, compact, multiple-input, self-contained data logging recording system for field or laboratory application. It can operate on power sources of 115/230 VAC, 50/60 Hz, internal DC battery, or external storage battery. It is ideal for data monitoring over long time periods in either portable or fixed station applications. The data logger provides a permanent data record when used with air and water quality, meteorology, geophysical, process control systems and laboratory instruments. The data logger accepts up to 14 data channels (up to 99 channels are available) and records time of day, day count, and channel identification number with each set of data points. This feature is very useful in enforcement and verification applications. Perhaps the main advantage is that the data logger greatly facilitates the accumulation and processing of numerous field data. A Model ADU Auxiliary Display Unit is available for monitoring the data logger.

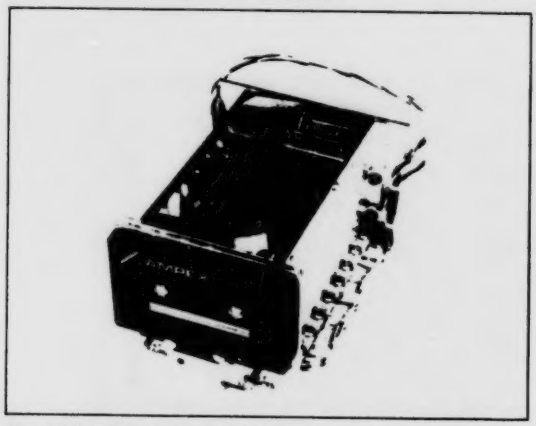
The Model DRS Data Reader is an economical self-contained unit designed to retrieve digital data from magnetic tape cassettes and to format the digital data for direct interfacing with data handlers and processors, such as computers, punch tape, modem, and digital printer. The instrument is fully compatible with magnetic tape cassettes recorded by any of the Series DAS Data Loggers. The information read from the tape is presented on a self-contained LED display and is simultaneously available at the output connectors. The unit will stop after reading out a number and will continue reading the next number only after receiving an internal or external "continue" command. The reader may be programmed to operate in one of the three modes: (a) reading digital magnetic tapes with an internal reading-rate control, (b) reading tapes with an external control, and (c) as a monitor and controller for any of the Series DAS Data Loggers.

Model AFP Alphanumeric Field Printer



The Model AFP Alphanumeric Field Printer was originally designed to operate with the Mark XV Water Quality Microprocessor. The Model AFP is controlled by an integral microprocessor and operates from its own rechargeable battery pack. The device utilizes a 16 character per line, dot matrix impact printer which prints approximately one line of alphanumeric data per second. The Model AFP receives data via an RS232 serial port at a data rate of 300 baud. A 2000 character buffer ensures that data over-run does not occur. The unit is normally maintained in a low-power, "idle" state where very little battery power is consumed. When data is received, the unit initiates its own power and begins printing. It will continue to print until its buffer is emptied, at which time it resumes the low power condition.

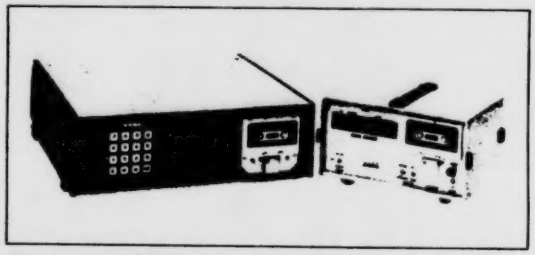
Model SDS Submersible Data Logger



The Model SDS Submersible Data Logger is a standard configuration of the Series DAS Data Acquisition and Telemetry System intended for *in situ* applications. The submersible logger may be packaged in a high-pressure housing designed to operate to water depths of approximately 650 meters, and equipped with waterproof connectors for carrying analog signals and power into the unit, as well as electrical lines to monitor and control the function of the Model SDS.

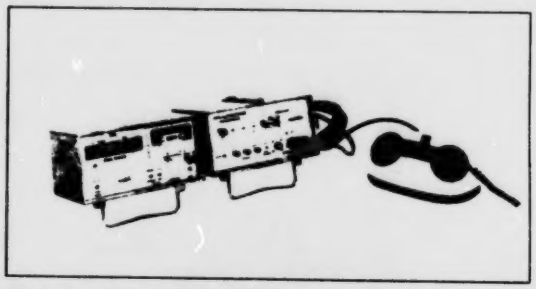
The number of active channels (up to 15 plus time of day) is selectable by a "last channel" control. By simply setting the PC board switches, the Model SDS will operate in one of three modes: (1) continuous operation, (2) On-Off mode, and (3) a single scan mode. In the ON-OFF mode, the system will turn on at a pre-selectable rate (from every 256 minutes to every 15 seconds) and will collect data for a pre-selected period of time.

Model DMP Data Microprocessor



The Model DMP Data Microprocessor features a modified Model DLS Data Logger which incorporates a microprocessor and simple keyboard control for data monitoring and system start-up that provides programmed operation for continuous data collection and analysis. The unit accepts up to 12 analog signals and will sample each data input every 30 seconds during its programmed operation. Samples are accumulated, averaged, recorded on the magnetic tape cassette, and outputted in serial format for remote data transmission. In addition to recording averaged data, the Model DMP stores and logs daily peak values and their respective times of occurrence for each data input parameter. Moreover, the Model DMP offers capability to control daily zero and calibration cycles which can provide maximum system accuracy and repeatability.

Model DRS Computer Interface



While the standard Model DRS Data Reader provides an output of parallel BCD, the DRS Computer Interface permits the Model DRS Data Reader to be interfaced with virtually any computer that accepts serial ASCII code. It is primarily designed to operate with a text-editing program. It can accept control characters for starting and stopping data transmission. A standard terminal is used to address the computer and print out echo data. It features selectable baud rates to 1200 baud with true 1200 baud throughput. It has RS232C and 20 ma loop input and output capability and permits local control of the data reader.

MARTEK INSTRUMENTS, INC.
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WELL WIZARD™ ...simplifies and speeds groundwater sampling.

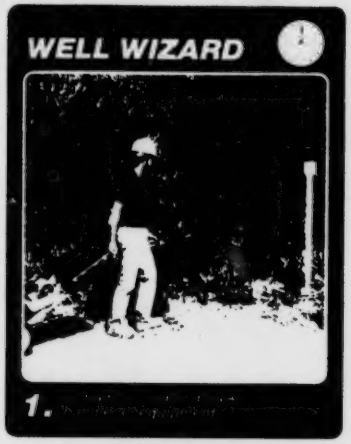
Groundwater monitoring, can be costly and ineffective without the proper sampling techniques and equipment.

The WELL WIZARD™ SYSTEM has been designed and engineered to provide fast, simple, cost-effective, contamination-free sampling for the duration of your monitoring program.

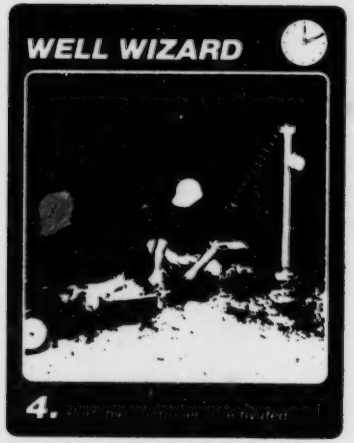
The WELL WIZARD™ SYSTEM consists of dedicated downwell pumps, well-cap assemblies and a portable controller easily managed by a labor-saving single man crew. Permanent installation of the system prevents introduction of contaminants to the well...virtually eliminating any need for costly resampling or reanalyzing.

The use of a bladder pump and pneumatic controls prevents damage by solids or dry pumping. This combination, proven superior through years of independent testing, makes WELL WIZARD™ the choice of industry leaders.

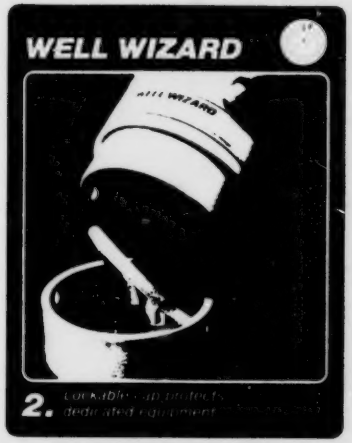
Reduce your sampling costs, improve your sample integrity and protect your investment with WELL WIZARD™. Equipment engineered with experience and supported with superior customer service.



1. [illegible]

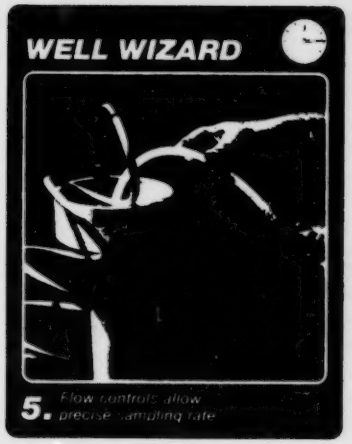


4. [illegible] achieved



2. Lockable cap protects dedicated equipment

3. One simple quick connect and system is ready [illegible]

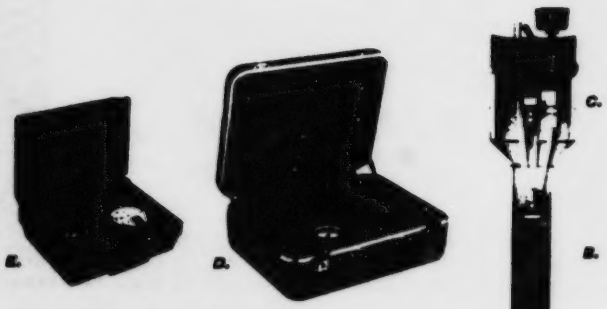


5. Flow controls allow precise sampling rate

6. Sampling complete on to next well

3708

WELL WIZARD : a complete system approach



A FLEXIBLE SYSTEM FOR YOUR SPECIFIC NEEDS

The WELL WIZARD™ SYSTEM represents a cost effective investment in a complete system designed to meet your groundwater monitoring needs. Exhaustive engineering and extensive field experience have helped produce a complete product offering sample reliability, ease of operation and years of maintenance-free service.

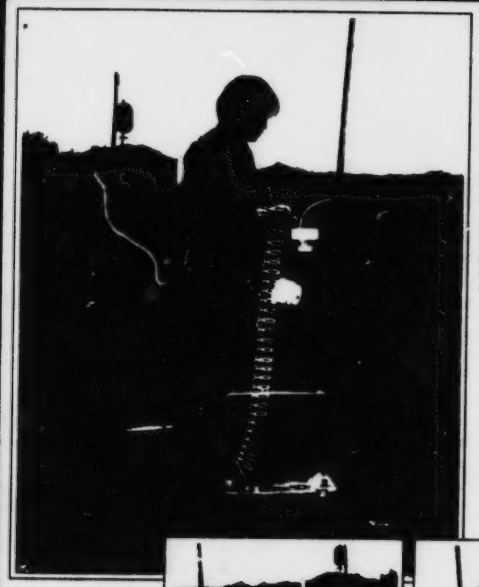
The use of dedicated components simplifies sampling by eliminating on-site assembly and set-up...protecting the sample from surface contamination.

The WELL WIZARD™ portable power and control systems are designed to meet a wide range of monitoring needs. You can choose from 3 different controller options, as well as a portable or dedicated liquid level indicator, depending on your requirements.

Whatever your monitoring demands dictate, WELL WIZARD™ saves you time and money by offering reliable standardized sampling through a flexible complete systems approach.

A. PUMP
B. PURGE-MIZER
C. WELL CAP HOUSING showing quick-connect fittings
D. DRIVER-CONTROLLER
E. LIQUID LEVEL INDICATOR

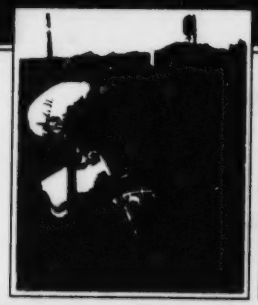
WELL WIZARD ™: a clean winner



◄ **WELL WIZARD™ KEEPS ALL WATER-CONTACTING COMPONENTS FREE FROM CONTAMINATION.**

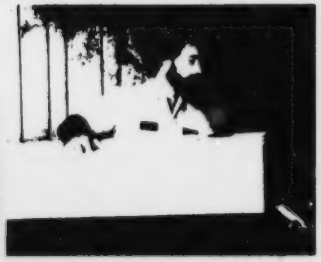
Dedication of sampling components saves time and money in setting-up, purging, sampling, cleaning and between-well transportation. Dedication of all water contacting components also helps encourage standardization of sampling techniques and controls contamination.

Other sampling ► techniques require moving pumps, tubing and cables from well to well. Costly and unreliable cleaning must be performed between sampling... dramatically increasing the potential for contamination...of the sample and the well!



3709

WELL WIZARD : personal guaranteed service



CUSTOMER SERVICE

At Q.E.D. we believe that service is the key to continued success. That's why we've developed technical assistance and service programs that assure your personal satisfaction. Our convenient "800" number guarantees you immediate attention from our fully qualified staff.

RAPID SERVICE AND DELIVERY

Responsiveness is the key word in our service and parts department. Our professional staff is always ready to receive your calls and promptly provide parts and assistance to keep your monitoring efforts running smoothly and efficiently.

"LIFETIME" WARRANTY

We are so confident our WELL WIZARD™ system will provide trouble free service for the life of your monitoring program, we will extend a lifetime warranty for WELL WIZARD™ system components. Please contact us for details on this unique protection policy.

WELL DEDICATED COMPONENTS

PUMP, TUBING AND CAP

WELL WIZARD™ MONITORING SYSTEMS control contamination, cost and sampling method by dedicating all water contacting components to each well. The pump, tubing and cap assemblies include all water-contacting components needed for individual wells. The pumps are a bladder type design and come in a variety of materials to meet specific monitoring requirements. The well-caps include quick-connect fittings and a lockable top. Lifts of up to 300 ft. are standard; lifts of up to 1000 ft. can be accomodated with modifications. Pumps fit wells 2" and greater.

PURGE-MIZER

Reduces Purge Volumes

Purge-Mizer is an expandable collar which effectively isolates standing water above the pump. This reduces purge volume requirements significantly. The Purge-Mizer is expanded prior to purging with the same compressed air source used to drive the pump.

NON-DEDICATED COMPONENTS

MODEL 3013 CONTROLLER

The model 3013 Controller is used to cycle the pump for purging and sampling with compressed air from an external compressor or air tank. The model 3013 is used primarily where an owner has a compressed air source readily available.

MODEL 3011 DRIVER-CONTROLLER

The model 3011 Driver-Controller combines the compressed air source with the pump controller in one lightweight portable unit. The compressor is powered by an external 12V DC 8.3 amp power source. This unit is designed for use where vehicular 12V power is available and when used with a battery pack provides for ultimate portability.

MODEL 3111 DRIVER-CONTROLLER

The model 3111 Driver-Controller combines a self-contained gasoline driven compressor with the controller into a portable unit. The 3111 is used for maximum pumping rates where no vehicle access to the well or rugged terrain and travel distance between wells require high portability. The large capacity compressor allows pumping of deep wells or up to three wells simultaneously.

MODEL 6010 LIQUID LEVEL INDICATOR

The model 6010 pneumatic water level system determines the static water level without introducing "outside" elements into the well. The system employs a dedicated probe and a lightweight portable air supply.

Please consult factory regarding additional information on the components and your specific requirements.

WELL WIZARD™
Dedicated Monitoring System

PRICE LIST

CONTROLLERS AND DRIVERS

Model No.	Description	Price (1984)
3011	Controller/Driver Case mounted, automatic fully adjustable pneumatic operation. Includes integral 12 V 60 psi oilless compressor.	$2,100.00
3111	Controller/Driver Controller module (Model 3013) with 100 psi gasoline-driven compressor with versatile mobile field transporter.	$2,890.00
3013	Controller Automatic, case mounted with adjustments for flow rate and well depth.	$1,695.00

NOTE: All of the above include self coiling quick connect lines.

Prices subject to change without notice.

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15-983

WELL WIZARD™
Dedicated Monitoring System

DESCRIPTION OF OPERATION

The Well Wizard is the only complete dedicated system for well monitoring. Permanent installation of the sampling device is the key to controlling the introduction of contamination to the well.

The Well Wizard system consists of dedicated downwell pumps, well cap assemblies and one portable controller.

The Well Wizard employs the use of a bladder pump. Water enters the bladder via a bottom check valve. When the bladder is full, compressed air is delivered, via an air line, to the space between the body of the pump and the bladder, which squeezes the bladder. This action closes the bottom check valve and forces the water contained inside the bladder through the upper check valve and into the attached water discharge tubing. There is no air-water contact. After the bladder is fully evacuated, the pressure inside the pump is released back through the air line to the surface. This action causes the upper check valve to close and the bottom check valve to open, refilling the bladder. Continuous operation of this pump relies upon alternating the compression/release cycle.

The small number of moving parts, the ability of this design to handle solids (including sand) without damage and the ability to withstand dry pumping make it very reliable and practical for permanent installation.

Additional advantages of this pumping method are the elimination of air/water contact, no loss of volatile organics due to air stripping and no change in sample temperature as sometimes experienced with electric pumps.

The pump is offered in two models. One is constructed entirely of rigid PVC. The other model is constructed entirely of teflon.* The bladders are also available in flexible PVC or teflon.*

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Ann Arbor, MI 48107 • (313) 995-2547

The pumping device is suspended inside the well by the lines that conduct the water and compressed air. These lines are available in polypropylene, polyethylene or teflon.*

The air and water lines terminate at the top of the well casing in a snugly fitting cap assembly. The cap has a lockable top to prevent tampering. Inside the cap assembly is a panel with a fitting for the water discharge tubing and a quick connect air fitting for the compressed air supply.

The compression/release cycling of compressed air that is required to drive the pumping device is managed at the surface by a portable cycle controller. The cycle controller has several features that add to the versatility of the system.

The controller is light and compact. Its design permits the use of virtually any compressed air source. A full range of compressors, both 12 VDC and gasoline-operated, is available or the system can be driven with compressed air cylinders.

In keeping with the general dedicated approach, a dedicated static water level indicator can be included with the system. The probe portion of the static water level indicator remains in the well with the pump and is actuated through a fitting in the cap assembly.

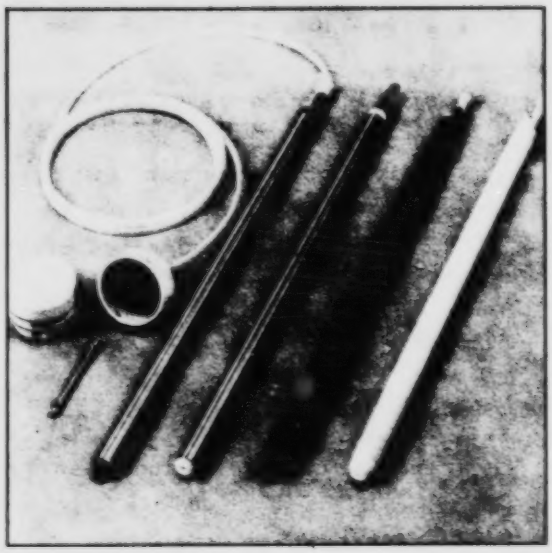
QED's objective continues to be to provide a high quality, low cost approach to groundwater sampling equipment and techniques. We believe that the Well Wizard meets this objective by eliminating several potential sources of sample contamination, adhering to very strict material standards, providing an efficient and simple design and by reducing the time and effort required for the collection of high integrity groundwater samples.

* Registered trademark of Du Pont

Groundwater Sampling

WELL WIZARD™

WELL-DEDICATED COMPONENTS



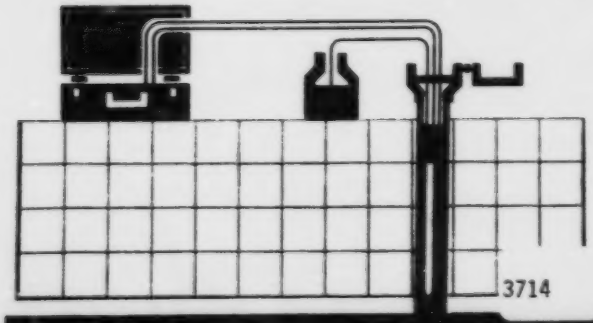
Well-Wizard™ Monitoring Systems control contamination, cost and sampling method by dedicating all water contacting components to each well.

The Pump, Tubing and Well-Cap Assemblies include all water-contacting components needed for individual wells: a down-well pump, connecting tubing, a locking well-cap assembly with sample tube, and quick-connect fittings for the air supply line. The pump is designed to prevent air-water contact and avoid sample contamination. Its rugged construction allows it to pump most solids, and to lift samples from 1000 feet with minor modifications. Dedicated water-level sensing components are optionally available.

Pump Models:	Materials			Max Lift:	Flow Rate:	Dimensions:
	Body	Assembly	Bladder			
P-1100	PVC	PVC	PVC	300 ft. (std.)	0.6 GPM at 75 ft. lift	1.66 inch diam.
P-1101	PVC	PVC	TEFLON	300 ft. (std.)	with 100 PSI	36 inch length
T-1100	TEFLON	TEFLON	TEFLON	300 ft. (std.)	drive air	36 inch length
P-1200	SS	PVC	TEFLON	300 ft. (std.)	0.75 GPM at 75 ft. lift	1.5 inch diam.
T-1200	SS	TEFLON	TEFLON	300 ft. (std.)	with 100 PSI drive air	37.2 inch length

Tubing available in Polyethylene or Teflon

Well Cap Assembly PVC body with lockable protective cover. Non-locking (unprotected) also available. Contains quick-connect fitting for drive air and sample delivery tube. Available with provisions for water level sensing. Standard Assemblies fit on 2-inch or 4-inch pipe; other pipe sizes also available.



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WELL WIZARD™

Dedicated Monitoring Systems

Patents Pending

3-84

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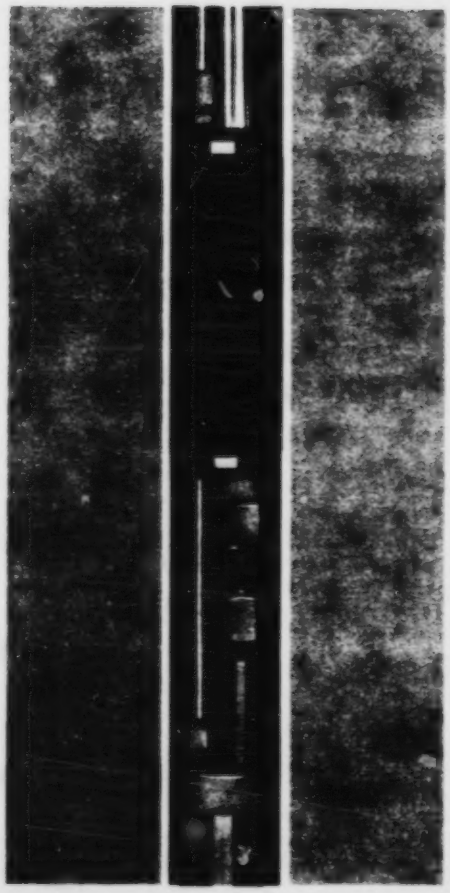
Groundwater Sampling

WELL WIZARD™

PURGE MIZER



Purge Mizer™ is an expandable collar which, when pressurized, isolates the sampling pump from stagnant water in the well. This technique substantially reduces the volume of water which must be purged prior to sampling—reducing field time and labor.

The Purge Mizer is located immediately above the Well Wizard™ pump and well screen area and is permanently dedicated to the well along with the other water contacting components of the sampling system. Air and sample lines to the sample pump pass through Purge Mizer uninterrupted and compression fittings position Purge Mizer in the well. Just prior to purging and sampling, the Purge Mizer is inflated through a fitting located in the well cap assembly. Air pressure is obtained from the portable pneumatic controller which is used to drive the pump. After sampling has been completed, the pressure in the Purge Mizer is released, allowing the device to deflate.

ıe Purge Mizer saves significant time and expense in groundwater sampling.

Material Specifications:

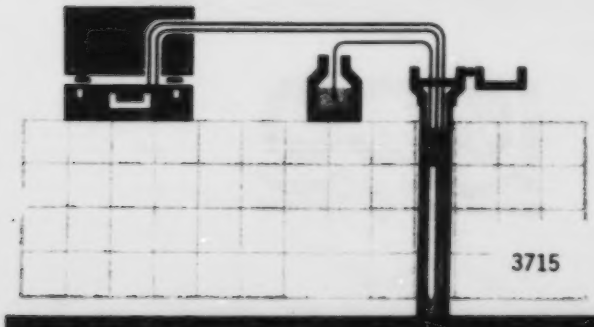
Rigid PVC body with Viton bladder and stainless steel clamp rings.

Purge Mizer:

Model 4200 for 2" wells
Model 4400 for 4" wells

Control Kit:

Includes all fittings, lines, gauge and relief valve
Model 4000A for 2" wells
Model 4000C for 4" wells



WELL WIZARD™

Dedicated Monitoring Systems

Patents Pending

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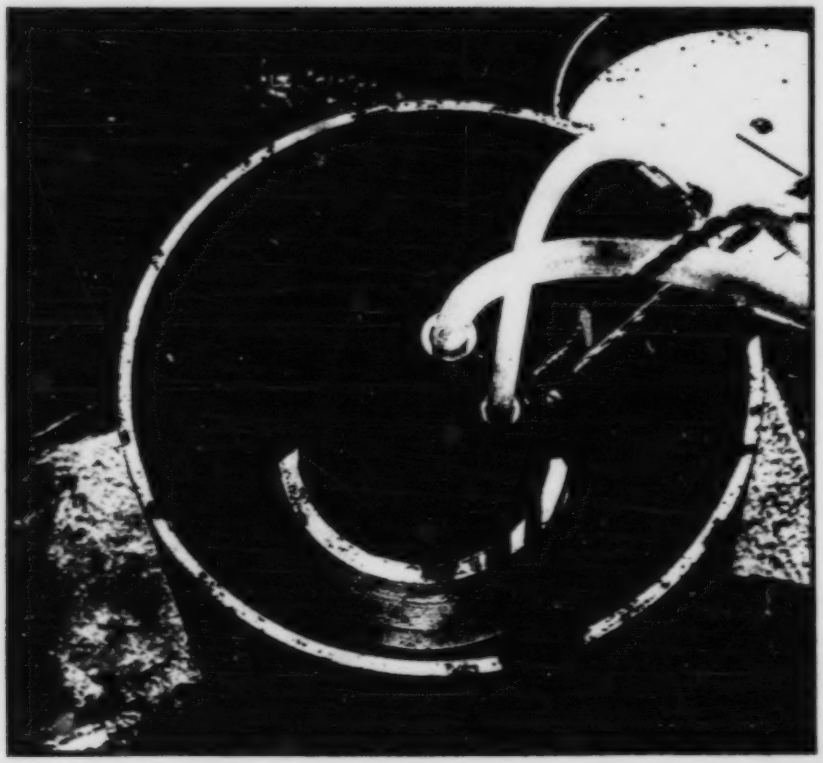
Model 2600
Well Sampler



ISCO

3716

Model 2600 Well Sampler features high pumping rate

ISCO's Model 2600 Deep Well Sampler is specifically designed to collect water samples from small diameter test wells, yet provides pumping rates high enough that larger diameter wells may be bailed of stagnant water and sampled with a minimum of time and effort. The pump will easily fit in wells as small as 2" I.D. and will efficiently sample at depths to 150 feet. Pumping rates using 110 psig vary from 0.5 gpm at 150 feet of head to as high as 2.0 gpm at 25 feet of head. Tanks of compressed gas are used to operate the pump.

Simple design

The pump is simple in design and operation. The control box automatically meters gas to the bladder. As the gas expands the bladder, it forces water through the upper check valve. Then when the bladder has reached its maximum expansion, gas pressure is released allowing water to enter through the lower check valve and the cycle is repeated.

Alleviates contamination

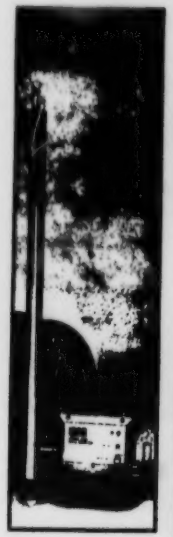
Gas does not contact the sample, eliminating the major objection to other types of gas-operated pumps. Samples contact only Delrin[1], medical-grade silicone rubber, polyethylene, and series 300 stainless steel.

Simple to use

Connecting the gas and liquid sample lines to the pump takes less than a minute. The pump is then lowered into the well to the desired depth by the polyethylene rope attached to the sample line. Connecting the gas supply and pump gas lines to the control box and setting the controls then readies the pump for operation once air is supplied.

Easy to control

Setting the sample line length switch controls bladder deflation rate, while the "sample volume" adjusts to compensate for the bladder inflation rate at varying lifts and gas supply pressure (120 psi maximum). A flow sensor in the controller monitors both direction and velocity of gas into and out of the bladder for maximum pumping efficiency.



Effective water displacement

Rapid inflation and deflation of the pump's silicone rubber bladder displaces water through check valves.

Rolling up lines

A lightweight spool is provided for convenience in rolling up lines and transporting them from site to site.

Pump efficiency*

sample line length (feet)	well head (feet)	gas pressure (psig)	gas consumption (scfm)	flow rate (gpm)
25	25	50	1.8	1.90
50	50	50	3.0	1.25
100	100	80	3.3	.90
150	150	110	3.5	.50

The table shows the most efficient pumping rates per gas consumption. Higher rates are achieved at higher gas pressure and consumption.

Specifications

PUMP:	
Physical Size:	Diameter: 1.75 in. (44.5 mm) Length: 48 in. (1219 mm)
Dry Weight:	7 lbs. 15 oz. (3.95 kg)
CONTROL BOX:	
Physical Size:	Length: 11.5 in. (292 mm) Width: 9 in. (229 mm) Height: 7 in. (178 mm)
Weight:	12 lbs. (5.44 kg)
Battery Capacity:	7 hours continuous use (rechargeable Nicad)
MAXIMUM GAS SUPPLY PRESSURE:	120 psig
MINIMUM GAS SUPPLY PRESSURE:	50 psig
MAXIMUM PUMP HEAD:	150 ft.

Optional

Sample containers with caps can be ordered in ½, 2½, 3, and 5 gallon polyethylene bottles and ½ and 2½ gallon glass bottles.

Ordering information

For a complete Model 2600 Well Sampler, you must specify the Pump, the Control Box, a Nicad battery charger, and the length of gas and sample line tubing you need (the gas and sample line tubing assembly includes the spool).

Model 2600 Pump	60-2604-001
Model 2600 Control Box with Nicad battery	60-2604-005
50' gas and sample line tubing assembly (includes reel)	60-2604-025
100' gas and sample line tubing assembly (includes reel)	60-2604-026
150' gas and sample line tubing assembly (includes reel)	60-2604-027
Control Box Battery Charger (117v)	60-2604-015
½ gallon polyethylene bottle with cap	68-2600-002
½ gallon glass bottle with cap	68-2600-003
2½ gallon polyethylene sample container with cap	299-0013-04
2½ gallon glass sample container with cap	291-0000-00
3 gallon polyethylene sample container with cap	299-0013-02
5 gallon polyethylene sample container with cap	299-0013-01
Gas line connector ferrule set	209-0171-05
Sample line connector ferrule set	209-0171-06
Extra silicone bladder tubing, 36-inch length	60-2603-032

ISCO P.O. Box 82531 • Lincoln, Nebraska 68501 • Telex 43-8028
Phone toll free (800) 228-4373 • In Nebraska (402) 474-2233

BROCHURE 60-2603-031 February 1984 3718

MODEL 2600 PRODUCT UPDATE

Dedicated pumps

To eliminate the need to clean the Model 2600 pump and the chance of cross-contamination, a pump and tubing assembly may be dedicated to each of a series of wells, and each well sampled using a single portable control unit. Lockable well caps are available to provide security for dedicated installations. In addition, quick-disconnect fittings for the gas line hose makes set-up fast and easy.

New cable

The sample line assemblies described in the brochure have been modified to improve their utility. The braided polyethylene support rope in the sample line assembly has been replaced by a polyethylene covered stainless steel cable. The cable provides increased strength and is much easier to clean (for portable use) than the rope previously supplied. The cable is connected to the pump using the stainless steel "U" clamp supplied.

The part numbers of the sample line assemblies with stainless steel cable, cable clamp, and storage reel are as follows:

50′ sample line assembly	60-2604-025
100′ sample line assembly	60-2604-026
150′ sample line assembly	60-2604-027

ORDERING INFORMATION FOR NEW ITEMS

Well caps

Lockable well cap for 1.5″ plastic well casing (includes pump support, fittings for gas and sample lines, and 18″ delivery tubing)	60-2604-039	$50.00
Lockable well cap for 2″ plastic well casing (includes pump support, fittings for gas and sample lines, and 18″ delivery tubing)	60-2604-036	45.00
Lockable well cap for 3″ plastic well casing (includes pump support, fittings for gas and sample lines, and 18″ delivery tubing)	60-2604-033	50.00
Lockable well cap for 4″ plastic well casing (includes pump support, fittings for gas and sample lines, and 18″ delivery tubing)	60-2604-030	60.00

Quick disconnects

Connector package — control unit to gas supply (12′ coiled hose with quick disconnect fitting to control unit and male ¼″ standard pipe thread to gas supply)	60-2604-040	50.00
Connector package — gas line, control unit to well cap (12′ coiled hose with coupler to control unit and quick disconnect fitting to well cap connector)	60-2604-041	50.00
Connector package for portable use — gas line, control unit to pump (12′ coiled hose with quick disconnect fitting to control unit and male, ¼″ standard pipe thread to pump)	60-2604-042	50.00

ISCO price list 278
march 15, 1984

MODEL 2600 WELL SAMPLER

Catalog No.	Price
60-2604-001	$375.00
60-2604-005	800.00
60-2604-025	120.00
60-2604-026	165.00
60-2604-027	210.00
60-2604-015	55.00
68-2600-002	6.15
68-2600-003	8.50

Catalog No.	Price
299-0013-04	$ 34.00
291-0000-00	20.00
299-0013-02	38.50
299-0013-01	42.00
209-0171-05	3.81
209-0171-06	5.48
60-2603-032	12.00

PORTABLE PUMP

Catalog No.	Price
60-3004-060	$545.00
60-1684-040	185.00
60-3004-070	55.00
60-1684-088	160.00
60-1684-093	160.00
60-3004-068	43.00
60-1394-023	32.00
60-1394-054	48.00
60-1684-035	54.00
60-1683-146	65.00
60-1683-144	130.00
60-1684-110	65.00
60-2103-093	11.00
68-1680-055	45.00

Catalog No.	Price
68-1680-056	$135.00
68-1680-057	235.00
68-1680-058	68.00
68-1680-059	210.00
60-1394-070	35.00
60-1394-071	35.00
60-2104-054	4.95
68-1680-061	23.00
68-2600-002	6.15
68-2600-003	8.50
299-0013-04	34.00
291-0000-00	20.00
299-0013-02	38.50
299-0013-01	42.00

Extra Instructions Manuals

Model 2600	60-2603-065	$14.00
Portable Pump	60-3003-184	14.00

ISCO, Inc.
mailing address: Lincoln, Nebraska 68501
telephone: (800) 228-4373
In Nebraska (402) 474-2233
telex: 43-8028

geotech

The Geotech Small Diameter Well Pump was designed and developed in conjunction with the United States Geological Survey, Quality of Water Branch. Its purpose is to fill the requirement for a device to remove a sample from a 2" diameter well, which is less costly to drill and maintain.

This unit is ideal for ground water sampling. Because the unit is constructed of Teflon* and stainless steel, it will not contaminate your sample in any way. It can operate entirely on inert gas. It is fully automatic, portable, and can be safely operated in an explosive gas atmosphere.

This compact unit, measuring 1-3/4" in diameter and 38" in length, is operated at the well head by either our Electronic Logic Unit, or the Pneumatic Logic Unit. Both units are fully automatic, and require compressed air, nitrogen, or an air compressor. The Electronic Logic Unit also requires an AC or DC power supply. It is variable from .3 to 30 seconds on both the charge and exhaust cycles. The Pneumatic Logic Unit requires no electricity. It is variable from 0 to 60 seconds on both cycles.

A bellows of Teflon protects the sample from contamination by the inert gas power supply and is encased in a stainless steel chamber providing durability and corrosion resistance.

Twin line Neoprene hose carries the power supply to charge and bleed the chamber from one line and exhausts the sample from the other.

The inert power supply can be in the form of compressed nitrogen, compressed air or an air compressor capable of providing one-half pound of pressure for each foot of well pump depth.

The following is a description of the well pump construction and product data.

#0500 WELL PUMP

Length	38"
Width	1-3/4"
Outer Casing	Stainless Steel
Center Shaft	Stainless Steel
Bottom Check Valve	Stainless Steel
Bottom Check Valve Ball	Teflon
Plastic Strainer Disks	Polycarbonate
Bellows	Teflon
Volume of Bellows	3/4 Liter
Fittings	Stainless Steel, Quick Disconnect with Safety Washers

#5503 & #5513 NEOPRENE HOSE

Twin Line charge/exhaust Neoprene hose with quick disconnect, stainless steel fittings with safety washers.

Standard Length	100 Foot Sections
Inside Diameter per each Hose	3/8"
Outside Diameter per each Hose	1/2"
Maximum Pounds per Square Inch	200
Air Hose Color	Red
Sample Hose Color	Green

#5505 ELECTRONIC PNEUMATIC LOGIC UNIT

This unit is recommended because of the ease of operation. Charge and exhaust cycles are electronically timed and very little adjustment is needed. The unit comes with AC and DC power cords.

Minimum Pounds per Square Inch	55
Maximum Pounds per Square Inch	200
Battery Amp Draw	0.694
Electronic Timers	0.3 to 30 second charge 0.3 to 30 second exhaust
Electric Power Source	115 VAC or 12 VDC
Pneumatic Power Source	Compressed Air or Nitrogen or an Air Compressor

#5504 PNEUMATIC LOGIC UNIT

This unit is recommended if an AC or DC power source is not available or if you are working in an explosive gas atmosphere. This unit is not recommended below a 300 foot depth.

Minimum Pounds per Square Inch	70
Maximum Pounds per Square Inch	200
Controls	Pneumatic Needle Valves
Pneumatic Power Source	Compressed Air or Nitrogen or an Air Compressor

#5501 TANK REGULATOR

This unit is used with a compressed air or nitrogen tank. It consists of two gauges, a single valve 3000 PSI inlet, and a 250 PSI outlet. It also comes with a ten foot hose whip with CGA 580 quick disconnect fittings.

COMPRESSED AIR/GAS POWER SUPPLY

The Small Diameter Well Pump is designed to be operated by any inert air supply. The most common is a compressed air or nitrogen tank, or an air compressor.

For any of the above named power supplies, you can calculate the air consumption as follows. With 100 feet of hose, in or out of the well, the air consumption is 125 cubic inches per cycle, with five cycles per minute. For each additional 100 feet, add 59 cubic inches. If you plan to use an air compressor we advise that you have one with a reserve tank to insure proper air supply to the pump.

In order for the well pump to operate efficiently, you must supply adequate pressure. For each foot of pump depth, the pump utilizes 1/2 psi. An additional 10 psi is needed to assure a satisfactory flow rate. With the Pneumatic Logic Unit a minimum of 70 psi is required, the Electrical Pneumatic Logic Unit requires only 55 psi.

#5504 PNEUMATIC LOGIC UNIT

Example #1

	Pressure to Operate
100 Foot Pump Depth	
1/2 psi per foot	50 psi
For operation & line loss	10 psi
	60 psi

Adjust regulator to the required minimum of 70 psi.

Example #2

	Pressure to Operate
150 Foot Pump Depth	
1/2 psi per foot	75 psi
For operation & line loss	10 psi
Adjust Regulator to	85 psi

#5505 ELECTRICAL PNEUMATIC LOGIC UNIT

Example #1

50 Foot Pump Depth	Pressure to Operate
1/2 psi per foot	25 psi
For operation & line loss	10 psi
	35 psi

Adjust regulator to the required minimum of 55 psi.

Example #2

100 Foot Pump Depth	Pressure to Operate
1/2 psi per foot	50 psi
For operation & line loss	10 psi
Adjust Regulator to	60 psi

ADDITIONAL NOTES

There is no set minimum water depth, the only requirement is that the pump be entirely submersed at all times.

For the Electronic Logic Unit, the maximum pumping depth is 400 feet, with the pneumatic logic unit it is 300 feet.

The water contained in 100 feet of 1/4 inch I.D. hose is 59 cubic inches or 0.26 gallons. There are 231 cubic inches in one gallon.

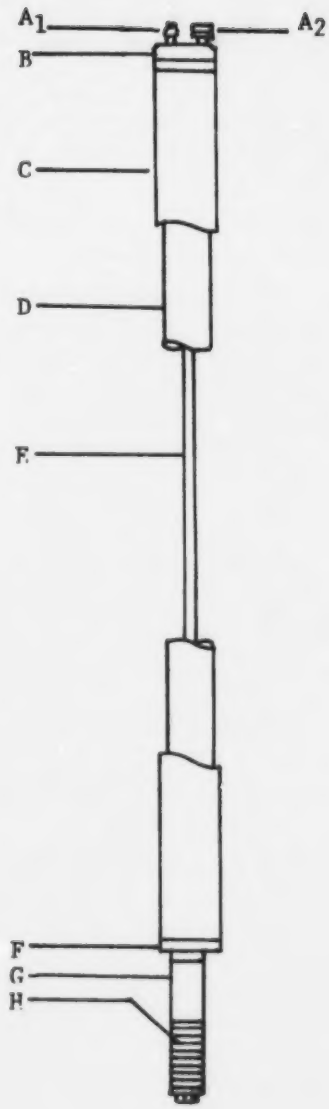
There are 46 cubic inches contained in the bladder of the 1-3/4 inch Well Pump.

The total amount of air used per cycle is 125 cubic inches. We came to this figure by adding the amount of air in the pump, 66 cubic inches, and the amount contained in 100 feet of hose, 59 cubic inches.

* Teflon is a registered trademark of E.I. duPont de Nemours, Inc.

DESCRIPTION OF OPERATION

Water enters through the strainer (H) and passes the check valve (G), filling the Teflon bellows (D) by way of the center shaft (E). When the bellows is full, air is compressed into the chamber (C) through the top air port (A_2). This pressure closes the check valve (G) and constricts the bellows (D), forcing the water back through the center shaft (E) and past the check valve (B) to the sample port (A_1) and up the sample tubing. When the pressure is bled from the chamber (C) back through the air port (A_2), the head pressure closes the check valve (B) and the cycle is repeated.



DESCRIPTION OF WELL PUMP PARTS

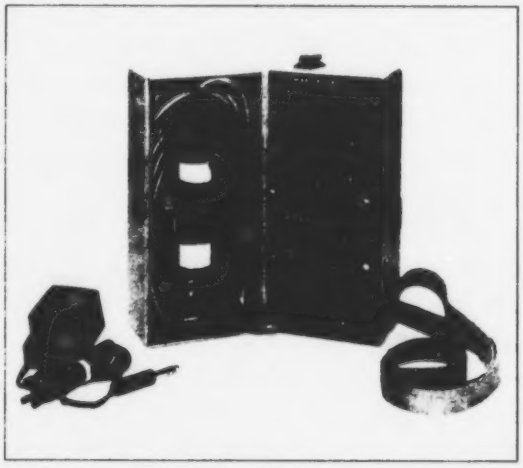
(A) Quick disconnect fittings.*
(B) Top cap and check valve.*
(C) Pressure chamber.*
(D) Teflon rubber sample bellows.
(E) Center shaft.*
(F) Bottom cap.*
(G) Bottom check valve and draw-nut.*
(H) Perforated strainer.

*Stainless Steel

MARTEK MARK X WATER QUALITY MONITOR

MARTEK INSTRUMENTS, INC. MANUFACTURERS OF ENVIRONMENTAL INSTRUMENTATION

. . . for field and laboratory accurate measurements of temperature, pH, conducitvity, and temperature corrected conductivity, or salinity in fresh or sea water bodies.



DESIGN AND PERFORMANCE FEATURES

- Direct in-situ measurements of temperature, pH, conductivity and temperature corrected conductivity or salinity.
- Digital panel meter display in engineering units for each parameter.
- Extended DC operation with internal, rechargeable battery pack.
- Designed for rugged field applications with simple operating controls.

DESCRIPTION

The Martek Mark X is an in-situ self-contained system for measuring temperature, pH, conductivity, and temperature corrected conductivity or salinity in the field or in the laboratory. The standard configuration, including the readout module, sensors, and 10 meters of cable which is stored within the readout module, weighs less than 6 pounds (2.7 kg); thus facilitating field monitoring under rugged environmental conditions. It can operate throughout the standard conductivity range of fresh to sea water samples without altering the conductivity sensor.

The Martek Mark X is simple to operate and provides quick, reliable and accurate data. Water quality measurements are performed by placing the multi-parameter sensor configuration in the water body or sample to be measured. A display selector switch is set to the desired parameter of measurement, which is presented on a four digit liquid crystal display. Selector switch positions are provided for reading of internal battery voltage, temperature, pH, conductivity, and temperature corrected conductivity or salinity. A conductivity "Range Selection" switch is provided on the front panel, which permits full scale conductivity sensitivities of 0-1, 0-10, or 0-100 millimhos/cm. Switching from one conductivity range to another will greatly enhance the system capability when operating in unknown water bodies, yet it will not affect the sensor calibration. Calibration controls are located under a convenient front panel access cover. Individual "Zero" and "Span" adjustments enable simple, two-point calibration of each sensor that maintains optimum system accuracy and data integrity.

The Martek Mark X system is furnished with: a readout module that incorporates a four digit liquid crystal display, a battery power supply, switch controls, front panel access to calibration controls, and a storage compartment for the 10 meter cable length and probes; battery charger, 10 meter cable length and temperature, pH, and conductivity probes; and a sturdy wooden storage and carrying case. The readout module is powered by two internal 6 volt, 0.9 amp-hour gel cell batteries. An average system current drain of less than 25 milliamps provides approximately 35 hours of continuous operation before battery charging is required. An encapsulated battery charger supplied with the system provides over-night recharge capabilities or continuous AC operation for laboratory or industrial applications. Due to its small size, light weight, simple operation and long term stability under harsh ambient monitoring conditions, the Martek Mark X is a valuable instrument for scientists, technicians, or engineers engaged in water analysis.

MARTEK MARK X SPECIFICATIONS

MEASUREMENT PARAMETERS	RANGE	ACCURACY	SENSOR TYPE
pH	0-14 pH	±0.1 pH	Combination pH electrode with internal silver-silver chloride reference electrode.
Temperature	0-50°C	±0.1°C	Thermo-linear array.
Conductivity (Range Selectable)	0-100 mmho/cm	±1.0 mmho/cm	Four electrode stainless steel.
	0-10 mmho/cm	±0.1 mmho/cm	
	0-1 mmho/cm	±0.01 mmho/cm	
Temperature Corrected Conductivity	Variable	±2% of range selected	

INSTRUMENT ASSEMBLY

Case Dimensions:	10 inches (25.4 cm) length x 4.5 inches (11.4 cm) width x 5.5 inches (14.0 cm) height
Overall Weight: Readout, Sensor and Cable	6 pounds (2.7 kg)
Sensor Dimensions:	
Conductivity and Temperature Sensors	2.5 inches (6.35 cm) length x 1.25 inches (3.28 cm) diameter
pH Sensor	5.5 inches (14 cm) length x 1.25 inches (3.28 cm) diameter
Power Supply:	Regulated, self-contained, two 6 volt, 0.9 amp-hour rechargeable batteries. Power drain is an average of 25 milliamps.

ENVIRONMENTAL CONDITIONS

Temperature:	Storage −20 to 70°C Operation: 0 to 50°C
Moisture:	Gasketed, splash proof construction throughout.
Corrosion:	Aluminum control panel and carrying case prepared to MIL specs for maximum corrosion resistance.

ORDERING INFORMATION

Part Number

170 Martek Mark X In-Situ Water Quality Monitor, includes readout module, 10 meter cable length with temperature, pH, and conductivity probes, battery charger, and storage case. NOTE: Specify 120 volts or 240 volts, 50/60 Hz AC for battery charger.

All prices FOB Irvine, California including 12 month product warranty against defects in material and workmanship.
Prices and specifications subject to change without notice.

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17302 DAIMLER STREET, IRVINE, CALIFORNIA 92713 PHONE (714) 540-4435 TELEX 692 317

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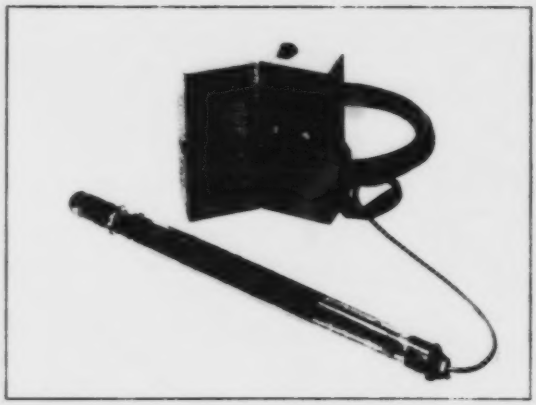
MARTEK® MARK XIV

MARTEK INSTRUMENTS, INC. MANUFACTURERS OF ENVIRONMENTAL INSTRUMENTATION

. . . in situ measurements of temperature, pH, dissolved oxygen, conductivity, and temperature corrected conductivity, or salinity in fresh or sea water bodies



DESIGN AND PERFORMANCE FEATURES

- Sensor configuration will fit two inch borehole.
- Direct in situ measurements of multiple water quality parameters.
- Digital display in engineering units for each parameter.
- AC/DC operation with internal, rechargeable battery pack.
- Designed for rugged field application with simple operating controls.
- Five element conductivity sensor operates from fresh to sea water ranges without need for changing cell constant.
- Recorder output signal for each parameter.

DESCRIPTION

The Martek Mark XIV Borehole Water Quality Monitor measurements are performed by placing the multi-parameter sensor configuration in the water body or sample to be measured. A display selector switch is set to the desired parameter of measurement, which is presented on a four digit liquid crystal display. Selector switch positions are provided for reading of the internal battery voltage, temperature, pH, dissolved oxygen, conductivity, and temperature corrected conductivity or salinity. A conductivity "Range Selection" switch is provided on the front panel, which permits full scale conductivity ranges of 0-1, 0-10, or 0-100 millimhos/cm. Switching from one conductivity range to another will greatly enhance the system capability when operating in unknown water bodies, yet it will not affect the sensor calibration. Calibration controls are located under a convenient front panel access cover. Individual "Zero" and "Span" adjustments enable simple, two-point calibration of each sensor that maintains optimum system accuracy and data integrity.

The Martek Mark XIV system is furnished with a readout module that incorporates a four digit liquid crystal display, a battery power supply, switch controls, front panel access to calibration controls, battery charger, 30 meter cable length, and a probe configuration consisting of temperature, conductivity, pH, dissolved oxygen probes and stirrer. The readout module is powered by an internal 12 volt, 1.9 amp-hour gel cell battery. An average system current drain of 50 milliamps provides approximately 35 hours of continuous operation before battery charging is required. An encapsulated battery charger supplied with the system provides overnight recharge capabilities or continuous AC operation for laboratory or industrial applications. Due to its small size, light weight, simple operation and long term stability under harsh ambient monitoring conditions, the Martek Mark XIV is a valuable instrument for scientists, technicians, or engineers engaged in water analysis.

APPLICATIONS

The Martek Mark XIV is ideally suited for in-situ water quality monitoring of ground water. The entire down hole sensor configuration is narrow to fit most two inch boreholes. In-situ monitoring avoids the problems associated with aeration, degassing, and other disturbances when samples are brought to the surface. Temperature and/or conductivity measured in boreholes may indicate the source of water at various depths or to define plumes which are usually warmer or more conductive than native ground water. Dissolved oxygen readings may be indicative of microbiological and bacterial reactions which occur in ground water. Simultaneous in-situ measurements of several parameters produces minimum disturbance of the fluid column and enhances monitoring of abrupt and irregular changes of ground water characteristics which often occurs during short intervals. The Martek Mark XIV may also be used for providing portable spot-tests, vertical profiles through water columns; bioassays; long term measurement of water samples aboard floating laboratories; in water treatment and waste water facilities; and for in-situ measurements of water bodies such as rivers, reservoirs, ponds, lakes, coastal and inland waters, and sewage and industrial plant effluents. Its unique circuitry permits digital operation under remote rugged field environments where AC power may not be available.

MARTEK MARK XIV SPECIFICATIONS

MEASUREMENT PARAMETERS	RANGE	ACCURACY	SENSOR TYPE
pH	0-14 pH	±0.1 pH	Combination pH electrode with internal silver-silver chloride reference electrode.
Dissolved Oxygen	0-20 ppm (mg/liter)	±0.1 ppm at temperature of calibration	Galvanic electrode with automatic temperature compensation and in-situ stirrer.
Temperature	0-50°C	±0.1°C	Thermo-linear array.
Conductivity (Range Selectable)	0-100 mmho/cm 0-10 mmho/cm 0-1 mmho/cm	±1.0 mmho/cm ±0.1 mmho/cm ±0.01 mmho/cm	Four electrode stainless steel.
Temperature Corrected Conductivity or Salinity	Variable	±2% of range selected	

INSTRUMENT ASSEMBLY

Case Dimensions:	10 inches (25.4cm) length x 4.5 inches (11.4cm) width x 4.5 inches (11.4cm) height
Case Weight:	6 pounds (2.7kg)
Sensor Dimensions:	1.75 inch (4.5cm) diameter x 32 inches (81cm) length
Sensor Weight:	3 pounds
Cable:	0.25 inches (0.6cm) diameter and 0.08 pounds per foot (0.11kg per meter)
Power Supply:	Regulated, self contained, 12 volt, 1.9 amp-hour rechargeable battery. Power drain is average 50 milliamps. Low voltage cutoff.

ENVIRONMENTAL CONDITIONS

Temperature:	Storage −20 to 70°C Operation: 0 to 50°C
Moisture:	Gasketed, splash proof construction throughout.
Corrosion:	Aluminum control panel and carrying case prepared to MIL specs for maximum corrosion resistance.

ORDERING INFORMATION

Part Number	
174	Martek Mark XIV Borehole In-Situ Water Quality Monitor, includes readout module, sensor configuration with temperature, pH, conductivity, dissolved oxygen probes and stirrer, 30 meter cable length, and AC battery charger. NOTE: SPECIFY 120 VOLTS OR 240 VOLTS, 50/60 HZ AC FOR BATTERY CHARGER.

All prices FOB Irvine, California including 12 month product warranty against defects in material and workmanship. Prices and specifications subject to change without notice.

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MARTEK INSTRUMENTS INC.

MARTEK MARK XIV BOREHOLE WATER QUALITY MONITOR

PRICE LIST NO. 12A

PART NUMBER	DESCRIPTION	UNIT PRICE
174	Martek Mark XIV Borehole In Situ Water Quality Monitor, includes readout module, sensor configuration with temperature, pH, conductivity, dissolved oxygen probes and stirrer, 30 meter cable length, and AC battery charger.	$4,000.00
174-10	Martek Mark XIV Borehole In Situ Water Qualtiy Monitor Readout Module with AC battery charger only.	$2,000.00
174-20	Martek Mark XIV Borehole complete Sensor Configuration with temperature, pH, conductivity, dissolved oxygen probes and stirrer, and 30 meters cable length.	$2,500.00
174-21	Mark XIV Temperature Sensor	$ 210.00
174-22	Mark XIV Dissolved Oxygen Sensor	$ 490.00
174-23	Mark XIV Dissolved Oxygen Stirrer	$ 350.00
174-24	Mark XIV Conductivity Sensor	$ 280.00
174-25	Mark XIV pH Sensor	$ 210.00

NOTE: (1) Specify AC adapter for 120 volts or 240 volts, 50/60 Hz.

(2) All prices FOB, Irvine, California. Prices and specifications subject to change without notice. Delivery 30 days after receipt of order.

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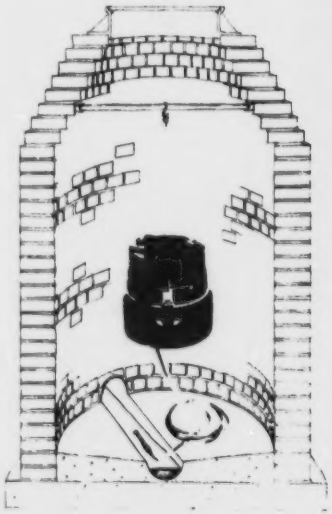
P.O. BOX 16487, 17302 DAIMLER STREET, IRVINE, CALIFORNIA 92713
PHONE: (714) 540-4435 TELEX: 692-317

ISCO

wastewater samplers

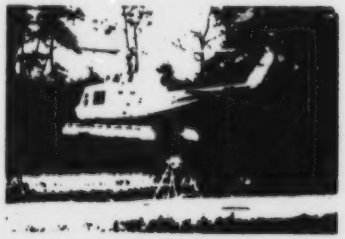
3731

high speed samplers



ISCO wastewater samplers are designed to collect individual or composite water samples taken from streams, manholes, or other sources at precisely timed or flow-proportioned intervals. Completely weatherproof, corrosion resistant construction and the ability to handle relatively large suspended materials suit them for use in industrial, food processing and meat packing plants, paper mills, and municipal sewage treatment plants or along rivers, sewers and tidelands.

Circular construction permits easy lowering into any standard manhole without dissassembly or tipping. The case is quickly snapped apart to expose all sections for servicing. Originated by ISCO, this efficient design has been field proven and copied by others. The sample compartment may be padlocked during operation to prevent tampering with collected samples.



Tripod-mounted sampler being installed into a sewer, tideland, or stream.

ISCO portable samplers can be powered by one of four sources: a removable, rechargeable Nicad or lead-acid battery located inside the sampler; an external automotive battery; or AC line. The dry Nicad battery has an extremely long recharge life, cannot spill acid, does not require refilling, and will not freeze. ISCO lead-acid batteries are of the sealed gel type and also will not spill or require refilling. A removable power converter/battery charger can be used to replace the internal batteries when AC line power is available.

The best feature of ISCO samplers — reliability — does not show up on the specification sheet. Time and again the many thousands of ISCO samplers currently in use have been shown to outlast competing samplers in adverse environments. ISCO samplers can be demonstrated in most areas by sales representatives. Contact the factory or your representative for more information on this equipment, or for formal specifications to help prepare your bid request.

P.O. Box 82531
Lincoln, Nebraska 68501

Sales (800) 228-4373
Service (800) 228-4374

60-3028

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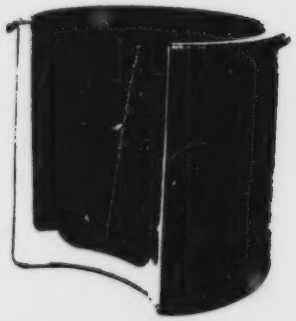
reliable, versatile control

In addition to normal timed collection, all ISCO samplers offer flow proportioned collection when used with an ISCO or other flow meter. Sample interval and volume can be set over wide ranges with simple switch controls. The controller cover has an erasable log to record sampling locations, battery recharging dates, and other data as needed. Programming instructions with examples are permanently attached to the controller lid for quick training of unskilled operators. Four wing nuts allow the controller mechanism case to be removed as a unit for servicing.

Sample size is determined with a typical repeatability of ±10 ml. Other samplers utilizing the vacuum principle determine sample size by overfilling a metering chamber and siphoning away the excess, frequently resulting in solids settling from the excess into the retained sample to artificially enrich BOD and suspended solids levels. ISCO's elimination of the metering chamber avoids this problem, reduces cross-contamination between samples, and prevents reliability troubles arising from grease-fouled electrodes, vacuum leaks, plugged valves, or other failures in the complex sequencing mechanism required for the operation of metering chambers.

rugged, watertight construction

ISCO samplers can withstand thorough cleaning with a hose and even prolonged submersion. All electrical and mechanical components—not just the controller—are sealed in a single watertight stainless steel housing to provide reliable operation in manholes and similar corrosive environments. Quick locking toggle clamps and a seamless gasket provides fast, secure sealing of the controller cover*. Switches have rubber boots for protection against wet fingers, and the housing contains a regenerable desiccant cartridge to absorb moisture seepage or condensation. An indicator tells when to oven dry the desiccant to restore its original absorptive capacity. All exposed hardware is stainless steel; there are no exposed painted or plated steel parts.



This composite sampler base was cut away to determine damage after drop testing. A complete sampler with a 40 lb. load was dropped three times at heights to 9'. The only damage was separation of the insulation visible in bottom corner. Inner and outer shells were intact and the sampler was completely serviceable.

The entire case is constructed of high impact plastic, and exhibits excellent mechanical strength. The case is resistant to gasoline and similar solvents in water, but is not compatible with chlorinated hydrocarbons. All ISCO sampler bases have an inner and outer shell, separated by rigid, foamed-in-place polyurethane insulation. Durability and insulating properties are far superior to samplers using modified plastic trash containers or one piece picnic cooler type moldings. Large compartments for block or crushed ice provide proper cooling for samples scheduled for BOD or TOC analysis.

All mechanical, pneumatic and electronic components are sealed in the watertight stainless steel case. The high speed, large bore pump is a rugged and virtually maintenance free.

*Watertight if seals are intact. Each unit is individually tested for leaks before it leaves the factory. However, once the conditions of use are beyond ISCO's control, maintaining watertightness is not guaranteed.

This Model 1680 sampler functioned perfectly after being dragged seven miles down a muddy river. No water leaked into the stainless steel case containing all motors and electronic components. Even the head battery was unaffected by prolonged submersion.

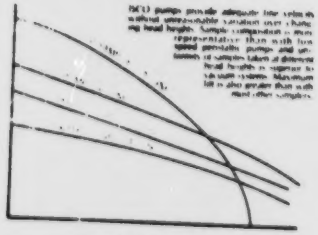
high speed, clog-proof pump

Samples are taken with a high speed, large bore (3/8") peristaltic pump. There are no valves or reciprocating parts — only a flexible tube through which the sample is forced by the squeezing action of moving rollers. This simple, clog-proof pump is extremely dependable and requires minimal maintenance. The peristaltic tubing is a separate length of silicone rubber, providing better performance and longer life than obtainable in pumps where the rollers run on a portion of the vinyl suction line. The silicon rubber pump and distribution tubing used in ISCO samplers is a special medical grade tubing which contains absolutely no organic material that will contaminate the sample or destroy its integrity.

Both before and after sampling, the pump reverses to air purge the suction line and minimize cross-contamination between samples. Suction lines have streamlined, weighted strainers to keep rags and other debris from entering the sampler. Suction lines of vinyl or Teflon®, 1/4" or 1/2" I.D., are available for general purpose or toxic pollutants sampling applications.

Intake velocity is close to optimum — fast enough to prevent settling of suspended solids, but not fast enough to pick up static bottom sediments which may provide an inaccurately high BOD value*. Although the EPA has no requirements regarding suction line velocity, its report EPA-R2-73-261 states (p. 221): "minimum velocity of two to three feet per second would appear warranted". The standard ISCO pump provides a typical line velocity of over 2'/sec with a 1/4" suction line at heads to 12'. If a higher line velocity is preferred for some unusual application, a superspeed pump operating at four times the standard rate is available. This provides a line velocity typically over 3½'/sec through a 3/8" suction line, but is not recommended for general sewage sampling as it can produce erroneously concentrated BOD and TSS samples if the strainer is too near the bottom of the stream.

The location of an ISCO sampler does not significantly affect sample composition, sometimes a real problem with vacuum operated samplers where suction line velocity, and hence sample composition, varies greatly with only a few feet difference in head height. An ISCO sampler, whether it's at the bottom or top of a manhole, always provides the same sample. Maximum head is 26'.



ISCO pumps provide adequate line velocity without unacceptable variation over varying head heights. Sample composition is more representative than with low speed peristaltic pumps and uniform vacuum taken at different head heights is superior to vacuum systems. Maximum lift is also greater than with most other samplers.

*In the last several years the EPA and other government agencies have thoroughly researched sampling methods and equipment. Their results show that suction line velocity is only one of many variables affecting sample composition, and that line velocity differences within a reasonable range (approximately 2 to 3'/sec) do not have a consistent effect on sample composition. Outside of this range, certain low velocity piston or peristaltic pumps and high velocity vacuum samplers often produce large composition deviations. EPA reports have repeatedly shown that vacuum operated samplers produce higher BOD and other composition values than grab samples.

model 1680 high speed sequential sampler

A Model 1680 sequential sampler can really simplify your pollution monitoring program. Reliable operation provides reproducible results you can trust; programming versatility insures against obsolescence due to changing regulations, and manhole-proof ruggedness withstands corrosive atmospheres, wear and tear, and frequent hosing or even total submersion. For taking a single composite sample, the standard 28 bottle sequential base section may be replaced with a base accommodating a single wide-mouth container.

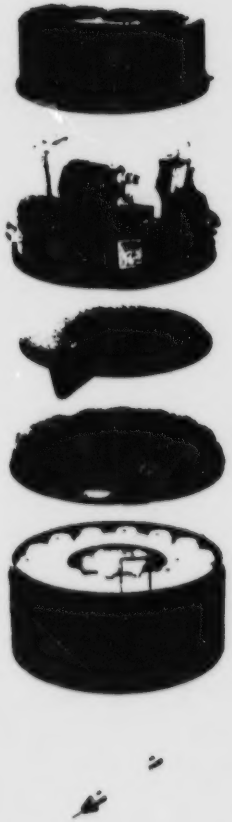
Typically, over one hundred full samples may be taken on an 18 hour charge of the removable Nicad or lead acid battery. An auxiliary battery within the controller maintains the logic for about eight hours in case of a power failure. While it will not power the pump, it accommodates power interruptions and battery changes without losing the program or time.

The one piece, clog-proof rotating tunnel carries samples to the distributor plate without passing through any rotating seals or hard-to-clean tubing; the steep trough angle prevents sedimentation. Samples are conducted into individual bottles by a distributor plate. Both the tunnel and distributor plate can be quickly removed for cleaning.

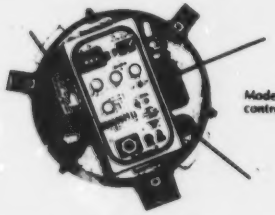
The base holds 28 bottles — four more than usual, to take the pressure off 24 hour servicing schedules. A large ice compartment is provided for cooling biological specimens. Its capacity is adequate to maintain samples at about 40°F below ambient for at least 12 hours, and 30°F below ambient for 24 hours. Construction is double-walled high impact plastic with foamed-in-place insulation having a nominal thickness of 1". Additional bases with covers and bottles may be obtained to retrieve samples from the field without interrupting collection. The cylindrical sample bottles are available in unbreakable, high density polyethylene (500 ml) or glass (400 ml). They are much easier to clean than wedge-shaped bottles since they have a wide mouth to admit a large brush and have no inaccessible corners. Polyethylene bottles can be washed in a dishwasher but not autoclaved. Glass bottles can be autoclaved and are also suitable for samples having organic components which may be absorbed by plastic bottles. All bottles are supplied with caps with polypropylene liners to insure safe handling. Teflon® lid liners are available separately for all ISCO bottles.

Outside dimensions are 21" high by 19½" diameter and the weight is 40 lbs. with battery and polyethylene bottles.

Accessory composite base



The all-electronic controller provides collection intervals determined by the 1 to 999 minute quartz crystal timer or by any ISCO flow meter. Up to 999 signals from the flow meter can be combined for each sample. This greatly expands the range of flowstream volumes originally available in the flow meter, and simplifies interfacing with flow meters or other manufacture. Sampling normally commences immediately upon setup, but the initial sample can be delayed up to 999 minutes if desired. All values are entered with a pushbutton digital switch. An LED display shows the interval remaining before the next sample is taken.



Model 1680 controller

Maximum sample volume is 500 ml selected with a 9 position switch. The switch scale indicates volumes for head heights to 21'. Another switch provides for the selection of six different suction line lengths. An optional multiplexer permits compositing 1, 2, 3, or 4 samples into each bottle, allowing a maximum of 112 samples to be placed into the 28 bottles. This provides more representative collection and reduces the danger of missing short term changes in stream composition. The multiplexer also can be used to distribute the sample over 1, 2, 3, or 4 bottles, permitting a larger sample volume or the use of several different preservatives. An automatic shutoff stops the sampling program after the last bottle is filled. An optional switch is available to by-pass the automatic 28th bottle shutoff when using the composite base accessory. When the sampler is returned to sequential sample collection, the switch may be placed in the shut-off position to cease sample collection after the 28th bottle has been collected.

For each complete Model 1680 you MUST SPECIFY the basic unit, a power source, and a suction line with strainer

THE BASIC UNIT

Catalog Number	Pump	Bottles	Multiplexer?
68-1680-06	Standard	Polyethylene	Yes
68-1680-068	Standard	Polyethylene	No
68-1680-069	Standard	Glass	Yes
68-1680-070	Standard	Glass	No
68-1680-071	Superspeed	Polyethylene	Yes
68-1680-072	Superspeed	Polyethylene	No
68-1680-073	Superspeed	Glass	Yes
68-1680-074	Superspeed	Glass	No

POWER SOURCES

Nicad Battery without charger	60-1684-080
Lead Acid Battery with clamp without charger	60-1684-062
AC power converter/battery charger. To power sampler from 115VAC 50/60 Hz line power or to recharge battery for use with standard speed pump samplers only	60-1684-046
Same as above except for use with superspeed pump samplers	60-1684-088
Same as above except for 230VAC 50/60 Hz line power and for use with standard and superspeed pump samplers	60-1684-071

SUCTION LINES

3/4" ID x 22' vinyl suction line with polypropylene braided inlet strainer. For use with standard speed pump samplers only	60-1194-054
3/8" ID x 20' vinyl suction line with polypropylene braided inlet strainer. For use with standard and superspeed pump samplers	60-1684-035

ACCESSORIES

Extra base with 28 polyethylene 500 ml bottles. Without cover	60-1194-069
Same except 28 glass 400 ml bottles. Without cover	60-1684-100
Cover for 28 bottle base	60-1194-067
Sample bottles, high density polyethylene, 400 ml with caps with polypropylene lid liners. For Models 1680, 1392 and late Model 1392. With caps removed will also fit Model 1580 or earlier Model 1392 with X or W in serial number. Set of 28	68-1680-029
Same. Case of 100. Without caps	68-1680-030
Caps for PE sample bottles. Case of 100	68-1680-031
Sample bottles, glass, 400 ml with caps with polypropylene lid liners. For use in 1580, 1581, 1582, 1680 for 1680 Samplers. Set of 28	68-1680-032
Teflon lid liners for 400 ml glass bottle, per each	60-1681-117
Composite base only. Does not include bottle container or locking insert. Sold separately below	60-1684-081
4 Gallon polyethylene container with lid and polypropylene lid liner. Requires locking insert below	299-0011-02
1 Gallon bottle, no locking insert	60-1681-020
5 Gallon polyethylene container with lid and polypropylene lid liner. No locking insert required	299-0011-01
2 ½ Gallon glass container with lid and polypropylene lid liner. Requires locking insert below	299-0000-00
2 ½ Gallon bottle, locking insert	60-1681-088
Teflon lid liner for 2 ½ Gallon bottle, each	60-1681-092
Cover for composite base, stainless only	60-1684-107
By-Pass Switch installed for composite sampling	**68-9680-064**
Extra silicon rubber pump tube, for Models 1680 and 1392, 17" long	60-1684-016
Extra silicon rubber pump tubing, bulk, 15' long	68-1680-063
Snap-on suspension harness	60-1394-014
Liquid level sampler actuator	60-1644-000
Automotive battery cable	60-1394-024

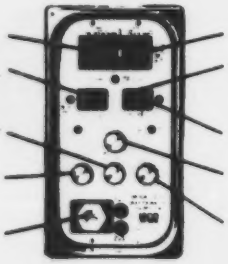
model 2100 sampler

Since the passage of the CLEAN WATER ACT of 1977, water sampling and testing has been expanded to include a class of substances known as "toxic pollutants". Because of the very low concentration limits that have been established for these substances, automatic samplers constructed of materials that do not contribute to or absorb from the sample are an absolute necessity. The ISCO Model 2100 Sampler has been designed specifically for toxic pollutant sampling and, because of this design is equally well suited for suspended solids and general purpose sampling applications. The versatility that has been built into the Model 2100 makes it possible for the user to adapt the instrument to a wide variety of applications.

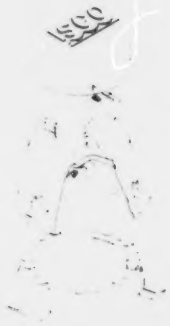
The Model 2100 is a portable automatic wastewater sampler designed to collect up to 24 separate sequential samples of a pre-determined volume. The samples may be collected in your choice of 350ml glass or 1000ml polypropylene bottles. Both bottles are interchangeable in the same base. The samples can be collected on a time basis using the internal quartz crystal clock, or on a flow proportional basis using a 12VDC pulse or isolated contact closure input from an external flow meter. In the time mode, the interval between samples may be set from 1 to 999 minutes in one minute increments or, in the flow mode, the interval between samples may be set from 1 to 999 flow pulses in single pulse increments. A manual sampling cycle may be initiated at any time. Sample volumes are adjustable in 10ml increments to a maximum of 1000ml. Each sampling cycle includes an air pre-purge and post-purge to clear the suction line.

A standard feature of the Model 2100 is an eight position multiplexer allowing up to eight sample bottles to be filled at each sampling interval or up to eight samples to be placed into each sample bottle. An LED readout indicates the bottle number and the multiplex step (if multiplexer is being used) of the next sample. A second LED readout indicates the interval in minutes or flow pulses remaining until the next sample is to be collected. Both LED displays are visible through a viewing window in the sampler control box lid, allowing the progress of the sampling program to be monitored without opening the control box. The sampler also features an adjustable time delay to the first sample providing the operator with up to 999 minutes delay before the first sample is taken. After the time delay, sample collection proceeds at regular time intervals.

The Model 2100 Sampler uses the proven ISCO peristaltic pump system to transport the sample from the source to the sample bottle. The flow rate is typically 3000 milliliters per minute. The sample is under pumped flow at all times: there are no metering chambers, valves, or gravity-fed internal distribution systems. The only materials in contact with the sample are the vinyl or Teflon® suction line, the polypropylene and stainless steel inlet strainer (use optional), and the silicone rubber pump and distribution tubing. The silicon rubber pump and distribution tubing used in ISCO samplers is a special medical grade tubing which contains absolutely no organic material that will contaminate the sample or destroy its integrity. These features make the Model 2100 eminently suitable for both suspended solids and toxic materials sampling. Cross contamination between samples is minimized by eliminating sites for sediment accumulation and by limiting the materials in contact with the sample to silicone rubber, Teflon® (when a Teflon® suction tube is used) and glass. Very stringent requirements regarding the cleaning and handling of samplers for toxic materials have been established. Cleaning the Model 2100 between sampling locations is accomplished by merely replacing relatively inexpensive lengths of tubing and washing the bottles in the prescribed manner. Ambient operating temperatures range from 32°F to 120°F in weather conditions including rain and dust. Basic construction is of vacuum formed ABS plastic and stainless steel. The controls and electronics are housed in a watertight stainless steel container. The 24 bottle base and the center section which supports the control box and which forms the cover for the base are well insulated and the base will hold at least 30 pounds of crushed ice for sample cooling. Power sources can be either 117VAC, 50/60 Hz line current (234VAC, 50/60 Hz optional), or a battery of 12VDC. ISCO customers will find the Model 2100 to be of the usual high ISCO quality and of advanced design and versatility.



Standard controls



model 2100 options

COMPOSITE SAMPLING — A special insert is supplied with the Model 2100 Sampler to allow composite sampling in the 24-bottle base. The insert positions one 2½ gallon glass or polyethylene container (container must be ordered separately). For larger composite samples, a larger base assembly is available to accommodate 3 or 5 gallon containers.

SPECIAL TIMING SEQUENCES — For certain applications (for example, run-off or combined sewer overflow studies) it may be desirable to collect samples in a timed mode where the time interval between samples does not remain constant, but changes in a preprogrammed manner as the sampling program progresses. Up to four such special timing sequences may be specified to be included in the sampler electronics as an extra cost option. Normally, an ISCO Model 1640 Liquid Level Sampler Actuator would be used when operating on the special timing sequence, but is not absolutely necessary.

In operation, the sampler would remain dormant until the water rises to a predetermined level, at which time the sampling program is initiated. The special timing sequence is normally established such that a number of samples are collected at rapid intervals to monitor the initial run-off, with the sample interval gradually increasing during the remainder of the sampling period.

OPTIONAL MODES OF OPERATION — The Model 2100 has four basic built-in optional modes of operation. These modes slightly modify the normal operation of the sampler to accomplish some special purpose. These modes of operation include a composite sampling mode, short purge mode when multiplexing samples into separate bottles, four liquid level sampler actuator sample initiation modes and a sample line pre-condition mode.

The composite mode is used for collecting composite samples. In operation, "NEXT SAMPLE" LED shows the total number of individual samples which have been placed in the sample container. The total number of samples to be placed in the sample container before the sampler is automatically shut off can be set on the MULTIPLEX switch to ensure that the container does not overflow.

The short purge mode is used when collecting more than one bottle per sample using the multiplexer. It disables the pre- and post-purge function between the bottles, substituting a short purge to keep the distributor from dripping between bottles, to conserve battery power and to reduce the time between samples to maximize uniformity. The pre-purge before the first bottle and post-purge after the last bottle in the multiple bottle sample sequence are unchanged.

The sample line precondition mode provides for a prewash of the sample line to reduce the chance of cross-contamination due to residue in the suction tube and pump from the previous sample.

The liquid level sampler actuator sample initiation mode provides four different sampling sequences by which the Model 2100 Sampler collects samples when used with the Model 1640 Liquid Level Sampler Actuator. Basically, this provides a means of controlling the time which the first sample is collected in relation to the balance of the samples.

The optional modes of operation are built into the Model 2100 and are selected by internal switches. It is relatively easy to return the Model 2100 Sampler to its normal mode of operation after being used in the optional mode.

model 2100 specifications

PHYSICAL SIZE	Height: 25 in Diameter: 14 in
DRY WEIGHT	40 lb
SAMPLE BOTTLE CAPACITY	24 with Teflon® lid liners
SAMPLE VOLUME	150ml in glass bottles, 1000ml in polypropylene bottles, incremental maximum 1000ml incremental volume, composite maximum
SAMPLE VOLUME REPEATABILITY	±10ml typical
SAMPLING FREQUENCY	1 to 999 minutes between consecutive samples in 1 minute increments, or 1 to 999 flow pulses in single pulse increments
SAMPLING MODES	Timed, or flow proportional to external flow meter
FLOW METER INPUT REQUIREMENT	12VDC pulse or isolated contact closure of at least 25 milliseconds duration
SUCTION INTAKE TUBING	3/8" I.D. x 20' vinyl 1/4" I.D. x 22' vinyl 1/8" I.D. x 10' or 20' Teflon®
SUCTION LIFT	26 feet maximum
PUMP RATE (1 cu HEAD)	1/4" I.D. suction tube: 2400ml/min 1/8" I.D. suction tube: 1000ml/min
LINE TRANSPORT VELOCITY (1 cu HEAD)	1/4" I.D. suction tube: 4.1 ft/sec 1/8" I.D. suction tube: 2.1 ft/sec
TIME BASE ACCURACY	Better than 0.01% quartz crystal controlled clock
AMBIENT TEMPERATURE RANGE	32° to 120°F
CONTROL BOX WATER TIGHTNESS	Maximum leak rate — 0.1 ml/hr at 1 cu head (1 oz in place), flow meter connector capped and battery or power pack attached to 12VDC connector
COOLING CAPACITY (with 30 lbs ice in bottle section and 24 bottles full of DI water	After 24 hrs: 35°F below ambient After 48 hrs: 25°F below ambient
POWER REQUIREMENTS	Sampler: 12VDC Power Converter: 117VAC, 50/60 Hz 234VAC, 50/60 Hz (optional)
EXTERNAL NICAD BATTERY CAPACITY	150 full bottles typical after 10 hr charge
INTERNAL NICAD BATTERY CAPACITY	Maintains internal logic and timing circuits 30 hr minimum when fully charged

For each complete Model 2100 you MUST SPECIFY the basic unit, a power source, and a suction line with strainer.

THE BASIC UNIT	
Model 2100 Sampler with multiplexer and 24 — 150ml glass bottles	60-2100-005
Same except with 24 — 1000ml polypropylene bottles	60-2100-006
POWER SOURCES	
Nicad battery, without charger	60-1684-060
Lead Acid battery, with clamp, without charger	60-1684-062
AC power converter/battery charger, 117VAC, 50/60 Hz	60-1684-068
Same except 234VAC, 50/60 Hz	60-1684-061
SUCTION LINES AND STRAINERS	
1/4" I.D. x 22' vinyl suction line with weighted polypropylene hooked strainer	60-1194-014
1/8" I.D. x 20' vinyl suction line with weighted polypropylene hooked strainer	60-1684-015
1/8" I.D. x 10' Teflon® suction line, Neoprene® rubber protective coating, without strainer	60-1683-146
Same except 20' length	60-1683-144
Weighted strainer only, 3/8" all stainless steel	60-1684-110
Teflon® suction line flaring tool to allow insertion of above strainer	60-2101-093
ACCESSORIES AND OPTIONS	
Extra base with 24 — 150ml glass bottles and caps	60-2104-021
Extra base with 24 — 1000ml polypropylene bottles and caps	60-2104-016
Special Timing Sequence — Add up to four special timing sequences through the addition of a special jumper on the MODE switch. Customer must complete Model 2100 information sheet	60-2100-004
Liquid level sampler actuator	60-1644-080
2½ gallon polyethylene container with cap, for composite sampling in 24-bottle base	299-0013-04
2½ gallon glass container with cap, for composite sampling in 24-bottle base	291-0080-00
Cover for extra base (for either standard or composite base)	60-2104-061
Composite base only. Does not include container or locating insert listed separately below.	60-2104-046
3 gallon polyethylene container with cap, for use in composite base. Requires locating insert below	299-0013-02
3 gallon locating insert	60-1483-020
5 gallon polyethylene container with cap, for use in composite base. No locating insert required	299-0013-01
Sample bottles, 150ml glass with Teflon® lined caps, set of 24	60-2103-001
Sample Bottles, 1000ml polypropylene with Teflon® lined caps, set of 24	60-2103-007
Sample Bottles, 150ml glass without caps, case of 100	60-2100-002
Caps for 150ml glass with Teflon® liners, case of 100	60-2100-003
Sample Bottles, 1000ml polypropylene without caps, case of 100	60-2100-008
Caps for 1000 ml polypropylene bottles, case of 100	60-2103-010
Extra silicone rubber pump and distribution tubing (3' length)	60-2104-054
Extra silicone rubber pump and distribution tubing, bulk (3' length)	60-1680-061
Snap-on suspension harness	60-1194-014
Automotive battery cable	60-1194-023

*Dupont

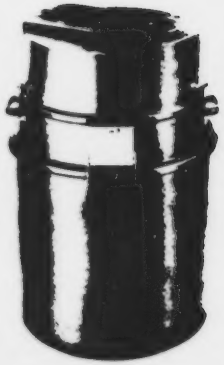
model 1580 composite sampler

The Model 1580 composite sampler pumps uniform, small sample increments into a single receptacle at programmed timed or flow-proportioned intervals. Although very economical, it has all of the ISCO features described on pages 1, 2, and 3. It adapts to battery or line power, and has an insulated ice compartment and automatic shutoff. The instrument is weatherproof with a single watertight, stainless steel housing for all electronic and mechanical components. Up to 40 gallons may be taken on an 18 hour charge of the optional Nicad or lead-acid battery.

Accurately calibrated switches allow precisely sized samples to be taken without involved computation. Sampling frequency can be continuously adjusted to any time from 2½ to 320 min, while the incremental volume can be varied from 40 to 600 ml. The intake line is purged before and after each increment to ensure that the sample is representative of the time at which it was taken, and to reduce cross-contamination. The Model 1580 composite sampler is available with either the standard or superspeed pumps.

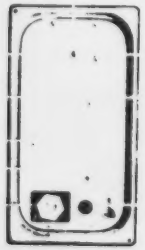
An optional ISCO flow meter enables the sampler to collect a composite based on the volume of passing fluid rather than on time. In the flow-proportioned mode, the uniform increments are taken at a frequency which is proportional to the flow rate of the stream. The Model 1580 can multiply, by a factor from 1 to 9, the volume that has been preselected on the flow meter.

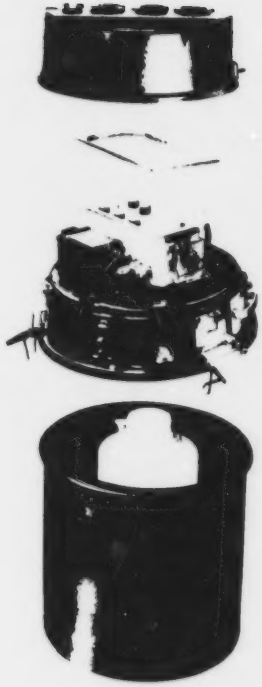
The sample is under pumped flow at all times: there is no gravity-fed internal tubing. Samples are collected in a three or five gallon high density polyethylene container or a 2½ gallon glass container. The container drops into the insulated base section without attaching any tubes or spouts, and has a mouth wide enough to insert an arm and brush for vigorous cleaning. An automatic, magnetically-coupled float shutoff terminates sampling when the container is full to prevent overflow if the sampler is not serviced on schedule. The base itself can be used for samples up to 10 gallons, and the controller section can be placed on a larger drum for special applications requiring unusually large samples.



Case sections, constructed of high impact plastic, snap apart to expose the entire unit for cleaning with a hose. The removable base section is constructed with thick foamed-in-place insulation, and can be iced to initially cool and keep a three gallon sample below 55°F for over 24 hours in 100°F environment. Stainless steel hasps allow padlocking to prevent tampering with the sample.

Diameter of the sampler is 19", height is 25½", and weight is 31 lb. See page 14 for sampler accessories.





For each complete Model 1580 you MUST SPECIFY the basic unit, a power source, suction line with strainer, and sample container.

THE BASIC UNIT

Model 1580 Sampler with standard pump	60-1684-015
Same, except superspeed pump	60-1684-017

POWER SOURCES

Nicad Battery, without charger	60-1684-040
Lead-Acid Battery, with charger, without charger	60-1684-062
AC power converter/battery charger. To power sampler from 117VAC, 50/60 Hz line power or to recharge batteries, for use with standard speed pump/sampler only	60-1684-046
Same as above, except for use with superspeed pump/sampler only	60-1684-060
Same as above, except for 234VAC, 50/60 Hz line power, and for use with both standard and superspeed pump/samplers	60-1684-061

SUCTION LINES AND STRAINERS

1/4" I.D. x 22' vinyl suction line with weighted polypropylene flutted strainer	60-1394-054
1/8" I.D. x 20' vinyl suction line with weighted polypropylene fluted strainer	60-1684-015
1/8" I.D. x 10' Teflon® suction line, Neoprene® rubber protective coating, without strainer	60-1684-146
Same, except 20' length	60-1684-144
Weighted strainer only, 1/8", all stainless steel	60-1684-110
Teflon® suction line flaring base to allow installation of above strainer	60-2101-094

SAMPLE CONTAINERS

1-Gallon polyethylene container with lid and polypropylene lid liner. Requires lex sling insert below	299-0011-032
1-Gallon bottle lex sling insert	60-1681-020
3-Gallon polyethylene container with lid and polypropylene lid liner. No lex sling insert required	299-0011-031
2½ Gallon glass container with lid and polypropylene lid liner. Requires lex sling insert below	291-0000-003
2½ Gallon bottle lex sling insert	60-1681-098
Teflon lid liner for 2½ Gallon bottle cap	60-1681-097

ACCESSORIES

Extra silicone rubber pump tube, 27½" long	60-1584-015
Extra silicone rubber pump tubes, bulk, 15' long	60-1640-061
Snap-on suspension harness	60-1394-014
Liquid level sampler actuator	60-1644-000
Automotive battery cable	60-1394-023

refrigerated samplers

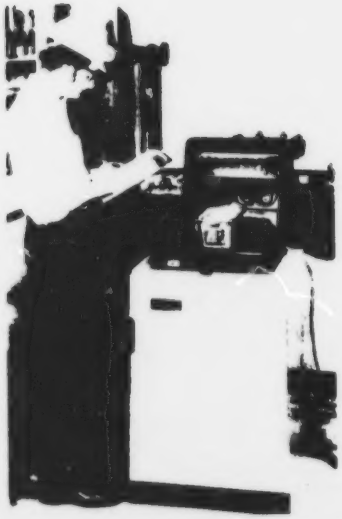
These three refrigerated samplers preserve biological specimens during and after collection. They are light and compact, and can be easily installed in any place affording reasonable protection from the elements. They are suitable for use whenever permanent installation is required. The controller/pump assemblies on two of these samplers are identical to, and interchangeable with, those of the Models 1680 and 1580 portable samplers. Information relating to sample collection will be found in the descriptions of these portable samplers. A refrigerated version of the Model 2100 is not available.

The Model 1580R refrigerated composite sampler can be supplied with a 3 or 5 gallon polyethylene container or a 2½ gallon glass container. These containers have a large mouth and are easily cleaned. When the container is filled to any predetermined level, a weight activated switch stops the sampling process and a red indicator light alerts the operator.

The Model 1680R uses the sequential controller and a slide-in 28 bottle rack. Ample room is provided for 32 additional loose bottles.

A third refrigerated sampler, the Model 1682R, takes eight samples of up to two liters each in either glass or polyethylene bottles. The standard controller includes a multiplexer so that eight identical composite samples may be taken with a different preservative in each bottle if desired. For other purposes, eight large sequential samples may be collected, with each sample being a composite of up to eight smaller increments. The Model 1682R has no portable equivalent. Controller specifications are basically the same as the Model 1680, but a Model 1680 controller cannot be converted to the eight bottle version.

Rigid foamed-in-place insulation stiffens the refrigerated compartment, and will not support bacterial growth or retain odors. Both the controller and sample compartment may be individually padlocked. The door utilizes a magnetic gasket for better sealing. Sample temperature can be selected from 32° to 46°F (0° to 8°C) with a calibrated control. A forced air condensing coil and front ventilation allow positioning the unit against a wall or in a corner without leaving clearance on the back or sides. Wraparound construction of the oversized evaporator coil provides quick and efficient cooling of the sample compartment. Defrosting is not required under normal operating conditions.



If it is desired to convert a presently owned portable sampler to a refrigerated unit, or to have both portable and refrigerated options on the same sampler, a refrigerator unit only may be ordered. These units are identical to the complete refrigerated samplers except the controllers (programmer and pump assemblies) are excluded. Changing a controller from the portable to the refrigerated version takes only a few minutes. Each refrigerated unit includes the sample container(s), suction line, and all standard accessories.

Height of the cabinet is 42½", width is 24¾", and depth is 25½". Net weight is 116 lb. Available for AC line power only.

A COMPLETE REFRIGERATED 1680R or 1682R SAMPLER CONSISTS OF:
1. THE BASIC UNIT
2. SUCTION LINE AND STRAINER

YOU MUST SPECIFY YOUR CHOICE OF THE ABOVE FROM 1 AND 2 BELOW:

1. THE BASIC UNIT

A. MODEL 1680R for 117VAC, 60HZ OPERATION

Catalog Number	Pump	Bottles	Multiplexer?
[illegible]	Standard	Polyethylene	Yes
[illegible]	Standard	Polyethylene	Yes
[illegible]	Standard	Glass	Yes
[illegible]	Standard	Glass	Yes
[illegible]	Super-speed	Polyethylene	Yes
[illegible]	Super-speed	Polyethylene	No
[illegible]	Super-speed	Glass	Yes
[illegible]	Super-speed	Glass	No

B. MODEL 1680R FOR 234VAC, 50HZ OPERATION

[illegible]	Standard	Polyethylene	Yes
[illegible]	Standard	Polyethylene	No
[illegible]	Standard	Glass	Yes
[illegible]	Standard	Glass	No
[illegible]	Super-speed	Polyethylene	Yes
[illegible]	Super-speed	Polyethylene	No
[illegible]	Super-speed	Glass	Yes
[illegible]	Super-speed	Glass	No

C. MODEL 1682R FOR 117VAC, 60HZ OPERATION

[illegible]	Standard	Polyethylene	Yes
[illegible]	Standard	Glass	Yes
[illegible]	Super-speed	Polyethylene	Yes
[illegible]	Super-speed	Glass	Yes

D. MODEL 1682R FOR 234VAC, 50HZ OPERATION

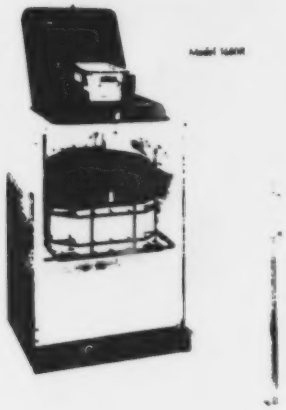
[illegible]	Standard	Polyethylene	Yes
[illegible]	Standard	Glass	Yes
[illegible]	Super-speed	Polyethylene	Yes
[illegible]	Super-speed	Glass	Yes

2. SUCTION LINES AND STRAINERS

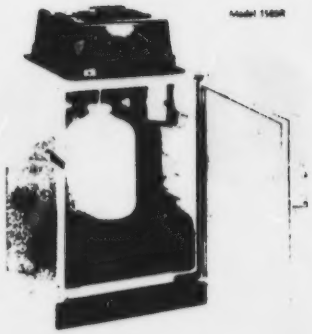
1/4" (ID) x 22' vinyl suction line with polypropylene heated inlet strainer, for use with standard-speed pump samplers only	[illegible]
1/8" (ID) x 20' vinyl suction line with polypropylene heated inlet strainer, for use with standard and super-speed pump samplers	[illegible]

ACCESSORIES FOR 1680R and 1682R

Extra 28 bottle rack for Model 1680R with polyethylene bottles	[illegible]
Extra 28 bottle rack for Model 1680R with glass bottles	[illegible]
For extra bottles only for the Model 1680R, see Page 6	
Extra 8 bottle rack for Model 1682R with polyethylene bottles	[illegible]
Extra 8 bottle rack for Model 1682R with glass bottles	[illegible]
Polyethylene bottles only for Model 1682R, set of 8 with caps	[illegible]
Glass bottles only for Model 1682R, set of 8 with caps	[illegible]
Teflon lid liners for 2 liter glass bottles	[illegible]
Extra silicone rubber pump tube for either Model 1680R or 1682R 17"	[illegible]
Extra silicone rubber pump tubing, bulk, 15' long	[illegible]



Model 1680R



Model 1580R

A COMPLETE MODEL 1580R REFRIGERATED SAMPLER CONSISTS OF
1. THE BASIC UNIT
2. A SAMPLE CONTAINER
3. A SUCTION LINE WITH STRAINER

YOU MUST SPECIFY YOUR CHOICE OF THE ABOVE FROM 1, 2, AND 3 BELOW:

1. THE BASIC UNIT

Catalog Number	Pump	Power Source
[illegible]	Standard	[illegible]
[illegible]	Super-speed	[illegible]
[illegible]	Standard	[illegible]
[illegible]	Super-speed	[illegible]

2. SAMPLE CONTAINERS

3 Gallon polyethylene container with lid and polypropylene lid liner	[illegible]
5 Gallon polyethylene container with lid and polypropylene lid liner	[illegible]
2½ Gallon glass container with lid and pump-type lid liner	[illegible]
Teflon lid liner for 2½ Gallon bottle only	[illegible]

3. SUCTION LINES AND STRAINERS

1/4" (ID) x 22' vinyl suction line with optional pump-protect heated strainer	[illegible]
1/8" (ID) x 20' vinyl suction line with optional pump-protect heated strainer	[illegible]
1/8" (ID) x [illegible] Teflon® suction line, "Neoprene®" rubber pump-tube coupling, without strainer	[illegible]
Same except 20' length	[illegible]
Weighted strainer only, 1/8" (ID) x [illegible]	[illegible]
Teflon® suction line, strainer tube, 1/8" (ID) x [illegible]	[illegible]

PUMP TUBING

[illegible]	[illegible]
[illegible]	[illegible]

REFRIGERATORS ONLY: COMPLETE EXCEPT FOR CONTROLLERS

Model [illegible] for use with Model [illegible]	[illegible]
[illegible]	[illegible]
Model [illegible] for use with Model [illegible]	[illegible]
[illegible]	[illegible]

accessories for ISCO samplers

BATTERIES. Nicad batteries have a self-discharge rate of one to two percent per day and are better suited than lead-acid or "GEL" batteries for applications where frequent recharging is necessary. Nicad batteries are compact, dry, have an extremely high recharge cycle life, can be left in a run-down condition indefinitely, are freeze proof and can't be overcharged when an ISCO charger is used. A short cord with a water proof connector provides quick and convenient installation.

The ISCO lead-acid battery is less expensive, sealed, and spill proof. It is not a motorcycle-type battery and never requires additional water. A porous filling between the plates greatly reduces the likelihood of freezing if uncharged. It has a water-proof connecting cord and requires a special clamp for mounting. Since the lead-acid battery has a much smaller self-discharge rate, it is better suited for applications where an installation may remain in a dormant condition for a long period of time before being actuated by the Model 1640 Liquid Level Actuator.

Both the ISCO Nicad and lead-acid batteries have a four amp-hour capacity. Battery life specifications are given elsewhere in this brochure. For those who desire to use an automotive battery, a connect cable is available.

Nicad battery. Without charger	60-1684-040
Lead acid battery, with clamp. Without charger	60-1684-062
Automotive battery cable	60-1394-023

AC POWER CONVERTER/BATTERY CHARGER. To power sampler from 117VAC 50/60Hz line power or to recharge battery for use with standard speed pump samplers only. 60-1684-046

Same as above except for use with super-speed pump samplers. 60-1684-080

Same as above except for 214VAC 50/60Hz line power and for use with both standard and super-speed pump samplers. 60-1684-081

SUSPENSION HARNESS. A snap-on, all stainless steel harness allows fast manhole installation by suspension from a rung or other projection.

Suspension harness for samplers 60-1394-014

SUCTION LINES. Each suction line has a weighted, streamlined strainer to prevent debris from entering the sampler. ISCO lines are specially extruded from clear vinyl, free of phenolic compounds, or teflon.

Vinyl tubing is available in bulk quantities for occasions when replacing the line is easier than cleaning it. Line replacement between surveys also assures no possible cross-contamination which can complicate legal proceedings. Bulk line is sold without the strainer.

1/4" I.D. x 22' suction line with polypropylene strainer	60-1394-054
3/8" I.D. x 20' suction line with polypropylene strainer	60-1684-015
1/8" I.D. x 10' Teflon® suction line "Hypodermic" rubber coupling, without strainer	60-1681-146
Same except 20' length	60-1681-148
Weighted strainer only, 1/4" polypropylene body	60-1394-070
Weighted strainer only, 3/8" polypropylene body	60-1394-071
Weighted strainer, 3/8" all stainless steel	60-1684-110
Fishing tool to allow mounting above strainer on Teflon® tubing	60-2101-093
Bulk 1/4" I.D. vinyl tubing only, 100'	60-1680-055
Same, 500'	60-1680-056
Same, 1000'	60-1680-057
Bulk 3/8" I.D. vinyl tubing only, 100'	60-1680-058
Same, 500'	60-1680-059

LIQUID LEVEL SAMPLER ACTUATOR. This unit causes a dormant sampler to begin operation when the liquid level in a stream rises to some predetermined height. It consists of a small controller which attaches inside the sampler cover, and a 22' cable ending in a rainproof detector. This detector can be staked at any level in the stream bed and will initiate a preprogrammed sampling sequence when the stream rises to this height. A switch can be set to terminate sampling when the stream lowers below the detector, or to continue to run out the program. It cannot be used at the same time as the flow meter without special modification. Contact the factory for details on these applications.

Liquid level sampler actuator 60-1644-080

Liquid level sampler actuator

flow proportional sampling

All ISCO samplers are designed to collect samples on a timed basis or proportional to flow using input signals from an external flow meter. Electronically, ISCO samplers require a 12 VDC input pulse or an isolated contact closure of at least 25 milliseconds duration to cause a sample to be taken and/or to register a flow pulse.

Connection of an ISCO sampler to an ISCO flow meter is easily made with finished connect cables supplied with the flow meter or purchased separately in the case of the Model 1870. ISCO flow meters can then be programmed to send a pulse to the sampler for every 10, 100, or 1000 increments of flow. ISCO samplers Model 1680 and 2100 can then be programmed to multiply these signals from 1 to 999 times to give a wide range of sampling frequency. The Model 1580 can be programmed to multiply input signals from 1 to 9 times.

Certain non-ISCO flow meters that have an isolated contact closure of at least 25 milliseconds duration can be directly interfaced with ISCO samplers. This is accomplished by using either the connector without cable or the connector with 22' cable listed below. The connector or connector with 22' of cable is attached to the FLOW METER socket on the ISCO sampler control unit. The connector with 22' of cable ends in bare wires which must be connected to the non-ISCO flow meter by using the appropriate connector and clamp which should be available from the flow meter manufacturer, or the cable can be hard wired into the flow meter.

Non-ISCO flow meters that do not produce an isolated contact closure will require a special interface device to convert the output signal to a contact closure. Output signals from these flow meters are generally either a pulse duration proportional to flow, a pulse rate proportional to flow, or more commonly a current signal (e.g. 4-20ma) proportional to flow. Current signals may either be proportional to flow or proportional to the flow squared. In order to pace an ISCO sampler proportional to flow from one of these flow meters, a special interface device must be used.

All ISCO interface devices are custom designed for each application and therefore, a data sheet (Isco Form #526a) must be completed and returned with the order. These data sheets are available from ISCO or from an ISCO representative. Because these interface devices are custom built, please allow up to 6 weeks for delivery. All interface devices are supplied with a 6-ft. cable and appropriate connector for attachment to the ISCO sampler. Each unit is also supplied with a 3-ft. cable with one end bare for connection to the non-ISCO flow meter. Longer cables may be specified at extra cost. The interface closure is NEMA Type 4.

ISCO interface devices Types A and B get their power from the ISCO sampler. Interface device Type C can get its power from a 117 VAC power source or from the ISCO sampler. If 117 VAC power is desired, a regular 3-prong grounded socket must be available nearby. If it is desired to power the interface from the sampler, then a different Type C interface is required. The sampler may be powered from 117 VAC or 12 VDC.

If it is desired to pace more than one sampler from one interface device, additional outputs can be ordered on the interface at $25.00 each.

Connector only, without cable, for use with non-ISCO flow meters having an isolated contact closure proportional to flow	60-1683-080
Same with 22' cable terminating in bare wires	60-1394-077
Interface Device Type A (converts pulse duration flow meter output proportional to flow to pulse output occurring at settable flow intervals)	60-1784-007
Interface Device Type B (converts direct flow meter contact closure or pulse rate proportional to flow to pulse output occurring at settable flow intervals)	60-1784-026
Interface Device Type C (for 117VAC operation. Converts current signal proportional to flow (4-20ma) to 30 Volts, 50 ms pulse output occurring at settable flow intervals)	60-1784-011
Interface Device Type C, powered by sampler	60-1784-003
Interface device Type C (for 117 VAC operation. Converts current signal proportional to flow squared	60-1784-020

Chapter 61

ANALYTICAL ADVANCES AND PROCESS CONTROLS

INTRODUCTION

Environmental protection regulations requiring ever decreasing metal concentrations create the need for reliable and improved analytical techniques. Mine and mineral processing environments are often remote, and there are needs for simple, and where possible, less expensive rapid techniques for these analyses. These analyses are needed for reporting purposes, to prove that the operation is operating within the law, and to provide some warning that contaminant levels are approaching regulated limits in time to implement corrective measures.

In this respect, it is equally important that the sample be taken in a reproducible manner, and that it is representative. Further, it should be handled in such a way between drawing of the sample and the actual analysis that no misleading changes take place.

A second equally important use of analytical techniques is to control reagent additions in metallurgical processes and in effluent treatment systems. Sometimes the reagent used to remove a toxic contaminant may itself be toxic--for example, chlorine addition for cyanide destruction, or Na_2S addition for hexavalent chromium removal or to polish solutions after heavy metal removal.

By monitoring metallurgical processes, reagent additions can be controlled continuously to cater to changes in ore quality. Not only will this help reduce reagent costs and improve metallurgical efficiency, but the cost of removing excess reagents can be kept to a minimum.

During this investigation, important progress was observed in Canada in the development of almost completely automated water treatment plants. This requires reliable means of controlling such processes by using microprocessors.

This chapter mentions just a few of the useful items of analytical technique and process control that were encountered. No deliberate survey of the field was carried out, and no effort was made to make a complete survey.

CYANIDE ANALYSIS

Cyanide analysis techniques are discussed in Chapter 40 on Cyanide. Of particular importance are the following developments.

- "Free" Cyanide Analysis

  The ASTM "free" cyanide titration method does not quantitatively determine all free cyanide of environmental consequence such as copper and nickel cyanides.

  The method has been improved by E. I duPont de Nemours & Co. by adding a small aliquot of zinc dust which liberates cyanide from both copper and zinc cyanide complexes which then makes these cyanides quantitatively measurable by titration.

  The titration is precise down to around 1 ppm "free" CN. Iron cyanide is not measured by the technique.

  The method is being further developed and tested to find out if it is applicable to the potentiometric titration, specific ion electrode, and Hachmeter rapid colorimetric field method which should have a detection limit around 0.1 ppm.

  Addotopma; cuamode ,pmotpromg ,etjpds were discussed at a conference on "Cyanide and the Environment" held at the University of Arizona in Tucson in December, 1984.

  More information on the "Cyanide Conference" is available from:

  DIRK VAN ZYL
  1512 Patton Street
  Fort Collins, CO 80524
  (303) 221-1476

  CIVIL ENGINEERING DEPARTMENT
  Colorado State University
  Fort Collins, CO 80524
  (303) 491-6081

  The new analytical method can be discussed with:

  E. I. duPONT de NEMOURS & CO., INC.
  Chemicals Dyes and Pigments Dept.
  Technical Service Laboratory
  Chestnut Run
  Wilmington, DE 19898
  (302) 999-4414
  Fred W. DeVries
  O. Mathre

- Cyanide Indicator

An indicator for the silver nitrate titration of "free" cyanide that provides a clearer endpoint than the normally used KI is 2-5 drops of an 0.03% acetone solution of 5-[p (Dimethylamine)-benzylidene]-rhodanine. CAS No. 536-14-4, Eastman Kodak No. 2648.

This indicator is finding increasing acceptance, and more information is available from:

KAPPES-CASSIDY & ASSOCIATES
Post Office Box 13687
Reno, NV 89507
(702) 356-7107
Daniel W. Kappes

- Continuous Cyanide Monitor

Gold Fields of South Africa, Ltd.: An automatic method for drawing samples of solutions from pulps and analyzing cyanide photometrically has been developed by Gold Fields of South Africa, Ltd. The patented system will ultimately possibly become available to other companies. The application for which the units have been developed is to control cyanide addition to leaching pachucas on a continuous basis to make cyanide additions much more precise. More information will in due course be available from:

GOLD FIELDS MINING & DEVELOPMENT, LTD.
Post Office Box 82582
Southdale 2135
South Africa
(011) 680-3466
G. W. Robartes
Chief Analyst

Witteck Development Inc.: A second ingenious continuous cyanide monitoring device is under development by:

WITTECK DEVELOPMENT, INC.
2640 South Sheridan Way
Mississauga, Ontario
Canada L5J 2M4
(416) 823-7381
Telex: 06:982328
Mrs. Peggy Witte

The device uses a programable microprocessor-controller designed and developed by Octant Computers Ltd. of which LAC MINERALS LTD. is a part owner and is in an advanced stage of development, although not yet on the market. Apparently, the device

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
CHEMICALS AND PIGMENTS DEPARTMENT
TECHNICAL SERVICES LABORATORY
CHESTNUT RUN
WILMINGTON, DELAWARE 19898

October 12, 1984

Dr. Hans von Michaelis
Randol International, LTD.
21578 Mountsfield Drive
Golden, CO 80401

MODIFIED FREE CYANIDE METHOD

Dear Hans:

As we discussed, here is the method we have recently released to cover weak-acid-dissociable cyanides. Proving the zinc cementation concept using the Hach Kit is in progress. If all goes well, Owen Mathre will report on this at Tucson.

Best regards,

F. W. DeVries

FWD:pag
Encls.

TECHNICAL INFORMATION

MODIFIED FREE* CYANIDE - FIELD TEST
TITRATION METHOD WITHOUT DISTILLATION

Principle

Gold and silver milling process streams generally contain complex iron cyanides, free sodium cyanide and a number of metal complexes that contain cyanide that is measured as weak acid dissociable (WAD) cyanide by generally accepted methodology. The cyanide is released from the WAD complexes by reaction with zinc dust in the presence of ammonia and sodium hydroxide. Sulfide, a common interference in determination of cyanide in mine process solutions and wastewater, is removed by reaction with lead carbonate to form lead sulfide which is filtered before the zinc treatment is started. There is also some evidence that some of the thiocyanate may be removed with the sulfide.

The released cyanide is finally measured by titration with silver nitrate.

[illegible]

Safety

1. Lead carbonate should be handled according to practices required for protection from acceptable exposure to the dust.

2. Zinc dust wet with alkaline solutions may be pyrophoric. Avoid letting air pass through the filter until it has been washed with water. Do not discard alkaline filter cake in containers or locations that contain combustible materials.

Apparatus

1. Buret, micrometer syringe type. The Hach Chemical digital titrator with standard solution supplied in plastic syringe cartridges has been used. The Gilmont digital pipet, "Teflon" piston, 2-mL size with a buret tip, has also been used with conventional standard 0.0200 N and 0.100 N silver nitrate solution.

2. Filter paper. Fast filtering paper is generally preferred. Medium speed filter paper should also be available if the fast filter paper does not remove all of the solids in the sulfide filtration.

3. Magnetic stirrer. These units are available from a laboratory supply house and may be powered with a battery powered tire pump. They will also run with ordinary laboratory air or water supplies.

4. Standard laboratory glassware. Graduated cylinder and pipets to measure samples, Erlenmeyer flasks or bottles to do the reactions and titrations in and a filter system (gravity or syringe operated pressure) for separation of solids (both lead sulfide and zinc are needed).

*Modified ~~free~~ cyanides include what are generally called "free cyanides" and "weak acid dissociable cyanides".

Reagents

1. Ammonia, ACS reagent.

2. Indicator, Deniges. Dissolve 10.0 g potassium iodide in 100-mL reagent ammonia solution. Use 2.0 mL for each 100 mL of solution to be titrated.

3. Lead carbonate, ACS reagent. It has been found that a 10% w/v solution of lead acetate can be used if the sulfide content is not too high. This reduces the possible exposure to dusts of lead salts during analysis. However, the excess reagent must be controlled more carefully.

4. Potassium iodide, ACS reagent. This is needed to make up the indicator solution.

5. Sodium hydroxide, 5 M. Dissolve 200 g sodium hydroxide in about 500 mL water. Dilute to one liter. Store in a plastic bottle.

6. Standard silver nitrate, 0.100 N and 0.0200 N. Prepare with dilute solution by diluting 20.0 mL of 0.100 N solution to 100 mL with deionized water.

   Alternately, the silver nitrate solution may be purchased in cartridges for the Hach digital titrator and used as supplied.

7. Zinc, dust. ACS reagent has been satisfactory. Granular zinc reacts too slowly and does not generally have enough surface area to be satisfactory for this procedure.

Procedure

Sample Preparation

1. Measure 50 mL solution into the reaction bottle or flask.

   If the sample is expected to contain less than 5 mg WAD cyanide/L, use 100 mL.

   If the sample is expected to contain more than 200 mg WAD cyanide/L, then use 10 mL of sample and add 15 mL deionized water to the reaction bottle.

2. Add about 0.1 g of lead carbonate to the sample and swirl vigorously to react the sulfide with the lead. If the black lead sulfide forms, then add 1 g more and swirl vigorously to react the sulfide. Filter through medium filter paper into another reaction bottle. Wash the filter with about 10 mL of water. This should have removed the sulfide. If there is doubt about it, then the procedure should be repeated.

   If it is known that there is no sulfide in the sample, then this step may be omitted.

3. Add 10 mL ammonia and 3 g zinc dust. Then add quickly 10 mL of 5 M sodium hydroxide.

4. Mix vigorously for 15 minutes. A mechanical stirrer is very helpful for this step. An air powered magnetic stirrer can be used with air, water or a compressed-like carbon dioxide in field use if they can be made available.

5. Filter the solution through a rapid filter paper into a titration bottle or flask. As soon as the solution is through the filter, wash the filter with 50 mL of deionized water.

   NOTE: Remove the filter from the funnel and put into a vented jar containing enough water to cover the filter paper. This will eliminate the chance of spontaneous combustion of the zinc dust.

Titration

6. Add 3 mL (4 mL if 100-mL sample was taken) indicator solution to the titration bottle.

7. Titrate the solution with the standard silver nitrate (0.0200 N) to the first cloud point. If the WAD cyanide content is expected to be above 40 mg/L, then use 0.100 N silver nitrate for the titration.

   The cloud point should be just "off white" in shade and should not be dark. If it is dark brown or black, it is quite likely that the sulfide was not removed completely. The analysis should be repeated. Test the solution after the lead carbonate treatment with lead acetate paper or with a bit of lead carbonate to determine if the sulfide removal is complete.

Calculation

8. CN, mg/L = mL $AgNO_3$ x N x 52/mL sample taken x 0.001

   NaCN, mg/L = mL $AgNO_3$ x N x 98/mL sample taken x 0.001

   NOTE: If the Hach digital titrator is used, then the cartridge will probably have the factor on it or it will be in the formation supplied by the vendor.

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0381L

measures differences in conductivity of a silver wire as cyanide reacts with the surface. Ways had to be developed to master interferences by sulfide and copper.

- X-Ray Fluorescence

A miniaturized portable X-ray fluorescence analyzer has recently become available which analyzes over 60 elements semiquantitatively.

By using two radioactive sources and a computer to wash out background effects, the instrument is claimed (by the makers) to be able to achieve much lower detection limits and to avoid interferences. It is claimed to be suitable for water analysis, detecting sources of metal contamination in the field and for continuous monitoring of effluents. Detection of some elements down to 10 ppb is claimed.

The unit is very lightweight, portable, and rugged.

Since it is new and since so many previous portable XRF units did not perform usefully, it is necessary to be skeptical. At the same time, this device has new features which claim to have solved many problems.

RANDOL INTERNATIONAL LTD. would be most interested to hear from anyone who is able to test this device to determine its applicability. Information on the ATX100 portable X-ray fluorescence spectrometor is available from:

AURORA TECH, INC.
620 West Center Street
Building 1
North Salt Lake, UT 84054
(801) 295-8145
Ronald E. Horrocks
President
Brent Merrill
Director of Marketing

ARSENIC

Arsenic is said to be very difficult to analyze accurately at low levels. According to GIANT YELLOWKNIFE MINES LTD., the silver di-ethyl carbamate method of AWWA Standard Methods works well down to 1 ppb and can detect as little as 1 microgram arsenic.

Description of Method

Inorganic arsenic plus zinc dust are reacted in a Gutzeit generator in an acid solution, and the gases passed through a scrubber with lead acetate impregnated glass wool to an absorber tube with silver di-ethyl carbamate dissolved in pyridene or chloroform.

As (Inorganic) + Zn + Acid = $AsH_3\uparrow$

Sulfides + Acid = H_2S + Pb Acetate $\rightarrow$ PbS

INTERFERENCES

Cr, Co, Cu, Hg, Mo, Pt, and Ag interfere with the generation of arsenic--but not in the quantities usually present in water. Antimony salts form stibnine which interferes by forming a red color with maximum absorbance at 510 nm.

Complete details are available from:

AMERICAN PUBLIC HEALTH ASSOCIATION
AMERICAN WATER WORKS ASSOCIATION

"Standard Methods for the Examination of Water and Wastewater," 15th Edition, Washington, DC.

CADMIUM

Evaluation of data for cadmium analyses prior to the mid-1970's seems to show a detection limit around 0.003 ppm - 0.01 ppm Cd. After 1975, AA as been able to detect cadmium down to -.001 ppm reliably with precision using the deuterium arc correction. The technique is essential to avoid misleading high readings by AA. Deunterium arc correction is available for most of the better AA units on the market today.

GOLD ANALYSIS

An AA technique is available which is capable of analyzing gold down to 0.01 ppm in solution without pre-concentration using a direct coupled plasma device. Such a device is now in routine use by, among other companies, WITTECK DEVELOPMENT, INC.

The units supplied by SPECTRAMETRICS, INC. (Beckman ?) sell for C$65,000 each. Photographs of the Spectrum are made as a permanent record.

MERCURY ANALYSIS

Solutions: The Jerome Model 511 gold film mercury analyzer is calimed to be able to measure mercury in solutions down to 1 ppb. The unit costs $3,950 and is in use at ST. JOE MINERALS, Monaca, Pennsylvania, CARLIN Gold Mine, and GETTY Mercur, Utah.

Air Samples: The Jerome Model 411 gold film mercury vapor analyzer measures gold in air down to 0.001 mg/m^3 up to 1.999 mg/m^3. It costs $3,750 for the basic instrument.

The Jerome mercury analyzers are available from:

JEROME INSTRUMENT CORP.
Post Office Box 336
Highway 89A
Jerome, AZ 86331
(800) 952-2566
(602) 634-4263
Telex§; 165-973

AUTOMATIC MICROPROCESSOR PLANT CONTROLS

As mentioned above, automated process control requires microprocessor control units. These were successfully installed at NORANDA's Geco Mine to control a high density sludge plant treating acid mine drainage. The individual who has mastered the design and programming of solid state controllers for that plant is:

WALTER LAWRENCE
Noranda Mines Ltd.
Geco Divison
Manitouwadge Lake, Ontario
(807) 826-3211

Another similar system has been installed at an automated HDS plant at the Waite-Amulte site:

NORANDA MINES LTD.
Horne Division
Noranda, Quebec J9X 5B6
(819) 762-7764
Bernard W. Brooks

LAC MINERALS OCTANT COMPUTERS LTD. MICROPORCESSOR CONTROL

The microprocessor control unit developed by OCTANT COMPUTERS LTD., a subsidiary of LAC MINERALS, has proven to be robust and reliable in several heavy duty asphalt plants in Canada.

The unit is being developed for application on continuous gold sampling and analyzing as well as for continuous cyanide monitoring by WITTECK DEVELOPMENT, INC. on behalf of the Canadian government and LAC MINERALS.

More details would be available from WITTECK DEVELOPMENT, INC. or:

LAC MINERALS LTD.
2105 North Tower
Post Office Box 156
Royal Bank Plaza
Toronto, Ontario
Canada M5J 2J4
(416) 865-0722
E. J. Wade
Vice President Engineering
and Administration

OMRON SYSMAC PRO 16 PROGRAMMING CONSOLE

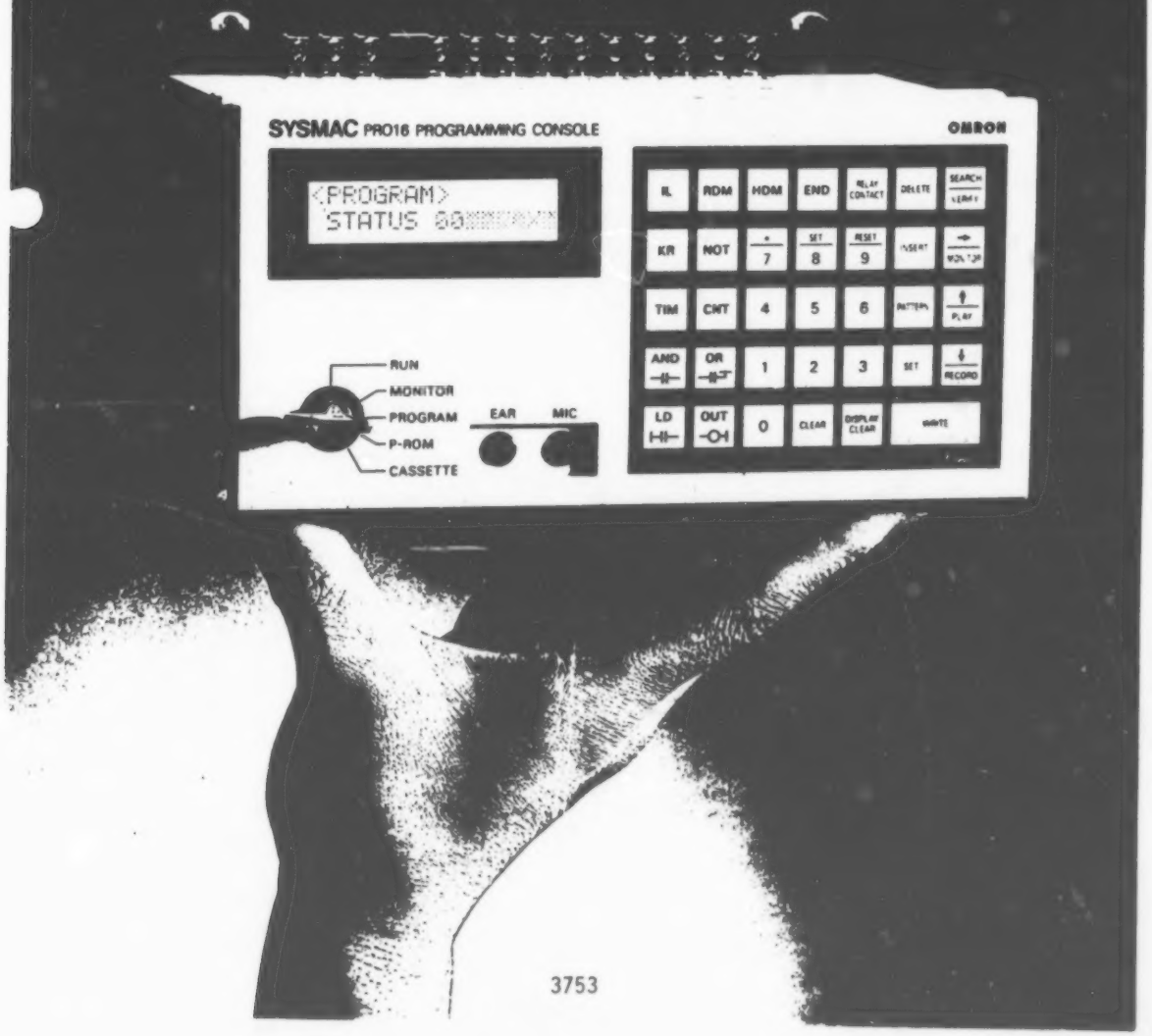
An extremely compact programable controller, OMRON, is available from:

YELLAND ENGINEERING (PTY) LTD.
Post Office Box 10993
Johannesburg 2000
(011) 833-2150
Telex: 8-4067
Guy Tribelhorn

OMRON ELECTRONICS, INC.
650 Woodfield
Schaumberg, IL 60195
(312) 843-7900
Telex: 910-291-2494

OMRON ELECTRONICS HK LTD.
No. 34 Hung To Road
Gee Lok Industrail Building
3rd Floor
Kwun Tong
Kowloon
Hong Kong
Telephone: 3-444210, 3-444219
Telex: 3021 41092 (Omron HX)

HOW MUCH CAN YOU EXPECT FROM A PROGRAMMABLE CONTROLLER THIS SMALL?



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WITH OMRON SYSMAC-S6

WITH FACTORY AUTOMATION SEIZING THE IMAGINATION OF THE INDUSTRIAL WORLD, demand is growing for programmable controllers (PCs). Controllers which must be compact and multifunction as well as economical and easy to use. For applications like controlling industrial machines or small assembly machines for today's flexible manufacturing systems.

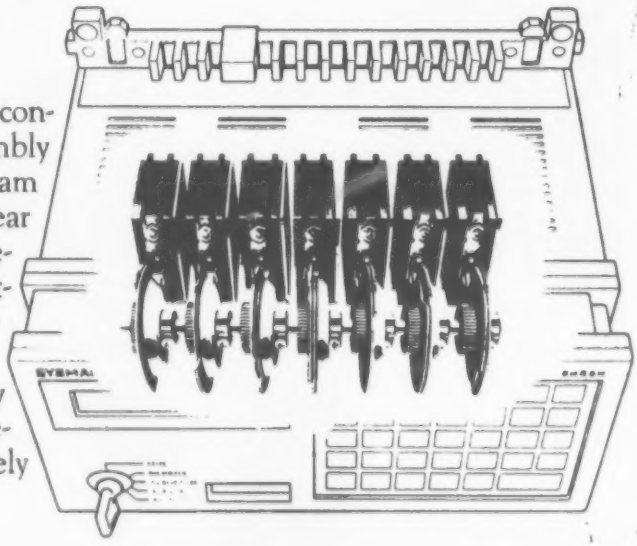
To meet such demand, Omron has developed the Sysmac-S6, a new-age PC which can be built into the machine it controls.

1 NO MORE THAN YOU NEED.

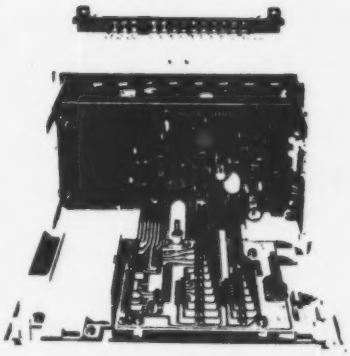
The compact Sysmac-S6 is a fully modular system. This means you can design a configuration that's no bigger than the optimum size for your application. So you get the performance you need at minimum cost, in the smallest space.

2 NO MORE WORN-OUT CAM SEQUENCERS.

Conventional job-step timing control of machine tools or small assembly machines is done mechanically by cam sequencers. And cam sequencers wear out fast. Now, the Sysmac-S6 has replaced mechanical control with software control, using its 32-output-position high speed and reversible counter instructions. Result: vastly improved reliability, drastically reduced operating costs and extremely sophisticated control.



THIS IS HOW MUCH YOU GET.

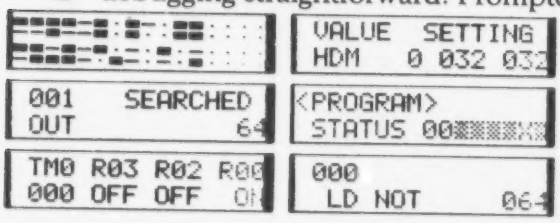


3 NO MORE RELIABILITY WORRIES.

The all-solid-state Sysmac-S6 is built rugged so it works dependably under any kind of punishment industry can dish out. Vibration, extreme temperatures, dust and electrical noise do not bother this tough little PC—or any of its modules. Such high reliability means virtually no down-time.

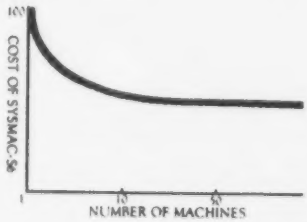
4 NO MORE PROGRAMMING HEADACHES.

The console's liquid crystal display (LCD) makes interactive programming and debugging straightforward. Prompted by messages, operators input information via easy-to-understand symbol keys, so no special training is necessary. Which makes even tricky control change-overs fast and fault-free, opening the way to new highs in ladder-diagram program development.



5 NO MORE UNNECESSARY DUPLICATION WORK.

For mass production applications, with just one removable programming console and PROM writer, you can copy your debugged program into as many PROM memory units as you need. Plug a PROM into each CPU, hook up the required I/O units (if any), and what you have is an innovative solution to unit cost problems.



6 NO MORE EXPENSIVE DOWNTIME.

When a fault occurs, swift detection is of vital importance. The Sysmac-S6's comprehensive self-diagnostics cover the programming console's LCD section, key-board and mode selector, and the CPU's various indicators. You can quickly pinpoint what's causing the trouble.

SMART I™

IMPROVED SAFETY, INCREASED PRODUCTIVITY. TOTAL CONTROL OVER THE MINING ENVIRONMENT.

Effective management of the mining environment is essential to profitability. That's why P&MT designed the SMART I system.

SMART I can manage a network of over 3,000 sensors and over 1,000 controlled responses, with split-second accuracy. It continuously monitors every aspect of the mining operation: belt functions, flow rates, bearing temperatures, the presence of toxic gases, etc. Then, it automatically responds to changes in that environment by activating or deactivating pumps, power centers, ventilating fans, and so forth, as needed.

The SMART I Central Monitoring Station is easy to operate and communicates in plain English. It features a powerful microcomputer with over 2 million bytes of information storage, a high-speed printer, and a full-color monitor that shows sensor status along with an exact-scale layout of the mine site. (There is even a 100:1 Zoom feature for a closer look.) And, all SMART I communication is completely self-checked with every data transmission.

The SMART I Remote Sensing Station has 24 sensor inputs, 8 controlled outputs, and a powerful warning horn and light that sounds an alarm whenever a sensor threshold is crossed. With a SMART I Magic Touch Hidden Switch, sensors can even be placed up to 7,000 feet away. During power-outs, it remains fully operational for up to three days, and stores data in memory for as long as thirty days. Housed in a rugged NEMA 12 enclosure, with rubber-sealed packing glands for protection against dirt and moisture, it will withstand the most severe environments. And, like all other SMART I components, it undergoes a Total System Checkout before being backed by P&MT's comprehensive onsite service and parts replacement warranty.

SMART I is easy to operate. It can monitor and control the entire mining environment. And it can operate manually, or automatically according to any control schedule you prefer. A SMART I system is probably the most cost-effective investment your mine could make this year.

For more information about the SMART I system and how it can improve your operation, call your mining, and most important, safety. Call or write today.

P&MT

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SPECIFICATIONS

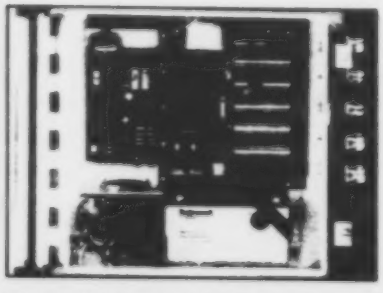
SMART I™ Central Monitoring Station

Microcomputer:	128K microcomputer with 2.4 Mb storage; RS-232C interface to FSK modem.
Printer:	High-speed dot matrix printer with 64K in-line buffer. Wide-carriage option.
Monitor:	14" high-resolution RGB color CRT.
Modem:	FSK at 4800 Baud; Automatic Gain Control; 30 mile range.
Data Transmission:	Uses 2- or 3-conductor twisted pair or, RG-59 coaxial cable.
Power:	120 VAC. Uninterruptable Power Supply available.

The SMART I Central Monitoring Station's high-speed printer prints screen displays and other documents while leaving the computer free to perform its remote sensing and control functions.

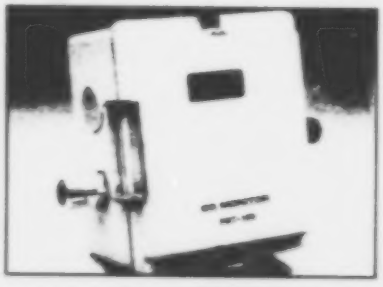
SMART I™ Remote Sensing Station

Intelligence:	4K RAM/4K ROM microprocessor (expandable to 64K); 8 analog and 16 digital inputs; 8 digital outputs.
Modem:	FSK at 4800 Baud; Automatic Gain Control; 30 mile range.
Enclosure:	NEMA-12 steel enclosure with entrance glands. Size: 20" x 20" x 8".
Data Transmission:	Uses either 2- or 3-conductor twisted pair or, RG-59 coaxial cable.
Power:	110 VAC via Hubbell connector; 24 amp/hour backup battery built-in.
Analog Input Range:	- 5 to + 5 VDC, without reference. Can be modified to accept other ranges.
Indicator Lamps:	AC power, DC power, Communication Input.



The SMART I Remote Sensing Station can store data in memory for up to thirty days and remain fully operational for up to three days during power outages.

SMART I™ Monitor With Magic Touch™ Module



The SMART I Status Monitoring And Remote Telemetry network is designed to interface with a wide variety of sensors, such as the SMART I CO Monitor with Magic Touch module. The Magic Touch module is an intelligent, stand-alone transmitter that can interface with the SMART I Remote Sensing Station by adding 8 sensor inputs (either analog, digital, or a combination of both) and extend its monitoring capabilities by up to 2,000 feet per channel. The Magic Touch option can be used with a variety of sensors, and is powered by a 3-wire connection directly from the SMART I Remote Sensing Station. Call P&MT for more information on availability (pending agency approval).

P&MT

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CHAPTER 62

IMPORTANT RESEARCH AND DEVELOPMENT FRONTIERS

There are so many directions in water management and treatment technology that need additional research and development that it is clear that the resources are not available to address them all at once. Available R&D resources should first be channeled to the most important problems. Since several problems are common to much of the industry, or at least to groups of companies on a regional basis, it is appropriate that some of the needed research is being conducted as a joint effort.

TAILINGS DISPOSAL AND ACID MINE DRAINAGE

Acid drainage from tailings containing sulfides is by far the most serious root cause of pollution. Several groups have been organized to study fundamental aspects of the problem and to seek better ways of treating or disposing of tailings to avoid long-term problems that the mineral processing and mining industry face.

In Canada, an industry group has been formed to conduct joint research into tailings disposal methods under the auspices of the Canadian Mining Association. It is believed that COMINCO, INCO, KIDD CREEK MINES, NORANDA, and FALCONBRIDGE are members of this group, and more information could be requested through:

JOHN K. WEGLO
Director, Environmental Control
Falconbridge Ltd.
Falconbridge, Ontario
Canada P0M 1S0
(705) 693-2761

Particularly farsighted research into sulfide-bearing tailings disposal from uranium as well as base metal recovery operations has been carried out by CANMET in Ottawa and at a research station at Elliot Lake. Their work aims to understand some of the fundamental processes that take place in tailings materials under different conditions. It is important to examine the root causes of acid mine drainage as well as methods to treat the symptoms of this problem. Having made such a good start, it is hoped that CANMET will continue this work funded by the Canadian government in their national interest:

CANMET
555 Booth Street
Ottawa, Ontario
Canada K1A 0G1
(613) 995-4124

The Chamber of Mines of South Africa is an industry-funded group conducting research into methods of tailings stabilization. Their interest has been mainly directed at inhibition of erosion and dust control. If and when current investigations reveal that tailings and wasterock disposal areas are, in fact, diffuse sources of tds that contribute to the salt load in the Vaal Dam, then further investigations of better ways of preventing or inhibiting them would likely be a natural extension of work by Chamber of Mines Pollution Control Group.

CHAMBER OF MINES OF SOUTH AFRICA
Pollution Control Unit
Post Office Box 2
Regents Park 2125
South Africa
(011) 86-6358
Dan Marsden

There are other industry supported research groups in the U.S.A. which serve the coal industry primarily, such as:

THE WEST VIRGINIA ACID MINE DRAINAGE
Technical Advisory Committee
Dept. of Geology
University of South Carolina
Columbia, South Carolina
(803) 777-3120
Frank Carruchio

Some interesting research which holds promise for the passive treatment of smaller abandoned minesites has been carried out by state organizations such as:

COLORADO DEPT. OF NATURAL RESOURCES
Bureau of Land Reclamation
1313 Sherman, #423
Denver, CO 80203
(303) 866-3567
J. David Holm

Having scored initial successes, this organization has been strapped for funds to take this work further.

Further valuable research into water technology has been funded by the U.S. Environmental Protection Agency which has spent enormous pools of money mainly on seeking ways to treat the symptoms than to find the root causes of acid mine drainage. The U.S. EPA seems to fund organizations and academic institutions with limited experience in the mining and metallurgical industries, and some very hard work has ended up being somewhat out of context at times. Unfortunately, bureaucratic cocoons within this mammoth organization seem to have prevented those charged with directing this research from drawing from the mineral processing industry or from calling on assistance from those in their own organization who have the most experience in this

industry. Partly too, the industry is so afraid of the EPA that this fear has inhibited real cooperation in the past.

In the United States, the Bureau of Mines in Pittsburgh, Pennsylvania, under Dr. Ralph L. P. Kleinmann has conducted very valuable research into how acid mine drainage processes work and how they can be inhibited, and more lately into new low capital cost ways of treating acid mine drainage. Results of their work is available to everyone in the form of publications and industry workshops.

In the end, it will be individual companies and researchers who will find the most practical answers, but the more institutionalized efforts are needed as a springboard if free enterprise principles still work, that is.

The most important R&D frontiers include the following:

1. Determination of tolerance to contaminants in the real life environment.

2. Acid mine drainage inhibition.

3. Water quality effects on metallurgical processes.

4. Water treatment technology for effluents and process water.

5. Biological Treatment processes including ecological engineering.

6. Disposal of precipitate sludges and desalination concentrates.

7. Groundwater quality modelling.

8. Salt balance modelling in metallurgical and mining complexes.

9. Resource recovery from effluents and tailings.

10. Better metallurgical industry insight into dispersants, coagulants, and flocculants.

11. Applicability of impoundment linings and how to install them.

12. Use of water treatment and desalination technology as resource recovery tools.

13. Use of minewater to generate HYDROPOWER.

1. Tolerance to Contaminants in the Real Life Environment

All too often the mining industry decries proposed regulatory limits for various contaminant species on the grounds that they are based on toxicity data established in laboratory tests which do not truly reflect real environmental conditions.

In order to argue convincingly on these grounds that a permit limit is too strict, the mining industry needs quantitative facts. Tolerance to a given contaminant probably depends on the site-specific nature of the environment, climate, and importantly, the other species present in the water as well as the biological species of concern.

Important pioneering work in this direction has been accomplished by Homestake Mining Company at Lead, South Dakota, where Terry Mudder, their environmental control manager, has demonstrated an in-situ bioassay approach in which he shows that sensitive species can and do survive in Homestake's treated effluent.

Demonstrating environmental compatibility of an effluent must surely be safer from an environmental protection standpoint than a set of derived numbers on a permit which were largely guestimates with inordinant safety factors.

This area of R&D, therefore, aims to expand industry's skills and knowledge of applicability of in-situ bioassay techniques as a means of replacing, or at least augmenting, regulatory contaminant limits. Once this has been developed, industry will have a better understanding of "what a particular environment can live with," which will provide a powerful argument to counteract "overzealous" or "anti-industry" idealistic elements in society and the few that still exist in government.

2. Acid Mine Drainage Inhibition

Acid mine drainage is the biggest environmental problem of the mining and metallurgical industry. Methods of treating acid mine drainage involve treatment plants that will have to be operated and maintained "in perpetuity" at enormous accumulating expense to industry and, therefore, indirectly to society.

R&D directed at inhibiting acid mine drainage would address better ways of disposing of wasterock and, particularly, sulfide-containing tailings. Acid mine drainage inhibition in mines is also a vitally important area for further work.

An interesting area of particular interest to explore would be ways to encapsulate the acid generators within the tailings to prevent water getting to these particles in the first place or acid from seeping out. These include application of "subaerial" or "semi-dry" tailings disposal which may require modification aimed specifically at reducing AMD. The

climatic conditions in which sub-aerial tailings deposition will work and types of tailings that will provide adequate encapsulation need to be established.

Another possibility would be to remove the acid generators from tailings for separate disposal or separate treatment, possibly even as a means of recovering valuable by-products in some cases.

Hence, acid mine drainage inhibition involves ways of disposing of tailings, ways of treating tailings, and ways of restoring tailings sites aimed at allowing the operator to walk away from a restored site on completion of the operation.

3. Water Quality Effects on Metallurgical Processes and Equipment

If one cannot discharge an effluent without expensive treatment, then costs can be saved by discharging less effluent. This is likely to mean recycling more process solutions which, in turn, results in a buildup of TDS and contaminant species. These can have serious impact both on metallurgical recoveries and cause corrosion and scale effects in the plant.

The precise effects and mechanisms of how various contaminants affect metallurgical processes need to be understood as well as a means of overcoming those that are detrimental. This may require modifying process conditions--e.g., grinding and flotation in nitrogen rather than air is one example of a way to reduce thiosalt generation in high sulfide ore treatment that could be explored if thiosalts are a problem.

Effects of water quality on flotation processes have been examined, and an interesting start has been made which needs to be carried further to build an insight into precisely what characteristics of water are the cause of detrimental process influences. For example, how can some treated sewage effluents be used in flotation plants without detrimental effects and not others?

Insight of this sort will allow the greater use of alternative sources of water which, at this time, are usually not considered suitable for certain metallurgical processes.

4. Water Treatment Technologies for Effluents and Process Water

Whereas environmental impact of contaminants is measured at levels in the parts per billion range, most water treatment processes in use remove these contaminants to the parts per million range.

Therefore, more powerful and cost-effective processes are needed for removal of many metal ion contaminants to levels that are of interest in environmental protection.

Removal of cyanide and metallo-cyanide complexes are another challenge that requires greater understanding, better technology, and less costly approaches. These may be emerging now in the biological degradation technology recently installed at Lead, South Dakota, and others being tested. Some of the other alternatives that have been applied, including FeS addition, may prove to be more universally applicable, but more practical ways of applying these powerful processes need to be demonstrated to make them more widely applicable. Enhanced natural degradation systems for cyanide destruction deserve attention.

Desalination technologies have been developed into powerful means of making potable water from the sea. However, typical compositions of mine-mill effluents and the need for high recoveries (conversely the need for small volumes of concentrate to be disposed of) is not compatible with conventional desalination equipment. The recent breakthrough in seeded slurry reverse osmosis in mine water treatment described in Chapters 15 and 24 represent the beginning of a whole new perspective for desalination which needs to be tested in more cases. At a treatment cost of R0.50-R0.60 (U.S. 0.25-U.S. 0.30) per m^3, this process is already less expensive than lime addition to high pH in areas located far from a lime source.

Another area where there is room to develop more powerful and more widely applicable technology for water treatment is the high density sludge (HDS) process. Not only does this have advantages in facilitating disposal of precipitates, but it also makes precipitation of contaminants more powerful than conventional precipitation and settling approaches. The HDS process may be expandable to other regimes to further enhance its applicability and usefulness, but this remains to be tested and proven, i.e., another important R&D frontier.

Innovative ways to catalytically oxidize ferrous to ferric iron at a low pH offers a key to iron removal prior to pH adjustment using cheaper limestone which otherwise would be passivated by iron precipitates. These systems need to be further explored.

New developments in cross-flow microfiltration and new equipment is available on the market. This now needs to be applied creatively in water treatment in the mine-mill environment, perhaps combined with creative precipitation techniques. After all, suspended precipitate particles in submicron sizes also contribute to contaminant levels in effluents.

New methods such as insoluble starch xanthates, cellulose xanthates, the Devoe-Holbein pseudo cell media, etc. claim to offer ways of polishing effluents to extremely low metal levels. These need to be investigated, evaluated, and possibly, new applications developed. Not doubt, ways of reducing the cost of these materials and their application will be needed.

As far as removal of suspended solids is concerned when the solids load is very small but must be removed to very low levels to remove suspended metal precipitates, then dissolved air flotation is a powerful technique that needs to be tailored to these needs. DAF may also be used in conjunction with organic solvent extraction or adsorbent removal to reduce effluent metal levels.

New needs for removal of abrasive suspended solids from recycled minewater seem to be emerging, and the new technologies need to be tested and possibly improved upon for specific applications.

5. Biological Treatment Processes Including Ecological Engineering

There is evidence in nature that biological processes can remove contaminants from water. This is nature's own way of cleaning the environment. Mine-mill effluents are more concentrated than most natural effluents and, therefore, to deal with them, natural biological processes need to be engineered to let them match the effluents' treatment requirements.

Interesting experiments have demonstrated useful results in the use of engineered natural marshes for the treatment of sewage. The same principles need to be tested to develop an engineered ecological system to remove contaminants from water in a way that the marsh can sustain itself without becoming destroyed by the toxicity of the metals it has removed from the water. Whereas most research in the past has explored metals uptake by plants, by algae, and by bacteria separately, the key here lies in an engineered ecological system which combines all three in coexistence with each other.

The rest of this century has been identified as the dawning of the age of bioengineering, and this is opening up new frontiers and understanding of biological processes as well as offering new equipment which will be useful in the treatment of mine-mill wastes and effluents.

Reference is made already to the use of bacteria in cyanide destruction of effluents. Research has also been identified into the use of bacterial to detoxify heap leaching tailings after cyanidation. This work is being pioneered by Envirologic Services International.

Advanced Mineral Technologies of Socorro, New Mexico, has developed a new biological process for the removal of metal ions from effluents, which they also are engineering as a means of recovering resources.

John Spisak of Anschutz Mining Corporation wrote about algae that take up very high concentrations of arsenic which could be useful as a means of removing arsenic from effluents.

David Holm of the Colorado Dept. of Natural Resources showed how natural marshes can remove contaminants from acid mine drainage, and there is evidence that a series of beaver ponds on streams have natural cleansing effects on water rendering AMD contaminated water viable for trout.

Japanese workers and CANMET have demonstrated that acid mine drainage can be treated by passing it through wood shavings or sawdust which support biological activity when augmented with organic nutrients.

Biological processes are known which convert sulfates to elemental sulfur or sulfide. These would be useful first to remove sulfates from water with high TDS level problems--e.g., minewater on the Witwatersrand--or to precipitate contaminant metals as sulfides. Sulfate removal and metal sulfide removal has been observed in natural settings and may be engineered into useful processes. The argument that too much land area would be required for marshes can be countered by showing the large areas surrounding tailings areas in various parts of the world that today already accommodate marshland.

Biological processes represent a promising frontier and, with research and development, more of these may be developed into useful techniques to help solve some of the many problems in water treatment facing the mining and milling industry.

6. Disposal of Precipitate Sludges and Desalination Concentrates

In treating large volumes of effluents to remove contaminants, most processes yield smaller volumes of much higher concentrations of these contaminants. These, of course, are usually more toxic or at least are less desirable than the original effluent and must be disposed of safely.

Various methods have been developed to encapsulate this type of waste, but these can often be expensive. It remains to determine whether the common practice of adding them back to the tailings pond is a safe permanent way of disposing of these materials, or whether it can be made to be so. Chloride levels would be an area of particular concern here.

Bethlehem Steel Company has shown that HDS sludges can be mixed with small quantities of cement or flyash and lime to form pozzolons suitable for disposal in sanitary landfills. This could be a start in a more widely applicable way of safe disposal of precipitates.

Deepwell disposal of desalination concentrates has been considered along the lines of toxic waste disposal by the chemical industry, but this is not very economical either.

Another technique of disposing of desalination concentrates may be through evaporation in ponds and, again, more needs to be known about how to make safe, leakproof evaporation

ponds, on liner selection and installation, and about final closure of these ponds on completion of a project or when they have filled with salts.

7. Groundwater Quality Modelling

Impoundment linings are very expensive and also, if seepage is eliminated, these can cause other salt and water balance problems in some metallurgical operations.

In some cases, natural geochemical attenuation of contaminants in seepage is sufficient to allow seepage to take place. To be able to know where this is safe and where it is not, more knowledge of groundwater quality modelling is needed.

8. Salt and Water Balance Modelling

Water balance modelling to take into account water gain and loss at each component of a mine-mill-tailings complex is relatively easy until complicated by naving to make decisions on routing of streams and degree of recycling of solution based on their salt load. This is where salt balance modelling would be most useful if it could be achieved reliably, based on experimental data.

Before a mine-mill-tailings operation can be licensed in most countries today, the operator must demonstrate how water will be used, how much may have to be discharged, and what its quality will be. Judgements must be made on the amount that can be recycled within equipment and process constraints. To do this in advance requires a good water and salt balance model. However, salt balances, especially for operations that recycle solutions allowing dissolved solids levels to build up, are very site specific and ore-specific. That is, the degree to which salts will dissolve into solution or be removed from solution also varies with chemistry of the gangue in the ore, and other site-specific aspects that may not be known in advance.

The problem of dealing with numerous equations expressing equilibria of various components in solution and numerous process streams and loops can be dealt with using powerful computers available today. However, how one contaminant affects another and the effects of gangue characteristics and reagents used or surfactants employed in the process on salt solubilities are not yet clearly quantifiable. Much more R&D is needed in this area to develop a useful salt balance modelling technique for complex solutions. This has been achieved for power station cooling water by CALGON CORP., and several consultants have made a good start in salt balance modelling technology. However, those interested in developing this technique should be prepared to invest many years and many millions of dollars before they might have a really reliable tool. This remains a most needed R&D frontier, however.

9. Resource Recovery from Effluents and Tailings

While the mining industry seeks ways of inhibiting acid mine drainage, a chemical engineer in the U.S.A. has developed a concept for hydrogen gas development as a source of energy. To him, an acid stream at pH 2, a source of granular pyrite and scrap iron, would be a potential bonanza.

Imagine if sulfide tailings could be disposed of in such a way that rather than inhibiting acid generation, ways are sought to accelerate sulfide oxidation (e.g., bacterial), thereby generating acid faster but also oxidizing the tailings faster to a point that they are exhausted in say 20 years as opposed to the present 300-500 year timeframe. Pyrite removed from the ore or tailings would be consumed as one galvanic cell electrode and scrap iron gathered locally from various sources as the other, to generate hydrogen. Such a concept is a "long shot," but it does have such a valuable potential if only to avoid the prospect of "perpetual" treatment plants and tailings site maintenance at the many mining centers around the world.

This concept has not progressed beyond the idea stage. It was conceived by:

PROFESSOR AL STILLER
Chemical Engineering Dept.
University of West Virginia
Morgantown, WV

The important point is that effluents may contain valuable by-products which can change one's approach. But more R&D is needed in this area.

Many effluents contain valuable metals. At most gold mills that discharge an effluent, residual gold values can be recovered from these effluents. Attempts are even being made to recover gold values from an acid mine drainage flow from an abandoned base metal mine in California, for example, as well as from oil field brines.

In Peru and Chile, copper is recovered from minewater. In the U.S.A., uranium is recovered from minewater draining from copper and uranium mines. On the Witwatersrand, a series of metals could be recovered by selective precipitation or selective extraction from gold and uranium mine effluents, if the price of cobalt, nickel, and manganese ever got high enough. Creative approaches at biologically accelerating AMD generation in sand dumps to yield recoverable gold and uranium values may be more realistic in the short term while helping to neutralize residual AMD generating capacity of low grade tailings.

Water treatment plant sludges containing high metal values have been disposed of with smelter or roaster feed where some incremental values have been generated.

In other industries, biomass generated in biological waste treatment is used to generate methane gas an an energy source--could .this be a possible by-product of biological effluent treatment in the mine-mill environment in some parts of the world?

In Scranton, Pennsylvania, mine drainage is reputedly used as a source of heat in winter and a means of cooling buildings in summer.

New developments have come to light in the recovery of cyanide values from gold mill effluents where the ore contains high concentrations of cyanide soluble copper. This was practised years ago in Canada and Mexico, but the new process has been demonstrated by MNR Reprocessing, a subsidiary of Metallgesellschaft, and Mountain States Mineral Processing, Inc. Cyanide recovery from effluents is certainly a worthwhile R&D frontier considering the cost of cyanide destruction alternatives.

Other areas in R&D include the use of desalination, e.g., electrodialysis, as a means of recovering reagents, e.g., H_2SO_4 and NaOH from Na_2SO_4 effluents. Elsewhere, the use of R.O. in water treatment to make potable water also generated a concentrated Na_2CO_3 stream with potential by-product recovery potential.

Through R&D, more examples and better economics of resource recovery from effluents can be expected. In general, however, recovery of base metals from most effluents does not look economically attractive at today's metal prices.

10. Better Insight into Dispersants, Coagulants, and Flocculant

As attempts are made to reduce the capital cost of installations by making smaller units work harder, increasing use is being made of reagents which are dosed at small amounts to modify or inhibit scale characteristics of water, reduce corrosion, enhance settling rates, and improve clarities or slurry rheology. Several water treatment chemical companies serve this market. Sometimes relatively cheap materials and even waste material from other industries are used as surfactants for these purposes.

Mineral processing operations would not dream of employing a metallurgical process, reagent, or item of equipment unless they know exactly what it is, how it works, or what impact it might have elsewhere in the plant. Yet, when it comes to water treatment services and products, they are usually satisfied to trust the supplier of those services and products implicitly. This may be recognition of the complexity of some of the chemistry sometimes involved or of the AXIOM that a little bit of knowledge is dangerous.

Many of these surfactants and water treatment additives are so powerful that the mining industry might benefit well from more R&D to learn more about the fundamentals and practical cost saving ideas in this [illegible] which, to most metallurgical and water treatment engineers involved in mining, rem[illegible] a "black art."

11. Applicability of Impoundment Linings and How to Install Them

Even based on a small sampling of installations, there have been enough cases of failure or problems associated with linings of impoundments for this to be added to the list of R&D frontier needs.

R&D in this area needs to think in terms of a lining system rather than just a lining.

Lining salesmen are a major source of valuable information on linings, but what is needed is a detailed survey of the practical aspects of selecting, testing, and applying linings for solution, tailings, and water impoundments, as well as a catalogue of pitfalls.

12. Use of Water Treatment and Desalination Technology as Resource Recovery Tools

Although several processes have been looked at as a means of treating water to make it potable, useable in metallurgical processing, or dischargeable as an effluent, some of the desalination techniques could possibly be developed into concentrating processes.

Examples include reverse osmosis and electrodialysis, liquid-filled membranes, biological processes, and certain adsorption processes, etc. Some attempts to develop electrolytic recovery techniques to both recover metals and remove contaminants have been made so far without economic success.

13. Use of Minewater to Generate Hydropower

When water is needed underground for whatever use, it usually is supplied from the surface. There is a significant hydrostatic head at the underground tap of a mine some thousands of feet below the surface, and special high pressure pipes must be used.

This hydrostatic head is being harnessed to drive hydropower generators and even to drive hydraulic tools and equipment. The latter was announced by the Chamber of Mines as a new development and, undoubtably, more R&D will turn this into a routinely used source of energy in underground mines.

The above list some of the R&D frontiers that need to be addressed. Undoubtably many more have been left out. Clearly, this a worthwhile area to invest research and development funds at this time. In many cases, processes or equipment already exist that can fulfill needs of industry. It is a question of finding and adapting them to fill specific needs.

CHAPTER 63

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APPENDIX

WATER MANAGEMENT & TREATMENT

FOR

MINING & METALLURGICAL OPERATIONS

1 JUNE 1985

RANDOL INTERNATIONAL LTD.
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GOLDEN, COLORADO 80401
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MICROMEDIA

APPENDIX I

CONTRACT SERIAL NUMBER OSQ83-00220

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MINING & METALLURGICAL OPERATIONS

1 JUNE 1985

RANDOL INTERNATIONAL LTD.
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NOTE

This report is based on information provided by literally hundreds of individuals in mining, engineering, and consulting companies. The author gratefully acknowledges this industry support without which RANDOL surveys would not be possible.

The information contained herein is submitted on a "best efforts" basis. Although an attempt has been made to avoid misleading errors, this report should be used by sponsors at their own risk and subject to verification. Since it deals with a pioneering field, it has not been altogether possible to avoid speculative assessments.

Some of the information may possibly be "sensitive." This report is submitted to you on condition that sponsors hold its contents strictly confidential.

CONVERSION FACTORS

Grains per gallon (U.S.)	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon (U.S.)	0.05841
Milligrams per liter	Tons per acre-foot	.001360
Tons per acre	Metric tons per hectare	2.217
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Gallons (Imperial)	Gallons (U.S.)	1.2009
Acre-feet	Gallons	325,851
Acre-feet	Cubic feet	43,560
Cubic feet	Cubic meters	.028317
Cubic feet	Gallons	7.481
Cubic meters	U.S. Gallons	264.2
Cubic meters	Imp. Gallons	220.0
1,000 m^3/d	I gpm	152.8
1,000 m^3/d	U.S. gpm	183.6
U.S. gallon	Cubic meter	0.3785

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CHAPTER 4 - REVIEW OF WATER PROBLEMS IN MINES AND MILLS
CHAPTER 5 - WATER RECYCLING IN METALLURGICAL PLANTS
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APPENDIX I

TRIP REPORTS AND OPERATION DESCRIPTIONS

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INTRODUCTION

The Beisa Mine was designed to produce uranium and gold from a typical Witwatersrand quartz pebble conglomerate ore. The mine is located south of Welkom on the southern edge of the Witwatersrand in what is known as the Orange Free State Goldfields.

The gold mill uses carbon-in-pulp. The uranium plant uses sulfuric acid leaching, belt filtration followed by solvent extraction.

The Beisa Mine is a wet mine and considerable quantities of water must be pumped from underground.

Beisa minewater is high in chlorides and until the 1982-4 drought resulted in the need for emergency measures, the water was evaporated to dispose of it. Since the drought resulted in a severe shortage of water, it has been settled and used in the process.

EVAPORATION POND QUALITY

pH	9
TDS	4042 ppm
Cl^-	2080 ppm
Total $CaCO_3$ hardness	370 ppm
$SO_4^=$	122 ppm
Suspended solids	Less than 10 ppm

WATER TREATMENT None, settling to remove suspended solids.

WATER USE

The operation was started up using Orange Free State Water Board fresh water. During the drought, the plant converted to using the high chloride minewater except where fresh water is essential - that is for solvent extraction and ADU washing in the uranium plant, for carbon elution in the gold plant.

EFFECTS OF WATER QUALITY

No ill effects had been noted on metallurgical recovery by the operators. Presumably, because there is an excess of water it does not have to be recycled many times so a further buildup of TDS is avoided and raffinates can be discarded to evaporation. No serious corrosion effects had been observed that could be blamed on water quality. The walkways on the gold plant were getting rusty. The gold filter plant uses stainless steel 316L which is corrosion resistant and no ill effects of the high chlorides have been observed yet.

The operators had some initial concern about using minewater as washwater on the belt filter plant. To their surprise they found that the high TDS, high chloride water gave a 20% faster filtration rate than OFS Water Board fresh water.

DISPOSAL OF EXCESS WATER

Beisa minewater is too high in chlorides to be discharged as effluent. Beisa disposes of excess water and solution bleeds by evaporation which has been found to be more cost effective than desalination and recycling. It was planned to pump excess water to the St. Helena mine and mill which is short of water and located just a few miles away.

EVAPORATION

It is believed that the following paper by BENTEL & JAMES (1983) refers to disposal of water from an OFS mine, presumably Beisa; it provides an interesting insight into design and costs of evaporation ponds in South Africa.

MINE WATER

Design aspects of EVAPORATION DAMS

General view showing typical land coverage of evaporation dams.

By D L BENTEL and B M JAMES, both of Steffen, Robertson & Kirsten, Mining and Geotechnical Engineers.

THE RECENT DEVELOPMENT of a new mine in the OFS goldfields has led to considerable quantities of underground water being pumped to surface.

In addition, disposal of effluent water from the mine tailings and raffinate dams is required. This underground and effluent water is not suitable for drinking, irrigation, stock-watering or discharge into a water-course.

Detailed analyses indicate that the cost of purifying the underground water, so that it conforms with regulations, is about three times the cost associated with evaporating the water. Consequently, the most economical and practical method to dispose of underground and effluent water is an evaporation-dam system.

This article describes the design philosophy adopted for both the

evaporation dam systems constructed to date and proposed future systems. Engineering, economic and environmental considerations are discussed.

Hydrological Considerations

Fig 1 illustrates the typical water balance affecting the evaporation-dam system.

Hydrological data from Hydrological Research Unit reports Nos 1/72 and 2/73 and Weather Bureau publications are used to determine the minimum area required to evaporate sufficient water to achieve an acceptable balance.

Tables 1 and 2 summarise average monthly precipitation and mean monthly evaporation figures for Odendaalsrus.

From these tables the theoretical minimum net monthly loss due to evaporation only (*i.e.* not including seepage losses), is in July and is of the order of 0,45 Mℓ/ha. The average annual net monthly loss due to evaporation is of the order of 0,85 Mℓ/ha.

Recent on-site measurements indicate that a total minimum loss (including evaporation and seepage) of the order of 1,0 Mℓ/month is reasonable for July. This figure has been used to determine the minimum evaporation area required.

It should be noted that an evaporation tank (Symons Type T) and a competent rain gauge have been installed to monitor on-site precipitation and evaporation and hence aid in the determination of variable inflows and outflows.

THE FOLLOWING section describes the design details used to develop an available area into an evaporation-dam complex.

Wall height

The minimum wall height is determined according to the criteria set out in regulations made in terms of Section 26 (c) and (d) of the Water Act, 1956 (Act 54 of 1956).

The relevant clause 11.1 states:

"The storage capacities of all sumps and dams shall be sufficient to ensure a freeboard of at least 0,5 m above the expected maximum water level, which shall be based on the average monthly rainfall figures for the catchment area concerned, less the gross mean evaporation in that area, plus the maximum precipitation to be expected over a period of 24 hours with a frequency of once in 100

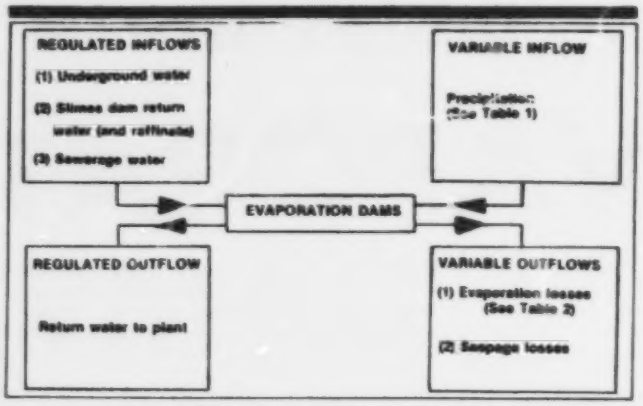


FIGURE 1: Water balance affecting evaporation system.

Month	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT
Precipitation (mm)	46	66	72	89	73	76	46	22	8	9	7	13

TABLE 1: Average monthly rainfall figures for Odendaalsrus

Month	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT
Evaporation (mm)	46	66	72	89	73	76	46	22	8	9	7	13

TABLE 2: Mean monthly evaporaton figures (HRU 2/73)

View of wall showing upstream and downstream rip-rap and crossfall on crest towards upstream side.

years, according to information obtained from the Secretary."

To comply practically with this regulation in terms of freeboard and storage capacity, the minimum wall height considered is of the order of 1,0 m. The spillway level is 0,5 m below the crest level.

The maximum wall height is of the order of 2,0 m. A higher wall of the same cross-section requires incorporation of underdrainage to control the phreatic surface. This involves additional expense (R30/m of wall). Dissipation of accumulated seepage water in the underdrains is impractical because ground slopes are flat and substantial "dead" area is required to gravitate water. This reduces the total evaporation potential of the area.

Wall construction

A typical wall cross section is shown in Fig 2.

Compacted earth wall and key

Sound engineering practice, as well as legal criteria, are the prime reasons for specifying compaction of earth walls and keys.

Clause 11.4 in the "Water Act" states: "All sumps and pumping

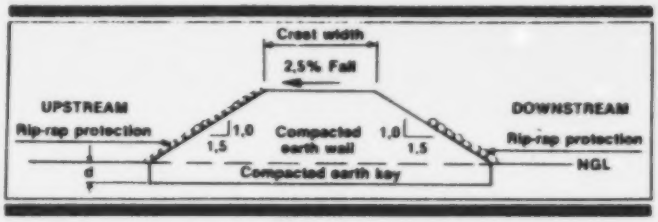


FIGURE 2: Adopted wall cross-section.

installations, including catchment dams for recycling of water, shall be of a design and of adequate capacity to prevent the uncontrolled release of water at any time."

Clause 12 states: "The manager of a mine or works shall ensure that any material, tailings and waste rock dump and any slimes, barrier or evaporation dam, stormwater drain or other waterway is as far as practicable located and designed so as to minimise the possibility of damage thereto by subsidence, settlement, shock, and cracking due to past, present and future operations at the mine or works."

Compacting the wall and key material increases the strength and hence decreases the permeability and seepage through such material. If compaction is not carried out on the in situ sands and clays the

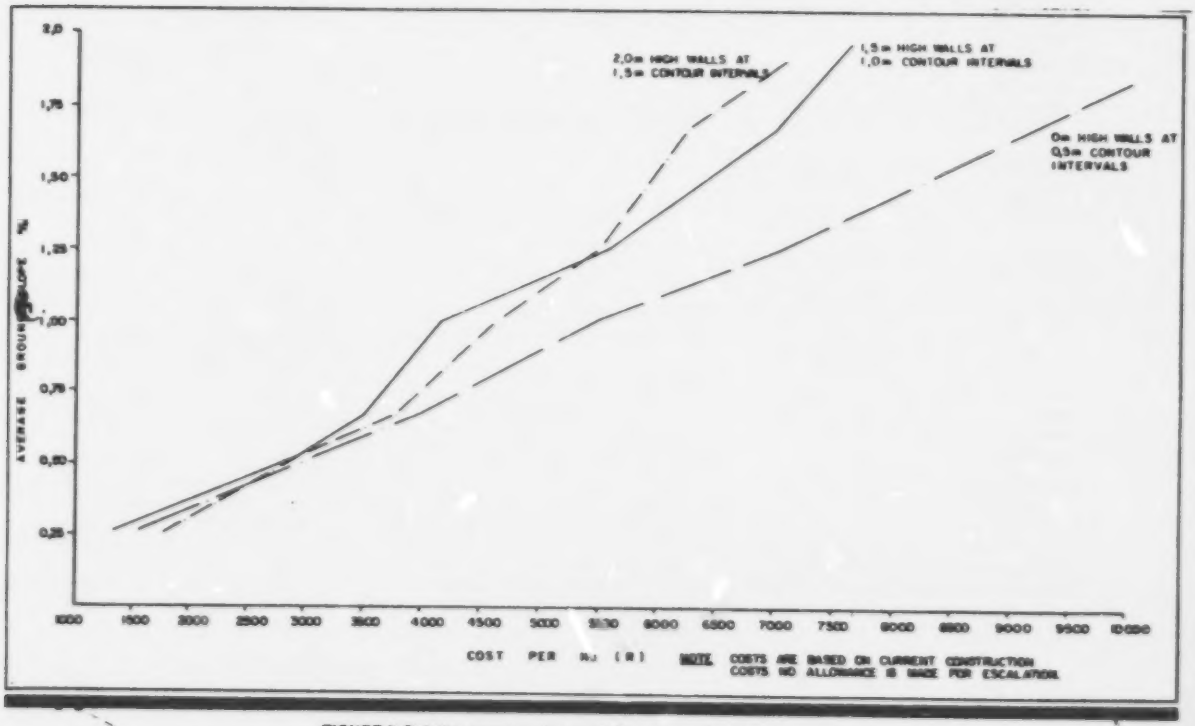


FIGURE 6: Relative construction costs for evaporation dam systems.

resulting seepage and inherent lack of strength would result in wall failure and hence uncontrolled release of water.

Inclusion of the compacted key ensures that the wall is not founded on in situ aeolian sands which display collapse potential. Differential settlement along the wall length is thereby minimised.

In addition, by extending the key to a reasonable depth below natural ground level, *i.e.* to a depth where the relative permeability of the in situ earth is much less than that of the highly permeable aeolian sands, seepage under the wall is reduced.

The least depth of the key is about 400 mm. This prevents differential settlement.

The greatest depth of the key depends on the seepage that may be tolerated. The depth of the key in walls adjacent to the farmer's should be greater than in internal walls, or in walls adjacent to mine property on which seepage water may be tolerated.

Crest

The crest width is determined according to the minimum width of plant required for compaction. The most economical method of constructing evaporation dams is with mechanical scrapers and conventional plant. A crest width of less that 3,0 m is thus both impractical and unsafe. A 2,5 % crest crossfall is incorporated to encourage stormwater falling on the crest to flow towards the upstream slope. This reduces erosion of the unprotected downstream slope.

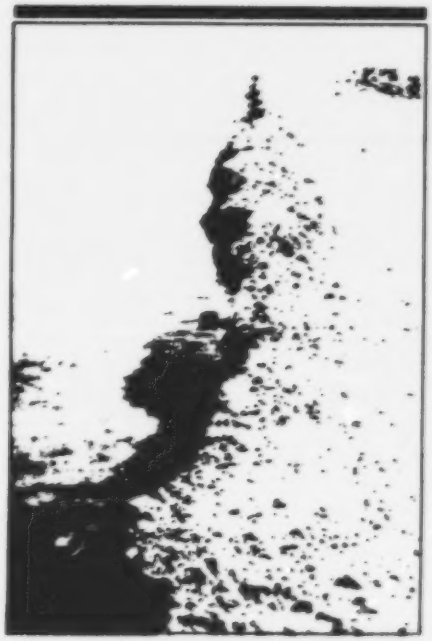
Sideslopes

The evaporation dam walls are constructed with in situ material which varies from silty sands to sandy clays. The strength and permeability characteristics for these materials have been used to determine the stability of the walls for operating conditions. Stability analyses have shown that for a crest width of 3,0 m, and a wall height that varies from 1 to 2 m, a minimum side slope of 1 (vertical) to 1,5 (horizontal) *i.e.* 33,7 %, ensures an acceptable factor of safety against sliding and slip-circle failure. In addition, this angle is less than the average angle of friction of the dump rock rip-rap protection. Hence sliding of the dump rock is minimised.

Rip-rap protection

Coarse waste-dump rock is specified for the entire upstream slope to prevent erosion of the earth wall due to wave action. The same is applied to the downstream toe to prevent erosion due to wave action as well as to form a toe buttress and toe drain. The maximum vertical height of the downstream rip-rap is of the order of 0,5 m.

Damage to wall resulting from wave action against inadequate rip-rap.



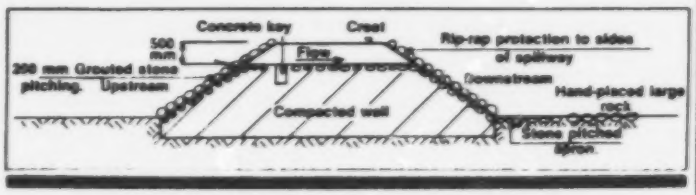


FIGURE 3 Adopted spillway cross section

Spillway construction

A typical spillway is shown in Fig 3.

Cut-off trenches and drains

Cut-off trenches and drains are required around the perimeter of the evaporation dam systems to prevent migration of seepage water into adjacent farmland.

Clause 11.3 of the Water Act states: "French drains and ditches to catch seepage water and carry it to evaporation dams or to sumps for recyling, shall be constructed at all tailings dumps wherever seepage occurs."

This clause has been applied to evaporation dams.

Two methods used to cut off seepage are shown in Fig 4 and Fig 5 (next page).

Cut-off trenches and drains are designed to gravitate towards sumps at low points adjacent to the system perimeter. From these sumps seepage water is pumped back into the system.

To reduce pumping, seepage water flowing within the cut-off trenches is gravitated, where possible, into downstream dams by means of weirs and pipes. The cut-off trench is designed, where possible, to in-

tercept seepage within the relatively permeable aeolian sands.

It should be noted that for economic reasons, the OFS mine has decided not to incorporate seepage cut-off trenches around all of the systems.

A DETAILED study has been carried out to determine the most cost-effective method of developing evaporation area for varying average ground slopes.

Fig 6 (next page) shows the relationship between construction costs per developed hectare, and average ground slopes, for varying wall heights, and the following information can also be otabained from the same graph.

(i) For ground slopes varying from 0,25 % to 1,2 % the most economical evaporation dam system is 1,5 m high walls at 1,0 m contour intervals.

(ii) For ground slopes greater than 1,2 %, the system based on 2,0 m high walls at 1,5 m contour intervals becomes most economical.

(iii) The system based on 1,0 m high walls at 0,5 m contour intervals tends to become highly uneconomical, as the ground slope increases.

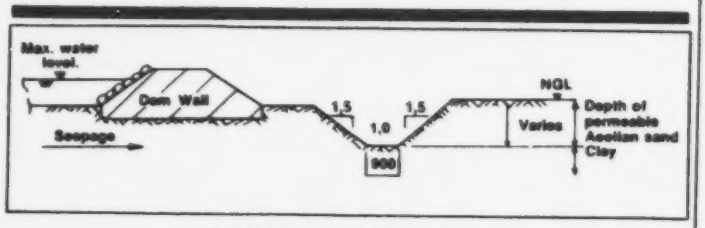


FIGURE 4: Open cut-off trench.

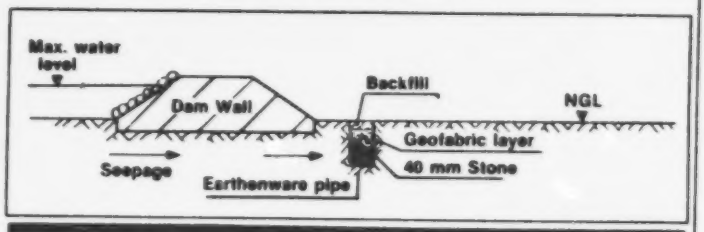


FIGURE 5: Closed drain.

DURING CONSTRUCTION of the evaporation dams, the following items have been found to be of major importance.

Survey and measurement

To ensure that maximum ground use is achieved, wall location and height, and spillway levels required great accuracy during construction. To this end, the contractor is required to submit survey data on a regular basis. These data are also required for accurate measurement of quantities.

Wall material and compaction

Constant control is required to ensure that acceptable borrow material is used for wall construction.

The present method of establishing borrow pits adjacent to the wall under construction, has led to the more sandy material (*i.e.* upper layers of borrow) being used in the lower regions of the wall, *i.e.* "key" and base.

Consideration should therefore be given to greater control of the location of borrow areas in order to achieve wall construction which incorporates the clayey material in the lower wall regions and hence minimises seepage. The more sandy material should be placed in the upper regions.

The borrow material is placed in loose layers not exceeding 200 mm in height and compacted by approved vibratory or impact compaction plant. The specified compaction is 100 % Standard Proctor density at a moisture content between 1 % below and 3 % above optimum moisture content. Compaction testing is carried out in each layer to ensure that the above specifications are met. A competent soils laboratory is required on site to ensure that the frequency of testing is sufficient to provide conclusive evidence of satisfactory compaction and to avoid delays in obtaining data.

Rip-rap

Loose material on the upstream face has a detrimental effect on the rip-rap layer in terms of post construction settlement. It is therefore essential to ensure that the upstream face is cut back to competent, well-compacted material prior to placing rip-rap. It is necessary for the contractor to over-build to achieve both the above criteria and the design cross-section.

The use of finely graded dump rock for rip-rap should be avoided where possible. If fine material only is available, as was the case in the construction of one of the evaporation dam systems, bad erosion can be expected.

The measures adopted as a result of the above are to increase the

height of the rip-rap, *i.e.* construct a "mound" of rip-rap on the upstream crest edge. Thus extra material was pushed down to reinstate eroded areas, with very limited success.

Increasing the thickness of the rip-rap may be considered. However, the cost of this is inhibitive. The most acceptable solution is to allow erosion and stabilisation of the rip-rap to occur, and then reinstate, using coarse material when it becomes available.

BAD EROSION of the downstream slope of the earth wall has taken place due to rainfall run-off, despite design and construction measures taken to prevent this, *i.e.* cross-fall on crest. The above is particularly bad at wall intersections. To prevent this, vegetaion should be established on the earth walls.

Regulated Inflows

The regulated inflow to each phase of the total system requires constant monitoring to ensure:

- That the depth of flow over spillways is not excessive in terms of acceptable freeboard;
- That optimum use of evaporation area is achieved.

Sufficient surge capacity is maintained by keeping topographically lower dams dry. As soon as spillage commences into the dams reserved for surge capacity, the regulated inflow into that system should be controlled to ensure that it is compatible with current achievable losses. A no-spill situation is set up while maintaining maximum allowable area coverage.

To achieve this, accurate measuring devices are required to record regulated inflows and outflows, precipitation, evaporation losses, and seepage losses. These measuring devices should be installed during construction of the dams.

Pollution

Periodic monitoring of boreholes in the immediate vicinity of the evaporation dams has revealed that little change in water quality has occurred since commissioning of the initial dams in 1980.

A change of surface-water quality has occurred at two seepage-trench sump areas where pumping of seepage water has been insufficient to prevent accumulation, and consequent migration into adjacent farm lands. It is therefore extremely important to ensure that the necessary equipment for dissipating seepage water is installed and fully functional before commissioning of any evaporation dam system.

In conclusion, the evaporation dam systems constructed to date have been successful in achieving their design function, *i.e.* to dispose of mine underground and effluent water in an environmentally acceptable fashion.

However, greater control is required with respect to the operation of these systems to prevent localised contamination of adjacent farmlands.

OPERATION (1)	COTTER CORPORATION SCHWARZWALDER URANIUM MINE RALSTON CREEK CANYON GOLDEN, CO 80401
TELEPHONE	(303) 642-3893
OPERATION (2)	COTTER CORPORATION Water Treatment Plant Ralston Creek Canyon Golden, CO 80401 (303) 642-7888
CONTACTS	Charles Palmer — Site Manager (303) 642-3893 Doug Pettinger — Operator
OPERATION (3)	COTTER CORPORATION Canon City Mill P. O. Box 751 Canon City, CO 81212 (303) 275-7413
CONTACT	Jim Cain — Radiation Control Officer
COMPANY	COTTER CORPORATION 9305 W. Alameda Parkway, #201 Lakewood, CO 80226 (303) 232-8218
CONTACTS	J. P. McCluskey — Executive Vice President Dave Munger A. O. Courtney — Director of Environmental Affairs

INTRODUCTION

Cotter Corporation is currently preparing an application for renewal of their operating permit from the Colorado Dept. of Health for the Canyon City Mill.

The company declined to provide information on their water management and/or water treatment facilities on the grounds that they are "not atypical of the industry." Cotter

Corporation has for a long time been under the scrutiny of environmentalists and regulatory authorities, perhaps more so than others because of the proximity of their operations to metropolitan areas and because water discharged from these plants migrates toward usable water sources for these areas.

It is appropriate to summarize some of the details of water management and treatment that is practiced by Cotter Corporation, much of which has been pieced together from fragments. The data is not completely as reliable but useful only to provide a broad picture of some of this company's challenges and achievements.

Of particular importance is the remarkable performance of a continuous ion exchange plant for removal of uranium from 2-3 ppm down to 10-12 ppb and less, which is a demonstration of just how effective fixed bed IX systems can be. This is the first continuous fixed bed system that has come to our attention.

DESCRIPTION - MINE

Cotter Corporation operates the Schwarzwalder uranium mine just north of Golden, CO. Ore is crushed and upgraded using radiometric ore sorting to produce a beneficiated ore for shipment to the Cotter Mill at Canon City, CO. Excess minewater is treated first to remove radium and then uranium. New effluent discharge limits in Cotter Corporation's permit were set at 40 pCi/l which is equivalent to 59 ppb U_3O_8 in 1979. A new ion exchange entraction process was developed by Cotter Corporation, Himsley Engineering and The Diamond Shamrock Company as described by JACOBS et al. (1979).

Flowrate of water treated is 500 USgpm and the treatment plant is operated at that rate. Water is pumped from underground resevoirs to a surge tank at the surface and arrives at the plant at a constant pH of 7.5 - 7.8 and requires no pH adjustment. Radium and uranium must be removed.

The primary treatment step is removal of particulates and radium. This is achieved by dosing $BaCl_2$ to the surge tank. Coagulants are added in a mixing tank downstream from the surge tank. There is adequate sulfate in the water at about 500 ppm to coprecipitate radium as $\underline{BaRaSO_4}$. At this point the water has 200-300 ntu turbidity (sometimes as high as 500 ntu.) This is followed by a 35' outdoor conventional clarifier and indoor filtration through two deep bed sand filters. Particulates at this point have been dropped to about 0.2 ntu's. To achieve this NALCO flocculant polymers of both the cationic and anionic types are added. Clarifier underflow sludge is dewatered on a drum filter and added to the ore. Sandfilter backflush sludges are returned to the clarifier.

The clarified water is next pumped at a constant rate of 500 USgpm to the downflow continuous moving bed ion exchange columns designed and installed by:

Himsley Engineering
250 Merton Street
Toronto, Ontario M4S 1B1

Telephone: (416) 485-4441
Contacts: Alec Himsley, President
Al Peterson

Finally the water discharges to the first of the original five barrens ponds leaving the remaining four ponds for use as an emergency catchment pond for use should any part of the facility be down for repair. The whole water treatment plant requires just one dayshift operator.

The Himsley continuous fixed bed ion exchange plant installed at the Schwarzwalder Mine is a unique and innovative design with an extraordinarily high efficiency. It consists of two downflow fixed bed ion exchange adsorption columns connected in series. The columns are closed tanks engineered as pressure vessels. The elution system consists of a single downflow column.

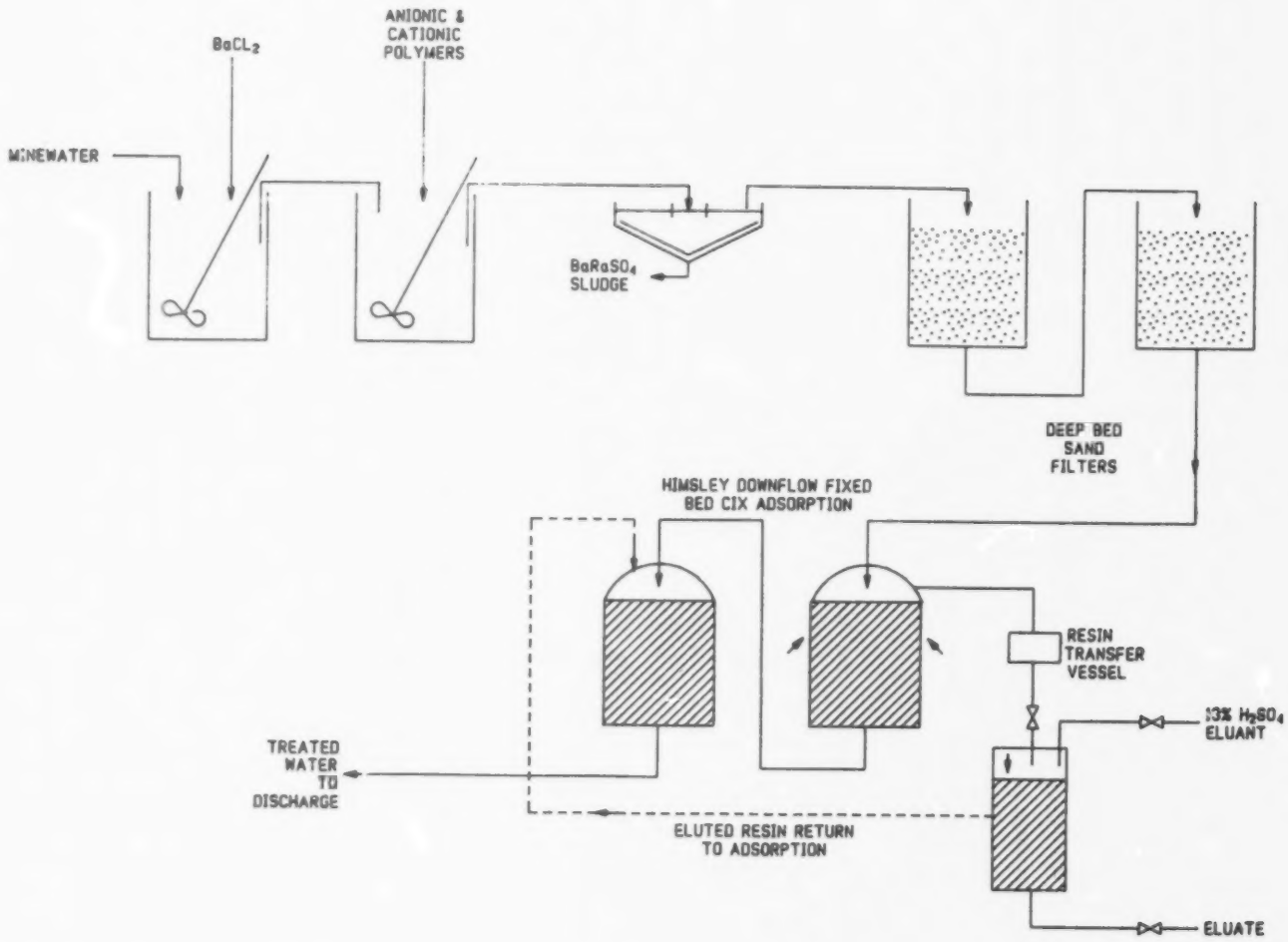
Uranium adsorbs as the uranyl carbonate complex and is reduced from 3 - 3.5 ppm U_3O_8 in the feed often to below 10 ppb in the effluent. Loaded resin is fluidized at the top of the lead adsorption column and transferred to the bottom of the desorption column via a 3 ft^3 measuring vessel. An intermediate step washes the resin with spent eluate to convert $CO_3^=$ to CO_2 which is vented. If this were not done, CO_2 gas in the fixed bed elution column would cause channelling and interfere with elution efficiency. Eluted resin is transferred from the top of the elution column to the bottom of the tail adsorption column. Transfer is via a pressure vessel and pressurized transfer of a resin slurry in water. The following details summarize the IX operation which was commissioned in 1982. The IX plant was described by PALMER, et al. (1984).

Loaded resin, after pretreatment with spent eluate is eluted with sulphuric acid. The eluate contains 10-15 g U_3O_8/l - in other words the ion exchange process achieves a 3,000 fold concentration ratio which is remarkable.

ADSORPTION

Flowrate	:	500 USgpm
Uranium in	:	3 - 3.5 ppm U_3O_8
Uranium out	:	10 - 20 ppb U_3O_8
Column diameter	:	4 - 7 feet
No. of stages	:	Two downflow columns in series
Resin depth	:	6 - 7 feet in each column
Column vessel height	:	10-12 feet (estimated)

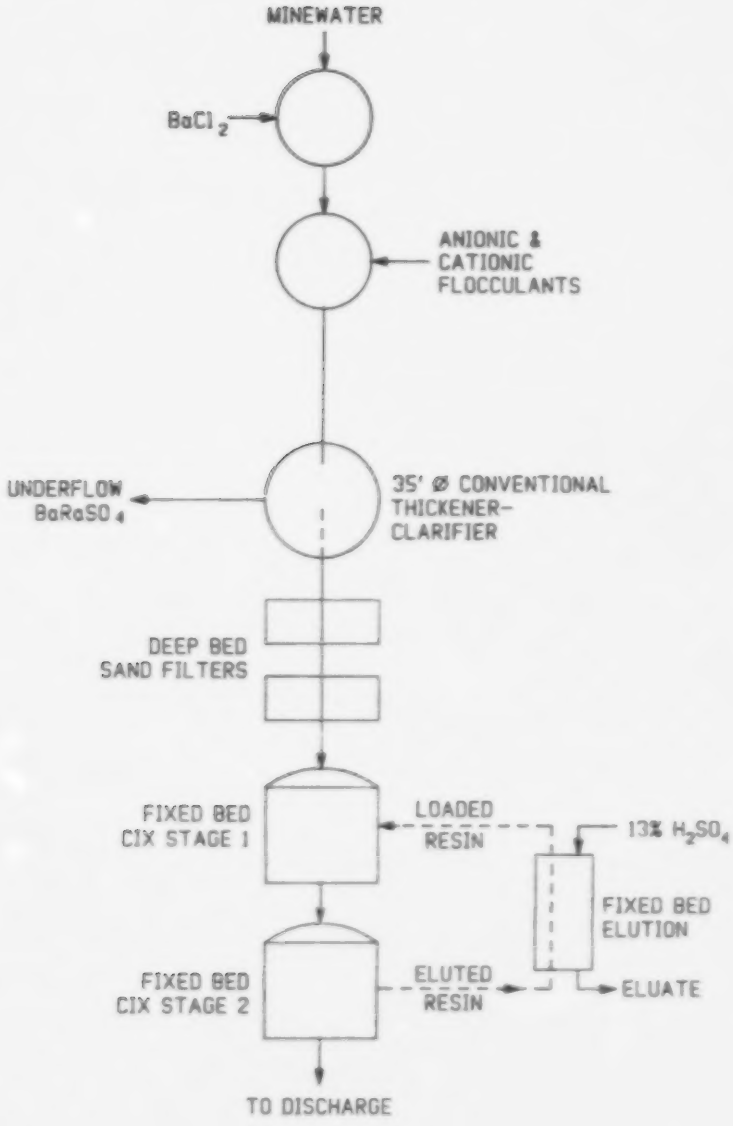
COTTER CORPORATION
SCHWARZWALDER MINEWATER TREATMENT

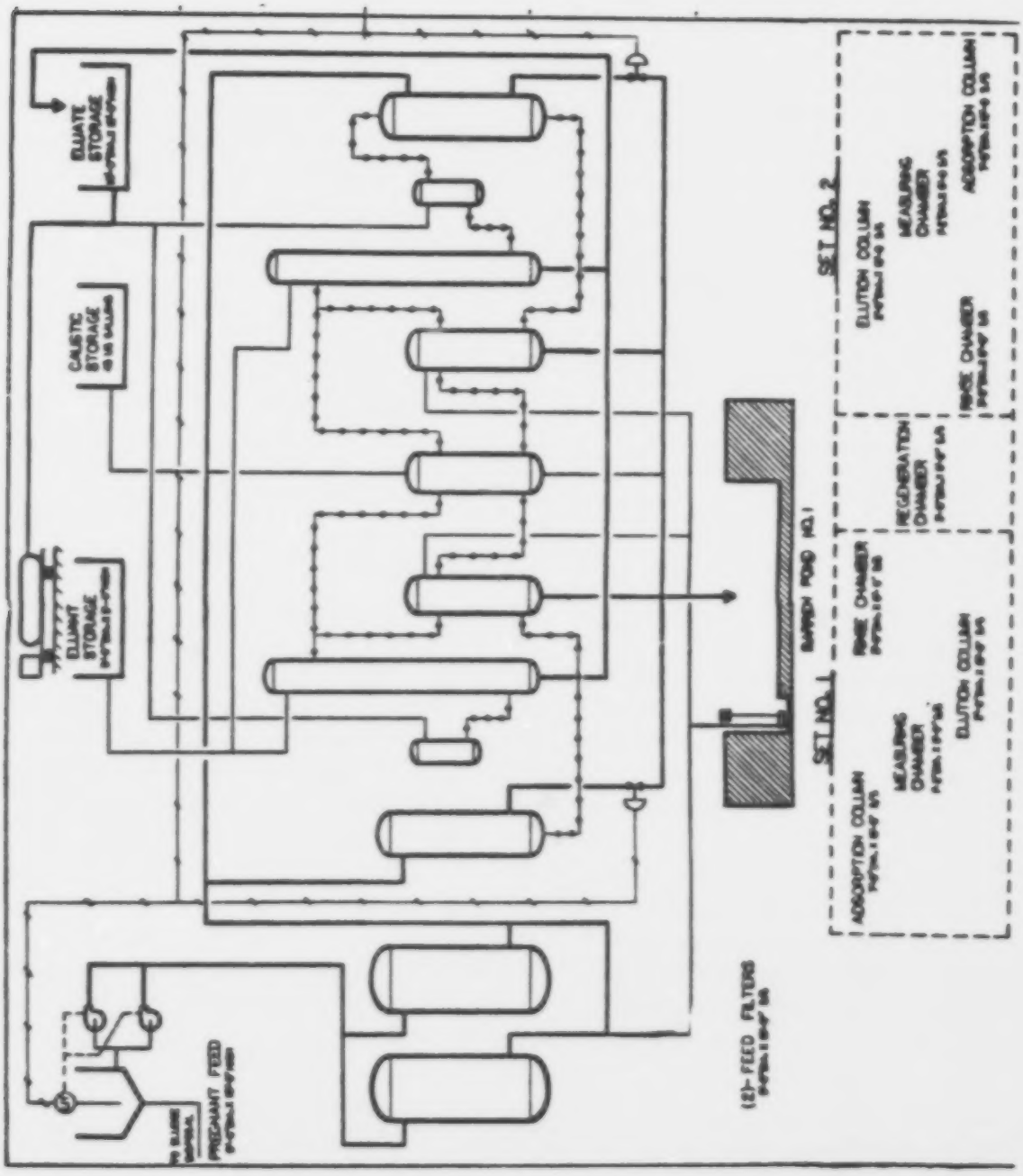


URANIUM REMOVAL FROM MINE WATER

Element	Feed (mg/l)	Typical IX Effluent (mg/l)	Discharge Limits (mg/l 30 day average)
Uranium (dissolved)	2-7	<0.010	0.06
Cadmium	.002	0.0004	0.0004
Copper	.02	0.005	0.005
Lead		0.005	0.032
Zinc	0.0026	0.05	0.05
Radium 226 (pCi/l) +228	50-100	5	5 total
Sulphate	800	800	N.A.
Chloride	60	60	N.A.
Barium		1.0	1.0
Arsenic		0.05	0.05

SOURCE: PALMER, HIMSLEY & BENNETT (1984)


MINEWATER
$BaCl_2$
ANIONIC &
CATIONIC
FLOCCULANTS
UNDERFLOW
$BaRaSO_4$
35' Ø CONVENTIONAL
THICKENER-
CLARIFIER
DEEP BED
SAND FILTERS
FIXED BED
CIX STAGE 1
LOADED
RESIN
13% H_2SO_4
FIXED BED
ELUTION
FIXED BED
CIX STAGE 2
ELUTED
RESIN
ELUATE
TO DISCHARGE



PROCESS FLOW SHEET FIG. 1

SOURCE: PALMER, HIMSLEY & BENNETT (1984)

Dowex resins are believed to have been used. Lately a test batch of Rohm & Haas anion exchange resin has been loaded into the system. A batch of Diamond Shamrock Duolite A101D anionic resin has been ordered to test. Cotter Corporation is looking for ways to reduce the cost of resin.

RESIN LOADING Resin is loaded to 35 g U_3O_8/l of resin.

RESIN TRANSFER

Periodically a measured volume of loaded resin is transferred from the adsorption column to a measuring vessel. The uranium loaded as uranyl tricarbonate is converted to uranyl tri-sulfute using free acid in the eluate with release of CO_2 in the measuring chamber.

ELUTION

Resin is eluted with 13% sulfuric acid also in a multi-stage downflow column. Loaded resin is injected into the bottom of the column and eluted resin extracted from the top of the column during the resin transfer cycle. Counter current elution of several batches of resin in series (U.S. Patent No. 401 8677) produces a more concentrated eluate than other systems, thereby reducing transportation costs to the mill. After a batch of resin leaves the elution column, it is washed with barren solution in the rinse chamber to remove excess sulfate before being transferred to the bottom of the adsorption column.

RECENERATION

A regenerating chamber is provided to clean the resin should it become fouled with silica or molybdenum. A selector switch on the control panel permits the operator to regenerate as much of the resin as necesssary to maintain the ash content at a level that will permit good loading and stripping to meet effluent regulations.

ELUATE

With feed concentrations at 3.0mg U_3O_8/l and barrens at less than 0.01ppm U_3O_8, the eluate averages 12g U_3O_8/l. Periodically it is shipped to the mill, which is about 125 miles from the mine and fed directly into the precipitation circuit for production of yellowcake.

RESIN LOSS Resin replacement has been about 7% per year.

OPERATORS

The CIX plant is the responsibility of Mr. Carles Palmer who also supervises the radiometric ore sorter plant. The CIX plant is operated by two full operators each working four 10-hour shifts per week and overlap on one day of the week. An alarm system alerts mine personnel to malfunctions while the plant is unattended.

OTHER ASPECTS

Copper, cadmium and lead levels in the water are said to be close to the permit limits. A study is in progress to determine the need for and processes available to remove these metals too.

MILL

Located at Canon City, Colorado, beneficiated ore from the Schwarzwalder Mine is leached to recover uranium. In earlier days unbeneficiated ore was treated which yielded larger volumes of tailings. At the Cotter Corporation Canon City facility there is an old millsite which is no longer in use and the new mill that replaced it is located on the same property. The old abandoned mill has been fenced off and it is expected that in 10-15 years or so it will be demolished and the site restored.

Several unlined old tailings disposal areas exist at the mill some of which are now used as ore stockpile areas for the new mill.

Numerous monitor wells are scattered around the Cotter Corporation plant and tailings site to define groundwater effects and migration of contaminants.

A few miles from the Cotter operations at Canon City is located Lincoln Park and a municipal drinking water SCS reservoir which serves the town. Seepage from the Cotter past and present operations is slowly migrating toward the reservoir and is contaminating groundwater with uranium, molybdenum and selenium.

A principle source of this contamination appears to be seepage through several old tailings impoundments which were in use since 1958. All tailings for the first 25 years of operation were deposited on unlined natural ground surfaces. The soil and groundwater underlying this area is contaminated by metals to the extent that it could take 50-100 years to decontaminate the groundwater by reversing the flow and flushing out the contaminants.

The migration rate of contaminated groundwater toward Lincoln Park is slow and is being monitored. The aquifer is artesian and the water table at places is 2-3 feet below the surface, elsewhere it is 30 feet deep. The main aquifer underlying the area is said not to be contaminated.

The contaminated soil layer covers 80 acres and is 6 feet deep. The soil is sandy and has become consolidated in places requiring ripping to penetrate. It is not vegetated.

Cotter Corporation is faced with two choices:

1) To remove contaminated topsoil
2) To isolate the contaminated material and prevent further seepage through it.

It is proposed to isolate the contaminated material by covering it with a 2 ft thick compacted clay layer. At the same time the already contaminated groundwater that is migrating toward the reservoir can be intercepted at a gap in the bedrock where it is planned to contain it. A series of measures including drains, downstream cutoff trenches and surface sealing are under review to determine the cost of solving the problem.

Morrison-Knudsen was retained to undertake an extensive investigation into the alternative remedial possibilities at the Canon City millsite and their costs. A report was due to be presented to Cotter Corporation mid 1984. The project manager for Morrison Knudsen at Boise, Idaho was Bill Gossett (208) 386-5422.

There is already a stockpile of clay rich soil that could possibly be used to install a compacted clay surface capping over the site. It is not known how surface cracking would be prevented except possibly by covering with topsoil and seeding.

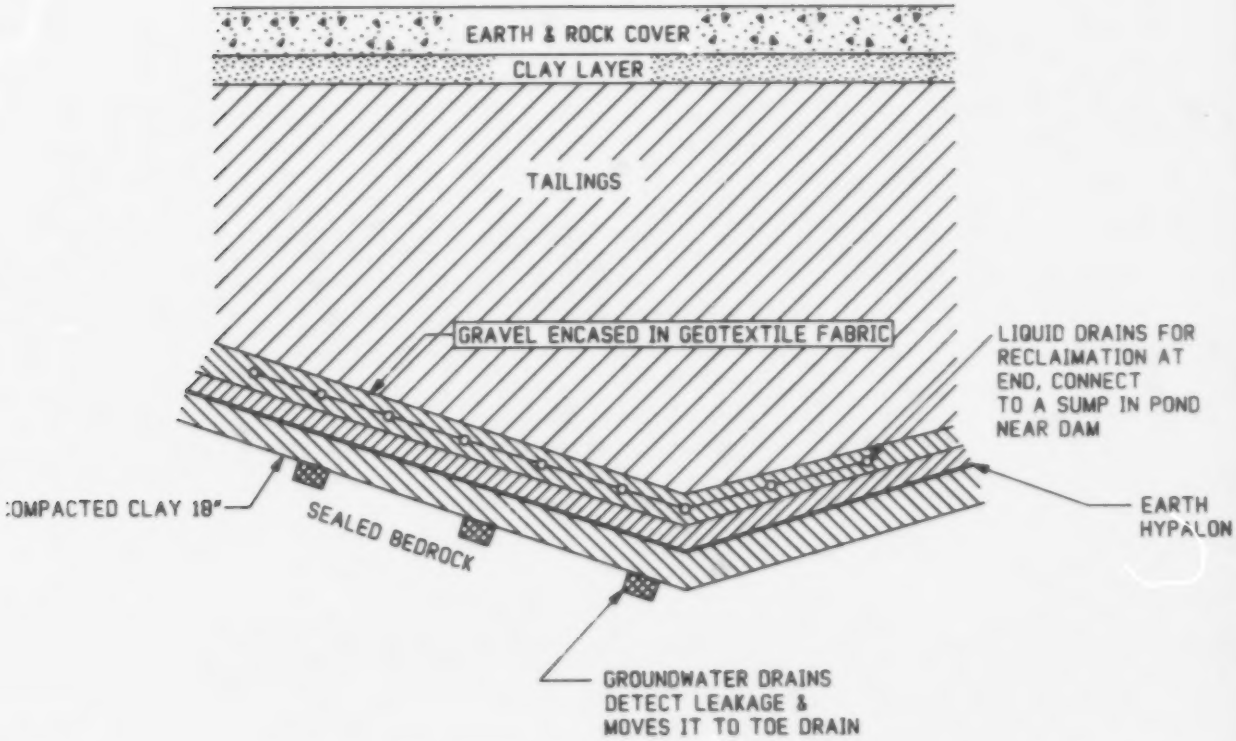
TAILINGS DAM

The Canon City tailings are now deposited in a lined tailings pond designed by:

Wahler Associates
1023 Corporation Way
Palo Alto, CA 94303
Telephone: (415) 968-6250
Contact: Forrest Gifford
Jack Wulff, President

The pond lining system is installed over an underground drainage system installed on the bedrock to catch and recover any seepage. The bedrock itself was cleaned and sealed then covered with an 18" compacted clay layer which acts as a base for a hypalon liner. An interesting feature of the lining membrane is that three thicknesses are used increasing with depth as hydrostatic head increases: believed to be 30, 35+ and 45 mil but subject to confirmation. The liner is covered with earth and finally a sequence of liquid drains installed over the lining system at the base of the tailings. When filled the

tailings pond will be covered with a layer of clay, then earth and rock followed by topsoil for seeding.



HIMSLEY A., U.S. Patent 4,018,677.

JACOBS, S., SCHEXNAILDER, S., URBAN, C., SMITH, T., and GONZALES, D. (1979) Recovery of Low-Level Dissolved Uranium Values from Treated Mine Water. October 1979.

PALMER, C., HIMSLEY, A., and BENNETT, J.A. (1984) Design and Operation of Continuous Ion Exchange Process for Treating Uranium Mine Water. 45th International Water Conference, Pittsburgh, PA, 22-24 October 1984.

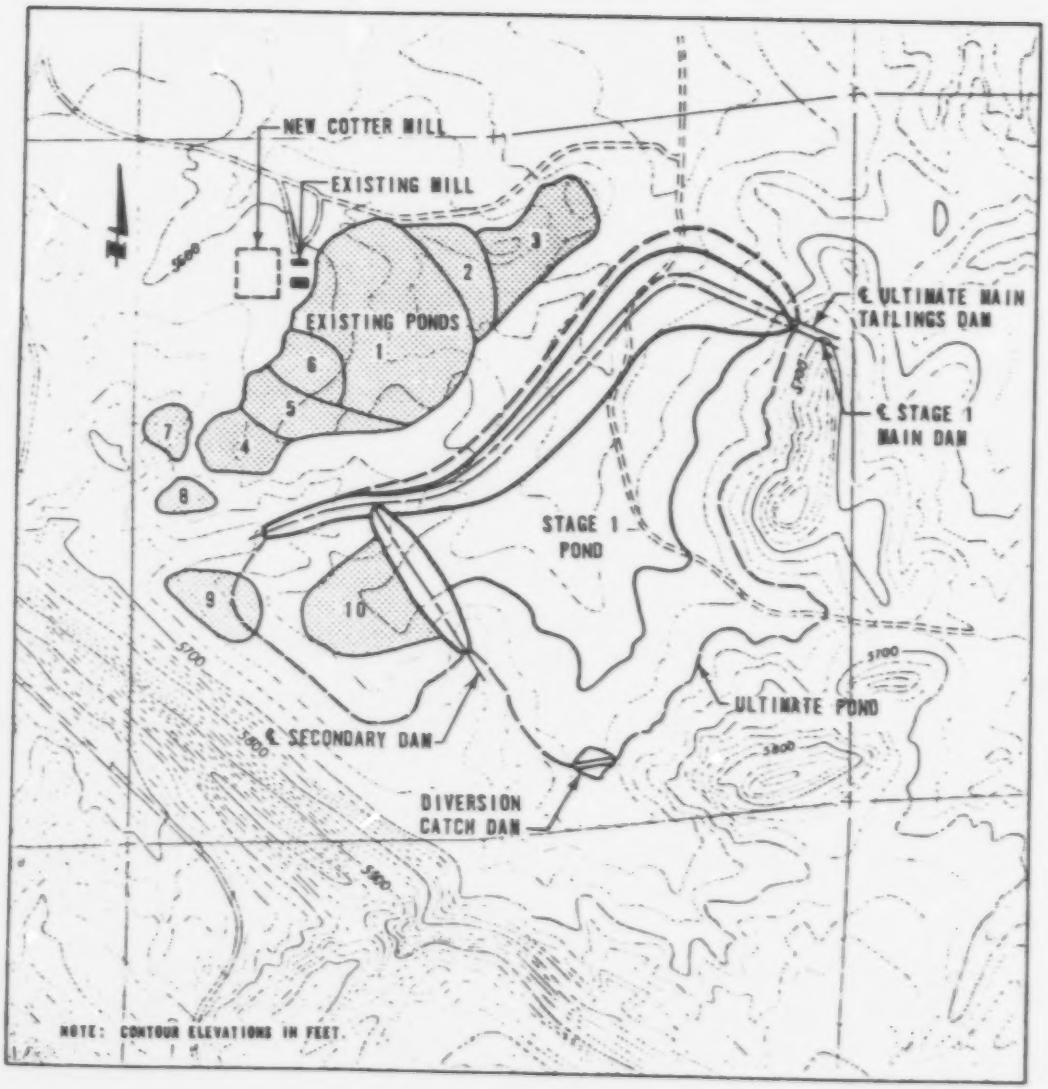


FIGURE II-1
GENERAL SITE PLAN

CURRENT PARAMETERS IN THE COST-EFFECTIVE DESIGN OF URANIUM MILL WASTE DISPOSAL SYSTEMS

J. G. Wulff, F. W. Gifford and D. Buranek

Wahler Associates
Consulting Geotechnical Engineers
P. O. Box 10023
Palo Alto, California 94303

Presented at First International Conference on Uranium Mine Waste Disposal, Vancouver, B.C., May 1980

COTTER PROJECT

Project Background and Setting

The Cotter Corporation began operating its first uranium mill in August 1958, near Canon City, Colorado. The original tailings dam was developed from a starter dike; further construction of the tailings impoundment was done with mechanical equipment using tailings sands, a normal method of construction at that time. Over the years, the plant expanded to meet the growing demands of the uranium industry. The tailings system was expanded along with the mill as required. In 1975 Cotter Corporation decided to construct a new mill adjacent to the then existing mill. The new mill, which has a capacity of 1360 metric tons per day (1,500 short tons) of ore, will handle new ores from various mines. It is planned that the refurbished old mill will reprocess tailings from the existing ponds for additional mineral resources recovery. The new mill produces acid wastes and the old mill produces alkaline wastes. Because of chemical considerations, the waste products are kept separate. Thus, two impoundments are required. No recycling of liquid wastes is performed. These will be disposed of by evaporation from the tailings pond. A plan of the facilities is shown on Figure II-1.

Since the solid and liquid wastes from uranium processing are toxic, one of the most important concerns in the design of the new tailings disposal facility was containment of the wastes, i.e. seepage control to prevent the degradation of downgradient waters. This is especially critical at the Cotter facility, because it is located at about Elevation 1700 m (5600 ft.) only 3 to 5 km (2 to 3 miles) upgradient of Canon City and the Arkansas River. In addition, the existing tailings ponds, which were constructed when proper uranium tailings disposal and pollution control were not fully understood or appreciated, have raised concerns related to groundwater degradation. The new ponds had to be made as liquidtight as practical to prevent further water degradation and to allow the existing problem to be corrected and eventually eliminated. Because of the importance of seepage control, the lining system designed for the tailings pond received very close scrutiny from the owners, the designers, and the various regulatory agencies involved in reviewing and licensing the project.

The reclamation of the existing tailings ponds and the existing mill was a primary consideration in the selection of Canon City as the new mill site. The problems with seepage from the existing unlined tailings ponds required corrective action. By having a new pond of high integrity available, solutions and slurries from the existing operation could be transferred into the new impoundment where they would be safely contained. The new impoundment is thus the key feature

in the reclamation of the existing mill area and tailings ponds.

Because of the proximity of the mill to Canon City, and because of topographic and geological conditions and the non-availability of additional suitable land, no satisfactory site off the property owned by Cotter Corporation was available. Thus, it was decided to construct the new tailings impoundment on the section of land that they already owned.

Topographically, the site is a northerly-drained alluvial valley, bounded by steep sandstone ridges on the east, southwest and northwest. Geologically, the mill and tailings ponds appear to be well sited, as they are in the middle of the bowl formed by the Chandler syncline, the axis of which bisects the project site. The surface bedrock unit underlying the tailings areas is the Poison Canyon Formation, which is some 250 m (800 feet) thick. It is composed primarily of sandstone interbedded with shales and some conglomerates. Core hole data at the site indicates interlensing of the different layers. Joints are primarily found only in sandstone and usually terminate at major bedding surfaces. Fracture frequencies are variable but, according to the core hole data, they appear to diminish considerably with depth. Figure II-2 shows a geologic cross section of the area.

Some 300 m (1,000 feet) below ground surface of the site are coal workings, mined out between 1908 and 1934. The coal seam, which averages 1.5 m (5 feet) in thickness, was mined by conventional room and pillar methods. Studies conducted during the tailings dam design indicate that collapse of the old workings would not cause detrimental subsidence at the surface.

Probably the most critical aspects of the site were the hydrogeological characteristics of the basin and the permeability of the basin area (see Figure II-1 for general site layout).

These were extensively investigated by field drilling and testing programs. Water injection tests in the exploratory core holes on the eastern flank of the retention basin, along the easterly hogback ridge, showed very high permeabilities. In most cases, all the drill water was lost in the holes. These high water losses were due to large, open fractures. However, in the central and western pond areas, the great majority of the injection tests indicated low permeability conditions. Most of the testing in these areas showed no water loss during the injection tests. However, pumpout tests conducted in observation wells downgradient of the existing ponds conflicted with the results of injection tests in the central and western pond area. The pumpout tests showed permeability values several orders of magnitude greater than did the injection tests. Furthermore, observations at cluster wells indicated that seepage flow from the existing pond is controlled by fractures or joints in the rock and this fracturing is erratic and complex.

Broadly, the results of this testing program were interpreted to mean that the eastern flank of the proposed new retention basin, where the permeability was high, would, without doubt, require lining. For the rest of the basin, the two basic data sources were in conflict. The results of the injection tests suggested that a lining would not be required, while the results of the pump tests in the wells downstream of the existing pond indicated that the lining of

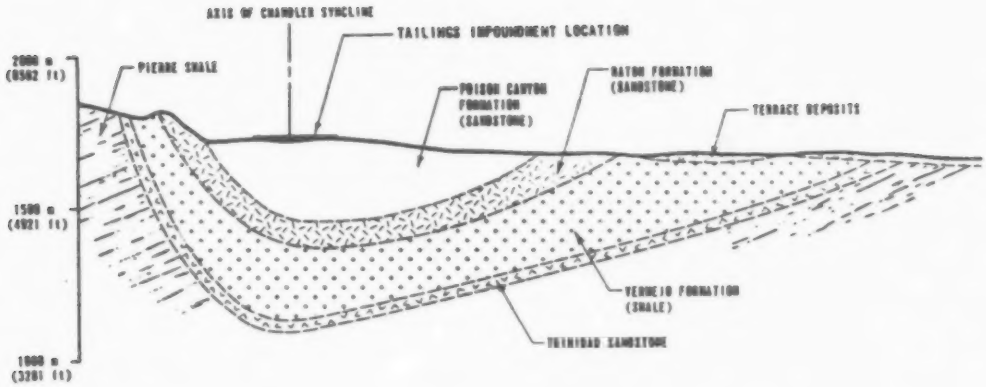


FIGURE II-2

SITE CROSS SECTION

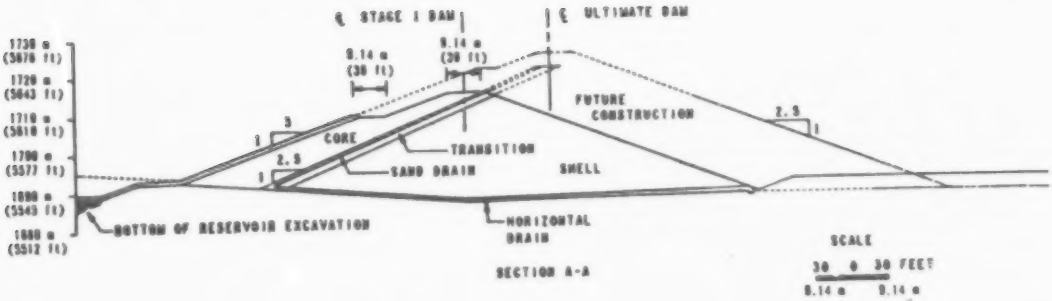


FIGURE II-3

TYPICAL MAIN DAM SECTION

the entire basin would be appropriate. After careful review of all the available information, and of the risks and liabilities involved, the Cotter Corporation decided it would be prudent and in everyone's best interests to provide a high quality lining system for the entire pond.

Selected Disposal System

Because of the topographic and geologic constraints on the property, below-grade disposal was not practical. The selected design is an above-grade disposal system consisting of zoned earth embank ments, a sophisticated lining system for the impoundment area, subdrains below the liner, and tailings dewatering drains above the liner. An idealized section is shown on Figure II-3.

The foundations for the embankments and lined impoundment areas are excavated to, or into, bedrock. As shown on Figure II-3, the embankments have an upstream sloping clay core, backed by a continuous sloping drain and a horizontal drain in the valley area. The portion of the embankment downstream of the sloping drain consists primarily of random fill. The lining system consists of three layers--a compacted 0.46 m (18-inch) clay subliner, a Hypalon membrane liner, and a 0.30 m (12-inch) soil cover. The clay subliner is provided as a cushion for the Hypalon to prevent rock perforating the membrane and to act as a secondary liner in case the membrane is inadvertently perforated. The Hypalon thickness varies from 0.91 mm (36 mils) for the shallower areas to 1.14 mm (45 mils) for the mid-depths, to 1.52 mm (60 mils) for the greater depths. The membrane liner has a reinforcing fabric scrim. The 0.30 m (12-inch) soil cover is provided to protect the Hypalon until it is covered by tailings.

The underdrain system consists of trenches excavated into bedrock, PVC pipe and gravel backfill. The purpose of the underdrains is to collect seepage emanating from areas of the bedrock and transport the collected seepage beyond the toe of the dam so that there is not a buildup of hydrostatic pressures that could displace the liner.

To futher reduce concerns about seepage over the very long term (i.e. after reclamation), the regulatory agencies requested that there be included a system to dewater the tailings to the greatest extent practical after the pond is decommissioned. Dewatering the tailings reduces the criticality of the lining system in long term containment of the waste. The dewatering system selected consists of a network of finger drains installed on top of the lining as shown on Figures II-4 and II-5. The dewatering system is to function only during reclamation and after the free water in the ponds has evaporated.

The pH is adjusted in the mill from 1.7 to 4.2. Raising the pH has the following benefits: (1) Reduces the concentration of contaminants in the liquid; hence, decreasing the potential for contamination by seepage. (2) Reduces the potential for precipitates clogging the dewatering drains. (3) Reduces precipitates covering surface of tailings after evaporation and reduces problems of placing reclamation cover. Costs for raising the pH are not included in this study.

System Quantities and Costs

The disposal system was designed to be constructed in stages. The ultimate height of the dam will be approximately 35 m (115 feet) with

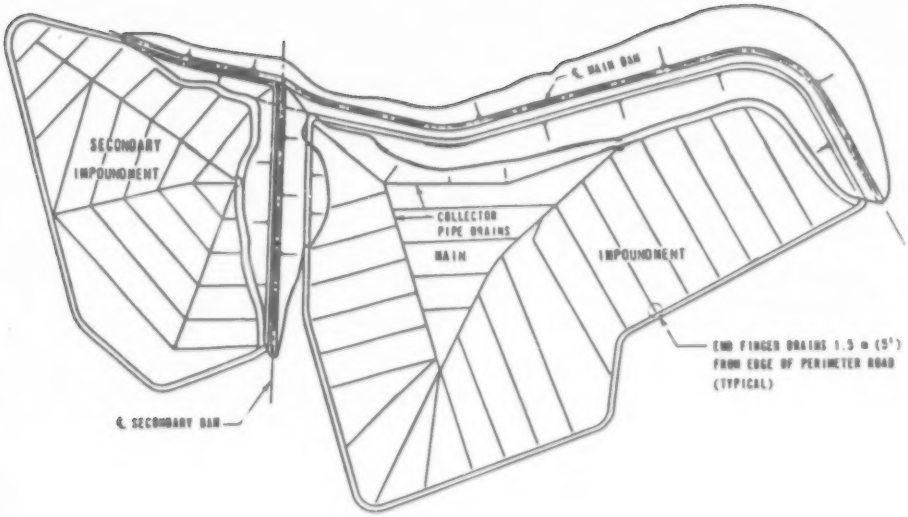


FIGURE II-4

TAILINGS DEWATERING DRAINS
LAYOUT PLAN

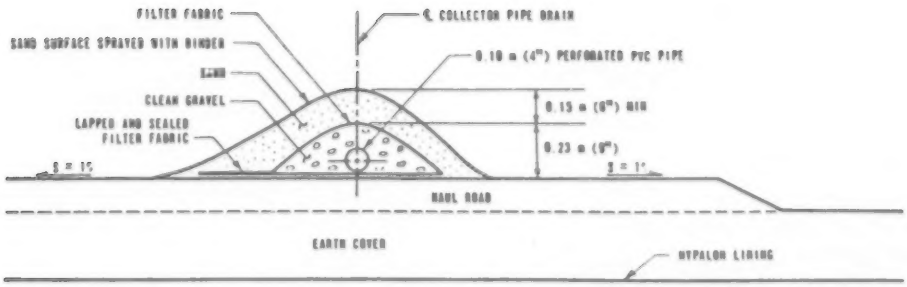


FIGURE II-5

TAILINGS DEWATERING DRAINS
DETAILS

a crest length of about 1524 m (5,000 feet) and a tailings storage capacity of about 9 250 000 m^3 (7,500 acre-feet). The first stage embankment is 31 m (101 feet) high, has a crest length of 1497 m (4,910 feet).

The total tailings solids storage capacity of the first stage impoundments is 3 million m^3 (2,400 acre feet). The first stage tailings storage will provide for approximately 3.4 million tonnes (3.8 million tons) of ore. Construction of the first stage tailings disposal facilities commenced in the summer of 1978 and was completed in 1979. Transfer of liquids from the old tailings impoundments began in the fall of 1979 and the new mill started operating in September 1979, with the disposal of tailings in the new main impoundment at that time.

Mountain States Engineers were the designers and constructors for the mill. Wahler Associates designed the tailings disposal facilities and Stafford Construction Co., served as the construction subcontractor for the earthwork.

All earthwork materials for the embankments and liners were derived from the reservoir area and an area downstream of the dam except for sands and gravels for the various drains. Sand and gravels came from a commercial plant located near Canon City.

The first stage main and secondary embankments consisted of about 2.2 million m^3 (2.9 million cubic yards) of fill. Including clearing, grubbing, stripping, foundation preparation, embankment materials procurement and placement, and elimination of two old tailings ponds, the first stage embankments costs were about $13,000,000, which is an average of $5.86 per m^3 ($4.48 per cubic yard) of fill.

There were about 3960 m (13,000 lineal feet) of subdrains installed at a total cost of $190,000, or $47.97 per m ($14.62 per foot) of subdrain.

There were 623,000 m^2 (154 acres) of lining installed for a total cost of $5,300,000, including subliner, membrane liner, and cover. This is a cost of $8.50 per m^2 ($0.79 per square-foot) of liner.

The tailings dewatering drains consisted of 8930 m (29,300 lineal feet) of drains and two sumps for installation of pumps. The total cost of the first stage tailings dewatering system was $303,000, for an average cost of $33.93 per m ($10.34 per lineal foot) of drain.

Construction of the remaining stages will provide 6.3 million m^3 (5,100 acre-feet) of additional storage. Data for storage provided by second stage construction and total storage are presented in Table II-1.

TABLE II-1

Future Stages and Total Tailings Storage Capacities

Future Stages		Total	
m^3	Metric Tons of Ore	m^3	Metric Tons of Ore
6.3 million (5,100 ac.ft)	7.3 million (8 million tons)	9.3 million (7,500 ac.ft)	10.7 million (11.8 million tons)

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INTRODUCTION

The Denison uranium mine was discovered in 1954 on the west side of Quirke Lake 11 miles north of the present town of Elliot Lake. The 120 million ton ore deposit has a grade of 2.78 lbs U_3O_8/st (1.18 kg U_3O_8/t). Production started at 5450 mt/d in 1957. By 1979 the Denison Mine had produced about 90 million lbs of U_3O_8. This gives an idea of the magnitude of the tailings disposal challenge - Some 25 million tons of tailings have already been disposed of, with another 100 million or so to go.

Several interesting aspects of water management were identified at the Denison operations. Four of these are of particular interest and are a shared problem with other large uranium mines in the area:

1) Macro water recycling and management for the mine, mill, tailings, townsite and lake system.

2) Disposing of hundreds of millions of tons of tailings containing 2-4% pyrite to handle the acid mine drainage challenge.

3) Removal of radium and other radionuclides from tailings decant water.

4) Limitations on use of recycled minewater for dust suppression underground.

5) Anaerobic underground sewage treatment system.

6) Underground leaching of uranium from mine stopes.

LOCATION — 11 miles north of Elliot Lake north of Lake Huron in Ontario.

CLIMATE — Mild damp summers, frozen winters with snowfall. The area has net precipitation over evaporation.

TOPOGRAPHY — Rolling hillsides with an intricate system of lakes and streams.

PROCESS

Ore is crushed and ground, then subjected to a conventional sulfuric acid leach followed by ion exchange. $NaOCl_4$ and recycled iron cake are used as oxidants in the leaching process. Ammonia is used to precipitate uranium from the eluate as ammonium di uranate (ADU). Nitric acid is used as the eluant to elute uranium from the loaded resin.

From a water management standpoint the use of ammonia could be expected to result in ammonia in the discharge to the lake which might be detrimental to the aquatic ecosystem.

The simplified process flowsheet is shown below.

WATER BALANCE

A water balance showing how water use is distributed to the various operating units at Denison Mines is shown. The numbers are in Imperial gallons per minute.

WATER UTILIZATION AND RECYCLE

The main source of water for the mines and mill at Denison Mines is Quirke Lake. The following volumes of water are used for the mines and mill from Quirke Lake.

To No. 1 Shaft area :	505 Igpm	3,300 m^3/d
No. 2 Shaft area :	1453 Igpm	9,500 m^3/d
Concentrator area :	2261 Igpm	14,800 m^3/d
Total	4219 Igpm	27,600 m^3/d

Gross water use works out to 5.1 m^3 water/ton ore based on 5400 mtpd ore throughput. Of this gross water intake, 1100 Igpm (7,200 m^3/d) that was used for compressor cooling is returned directly to Quirke Lake. Of the 3150 Igpm (20,600 m^3/d) pumped to the tailings pond with tailings, presumably 40% or so finds its way back to the Quirke Lake thereby constituting a macro recycle, but it is not recycled to the process directly.

The mine

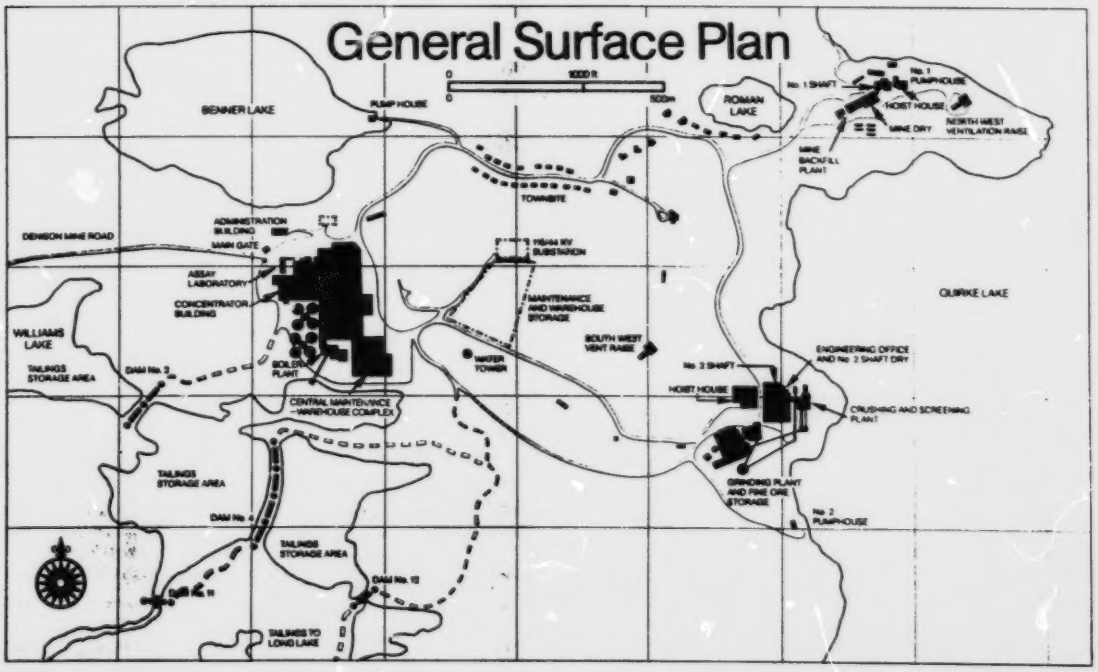
The Denison mine, more than 6,400 acres (2,600 hectares) in surface area, is located on the north limb of the famous Quirke Lake syncline. The main ore zone, consisting of the two uranium-bearing conglomerate beds, dips from north to south at an average inclination of 20 degrees. At the upper end it lies 550 feet (168 metres) below the surface and deepens to 3,100 feet (945 metres) at the south property boundary.

In many areas mining of the main ore zone is carried out over the entire section comprising the two conglomerate beds and the interbedded quartzite. In other areas the conglomerate beds are selectively mined, depending on the thickness of the interbedded quartzite. Minor undulations occur throughout the orebody and faults, dykes and sills have been encountered in several locations.

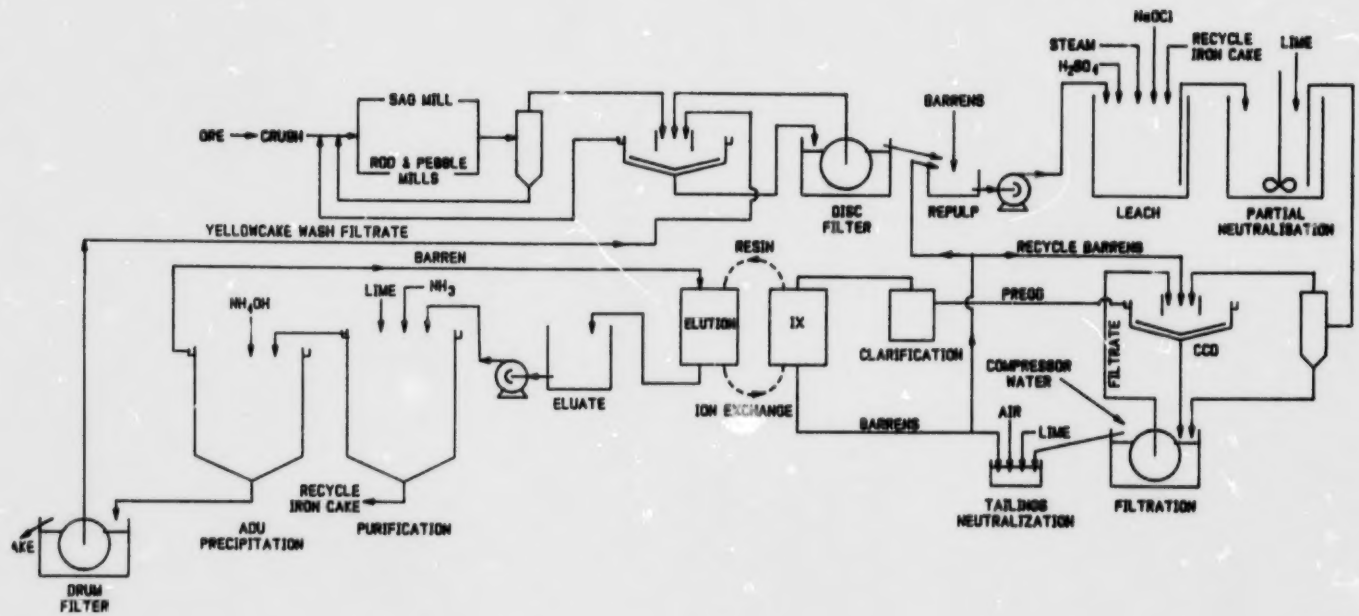
The three shallower reefs above the main ore zone will be mined sequentially when required.

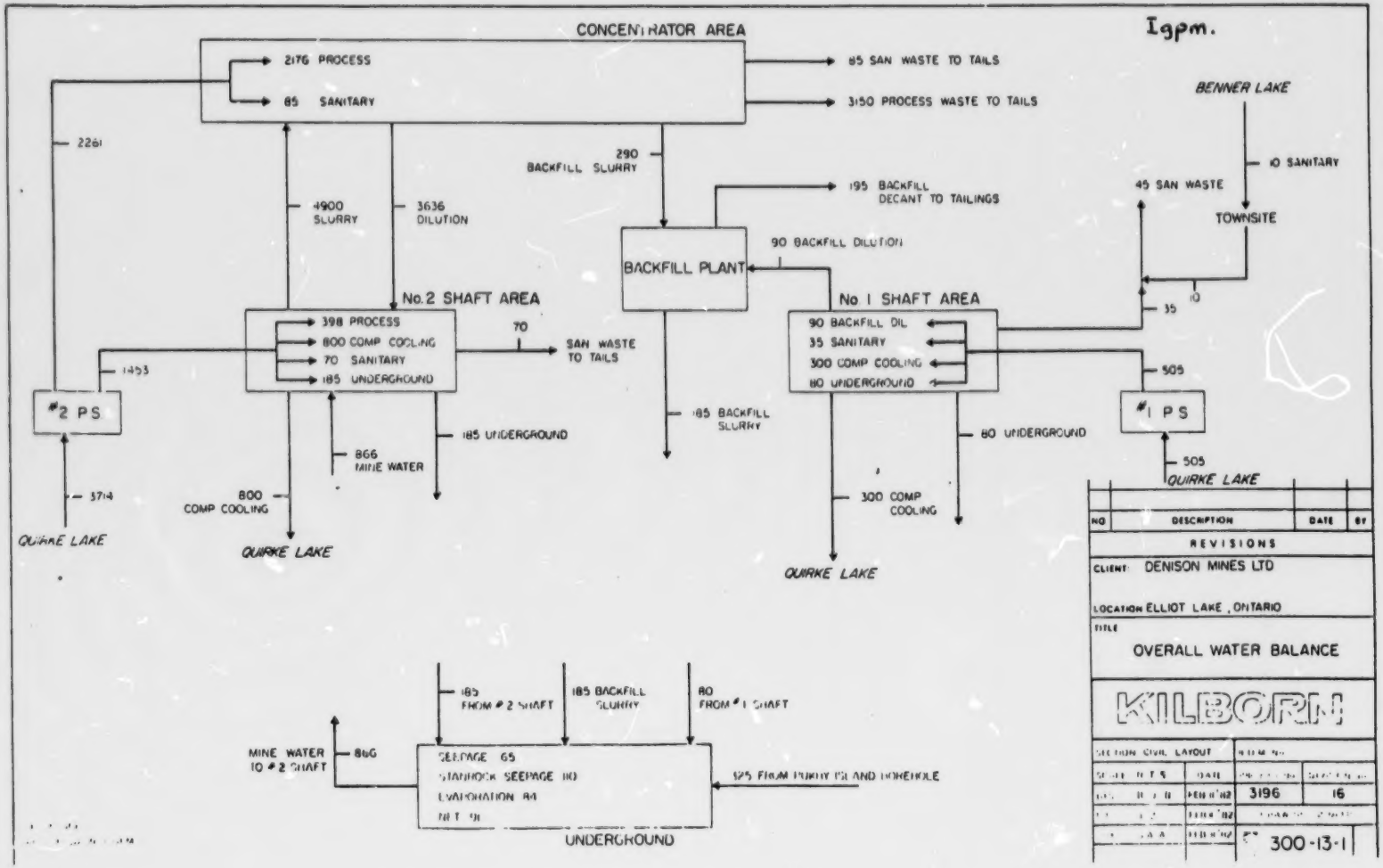
The uranium-bearing conglomerate beds are reached by two main vertical shafts, approximately 2,600 feet (800 metres) apart. The first shaft gives access to the orebody at the 1,600 foot (488 metres) level and the second shaft, farther down-dip, intersects the main ore zone at the 2,465 foot (752 metres) horizon. The mining method requires only one main underground station at each shaft.

Two other shafts at the east end of the property, formerly part of the neighboring Can-Met mine, have been connected with the Denison underground workings for ventilation purposes. The two Stanrock shafts eventually will be connected to the main Denison underground workings.



DENISON MINES LTD




Igpm.
CONCENTRATOR AREA
2176 PROCESS
85 SANITARY
85 SAN WASTE TO TAILS
3150 PROCESS WASTE TO TAILS
2261
4900 SLURRY
3636 DILUTION
290 BACKFILL SLURRY
195 BACKFILL DECANT TO TAILINGS
BACKFILL PLANT
90 BACKFILL DILUTION
BENNER LAKE
10 SANITARY
45 SAN WASTE
TOWNSITE
10
35
No. 2 SHAFT AREA
398 PROCESS
800 COMP COOLING
70 SANITARY
185 UNDERGROUND
70
SAN WASTE TO TAILS
1453
#2 PS
3714
QUIRKE LAKE
866 MINE WATER
185 UNDERGROUND
800 COMP COOLING
QUIRKE LAKE
185 BACKFILL SLURRY
No. 1 SHAFT AREA
90 BACKFILL DIL
35 SANITARY
300 COMP COOLING
80 UNDERGROUND
505
#1 PS
505
QUIRKE LAKE
80 UNDERGROUND
300 COMP COOLING
QUIRKE LAKE
185 FROM #2 SHAFT
185 BACKFILL SLURRY
80 FROM #1 SHAFT
MINE WATER TO #2 SHAFT
866
SEEPAGE 65
STANROCK SEEPAGE 80
EVAPORATION 84
NET 96
525 FROM FURDY ISLAND BOREHOLE
UNDERGROUND
NO
DESCRIPTION
DATE
BY
REVISIONS
CLIENT: DENISON MINES LTD
LOCATION ELLIOT LAKE, ONTARIO
TITLE
OVERALL WATER BALANCE
KILBORN
3196
16
300-13-1

Water management practice at Denison Mines Ltd. and other Ontario uranium operations contrasts with that at Rössing Uranium Ltd. in the Namib Desert which uses about one fifth the amount of water or less, per ton of ore treated.

In the metallurgical treatment process, water is recycled primarily to segregate the acid and neutral circuits to save corrosion and reduce overall acid consumption. In-plant water recycling loops are as follows:

1) Neutral water added to the grinding circuit is recovered from the ground pulp ahead of acid addition for leaching, by thickening and filtration, and is recycled to the grinding circuit. Dewatered pulp is repulped with recycled acid barrens.

2) Acid solutions are recycled after leaching, solid-liquid separation and ion exchange when barrens are recycled to the repulper at the head of the leach train. In this way acid consumption is reduced.

3) Eluate, after purification and precipitation of the ADU product, is decanted and recycled as fresh eluate after addition of nitric acid.

4) Compressor cooling water is used as glandwater.

5) Compressor water is used in spraybars for the second step filtration of leached pulp to wash tailings. This use of compressor water replaced one application of fresh water. Barrens are used for primary filtration wash.

6) 866 Igpm (5700 m^3/d) underground minewater is recycled to the metallurgical process.

FRESH WATER FROM QUIRKE LAKE IS ADDED FOR:

1. Underground mining operations for dust suppression.

2. Compressor cooling

3. Boiler water for steam

4. Pump glands

NON-RECYCLABLE WATER

1) Since nitric acid is used in the elution circuit, the use of barrens after uranium precipitation in the front end of the process would be a problem as the contained nitrates could interfere with the strong base ion exchange adsorption process.

2) Water is required for dust suppression in the quartz rich underground mine. The Ontario Ministry of Labor does not allow the recycle of water underground. They are worried about increased silicosis risk if recycled water containing silica is atomised in the stopes. Silica levels in the water are less than 10 ppm (total suspended solids). However, with high gypsum levels which would result from recycling of the water, the nozzles could become encrusted and dust suppression waterflow might is choke off. Also, if water is recycled and gypsum levels build up, this could cause a problem if mineworkers drink the water.

REGULATORY FRAMEWORK

Mining in Canada is controlled by the Federal Metal Mines Regulations which were promulgated under the Canada Fisheries Act. The Provincial government has a Mininstry of the Environment which can enter into an agreement with the Federal Government to apply the Fisheries Act to which provincial regulations can be added. Ontario has elected not to enter into this agreement. Consequently in Ontario the Mininstry of the Environment (MOE), does not have regulatory authority over metal mines. MOE does, however, review all mining operations, set environmental objectives, criteria etc. The MOE regional director has the authority to write rules on a case by case basis, and can insert some control on a case by case basis via an order on effluents that affect receiving waters.

Uranium mines fall under the ultimate jurisdiction of the Atomic Energy Control Board as set out in the Atomic Energy Control Act. The AECB can develop regulations to control uranium mines and mills or it can do so through issuing individual site specific licenses which is the approach that it has elected to use.

EFFLUENT LIMITS

Denison Mines Ltd. must comply with two sets of regulations - The AECB effluent discharge limits and the Federal Fisheries Act regulated by Environment Canada.

	AECB License Grab Sample (ppm)	Federal Metal Mine Regulations	DENISON MOE Objective
pH	6.5-9.5		
Cu Max	0.6		
Ni Max	1.0		
Pb Max	0.4		
Zn Max	1.0		
Cumulative Zn, Pb, Cu, Max	1.0		
Suspended Solids	15.0 (grab)		
	7.0 (Monthly Ave)		
Radium 226 pCi/l	5.0 (Monthly Ave)	10 pCi/l Monthly Ave	3.0 pCi/l
		5 pCi/l Annual Ave	
		10 pCi/l Composite	
		15 pCi/l Grab Sample	

The Federal drinking water objective for Radium-226 has been set at 27 pCi/l which means the level required for mine water discharge is very much stricter than drinking water levels for reasons not explained.

PLANT RUNOFF

Plant runoff from the mill area drains into the same catchment as the tailings drainage basin including the stormwater sewer.

Ore stockpiles are in the open, but normally coarse ore is not stockpiled. There is an unlined area that can be used for ore stockpiles if needed. This is located in the Waste Management Catchment area. Fine ore bins for the rod mills are covered. ROM feed for the SAG mill is also in a covered bin.

All water draining from these areas is collected, settled and treated with $BaCl_2$ for radium removal.

SEWAGE

The septic tank system is employed with effluent going to the tailings area. Septic tank sludges are pumped to the tailings dams.

Previously chemical toilets were used underground and the waste was dumped with the mill tailings. Now an anaerobic toilet sewage system is employed underground. The

overflow from the anaerobic system goes to the minewater mine-sump. The anaerobic sewage plant was supplied by Fitzpatrick Ltd., Sault Ste. Marie, Ontario.

MINEWATER

During 1983 minewater was pumped from underground at an average rate of 70 l/s (924 lgpm, 6048 m^3/d) and used in the grinding circuit. This water is used for underground leaching of uranium from the stopes at the same time as suppressing dust. No oxidant is added nor nutrients. Composition of the minewater is in mg/l is:

pH	2.7
Fe	300 ppm
Zn	4.5
Cu	1.28
Ni	0.84
Mn	1.9
Pb	5.05
$SO_4^=$	2050
Ca	176
Cl^-	113
NH_4^+ as N	47
NO_3^- as N	60
K^+	99.6
Mg	20
U_3O_8	104
Ra-226 Dissolved	40 pCi/l
Ra-226 Total	60 pCi/l

Underground leach solutions goes to the mine sump with all other minewater and is pumped to the surface after pH adjustment.

TAILINGS DECANT SOLUTION - FINAL EFFLUENT

Tailings pulps are neutralized to pH 8.3 and after decanting and treatment for radium removal, a final effluent is discharged at an average flowrate of 272 l/s (23,500 m^3/d, 3500 pgm) with the following composition compared with the regulatory limit:

	Tailings Solution after Neutralization	Final Effluent Composition	DENISON Regulatory Limit
pH	8.1	8.2	6.5-9.5
Radium (pCi/l)	1411	3.3	5,10 pCi/l
NH_3 (N)	97	60	No limit
NO_3^- (N)	143	81	No limit
TDS	3800	2852	No limit
Mg	48	24.8	No limit
SO_4	1750	1572	No limit
Cu	0.04	0.02	0.6 } combined max 1.0 ppm
Pb	0.25	0.109	0.4 } combined max 1.0 ppm
Zn	0.01	0.02	1.0 } combined max 1.0 ppm
Ni	0.01	0.12*	1.0 } combined max 1.0 ppm
Co	0.02	L T 0.02	
Mn	0.01	0.44*	
Ca	480	509	
K	146	80	
Cl	159	110	
Fe	0.06	0.35	
Na	396	87	
Kjiedhahl N	-	15	-
Ba	-	L T 0.11	No limit
PO_4^{3-} as P	-	0.09	-
Suspended Solids	-	2.5	15
Alkalinity as $CaCO_3$	-	46	-
U_3O_8	-	0.1 ppm	-

TAILINGS DISPOSAL

Tailings pulps are neutralized with lime to pH 8.2 and pumped to the tailings dam which is the first impoundment in the tailings system.

The biggest challenge facing uranium mill tailings disposal is the acid mine drainage problem that results from the pyrite content of the tailings. The acid generated is harmful to the water system in itself but also leaches out other radionuclides, for example, thorium and lead 210. A satisfactory long term method of disposing of pyrite containing tailings is needed.

Denison tailings are ground to 50% minus 200 mesh. Tailings at Denison and the Stanrock property which was acquired after it shut down, are disposed of both in above-ground

tailings ponds and underwater in lakes. In all cases so far the tailings generate acid mine drainage which has to be neutralized by lime addition after decanting.

Decanted tailings effluent is treated with $BaCl_2$ to precipitate radium-226 as discussed below.

Denison has found that when pyrite bearing tailings are disposed of under water, the pyrite will oxidize chemically only if water passes through the pond. Since all tailings dams leak, oxidation of pyrite is inevitable. However, chemical oxidation of pyrite will be slower than in the typical above ground tailings dams with their seepage and runoff.

The use of subaerial layered impoundments in which the tailings never become saturated with water and in which the tailings are emplaced in impermeable layers has been tested with success at Key Lake Uranium where permeabilities as low as 10^{-7} to 10^{-8} cm/sec are achieved. This process is labor intensive and expensive for low grade ores. The same applies to the South African technique of dry tailings disposal with underdrains, which is more applicable in the Witwatersrand climate.

Another possibility considered by Denison is the use of accelerated oxidation and neutralization before emplacement of the tailings. This was found to require too much lime. However, it potentially yields an inert tailings that do not require perpetual treatment. It is noted that sulfuric acid is purchased for the leaching of uranium. Processes that generate sulfuric acid from the pyrite in the ore are available either by pressure oxidation of the ore or by floating pyrite from the ore and roasting it. Either of these represent a way to reduce the acid mine drainage problems at Denison Mines Ltd. but would require extra capital and operating costs and would be ruled out in the currently depressed uranium market.

The Robinsky thickened tailings disposal method was tested on an experimental 12,000 t pile with a 5% slope. Over a 2 year period little erosion was noted and vertical permeability was reduced. The test heap was seeded and fertilized without any mechanical problems, but massive seedkill occurred in places. Slopes are steeper on thickened tailings and runoff is faster. The material is kept homogenous and does not filter well because of the way slimes are mixed with the coarser particles. Thickened tailings with only 25% moisture can be achieved, and the remaining water can be neutralized and disposed of in the same pond. Thickened tailings achieve these characteristics by preventing separation of sand/slimes in the pond.

Covering the tailings with compost to establish plant growth in some cases unexpectedly enhanced the rate of oxidation and was not effective in all cases. It is fair to conclude that the optimum solution to disposal of Elliot Lake uranium tailings has still be be found. It has been the subject of a massive research program funded by the Federal Government. CANMET is carrying out excellent accelerated tailings oxidation tests in Atlanra in which a bactorstat has been added, seeding with fertilzer, compost cover at different thicknesses are compared with disposal as received. More information is available from:

CANMET
555 Booth Street
Ottawa Ontario K1A 0G1
(613) 995-4194
Contact: Eddie Joe, Gordon M. Ritcey

A 10:1 acceleration rate has been achieved in the test. The leach test with the 30 cm compost cover resulted in pH 5 seepage indicating minimal acid generation which is encouraging.

RADIUM REMOVAL

Denison has found that radium in the final effluent is a function of the volume of effluent. Radium dissolves as a function of the amount of water in the mill. If ore is washed in fresh water, radium continues to dissolve from the matrix, so the amount of water is reduced by recycling.

In the solids fraction of mill tailings there is an average of 256 pCi/g radium. The water in the mill tailings after being neutralized contains 1411 pCi/l radium i.e., 1.4 pCi/g and 4000 mg/l TDS, mostly as $CaSO_4$. Before $BaCl_2$ addition, soluble radium in the decanted tailings effluent runs about 370 pCi/l which indicates that a lot of the radium gets left behind tied up in gypsum as the tailings are neutralized. After a few weeks aging, the dissolved radium in the pulp drops to 125 pCi/l as it attaches to solid particles. After about twenty years aging if the tailings are not altered chemically radium in the saturated pore solution will have dropped to 120 pCi/l.

The behavior of radium in tailings solutions under various conditions has been intensively studied by:

Al J. Vivyurka
Senior Environmental Engineer
Rio Algom Ltd.
P. O. Box 1500
Elliott Lake, Ontario
Canada P5A 2K1
Telephone: (705) 461-2518
Telex: 067-7338

After $BaCl_2$ treatment of the tailings pulp, radium drops to 3.3 pCi/l average. The ratio of total to soluble radium varies depending on conditions, turbulence, etc. Radium is settled out as coprecipitated $BaRaSO_4$ in which radium levels typically fall in the range 500-5000 pCi/g.

According to Mr. Chakravatti the amount of radium in the residual effluent is almost independent of the barium chloride dosage. It depends on how it is contacted with $BaCl_2$, i.e., contact time, settling capacity, pH etc. At high pH the flocs don't settle as well as at low pH. Also, the higher the sulfate concentration in the solution, the more effective the radium removal process. It was found that by adding $BaCl_2$ much more $SO_4^=$ and gypsum are precipitated than would be expected.

Concentration of radium in the sludge precipitated at higher pH is lowered by gypsum that precipitates too. In such cases the radium level in the sludge can be significantly diluted by the gypsum and may be in the hundreds of pCi/g rather than in the thousands of pCi/g. If $BaCl_2$ is added to a slightly acid effluent, radium precipitation works better than adding $BaCl_2$ to high pH effluents.

Precipitation of $BaSO_4$ is pH dependent like all sulfate precipitation reactions. When lime is added to the solution, a range of species such as $CaSO_4$, $BaSO_4$ and Ca-$BaSO_4$ will precipitate. The precipitation on addition of $BaCl_2$ goes faster at pH5-6 for some reason than when $BaCl_2$ is added to high pH solutions from which mainly $BaSO_4$ would precipitate.

The result of lower pH $BaCl_2$ is:

1) More radium is precipitated
2) Ba-Ra-SO_4 precipitates in a bigger volume of precipitate

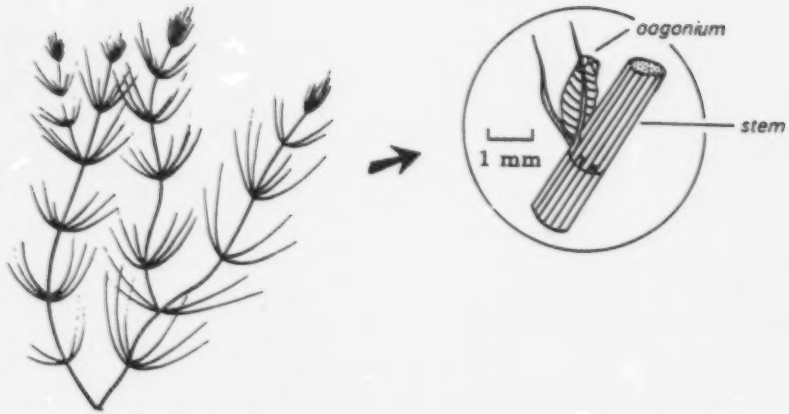
Denison Mines adds $BaCl_2$ to the effluent at pH 8 and does not have a subsequent pH adjustment like Rio Algom's Panel operation. Denison achieves a final effluent with 3pCi/l Ra or less.

AMMONIA

The Denison final effluent runs around 60 ppm NH_3. As water recirculates from the tailings decant dam to the huge volume in Quirke Lake there is such a long residence time that some nitrification of ammonia occurs which reduces the ammonia level. During ammonia oxidation hydrogen ions are generated which drops the pH. At the higher levels in Quirke Lake the rate of NH_3 oxidation is faster and this brings the pH back down again, by the reaction

$$NH_4^+ + 0_2 + = NO_3^- + H^+ \text{ (unbalanced)}$$

CHAROPHYCEAE



In this way ammonia tends to stabilize the pH of the lake.

The main source of NH_3 in the effluents is from its use in precipitating ADU. NH_3 in effluent could be avoided by converting to magnesium oxide for uranium precipitation as recommended by MOE. However, Denison has a Mg penalty clause in their sales contract for yellowcake. It was felt that the inventory of ammonia in the lake was already so high that there would not be a marked reduction in $[NH_4^+]$ in the lake for a long time, i.e. whaterever damage will be done has already been done.

Peroxide precipitation of uranium would avoid the magnesium contamination of product, but was ruled out because of the extra expense.

ECOLOGICAL ENGINEERING

For some time now Denison Mines Ltd. and has Algom Ltd. have hosted botanical research into finding various aquatic plants that will grow in the low and high pH effluent and tailings environment found in the tailings and decant plant. This work has been carried out by:

Boojum Research Ltd.
26 Geneva Avenue
Toronto, Ontario M5A 2J8
Telephone: (416) 922-9002
Contact: Margaret Kalin, PhD

This work aims to identify and grow plants that can survive in the severe (for plants) pH conditions in the Elliot Lake tailings and effluent environment. Some species will hopefully prove useful either as a means of removing metal ions from water or by creating a layer of organic material on the solids-aqueous interface of submerged tailings which would create a reducing environment that will prevent further oxidation of pyrite in the layers of tailings below. The work undertaken to date has been exploratory and no firm conclusions can be drawn yet. One very interesting species of aquatic macro algae known as Chara is one on which researchers' early hopes have been placed.

CONCLUSIONS

1. The acid mine drainage problem from pyrite bearing Elliot Lake uranium tailings is far from resolved. A tour of several tailings sites brings home the magnitude of this problem which will arise on closure of this and other similar mines. Will perpetual treatment be required?

2. $BaCl_2$ addition is very effective for removal of radium from effluent solutions and works best at pH 5-6 with very small doses.

3. In areas such as Elliot Lake where water is abundantly available, this is reflected in the water usage of an overall 8 m^3 per ton ore treated (including mining).

4. Denison Mines practices an interesting form of in situ leaching in which incremental uranium is recovered from the stopes by irrigating them with water. Natural pyrite oxidation drops the pH to leach uranium to 100 plus ppm.

OPERATION	KEY LAKE MINING CORPORATION 229 4th AVE. SOUTH SASKATOON, SASKATCHEWAN S7K 4K3	
CONTACT	Mr. Bernard Rosner	Engineering Manager
	Mr. Manfred Nevin	Metallurgist
	Mr. Joe Anderson	Environmental Manager
	Mr Bob Steen	Metallurgist
	Mr. Joe Sposo	Site Manager
	Mr. Peter Courtney	Environmental Engineer
	Mr. Nick Hall	Dewatering Engineer
TELEPHONE	(306) 665-7000	Saskatoon Office
	(306) 884-2100	Site Office

DATE OF VISIT 7 August 1984 to Key Lake Mining Offices

INTRODUCTION

Key Lake Mining is one of the very high grade uranium ore mines in Canada. Several interesting features have been observed:

1. The ore contains nickel, arsenic, radium etc. which must be taken into account in water management and environmental control.

2 Bentonite stabilized soil has been used as the main lining for the tailings pond which is also covered with a 3 ft thick sand layer over a drainage system to collect and remove solutions.

3. Sub-aerial tailings disposal is practised. Decant is recycled to the plant. Before it reaches the plant, however, arsenic and nickel are removed. An interesting oxidation and precipitation procedure is described as well as an interesting way to achieve a high precipitate sludge density.

4. The operation employs a two stage leach, the second of which is pressurized with oxygen addition. The plant started up using air as oxidant in the pressure leach but it was found that the high arsenic ores needed O_2 for good uranium leach recovery.

5. Raffinate is kept separate and is treated by lime precipitation. An expensive effluent storage and management step has been required employing five lined

monitoring ponds. Each day's effluent, after treatment, is collected in a pond while it is sampled and analyzed. If it meets the effluent limits, it is released to the lake, if not, it is retreated.

6. Lining failure in the monitor ponds even before they were filled with effluent provides and interesting case study on membrane linings. The membranes in this case were underlain by bentonite stabilized soil as a safety measure.

7. The high grade of the deposit economically justifies expensive water treatment and tailings impoundment measures employed including the installation of utilidors, concrete tunnels through which all slurry and solution lines are channelled.

8. Precipitate density in the water treatment step is higher than expected in the design. The Lamella thickener sumps had to be modified to be able to handle the sludges.

9. Gypsum scaling problems have caused a severe problem requiring replacement of buried pipelines which could possibly have been avoided by installing flexible above-ground lines to start with.

10. The Radium precipitation procedure followed at Key Lake is very fast and accomplishes in hours what in other mines, such as Elliott Lake and Rabbit Lake, takes days or weeks.

11. Barium chloride addition to semi-treated effluent results in a further reduction in arsenic levels to less than 0.01 ppm As in the effluent. Precise reasons for this excellent reduction are not completely clear, but it does occur.

12. In January 1984 a water reservoir at Key Lake Mining overflowed while under ice cover resulting in a public outcry, even though no damage was done. When a dam overflows under its ice and snow cover, the leakage is invisible at the time. Special measures have been adopted to prevent a recurrence, which would be useful at other operations in the similar climates.

13. Exceptional measures have been incorporated in the design to reduce the risk of leakage of undesirable metals, reagents and radioactive isotopes to the environment.

Although a small mine at 700 tpd ore, a total of 21,000 tons per day of wasterock must be moved. Based on production of 12 million lbs/year U_3O_8 Key Lake must be one of the largest if not the largest uranium producer in North America.

OWNERSHIP Key Lake Mining Corporation, the operating company is owned by:

Saskatchewan Mining & Development Organization	50 %
Uranerz	33.3%
Eldorado Resources	16.6%

STARTUP October 1983. The first Key Lake ore deposit was discovered in 1975.

PLANT CAPACITY 700 tons per day ore mined; 12mm lbs U_3O_8/year.

MINING RATE 30:1 Mining Ratio

CAPITAL COST $450 million investment

CLIMATE
Extremely cold subarctic winters
Evaporation is almost equal to precipitation
Temperatures to minus 40°C in winter
Extended period of snowcover

ORE TYPE

The uranium is associated with arsenosulfides mostly a nickel arsenosulfide $NiAsS_2$ gersdorffite. The ore is clay rich and extremely variable in grade (0.01% U_3O_8 to over 20% U_3O_8).

WASTEROCK Inert material low or devoid of sulfides.

PROCESS

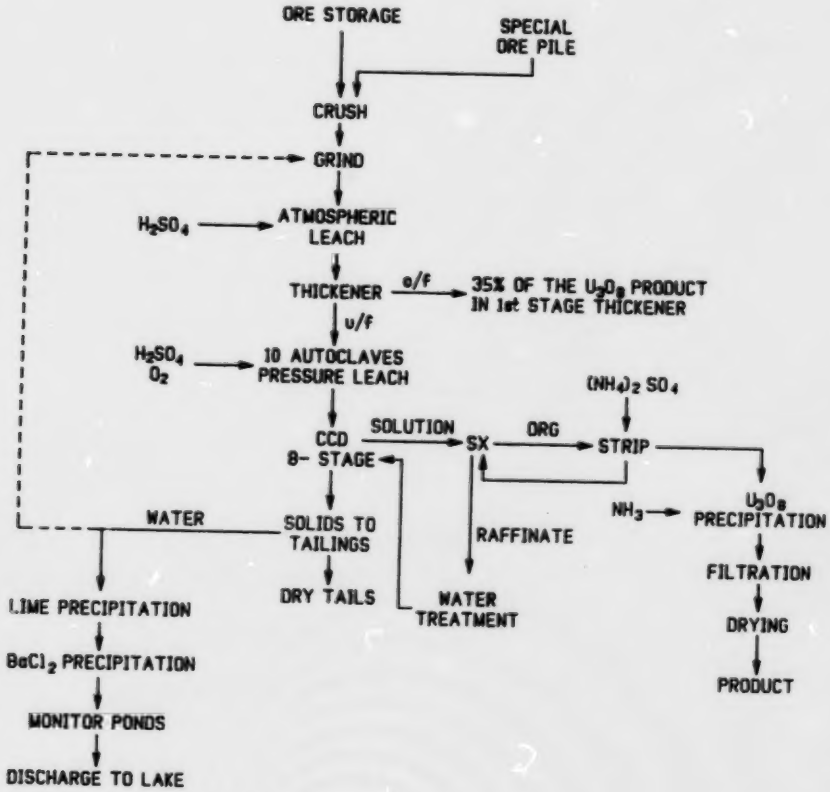
Because of the very high grade of ore, high leach recoveries of 99% plus are required. To achieve this a 2-stage sulfuric acid leach is needed using oxygen as oxidant in the second stage leach. The final metallurgical process was developed by:

Sherritt-Gordon Mines Ltd.
Fort Saskatchewan, Alberta
Canada T8L 2P2

Telephone (403) 988-6911
Contacts: Herb Veltman, Director
D. Robert Weir, Manager Process Research
Roman Berezowsky, Senior Research Metallurgist

An excellent detailed account of the process development for Key Lake is provided by CLARKE et al. (1980).

KEY LAKE MINING COMPANY



AFTER CCD

Uranium is recovered by SX followed by ammonium sulfate strip. Overall plant recovery of 97% is achieved. Ammonia is recovered for reuse using a lime-boil process primarily as an environmental control measure.

ACID PLANT

A small Krebs sulfuric acid plant generates 200 tpd H_2SO_4 from sulfur feed.

ADDITIONAL INFORMATION

1) Additional detailed information on the Key Lake Mining operation can be found in a review document at the Atomic Energy Control Board, Ottawa.
2) Canadian Mining Journal, June 1984
3) Canadian Chemical Processing, April/May 1984 pp. 20-26

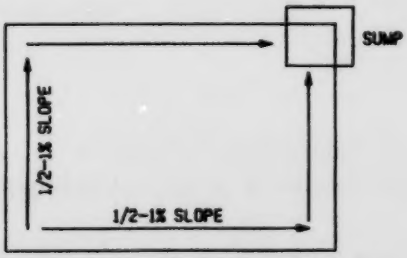
PLANT CONSTRUCTION

Wright Engineers, Vancouver, were the plant engineers.
Commonwealth Construction, construction managers.

TAILINGS POND CONSTRUCTION

The soil stabilized bentonite seal was installed by a subcontractor. 12 Kg Bentonite per m^2 was spread and then mixed in to a depth of 1 ft. The mix is believed to have been moistened and compacted but this detail is not certain. The bentonite stabilized soil achieves a satisfactory low permeability.

The bentonite stabilized lining is covered with a 3' layer of porous sand covering a system of perforated pipe to drain any fluids from the sloped lining. The tailings impoundment floor is sloped at ½ - 1% in two directions to move drainage to a sump.



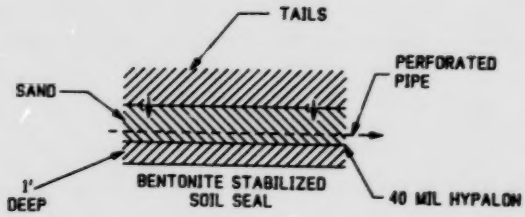
Bentonite stabilized soil linings of the tailings pond and the five monitor ponds were proposed by Knight and Piezold, Geotechnic Consultants in Vancouver, who were also consultants to the project:

Knight & Piezold
409 Granville
Vancouver, BC V6C 1T2
(604) 685-0543

R. Bruce Knight - Partner

TAILINGS DISPOSAL

The tailings are pumped to a permanent storage pond where they are spread in sequenced 100 mm (4") layers which become hardened and almost impermeable. The pond itself is underlain with a sealing layer of till and bentonite. A network of pipes under the tailings with upcomers collects supernatant water which is returned to the bulk-neutralization plant. Upon decommissioning of the project, the tails will be covered with a surface sealing layer. The drainage system will remain in place so that any seepage can be monitored.



The thin layer dry tailings disposal concept also known as "sub-aerial" was also proposed for this project by Knight & Piezold. The tailings are spread over paddocked sections of the tailings pond in thin layers. Solution is decanted from each layer and removed either for reuse as recycle or to be treated and discharged. After being decanted and dried the surface layer of tailings shrinks and cracks. The cracks are however filled by the next layer of pulp. To achieve this the tailings pulp is spread at a relatively low pulp density of 35-40% solids which allows even spreading and the desired particle size segregation in each layer.

The tailings are limed to pH 11 before being pumped to the tailings pond after blending of water treatment plant sludges consisting of metal precipitates with an excess of lime.

Tailings pulp at 35-40% solids are spread over the previous decanted surface in a 10 cm (4") thick layer and decanted. On drying the top layer shrinks and cracks.

The layered dry tailings system results in material with a low permeability of 10^{-9} to 10^{-11} which is remarkable. The system is compact and in any case is protected by the sand layer with underdrains and a low permeability bentonite stabilized soil lining. If the system consistently performs as described the design would appear to be over-conservative and it is conceivable that it future modification could safely reduce costs.

The dry laminated tailings system was pilot tested at Sherritt-Gordon with 7 layers of tailings under simulated conditions. The paper by CLARKE et al. (1980) discusses how these tests were performed.

Sherritt-Gordon also pilot tested the pressure leaching process employed at Key Lake Mines, an interesting aspect which nonetheless is not a focal point of this study except from the point of view of its impact on dissolved metal concentrations in the leached pulp which are greatly enhanced by pressure leaching, particularly arsenic when oxygen is used.

In August, 1984 there were not yet enough tailings to cover the entire lined tailings area. Nor had the innovative system been applied through a whole winter.

ORE GRIND	100% minus 500 u	(35 mesh)
	45% munus 44 u	(325 mesh)

This indicates a very fine grind.

WATER CONSIDERATIONS

There are two main aspects of collecting and treating water:

Minewater

Key Lake operates two mine pits, both of which are surrounded by lakes. Both deposits were located underneath lakes that had to be drained and dewatered before the ore could be mined.

Around each mine pit there are a number of dewatering wells. Dewatering of each pit requires a constant discharge of 0.3 m^3/second (26,000 m^3d) to the lake system. This minewater has high radium levels of 30 Bacquerel (about 900 piC/l.)

(37 Millibacquerels $\underline{=}$ 1 PiC/l)

The water also contains traces of As, Ni and U_3O_8. Approximately 1200-1500 m^3/d is used as process water, but at 300 l/sec from each of 2 pits the total water to be discharged works out to over 50,000 m^3/day.

SX Raffinate

SX Raffinate is treated with lime to precipitate gypsum and metals. Thereafter the solids are settled in lamella thickeners and the decant pumped to one of five monitor ponds each with 5000 m^3 capacity, enough for about one day's storage. As soon as a pond fills it is sampled and analyzed. If it is within the regulatory limits it can be released to the lake.

During neutralization soluble arsenic is dropped to less than 0.5 ppm As.

Water after treatment is sampled and analyzed in batches. If any of the regulatory limits are exceeded the water is returned to the treatment plant.

REGULATORY LIMITS

The Atomic Energy Control Board in conjuntion with the Province of Saskatchewan have set the following limits for effluents from Key Lake. The comment was made that Saskatchewan has generally stricter limits than the AECB.

	Maximum Monthly Mean (Arithmetic)	Composite Sample	Maximum Grab Sample
As	0.5 ppm	0.75	1.0 ppm
Cu	0.3 ppm	0.45	0.6 ppm
Ra	0.37 Bq/l		
	10 PiC/l	20.0 PiC/l	30.0 PiC/l
U	0.50 ppm		
Ni	0.5 ppm	0.75	1.0 ppm
Pb	0.2 ppm	0.30	0.4 ppm
Zn	0.5 ppm	0.75	1.0 ppm
Suspended Solids	25 ppm	37.5	50.00 ppm
$NH_4^=$	30 ppm at pH between 5-7		
pH	6 min	5.5 min	5.0 min

BULK NEUTRALIZATION

All solid and liquid wastes from the Key Lake operation are treated in the bulk neutralization plant. These include the raffinate from the solvent extraction plant, underflow from the CCD thickeners and all contaminated water from the mine, shops, mill and plant site. Clean water that can be released into the environment and solid wastes, or tailings, in which contaminants are immobilized are produced.

There are four main steps in bulk neutralization: neutralization; radium removal, pH adjustment and filtering of liquids; and slurry treatment and filtering. Throughout the process, the pH must be strictly controlled to aid in the removal of solids and to fix contaminants in insoluble compounds. Microprocessor control provided by UCS No. 5 makes this possible. The pH of liquids is first raised so that metals can be precipitated. It must then be lowered to 7.0 before release into the environment.

WATER TREATMENT PLANT

Capacity	(implied 5000 m^3d	= 58 l/sec)
$BaCl_2$ consumption	20g $BaCl_2$/Kg U_3O_8	= 109 Mt/year
		= 450g $BaCl_3$ per ton ore
Lime consumption		= 130 Kg/ton ore

1) Raffinate and minewater to be treated are neutralized in four air agitated pachucas in series with flash mixers for lime addition before each pachuca. The flash mixers are fitted with propeller agitators.

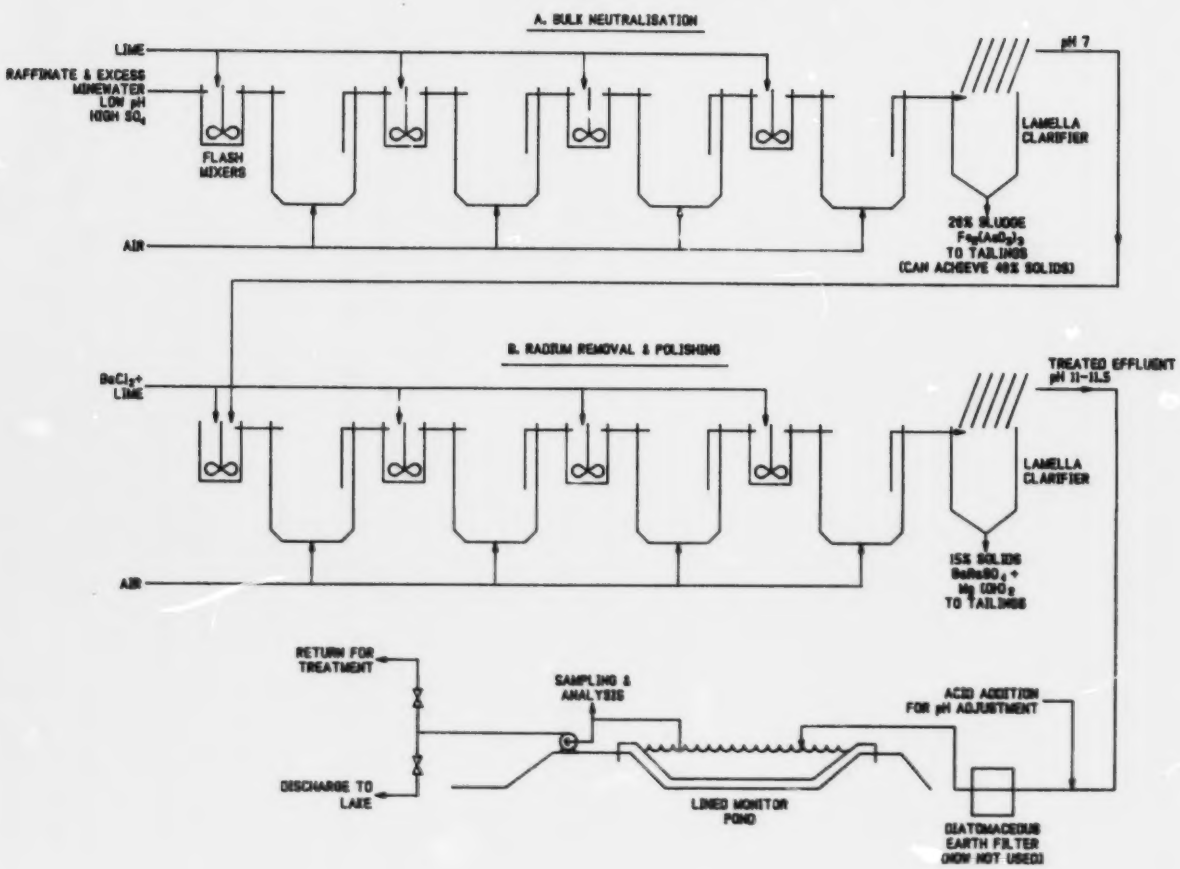
2) The precipitate is settled in Axel Johnson lamella clarifiers.

3) Underflow from the clarifier is mixed with the CCD underflow i.e., with ore tailings after leaching and washing.

4) Overflow from the clarifier is mixed in the next row of flash mixers and pachucas. Lime, $BaCl_2$ are added. The pH is now 11 to precipitate Ra Ba SO_4, Ba Ra Arsenate and Mg $(OH)_2$.

5) Residual arsenic is precipitated as $Ba_3(AsO_4)_2$ which according to CLARKE et al. (1980) is much less soluble than Calcium Arsenate ($8x10^{-51}$ at 25°C) although this fact is disputed by ROBINS (1984 personal communication). Possibly, the further reduction of arsenic levels in the treated effluent is due to enhanced removal of particulates with the $BaRaSO_4$ precipitate.

KEY LAKE MINING EFFLUENT TREATMENT



6) The second stage neutralization water is next clarified in clarifier 2. The No. 2 lamella clarifier underflow is mixed with the No. 1 lamella underflow and disposed of with the CCD underflow to the tailings impoundment.

7) Overflow from lamella 2 is filtered through diatomaceous earth filters (as of July 1984 this diatomaceous earth filter was not in use as the suspended solids levels are low enough for it not to be needed.)

8) pH of treated, clarified solution is adjusted from pH 11 to pH 7 by adding H_2SO_4.

9) The treated, pH adjusted effluent water stream is next directed to one of the 5 monitor ponds (500 m^3 each). If the water quality meets the effluent standard, it is discharged. If not, it is pumped to one of the two water reservoirs (250,000 m^3 and 120,000 m^3 capacity.)

EFFLUENT QUALITY

Effluent quality as determined in the Sherritt Gordon pilot tests are shown below, indicating a very effective process.

Table
Effluent Water Quality

Element	mg/l	Element	mg/l
Aluminum	LT 0.01	Molybdenum	0.04
Arsenic	LT 0.01	Nickel	LT 0.01
Barium	LT 0.4	Phosphorus	0.14
Calcium	701	Potassium	54
Chloride	20	Selenium	LT 0.01
Chromium	0.02	Silicon	0.38
Cobalt	0.01	Sodium	55
Copper	0.01	Sulphur	640
Fluoride	2	Titanium	0.01
Iron	0.06	Uranium	0.85
Lead	LT 0.01	Vanadium	0.01
Magnesium	0.65	Zinc	LT 0.01
Manganese	LT 0.01		

LT = Less Than

The radiological composition of the final effluent achieved during the experimental program is shown in the Table below and compared with target levels for radioactive isotopes in the effluents. All targets were met.

Table
Radiological Composition of Final Effluent

Isotope	Pico Curies Per Liter Activity	MPCw
Radium 226	1.6	10
Lead 210	0.5	100
Polonium 210	0.3	700
Thorium 227	0.5	
Thorium 228	1.4	7000
Thorium 230	0.8	2000
Thorium 232	1.4	2000

These reservoirs store water which is used for process water and as feed to the treatment plant. Tailings decant water also gets directed to these reservoirs.

One of the operating surprises encountered when the plant was commissioned was that the limed precipitate settled very much faster than expected in big crystals. As a result the lamella thickener rakes were overloaded and the mechanism jammed. This problem was overcome by installing cone bottoms on the thickeners. Initially drum filters were installed with a view to dewatering the clarifier underflow sludges but these are not needed in practice.

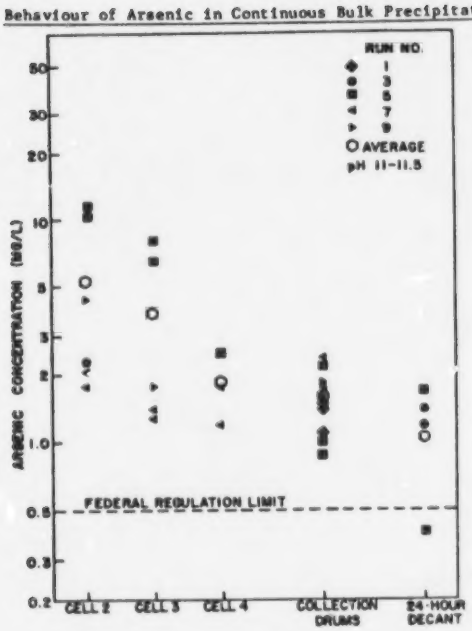
A major advantage of the Key Lake effluent treatment system is that the indoor process is very rapid. It can be monitored and if there is a problem it can be detected and corrected much more quickly than is possible when radium is removed by adding $BaCl_2$ to a large pond with a long residence time. The water treatment plant was designed by Wright Engineers based on a Key Lake proven concept that was tested by Sherritt-Gordon Mines.

WATER IMPOUNDMENTS

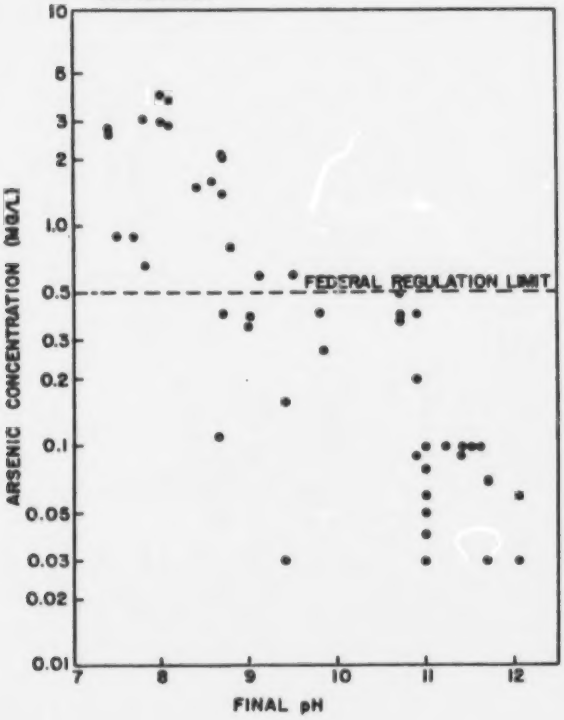
The plant includes the following water impoundments:

- 5 monitor ponds to collect treated minewater plus Raffinate prior to discharge

Behaviour of Arsenic in Continuous Bulk Precipitation



Effect of pH on Terminal Arsenic Concentration After $BaCl_2$ Addition: Treatment of Bulk Precipitation Waste Waters



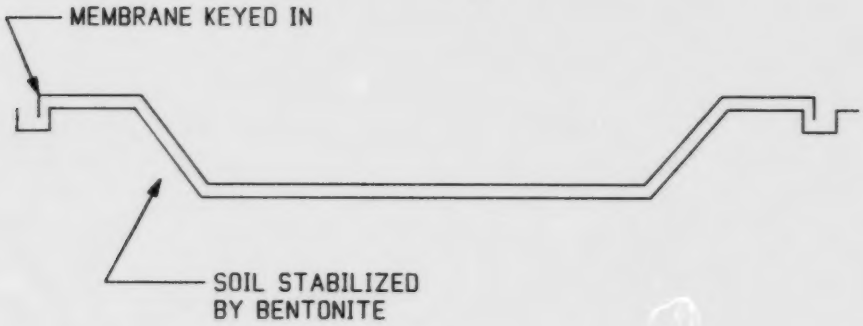
- 2 water reservoirs
  - plant water
  - potable water

- 1 fire fighting water pond at the mill

POND LININGS

Initially all impoundments were lined using 40 mil hypalon (1 millimeter) over bentonite stabilized soil. The monitor pond linings were installed in the summer of 1982 well before plant startup. Since the ponds are to be used intermittently with fluctuating solution levels there should have been no problem in leaving them empty.

By 1983, even before the ponds were put in use the linings delaminated and seams came loose at many spots to the extent that the lining had to be replaced.



NEW POND LININGS

The hypalon membrane was replaced by 100 mil HDPE supplied and installed by Schlegel in 1983, as described in a recent Schlegel advertisement inserted below.

Recently Columbia Impoundment Systems of Calgary, Alberta, have demonstrated an HDPE lining installation method with a double seam and air test.

LEVEL CONTROL

In January 1984 there was a spill form one of the Key Lake water reservoirs. The problem arose during winter when the reservoir was covered by snow and ice, and operators were not aware of the spill as the overflow stream was hidden from view by the snowcover. Controls are needed to detect when snowcovered impoundments are full. In this case there appears to have been no damage of consequence to the muskeg.

ENVIRONMENTAL CONTROL AUTHORITIES

Key Lake Mining is regulated by the Atomic Energy Control Board of Canada and the Saskatchewan Department of the Environment, Prince Albert, Saskatchewan.

ENVIRONMENTAL CONSULTANTS

Beak and Associates

SPECIAL ENVIRONMENTAL PROTECTION MEASURES

- $(NH_4)_2SO_4$ is employed to strip the SX organic and NH_3 to precipitate uranium thereafter.
- Yellowcake filtrate solutions have to be treated at Key Lake to recover $(NH_4)_2SO_4$ to prevent NH_4^+ discharge in the plant effluent if it were to be discharged with tailings or treated raffinate solutions. Sherritt-Gordon Mines Ltd. designed the $(NH_4)_2SO_4$ recovery plant.
- 1 m wide X 50 cm deep concrete "utilidors" are installed to contain any breaks in the tailings line. The utilidor is fitted with a sump to contain the volume of tailings that could leak into it in the event of a break. The utilidors are covered and heated in winter.
- A 1700 m utilidor is installed from the ore crushing plant to the main metallurgical plant. It carries ten pipes.

REFERENCES

CLARKE P.J.; JANTZON, F.G.W.; NEVEN, M.; WEIR, D. ROBERT; MASTERS, I.M.; BEREZOWSKY, R.M.G.S.; & DAY, M.D. (1980) The Key Lake Uranium Process, 19th Annual Conference of Metallurgists of the CIM, Halifax, N. S. August 1980.

IN·SITE

Schlegel®

A PUBLICATION FOR LINING SYSTEM USERS FROM SCHLEGEL LINING TECHNOLOGY. VOL. 1, 1984

ARE GEOTEXTILES NECESSARY WITH THICK LINERS?

Puncture and Tear Resistance Not Necessarily Improved

POLLUTION ENGINEERING magazine in its November 1983 issue reported the results of a study made by a geotextile manufacturer in which various geomembranes were evaluated for their puncture and tear resistance, alone and then with the addition of three different grades of geotextile. A laboratory procedure was developed to simulate the effects of equipment moving over the geomembrane. According to the magazine article, "Although there were major differences in the resistance of various membranes, the geotextile fabric offered significant protection from aggregate cutting, puncture and abrasion . . . "[1]

Is a geotextile always necessary for cushioning and protection against puncture and tear? The incorporation of a geotextile with a geomembrane may serve many important purposes, including filtration, soil stability, overburden stabilization, drainage, gas ventilation and so forth. But an appropriately thick liner, which Schlegel Lining Technology defines as 2.0 mm (80 mil) or more, is usually thick enough to resist both high and low speed puncture and resultant tear without the expense of

Continued on page 2.

World's largest uranium mine lines reservoirs with 100 mil HDPE

In the summer of 1983, officials of Key Lake Mining Corporation (KLMC) were faced with the task of having to reline two reservoirs and five monitoring ponds. These are sited adjacent to the mill and tailings deposition area on surficial materials of glacial till, sand and gravel.

Key Lake Mine will eventually be the largest uranium mining/milling complex in the world. Ore is extracted from two discrete deposits by open pit mining methods. The mill is designed to process 780 tons of ore per day using conventional separation and extraction techniques.

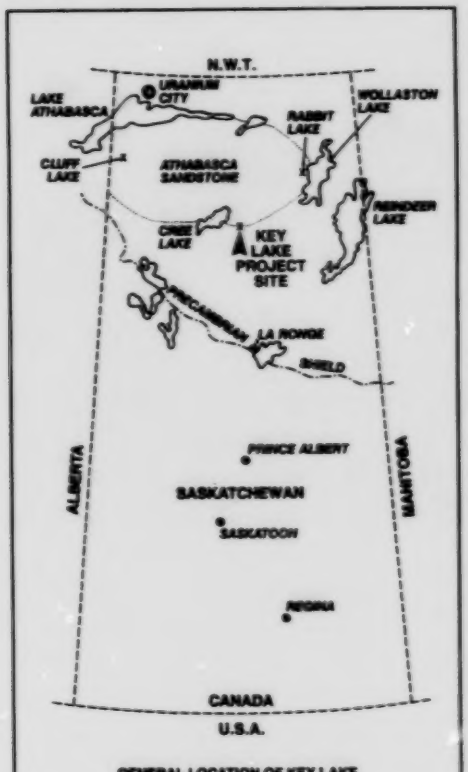
The Key Lake Mine site is located 400 miles north of Saskatoon, in Saskatchewan, Canada. Severe winters, featuring temperatures as low as −40°F, are the norm.

The purpose of the reservoirs is to store contaminated water from the open pit and ore stockpile areas. The first reservoir, with a capacity of 240,000 m^3, holds mine water and site and stockpile runoff. All runoff from the ore stockpiles, the open pits and the mill is considered contaminated, and is collected and stored in this reservoir. This reservoir also serves as a source of process water for the mill, as no free water is ordinarily introduced into the milling process, other than what is collected by dewatering. This reservoir was lined with 37,000 m^2 (400,000 ft^2) of HDPE material.

The second reservoir holds supernatant water from the tailings area, as well as any other water requiring treatment before it is recycled or discharged to the environment through the monitoring ponds. The capacity of this reservoir is 120,000 m^3; it was lined with 20,800 m^2 (224,000 ft^2) of HDPE liner.

The five monitoring ponds with individual capacities of 5,000 m^3, hold treated supernatant water from the process plant and are used to test treated water before it is

Continued on page 5.



GENERAL LOCATION OF KEY LAKE

Uranium mine lines with HDPE

Continued from page 1

discharged. Unacceptable water is recycled for further treatment. Each monitoring pond was lined with 3,100 m^2 (33,600 sq. ft.) of HDPE.

It was necessary that the liner withstand the severe climate and the icing conditions that would form in the reservoirs and ponds. (The tailings pond was not lined with geomembranes, because the subaerial technique used at Key Lake for depositing results in a laminar structure with vertical segregation of sands and slimes, and thus a very low coefficient of vertical permeability.)

HDPE Specified For Climatic Conditions

KLMC amended its previous specifications to require either 60 or 100 mil HDPE liners. The invitation to tender read: "The HDPE liner shall be capable of withstanding the climatic conditions as outlined.

During regular operation of these facilities, liquid levels will vary continually over a range from full to empty throughout the year.

Parts or all of the liners may be exposed to the full range of climatic conditions for extended periods of time and must be capable of withstanding the effects of sun, wind, rain, hail, snow, etc."

Thus, ice would not only form on the reservoirs and ponds, but it would continually ride up and down the slopes as liquid entered the impoundments and also as treated effluent was discharged.

Ice Loading

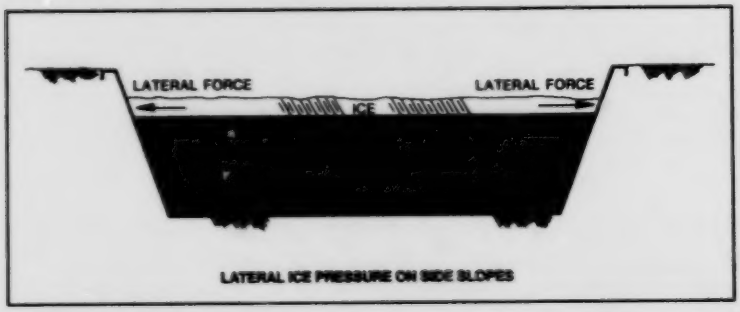
Two forces can be exerted by the formation of ice in a lined basin. The first is lateral pressure that is brought to bear on the side slopes of a basin when the entire surface freezes. The second occurs, usually in springtime, when large chunks of ice that break off from the main body are driven by wind and wave action into the side slopes, creating localized point source forces on the liner. Portions of the ice cap may also literally hang on the liner and tear it easily if enough mass has accumulated.

A basin designer can mitigate the destructive potential of ice loading by employing a relatively mild slope, by avoiding materials with a tendency to stick to ice, and by specifying a high strength material in an increased thickness for better puncture and tear resistance.

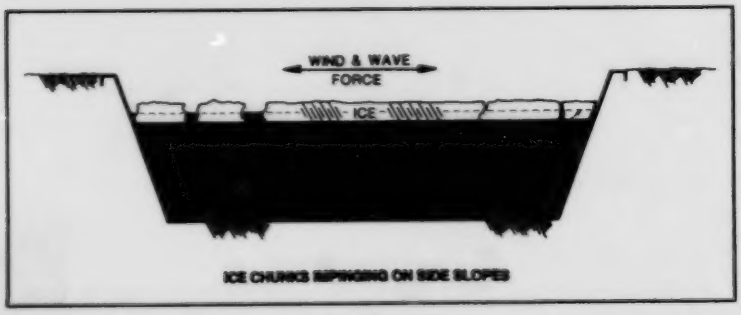
A mild slope (e.g., the 2.5:1 used at Key Lake) will ease the lateral pressure of a solid ice cap and permit it to ride up the slope rather than impinge on the liner in a direction perpendicular to it. Adherence of ice to a lining material occurs more frequently with roughly textured liners.

Beating the Freeze

The two reservoirs and five ponds had to be relined by September, 1983, before freezing weather conditions set in. On June 27, 1983, KLMC representatives flew to Houston to meet with two



LATERAL ICE PRESSURE ON SIDE SLOPES



ICE CHUNKS RIPPING ON SIDE SLOPES

Texas-based manufacturers of high density polyethylene liners. After an initial consultation, both firms prepared quotations, delivering them the following day, June 28.

Schlegel Lining Technology recommended its 100 mil SCHLEGEL® sheet in order to provide extra security against liner puncture and tear that could result from ice loading conditions. SCHLEGEL sheet has a low coefficient of friction; therefore, it would not have a tendency to stick to ice as might roughly textured liners. Schlegel Lining Technology also offered single-source responsibility to the lining project, from manufacturing the liner through installation and post-inspection. Other lining suppliers who had been considered for the job work only through general contractors or independent installers. It is not uncommon for a lining system to pass through several firms before it reaches the end user.

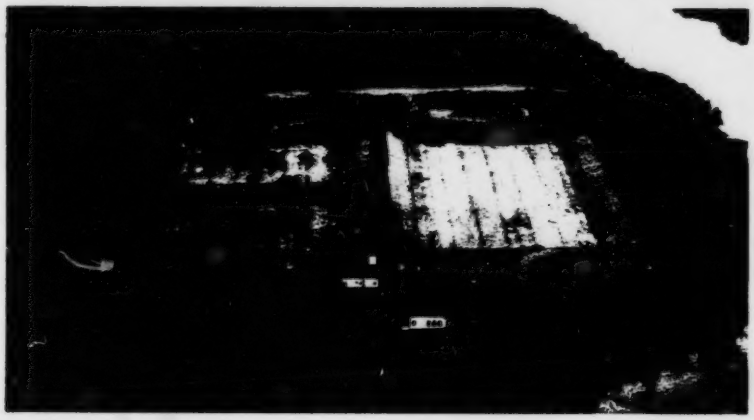
On June 29, 1983, Schlegel Lining Technology was informed that it had been awarded the contract. KLMC had decided to accept an HDPE liner in a 2.5 mm thickness, rather than the allowable alternate thickness of 1.5 mm, on the basis of data showing that any plastic material's resistance to puncture and tear is a proportional function of its thickness. The incremental cost of the increased thickness was relatively low.

During the month of July, more than 200 rolls of SCHLEGEL sheet were delivered to the Key Lake Mine site. The reservoirs and ponds were constructed in a priority order, determined by the operating needs of the facility. The larger water reservoir was installed first, followed by the second reservoir and then the five monitoring ponds.

Installation of the 73,300 m^2 of liner was accomplished in 36 work days, out of 37 elapsed days, using two shifts of 10-man crews.

Key Lake Mine began full operations in October, 1983.

Potential ice loading problem averted



Schlegel Lining Technology's experience with cold climate liner installation and operation can be seen in the work completed in the summer of 1983 at a new wastewater treatment facility in Caribou, Maine. Caribou is near the northernmost point of the continental United States, where winter temperatures often reach – 30 °F.

Protection of ground and surface waters was a serious consideration in construction planning for the facility owned by the Caribou Utility District. The specifications issued by the joint venture awarded the design-build contract called for lining the three treatment ponds with a high density polyethylene liner.

The ponds are sited 100 feet from the Aroostook River; the substrate on which they were built is coarse, porous gravel. Although the ponds are aerated year-round, they ice over during the winter months.

The mechanical toughness of SCHLEGEL® sheet and its ability to withstand the ice loading conditions prevalent in Caribou during the winter were demonstrated to the customer's satisfaction with case studies of similar installations that are now in operation. Schlegel Lining Technology installed 550,000 square feet of SCHLEGEL sheet at the Caribou project. Post-inspection reports indicate no problems with the lining.

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INTRODUCTION

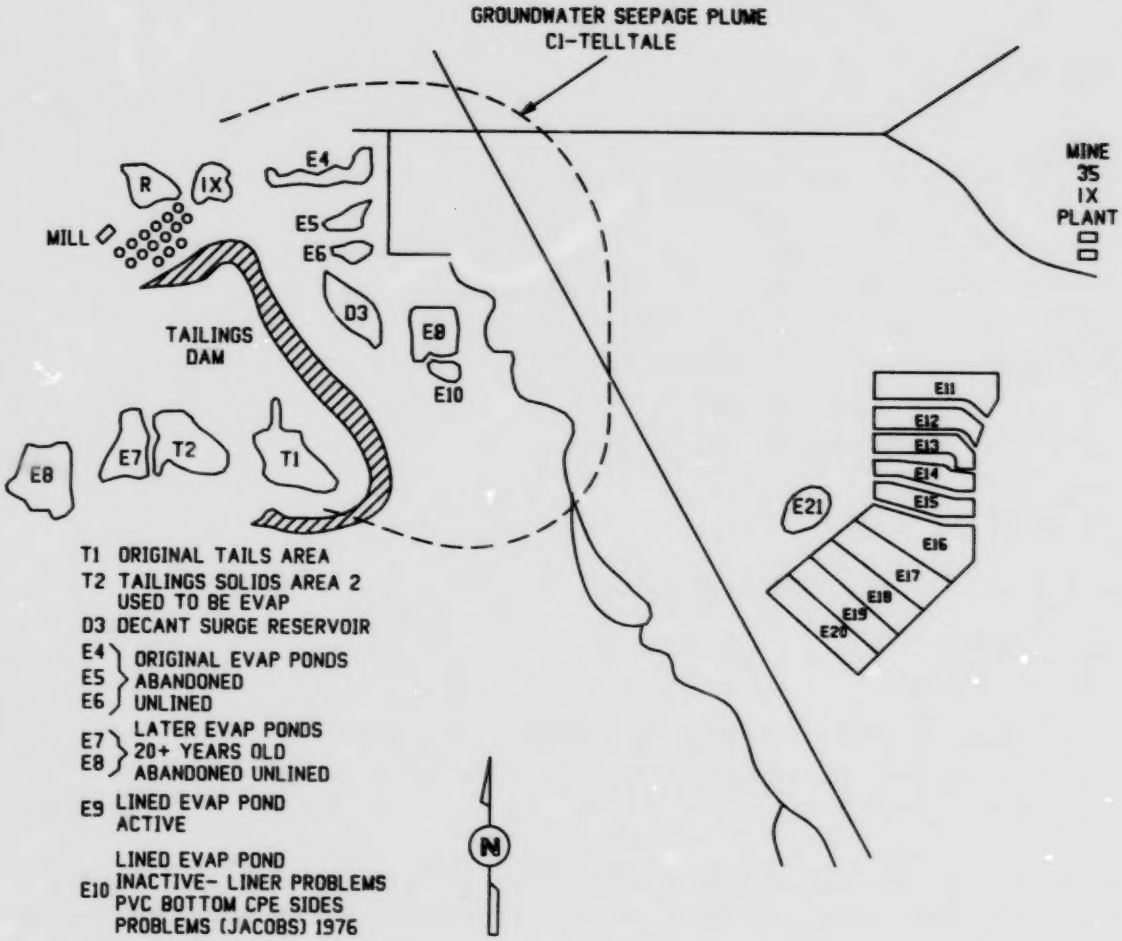
Quivira Mining Company's Ambrosia Lake operations with a design capacity of over 6,000 stpd is the largest uranium mill in the USA. It is served by six underground mines located in the vicinity.

Quivira Mining Company (formerly known as Kerr McGee Nuclear) operated one of the neatest and tidiest mining and milling complexes in the USA until the plant shut down in 1985.

There are several noteworthy water management features at this operation, now operating at a reduced throughput in tune with the market for uranium yellowcake:

1) Macro-recycling of water occurs between Mines-Mill-Tailings-Nearby Mines. Excess water pumped from the mines is discharged to a creek after uranium recovery by CIX and radium precipitation. This water evaporates in part and some returns to an aquifer. Buildup of competing ions due to seepage from the tailings pond results in a deterioration in efficiency of ion exchange recovery uranium from such streams.

2) Excess process water is decanted from the tailings dam and pumped to a series of membrane lined evaporation ponds. Much can be learned with respect to evaporation pond design and lining membrane selection from the early evaporation ponds, and the remedial measures that are employed.



T1 ORIGINAL TAILS AREA

T2 TAILINGS SOLIDS AREA 2
USED TO BE EVAP

D3 DECANT SURGE RESERVOIR

E4, E5, E6 — ORIGINAL EVAP PONDS
ABANDONED
UNLINED

E7, E8 — LATER EVAP PONDS
20+ YEARS OLD
ABANDONED UNLINED

E9 LINED EVAP POND
ACTIVE

E10 LINED EVAP POND
INACTIVE- LINER PROBLEMS
PVC BOTTOM CPE SIDES
PROBLEMS (JACOBS) 1976

E11 ↓ E15 — LINED EVAP PONDS
1977,1978
PVC AND CPE SIDES
HEAVER GUAGE WATERSAVER

E16 ↓ E21 — LINED EVAP PONDS
1979,1980
PVC AND HYPALON SIDES

R MINEWATER- PROCESSWATER RESERVOIR
ALSO USED FOR FIRE PROTECTION

35 SETTLING $BaSO_4$ PONDS

3) CIX performance has dropped off in comparison with original design parameters probably because of a general increase in dissolved salts - competing ions and fouling species - in the water. In order to maintain a 1 ppm U maximum discharge to the creek, the resin must be eluted up to 100 times per month compared with the initial design of 16 times per month when TDS (e.g., Cl^-) was lower in the solution.

4) Quivira Mining Company employs in situ leach of worked out stopes on a small scale. The water recovered from the mines is processed by ion exchange to recover uranium which accounts for about 5% of the present reduced U_3O_8 production rate of the operation of about 2.0 mm lbs per year. At mines 5 and 36 which are the furthest from the mill, treated water is discharged for use in irrigation by local ranchers after uranium recovery and Ra precipitation.

5) Water treatment practised at Quivira's Ambrosia Lake operations include:

° Boiler Water Treatment	Anthracite Filtration IX Cation Softening Anti-Scalant Addition (phosphonate) De-Aeration O_2-Scavenging
° Acid Cooling Coil Waters	Anti Scaling Chemicals added
° Domestic Water Treatment (for showers and toilets)	Sand Filtration chlorination
° Potable Water	Treatment of "domestic water" by charcoal filtration Reverse Osmosis
° Uranium Recovery from Minewater	Continuous Ion Exchange and Elution
° Radium Removal from Minewater for discharge	$BaCl_2$ addition
° Sewage	?

6) Quivira Mining Company does not have a problem in water conservation or supply. There is a relatively high cost of disposing of contaminated tailings decant water.

7) Water balance at the mill is regulated on a chloride level in mill water - i.e., chloride balance is the critical issue.

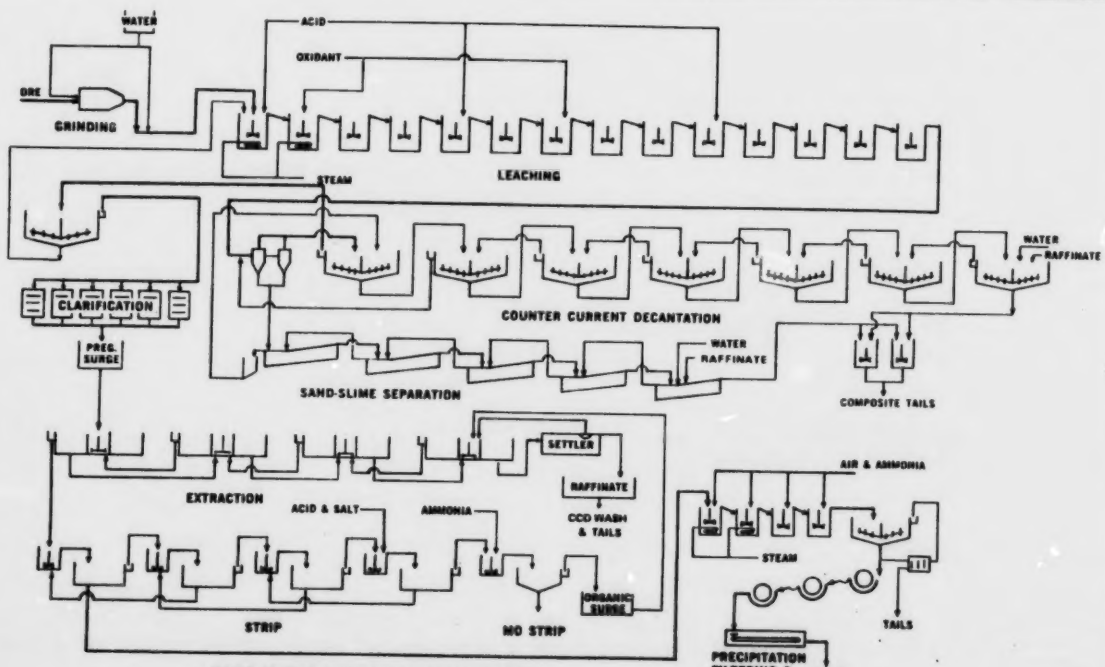
8) The tailings impoundment is unlined and is located on an alluvial plain - it is therefore porous and loses water through seepage. A seepage collection trench is currently under construction at the toe of the dam at a cost of around $500,000.

9) Tailings are not neutralized before being pumped to the pond. During seepage through the alluvia pH increases.

10) A major source of Cl^- to the system is from the stripping of the loaded SX organics using 0.6 Molar NaCl. This adds Cl^- to the raffinate and through discard of yellowcake filtrate to tailings at 0.3M concentration.

11) Biological processes observed in the minewater ponds before discharge appear to remove some uranium, selenium and molybdenum from solution.

12) As excess process water excess is evaporated the rate of evaporation from the ponds decreases as the salt concentration increases in the pond. Frest water evaporates at 48" per year, yet the salt laden solution in the pond evaporates at only 40" per year. There is a distinct odor downwind from the evaporation ponds.



KERR-McGEE NUCLEAR CORPORATION
URANIUM PROCESSING FLOWSHEET

LOCATION 25 miles north of Grants, New Mexico

OPERATION STARTUP 1958

CLIMATE:

Arid continental climate. Rainfall 9 - 10 inches per year. Evaporation 48"/yr for water.

MILL THROUGHPUT	Design Capacity	6200 stpd
	Present Operating Rate	2500 stpd for a 4 day week

URANIUM GRADE 0.18% U_3O_8 3.6 lbs U_3O_8 per short ton ore

WATER SOURCE Underground Mine dewatering

NET WATER CONSUMPTION
(based on flow rate)

At full production	1500 USgpm for 6200 stpd ore
i.e., 10,800 s tons water per day	= 1.74 tons water/ton ore treated
At reduced production	500 USgpm for 2500 tpd (4d/week)
3600 s tons water per day yearround	= 6300 s tons per operating day
	= 2.52 s tons water per one ore

NET WATER CONSUMPTION
(based on Metallurgical Balance)

1.3 - 1.5 t new water consumed per ton ore

SOLUTION REQUIRED PER TON ORE

1.7 - 2.0 tons water/ton ore milled
includes 0.45 tons recycled process water to mill

The sandstone ore is mined at depths of 600 to 1400 ft. Each mine generates 200 to 2000 USgpm water. Ore is hauled to the mill by truck. Ore stockpiles at the mines are not lined.

METALLURGICAL PROCESS

Ore is crushed in two stages to minus 1" then sampled prior to milling in open circuit rod mills. It is ground to minus 28 mesh and leached at 70% solids in sulfuric acid using

sodium chlorate as oxidant. Leaching takes 3 - 4 hours and is accelerated by steam heat. Heat is provided by wasteheat recovery from the acid plant supplemented by boilers. Cooling water from the acid cooling coils is added to the rodmills at 80-90°F. Sand and slime are separated by cyclones. Sand is washed in acid solution in five stage rake classifiers prior to being disposed of to the tailings pond.

Slime is washed in 7 stage CCD circuits of which the final stages are Enviroclear high rate thickeners.

Solution is filtered and clarified and fed to an SX circuit where uranium is extracted by a tertiary amine in an organic kerosene phase containing isodecanol. Organic advances at one third the rate of aqueous solution advance through the SX plant to achieve a 3-fold concentration.

Raffinate is returned to the CCD and rake classifier circuits as wash solution with 20% bleed to tailings.

Uranium is concentrated a further ten times in a 4 stage stripping circuit using a sodium chloride solution. Uranium is preipitated using anhydrous ammonia, air and steam, thickened and settled, then dewatered and washed in three stages of drum filtration. The yellowcake filtrate is pumped to the tailings pond. Yellowcake is dried and drummed, or more lately shipped in slurry form to the refinery.

RECOVERY

Overall uranium recovery is 90-97%. Soluble loss of uranium in the CCD circuit at the current reduced throughput is 0.25%.

OPERATING COSTS

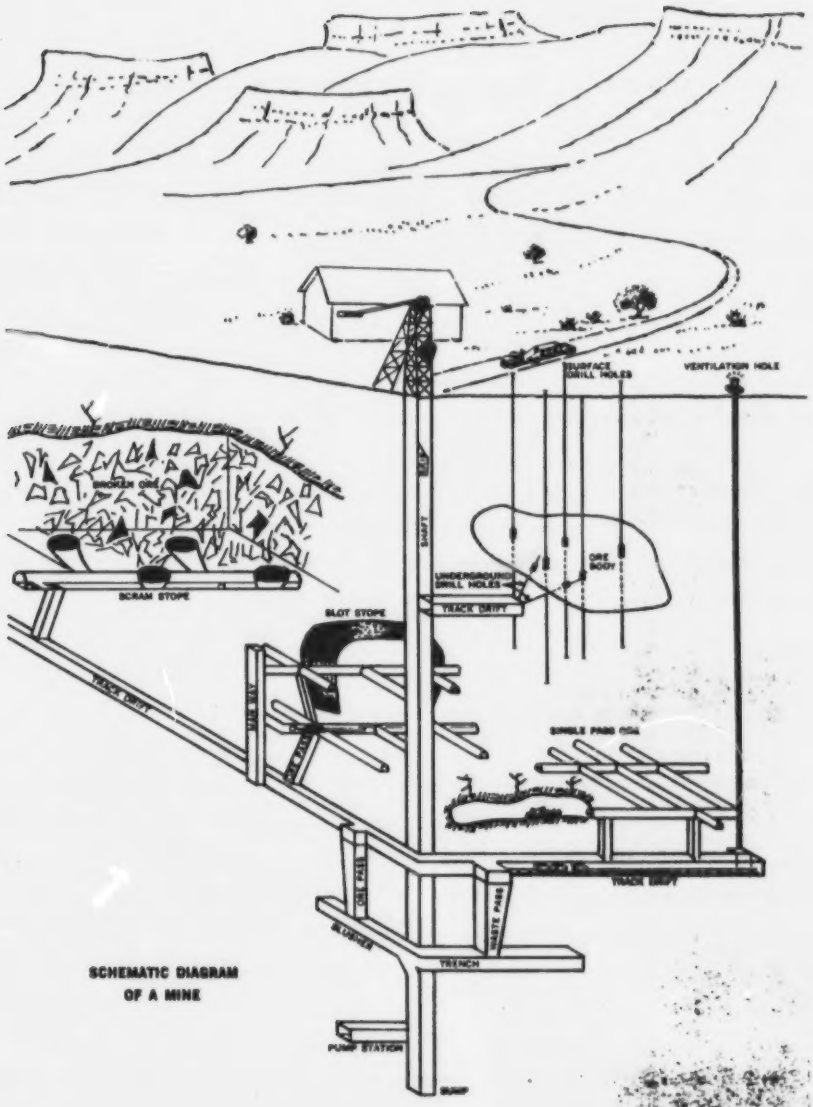
Mining accounts for two thirds the total operating costs. Sulfuric acid is the biggest single expense.

ACID CONSUMPTION

130 lbs concentrated H_2SO_4 is required to process each short ton of ore. Sulfuric acid is produced on site by burning sulfur.

NACL CONSUMPTION

6 - 7 lbs NaCl per ton ore treated. Additional chloride is added to the system as chlorate used as the oxidant.



SCHEMATIC DIAGRAM
OF A MINE

4

U_3O_8 RECOVERY SELECTION

Leach Liquor

The Ambrosia Lake ores contain several elements that also dissolve in sulfuric acid e.g., iron, selenium, vanadium, molybdenum.

The ore grade at 3.6 lbs/ton ore is high grade and the CCD wash solution has a relatively high tenor.

SX is economical to use at this concentration and favored over IX because it is more selective for uranium recovery from the leach liquor.

Minewater

Concentration of competing ions in the minewater especially at the time the IX plants were designed, was very much lower than in the leach liquor.

SX is not economical for treatment of very dilute solutions because organics entrainment losses are a function of flow rate rather than uranium tenor. Consequently the solvent losses for very dilute solutions are expensive in relation to the uranium values recovered - also the SX loadings from such low tenor solutions is low.

Consequently ion exchange is preferred for U_3O_8 recovery from mine solutions of the tenor encountered i.e., 5 - 12 ppm U_3O_8.

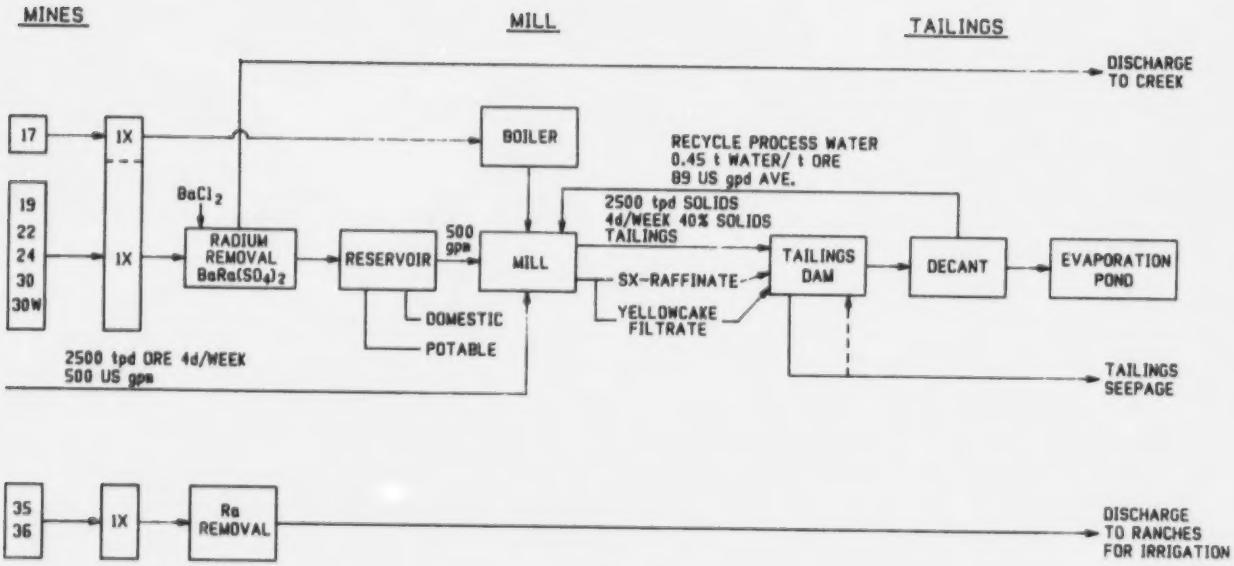
Because of the higher concentrations of competing ions in minewater feed to the IX plant, ideally a multi stage CIX plant would be required. However, given the mere 100,000 lbs per year U_3O_8 recovery by IX at a market value of $2 million/year it is difficult to justify a suitable multi stage CIX system such as NIMCIX requiring an investment of about $1.5 million, when the existing less efficient 2 stage IX systems do work after a fashion - albeit requiring many more costly elutions and undoubtably greater annual resin consumption costs.

Minewater from section 17 is generally lower in chloride than the rest and is used as boiler water after demineralization and addition of anti scaling agents.

Investigations carried out in 1979-81 were described showing how a variety of biological processes take place in the Quivira Mine effluent ponds which remove some of the residual pollutants including metals and sulphates, with algae acting as biofilters to remove suspended solids and removing soluble metals by adsorption.

Although not deliberately employed for this purpose, these processes have been described

by BRIERLEY, et al. (1980) and BRIERLEY AND BRIERLEY (1981) available from Randol International Ltd. on request.



1) <u>Water to Tails</u>

2500 tpd solids to tails @ 40% solids = 3750 stpd Water 4 d/week

= 297.6 USgpm Water to tails

2) <u>Water Recycled from Tails</u>

2500 tpd 0.45 tons water/ton ore X 4days/7dweek = 89 USgpm ave.

QUIVIRA

WATER QUALITY (ppm except where otherwise indicated)

	Mine 17 used for Boiler Water	Mine 19	Mine 22	Mine 24	Mine 30	Mine 30W	Mine 35	Mine 36
FLOW RATE USgpm								
pH	±8						±8	
TDS	1200-1300						1100-1200	1200-1500
Hardness	400-500						340	
Ca	100-140							
Mg	28-95							
Na								
$SO_4^=$							800	
Cl^-	5-10						10	
U_3O_8	5-10							
Se	0.004-0.36*			0.03-0.5				
MD	N1.0							
Si	8-15							
Ra								
Flow Rate								
Ultimate use	° Boiler Water ° Balance discharged to creek	Used as process water makeup balance treated by CIX and after Ra Removal discharged to creek					After CIX Recovery of U_3O_8 and radium discharged to ranchers for irrigation purposes	

* Analytical quality of data in question for 0.36 ppm reading. with some leakage back to

WATER QUALITY (ppm unless stated otherwise)

	Proven Water Reservoir	CCD Overflow Preg	SX-Raffinate	SX Organic Loading	SX Strip Solution Loaded	Yellow cake Filtrate	CIX Tails	Tailings Plant Decant
Flow (USgpm) Rate	500 gpm to mill		1200 US gpm		20 gpm	40 gpm		
pH		1.2	1.5				8	
TDS	2286		30,000					
Hardness	900							
Ca	200							
Mg	80							
Na	300							
$SO_4^=$	1300				60-70g/l	30 g/l		
Cl^-	112	1,300	1,600		0.7Molar	0.4Molar		
U_3O_8	2.3			3 g/l			1ppmU	
Se	0.2							
Mo	0.75			0.3-0.40/l				
Si	10							
Ra								
Ultimate use or disposal		to SX Plant then becomes raffinate	20% of Raffinate bled to tailings pond			dis-charged to tailings	Some used as Process water Excess dis-charged to creek	
Inflow Streams Source								

WATER TREATMENT

Boiler water and drinking water are treated as a service by Dearborn Chemical Company subsidiary of W. R. Grace & Co.

Mr. Jim Whitaker
Dearborn Chemical Company
12800 Lomas Boulevard NE #D
Albuquerque, NM 87112
(505) 292-0668

Head office: Dearborn Chemical Company
Lake Zurich
IL 60047
(312) 438-8241

Dearborn supplies anti-scaling reagents for the acid cooling coil circuit and the boilder feed water.

ION EXCHANGE U_3O_8 RECOVERY - MINEWATER

Quivira Mining Corp. recovers uranium from minewater before it is released to the creek. After ion exchange uranium recovery, radium is precipitated by $BaCl_2$ addition at the discharge from the IX plant and settled.

The IX plant was installed in 1963. There are now 5 IX circuits at the mill plant each with two stages of upflow adsorption in contactors designed by Kerr McGee Corp.

At Mines 35 and 36, there are a further three CIX circuits.

A multistage continuous CIX contactor was purchased from Solution Engineering, Denver, but was later abandoned in favor of the simpler K-M 2 stage system. The price of this installation was reported in 1980 to be $500,000 compared to $1.25 million for a comparable NIMCIX unit.

In the late 1950s when the operation started there was virtually no uranium in the minewater. Uranium levels gradually increased over the years until a point was reached when the ion exchange recovery yielded the present level of about 10-12,000 lbs U_3O_8 per year.

Details of the ion exchange recovery system and performance were obtained from the SLOAN & MA (1976) and RANDOL (1980).

WATER QUALITY (ppm unless stated otherwise)

	Mill CIX Plant Feed 8/84	Mill CIX Plant Tails 8/84	Mine 34 & 35 IX 8/84
Flow Rate (USgpm)			
pH	8	8	8
TDS	2800	2800	1300
Hardness			340
Ca			
Mg			
Na			
$SO_4^=$	1600	1600	800
Cl^-	150	150	10
U_3O_8	10-12	1-1.5	
Se			
Mo			
Si			
Ra			
Ultimate disposition/ use			
Source:	Mines 17,19,22 24,30,30W		

Since the original description of the KERMAC ion exchange recovery of uranium several changes have been noted:

1) Quality of minewater delivered to the Mill CIX unit has changed and now contains 28000 ppm TDS including 1600 ppm $SO_4^=$ and 150 ppm Cl^-.

   Under these conditions the U_3O_8 (still 10-12 ppm in the feed solution) loads to only 0.6 lb.ft³ (10g/l) before breakthrough occurs.

2) Minewater from Sections 35 and 36 runs 1300 ppm TDS, 1600 ppm $SO_4^=$ less than 10 ppm Cl^- and loads resin to 2 lbs U_3O_8/ft^3.

3) Resin fouling, believed to be SiO_2 and $CO_3^=$, is overcome by acid washing in pH1 HCl every few months using recirculating solution to clean the resin.

4) Original design called for 16 resin elutions per month. Currently it is necessary to elute 100 batches of resin per month. This reduces the economics of the operation.

5) Resin from Section 34 and 35 Mine IX plants are transported to the central mill for elution. Transfer of resin so often is labor intensive and expensive. Quivira is anticipating changing to an elution of resin inside the adsorption vessels and it is expected that the epoxy coated carbon steel vessels will corrode.

6) Because of the reduced loading achieved in the IX plant, the resin inventory has had to be increased to keep U_3O_8 in the minewater effluent within permit limits of below 2 ppm U_3O_8. This in turn has required a much greater load on the resin elution circuit with correspondingly greater cost of reagents.

7) Eluate is now mixed with the SX strip solution for direct precipitation of yellowcake.

KERMAC CIX

The Kermac System is described in the Randol Report on Continuous Ion Exchange/Resin in Pulp and by SLOAN & MA (1976). Very similar contactors are used at the The Uranium Resources Corporation, Benavides in situ leach plant in Texas.

Uranium is loaded on resin in two upflow fluidized beds in series. Feed solution flows down a central feed pipe to a conical section at the bottom of the contactor, then up through a perforated plate through the expanded bed of resin occupying the greatest part of the vessel. Solution then overflows across a launder and flows by gravity to the second column identical to the first.

When breakthrough is observed in the barrens from the tail column, the resin contents of the lead column are transferred to the elution vessel. Partly loaded resin from the tail column is transferred to the lead column and loading recommenced. Resin is transferred using hydraulic venturi eductors.

Resin is eluted in a downflow packed bed chamber using a split elution sequence to achieve higher eluate concentration.

This two stage system works well for very dilute feed solutions such as minewater as long as equilibrium is not depressed by competing ions.

This system is very similar to the so-called UTAH-type contactors used by several South Texas in situ leach operations. The name UTAH-type is derived from the first application of this type of contactor at the Utah Copper Company where they were designed by R. Porter.

CONSTRUCTION OF COLUMNS

8' x 8' with cone at bottom. There are no baffles in the tanks. At the bottom of each tank is a perforated disc with 1/8 inch holes on 3/4 inch centers.

Originally there were twice this number of holes in the solution distributor disc, but it was found to work better if half of them were plugged.

MATERIALS OF CONSTRUCTION

Mild steel loading columns without any coating.

Elution columns are of mild steel lined with a special epoxy designed to resist the high chloride content. The epoxy coating has lasted since the original application in 1962.

RESIN TRANSFERS

Resin is transferred from the loading columns to elution tank by means of water jet eductors at the bottom of each column which enter each tank below the perforated plates. Resin is transferred four times in each cycle. A single 5HP high speed water pump powers all eductors for resin transfers from one tank to another and in/out of the elution vessel.

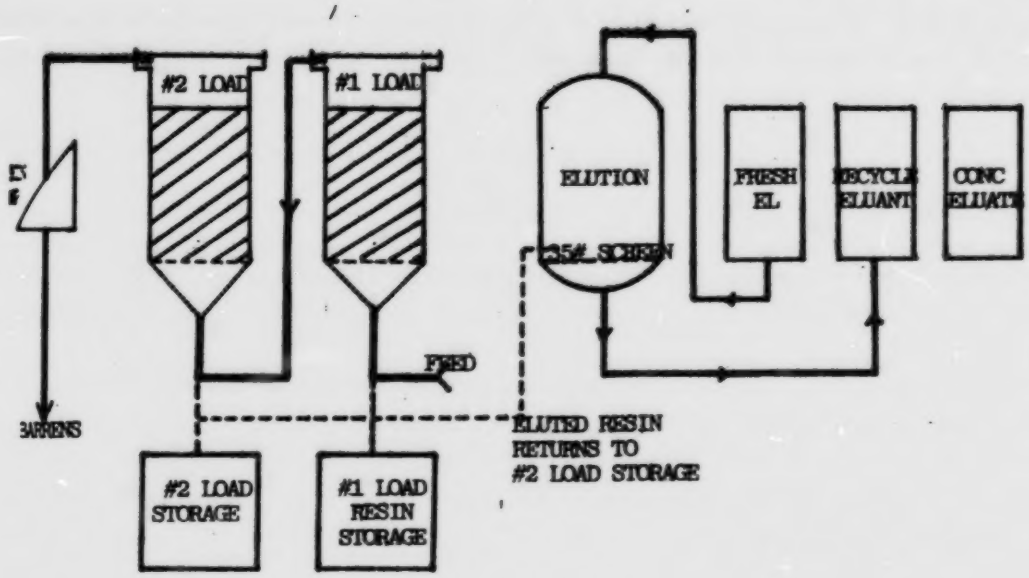
ELUTION CYCLE

As uranium levels in the CIX barrens start to rise in the tail of the two loading columns, the lead column is taken off line and resin transferred to the elution tank for elution.

The present elution system consists of two tanks (350 and 125 U.S. gal.) in series.

A split elution process is employed whereby the second elute from the previous day is used as a primary eluant to yield a rich eluate. This rich eluate runs about 10 g U_3O_8/l which is a very good tenor indeed. Then the partly eluted resin is eluted further using wash solution from the previous day.

The 3 stage split elution requires 6 hours downflow elution with 1.8 molar NaCl at pH 8.0-8.2.



During the cycle, resin moves as follows:

1. Eluted resin is held in storage in a tank.

2. When required eluted resin is transferred into the #2 loading tank (tail tank) where it is loaded for several days.

3. Once barrens from the tail tank rise indicating breakthrough, resin from the lead tank #1 is transferred to elution, and resin from the tail tank is transferred to the lead tank #1.

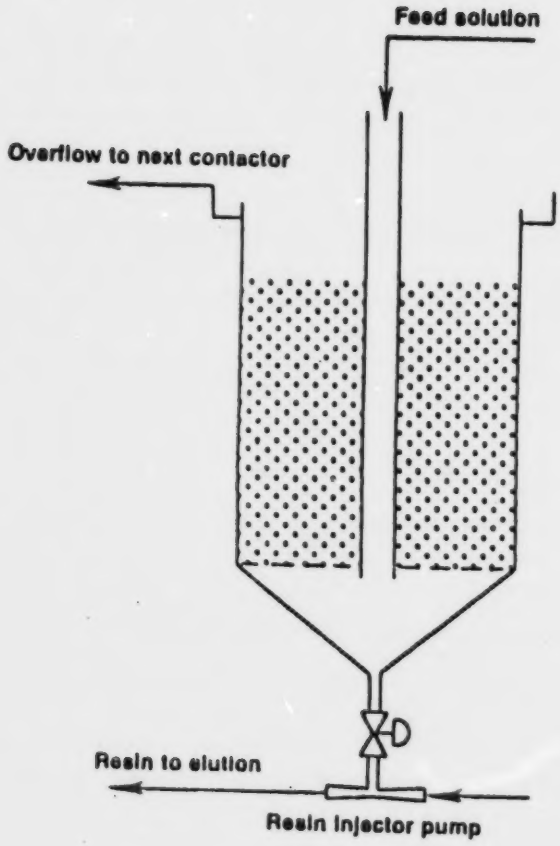
4. When the new resin batch in tank #2 loads to a point that barrens approach 1PPM U_3O_8, the resin in the lead tank is transferred to the elution tank.

5. After elution, the resin is rinsed and transferred back to the eluted resin storage tank or direct to the tail tank #2 as required.

ADVANTAGES OF KERMAC SYSTEM

1) Very simple to design and operate

2) Works very well for low concentrations of Uranium to be recovered in the presence of low competing ion concentrations.



Loading Kurmac CIX column in a two-column cascade

DISADVANTAGES OF KERMAC SYSTEM

1) High competing ion solutions would require numerous Kermac contactors in series at which point capital cost and resin inventory would go up to make this system uncompetitive with multiple stage column contactors.

2) In multiple stage configuration the Kermac contactor would resemble a Porter CIX system only it would not run truly continuously as the forward flow through each contactor is halted during resin transfer.

3) Scaleup of contactor diameter is limited. Distribution of feed solution across the contactor is achieved using a perforated plate. This works well only up to a certain tank diameter beyond which channeling can be expected to occur on account of the feed having to be distributed from the central pipe.

   For large flowrates several lines of contactors are required.

   Further contactor scaleup would require installation of more sophisticated feed distributors such as the patented Proter system.

RADIUM REMOVAL

Radium must be precipitated from minewater to meet the 3 piC/l radon effluent limit imposed by the state.

$BaCl_2$ in a saturated solution is mixed via a chemical feed pump to the ion exchange plant effluent.

0.023 lbs. $BaCl_2$ per ton water is consumed in this way. Barium Chloride costs $450/st i.e., based on an effluent flow of 4000 gpm, $BaCl_2$ is calculated at 662 lbs/day at a cost of $149/day.

After $BaCl_2$ addition the water is settled in two unlined ponds in series before the water is discharged in one case to a "creek" and in the second case to a ditch from which the ranchers draw irrigation water.

IMPACT OF MINEWATER DISCHARGE TO ENVIRONMENT

Impact of uranium minewater seepage on groundwater at Ambrosia Lake is similar to that at other Quivira Mining Company operations such as at Churchrock No. 1 Mine, with the

exception that at Ambrosia Lake, uranium is recovered by IX, but not at Churchrock No. 1.

TAILINGS DAM

Tailings at pH 1.2 and 40% solids or less are pumped to the tailings pond and discharged via perimeter spigots. The tailings are coarse. Ore grind is to Minus 28 mesh, 33% minus 150 mesh and 20% minus 200 mesh.

The original tailings dam was designed and built by Stearns Rogers in 1958 long before there were any environmental concerns about tailings disposal.

Every four months a state approved engineer must submit a report on the tailings pond to demonstrate that it conforms to the Bureau of Mines stability test.

Tailings are discharged to make a very wide peripheral beach with a small pond. No underdrains are installed to drop the phreatic level at the wall as such design features had not been considered when the dam was built.

At the date of the latest Randol visit the dam was reaching an estimated height of 100-150 ft. A new seepage collection trench is being excavated at a cost of $500,000 and it was clear that a significant volume of seepage solutions were collecting in the trench.

The site was visited just after a heavy rainfall and erosion features were noted on the outer surface of the dam wall. These were being filled in. Ever since the failure of the Churchrock tailings dam of an operation belonging to another company, uranium tailings dam construction has been very strictly monitored by the state.

SEEPAGE FROM TAILINGS

50 - 70 monitor wells are scattered around the Quivira Mining Company site, many of them around the tailings dam. Collecting samples of water from these wells is the fulltime task of Felix Vigil. Monitor wells go down to the contact at the bottom of the alluvia with bedrock - normally a shale at a depth of 10 - 50 feet below the surface.

Monitor well samples indicate that a plume of seepage from the tailings dam extends about half a mile east of the dam.

Seepage water quality indicates that there is some improvement in quality of tailings solution as it migrates through the alluvia as has been observed at several other uranium tailings sites.

High chloride levels in minewater from the vicinity of the tailings pond indicate that seepage losses do occur. Leakage into the mines may occur due to horizontal migration of solution until intercepted by vertical leakage points such as sample drillholes, ventilation shafts, etc. Minewater as high as 200 ppm Cl^- has been encountered as evidence of such seepage.

Also, when a lined evaporation pond was constructed close to the toe of the dam, large gas bubbles accumulated beneath the lining even as it was being laid down which were assumed to be carbon dioxide from a reaction between acid seepage from the tailings pond and carbonates in the soil.

It is almost certain that in 1984 a new uranium mill would not be allowed to discharge tailings to an unlined pond in an alluvial plain except under the most convincing circumstances where it could be shown that local factors would remove undesirable species from the solutions or that they would be contained in an aquifer that already was so poor in quality as to render the natural waters totally unusable before the impact of tailings seepage.

In this case mill tailings seepage and leakage into nearby mines has resulted in a gradually increased cost and deterioration in efficiency of the ion exchange minewater treatment process.

ENVIRONMENTAL PROTECTION AUTHORITY

New Mexico is an "agreement state" and as such falls under the state regulators as far as environmental protection is concerned. This means that the operation must comply with state regulations which are supposed to be at least as strict as those of the Federal Nuclear Regulatory Agency.

Water discharged to navigable streams must comply with the NPDES permits - National Pollution Discharge Elimination Service. These require maximum 2ppm U/l and 3piC/l Radium in discharged effluents. It is questionable whether such regulations apply in this case since the watercourse into which the treated minewater is being discharged is normally dry and is certainly not a navigable waterway.

Limits on discharged water	U	1 ppm max
	Ra	3 piC/l max
	pH	6 - 9

Remainder of environmental regulation is by the New Mexico Department of Environmental Improvement soon to become a cabinet position removing it from the Department of Health.

EVAPORATION PONDS

Once water has been involved in uranium mineral processing it may not be discharged except to a lined evaporation pond.

Initial evaporation ponds were not lined until the law was changed. Since then the first two sets of a total of 5 lined ponds have been abandoned. As water is recycled, so dissolved solids and chloride build up and must be bled.

EVAPORATION POND NO. 8 & 10

The first attempt to line a pond was pond 8 at the toe of the tailings pond. It was planned to line the pond with PVC on the floor and chlorinated polyethelene on the sides. In doing so a problem arose in that gas bubbles developed under the membrane and lifted it in such a way that they could not be removed. The gas generation was ascribed to a reaction between acid seepage from the dam and carbonates in the alluvia beneath the pond. A similar effect would be observed if acid effluent were initially discharged to the pond before it was lined.

Several "burpvalves" supplied by Watersaver Company were tested without success as a means of getting rid of the gas.

Soil covers were applied to try and weigh the lining membrane down.

Eventually pond 8 was abandoned. PVC floor lining where covered by sediment appears still to be in good shape. When exposed to the New Mexico sun and heat, however, plasticiser evaporates and the membrane soon decrepitates.

From this experience it can be demonstrated that evaporation ponds adjacent to seeping acid tailings dams may be impossible to line satisfactorily if located over carbonate containing strata. "Burp valves" do not work as a means of releasing such gases.

Pond 10 was designed and installed by Jacobs Engineering in 1976.

EVAPORATION PONDS 11 - 15

Ponds 11 - 15 were installed with PVC floors and 20 mil CPE sloping sides in 1977-8. The ponds were designed and installed by Jacobs Engineering and the membranes supplied by Panasall.

The membrane panels are installed with the long side seams parallel with the wall of the

pond. Sides are sloped at a gradient of 2.5:1 against sandy material making up the ponds walls. The ponds are quite large - the five ponds totalling 110 acres were installed for $2 million in 1978.

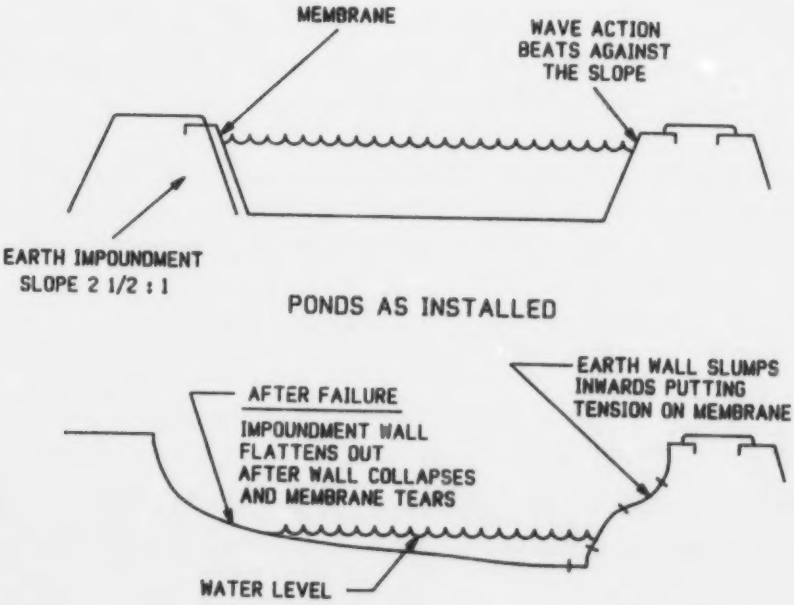
Several problems have been experienced:

- The steep sides are vulnerable to wave action - slope stability of the earth walls was inadequate and the soil beneath the membrane sloughed inward putting the membrane liner sides under tension.

- The membrane panels were factory seamed parallel to the wall of the dam. These seams have failed in places due to tension.

- Rodents found their way to the membrane from below and gnawed holes through the plastic. The holes allow water to the underside of the membrane allowing the earthen wall of the pond to become wet and plastic.

Ralph Yetter, plant engineer for Quivira Mining Company has been responsible for maintainence and repair of the pond linings and concludes after observing these ponds since they were installed that failure is due mainly to the steep 2.5:1 sides of the ponds.



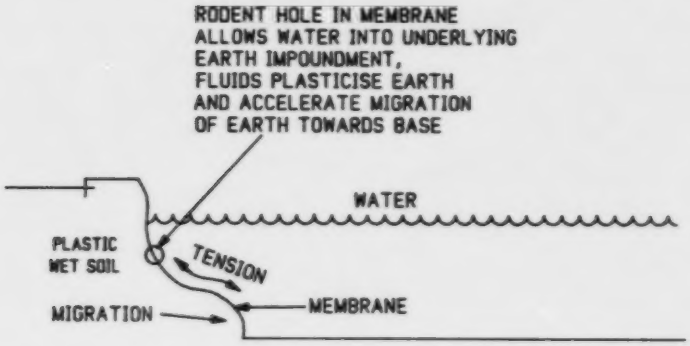
I-83

Wave action combined with slope instability has been the main cause of lining failure. The failures were exagerated by improper panel orientation, rodent holes, membrane embrittlement and seam failure on the 20 mil CPE membranes on the sides. The basic design of the pond appears to be failure prone regardless of membrane selection as discussed below.

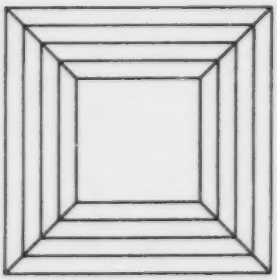
PONDS 16 - 21

Ponds 16 - 21 were designed and installed by Kerr McGee Corp. along the lines of the Jacobs Engineering design of ponds 11 - 15. These ponds covering 160 acres were installed in 1979-80 at a cost of $3.2 million. In these ponds the floor is again PVC with hypalon sides. The basic wall configuration of the ponds is similar to that of the earlier ponds installed by Jacobs Engineering with a 2.5:1 vertical slope.

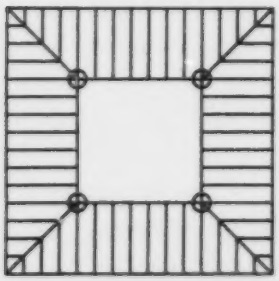
Once again wave action against unstable slopes of the earthen pond walls has caused the wall material to slump behind the hypalon lining membrane. This has caused tension in the membrane and resulted in failure.



EXISTING DESIGN



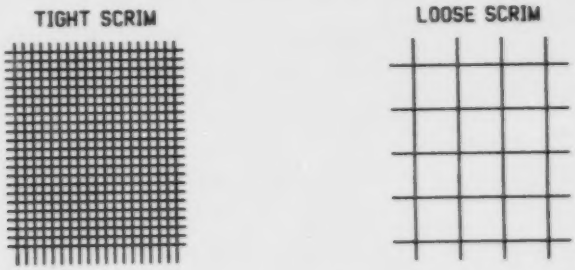
HINDSIGHT RECOMMENDATION



In ponds 16 - 21 the membrane panels are oriented parallel with the walls making them apparently more susceptible to seam failure than if the panels were oriented across the slope.

Again rodents have gnawed holes in the membranes on the exposed sides which allowed moisture to get behind it and to fluidize the earthen wall material in conjunction with wave action. The diagram illustrating how this caused failures on side slopes of dams 11 - 14 applies equally well in this case.

After the nylon reinforced hypalon membranes were installed at Quivira Mining Company's ponds, there has been some discussion as to the reason for delaminations in some installations. One possible contributory factor noted by Ralph Yetter is that the individual strands of nylon reinforcement are too close together.



One observation made (No qualitative test data available) is that when reinforcing fiber with a scrim that is too tight is used, then the bonding area in the spaces between fibers is too small for a good bond between the two layers of membrane.

The observation seems plausible and is an aspect of thermobonded reinforced membranes which is worth being aware of and further investigation.

MEMBRANE REPAIR

Where membranes on the walls of the evaporation ponds are damaged, this usually occurs in the form of failure along seams where the supporting wall embankment has slumped and put stress on the membrane.

The cost of changing the slope profile of the walls of the impoundments would be exorbitant. To date the repairs that have been made involve replacement of parts of the membrane panels. Several alternatives have been tested:

1) Chevron Industrial Membrane CIM painted over fiberglass reinforcement to make a new membrane to span holes and rips in the hypalon liner on the side of pond No. 16.

   Five gallons of CIM were required to cover an area about 15' long X 2' wide at a cost of $15/gallon plus fiberglass. The roller application of the liquid membrane was found to be messy and time consuming although Quivira Mining described CIM as a "very good product."

2) Hypalon patches on hypalon. These proved difficult to glue.

3) CPE patches adhered to hypalon using Staff Industries CC801 adhesive works very well. Expansion flaps are left in the inserted CPE panels. Liberal amounts of adhesive are applied to both membrane surfaces before pressing the two together. The glue works best in warm weather. It was supplied by:

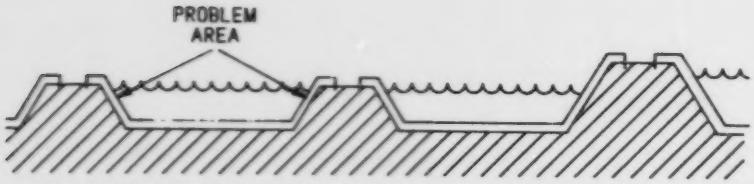
   Staff Industries Inc.
   240 Chene Street
   Detroit, MI 48201

SUGGESTED ALTERNATIVE EVAPORATION POND DESIGN

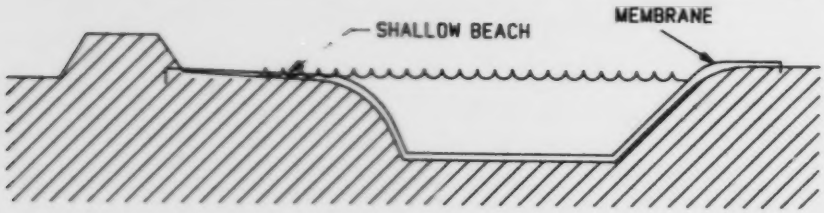
Since wave action appears to try to turn a steep wall into a low angle beach, Quivira Mining believes that the beaches of the evaporation pond should be constructed that way to start with.

At Quivira Mining Company it has been observed that where the water level is dropped so that the waves run up a shallow beach, then there are no slopes to become unstable. The shallow beach areas become protected by a layer of silt. In order to get the volume required in the ponds it is necessary to have an adequate depth. To achieve this an inverted "tophat" profile design has been suggested. Such a design would require more real estate but hopefully would avoid the expensive maintenance and potential for leaks.

OLD "FARM-TYPE" POND PROFILE



PROPOSED IMPROVED "INVERTED TOP HAT" PROFILE



BRIERLEY, J. A., BRIERLEY, C. L., and Dreher, K. T. (1980) "Removal of Selected Inorganic Pollutants from Uranium Mine Waste Water by Bacterial Methods." Chapter 27 in Proc. First International Conference on Uranium Mine Waste Disposal, AIME-SME, 19-21 May 1980, Vancouver, B. C., Ed: C. O. Brawner.

BRIERLEY, Corale L., and BRIERLEY, James A. (1981) "Contamination of Ground and Surface Waters due to Uranium Mining and Milling." Vol. 1. Biological Processes for Concentrating Trace Elements from Uranium Mine Waters, U. S. Bureau of Mines Report, October, 1981, Contract J029 5033, University of Colorado at Denver, Vol. I.

OPERATION RABBIT LAKE OPERATIONS
ELDOR MINES LTD.
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P.O. BOX 2070
SASKATOON, SASKATCHEWAN S7K 3S7

TELEPHONE (306) 382-0505

CONTACT Art Carino, Metallurgical Manager

LOCATION Northern Saskatchewan, 198 miles southeast of Uranium City and 134 miles northwest of Lynn Lake, Manitoba.

INTRODUCTION

The following draft paper was located in RANDOL files and unfortunately does not indicate the author's name. Nonetheless this paper is of interest for the following reasons.

1. A systems approach is described - In this case after Rabbit Lake ore was depleted, ore from nearby Collins Bay "B" Zone is sufficiently different to require a change in metallurgical process. Increased levels of environmentally sensitive metals in the effluent from the treatment of new ore lead to a change in metallurgical process, and inclusion of new purification and effluent treatment processes.

2. Useful methods for removal of zirconium and arsenic etc. from effluents are described.

   - Precipitation of zirconium as a phosphate by addition of phosphoric acid, and filtration.

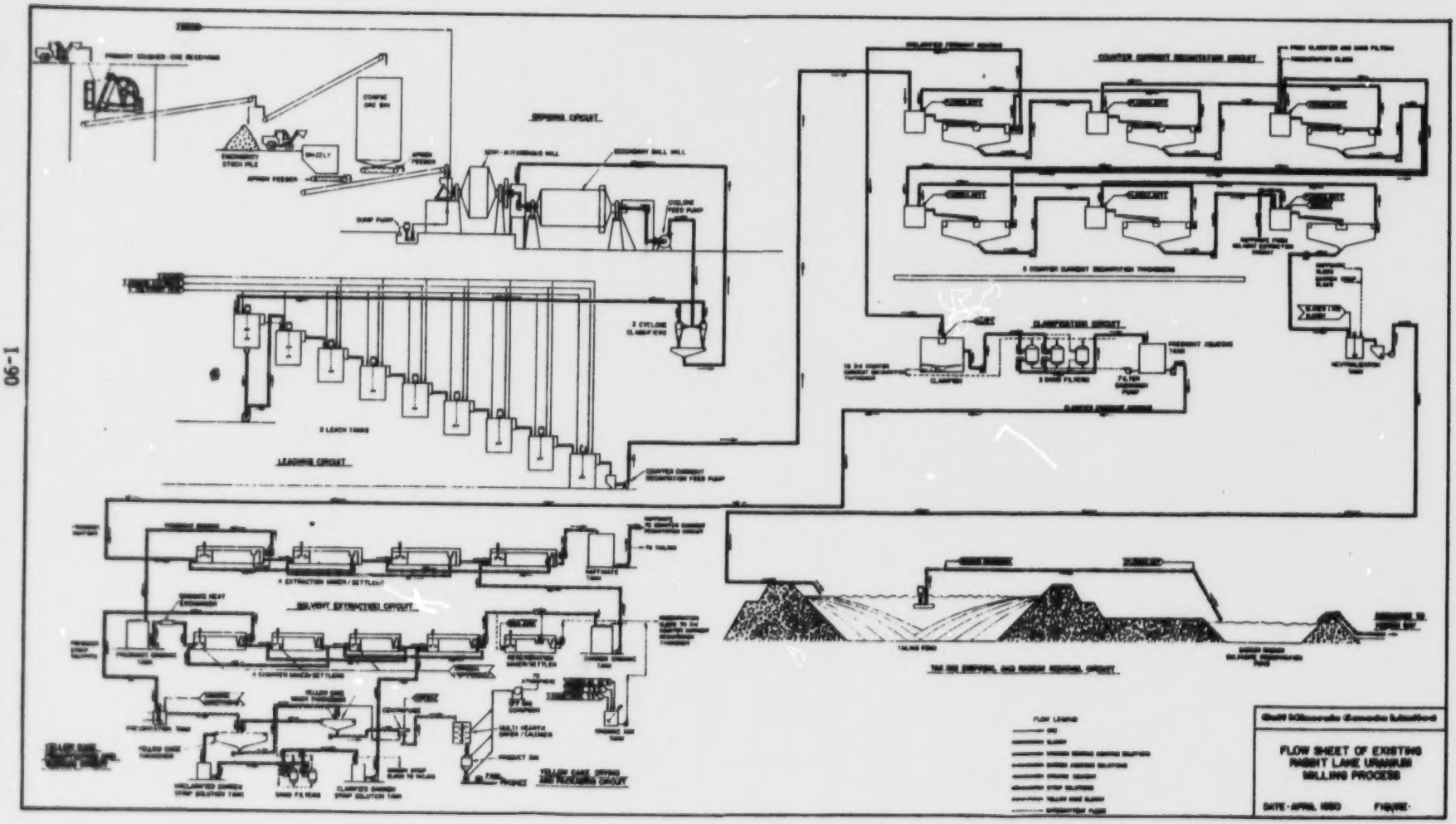
   - Precipitation of arsenic as ferric arsenate at pH 3.8 while is pH is adjusted by MgO addition to yield an iron cake.

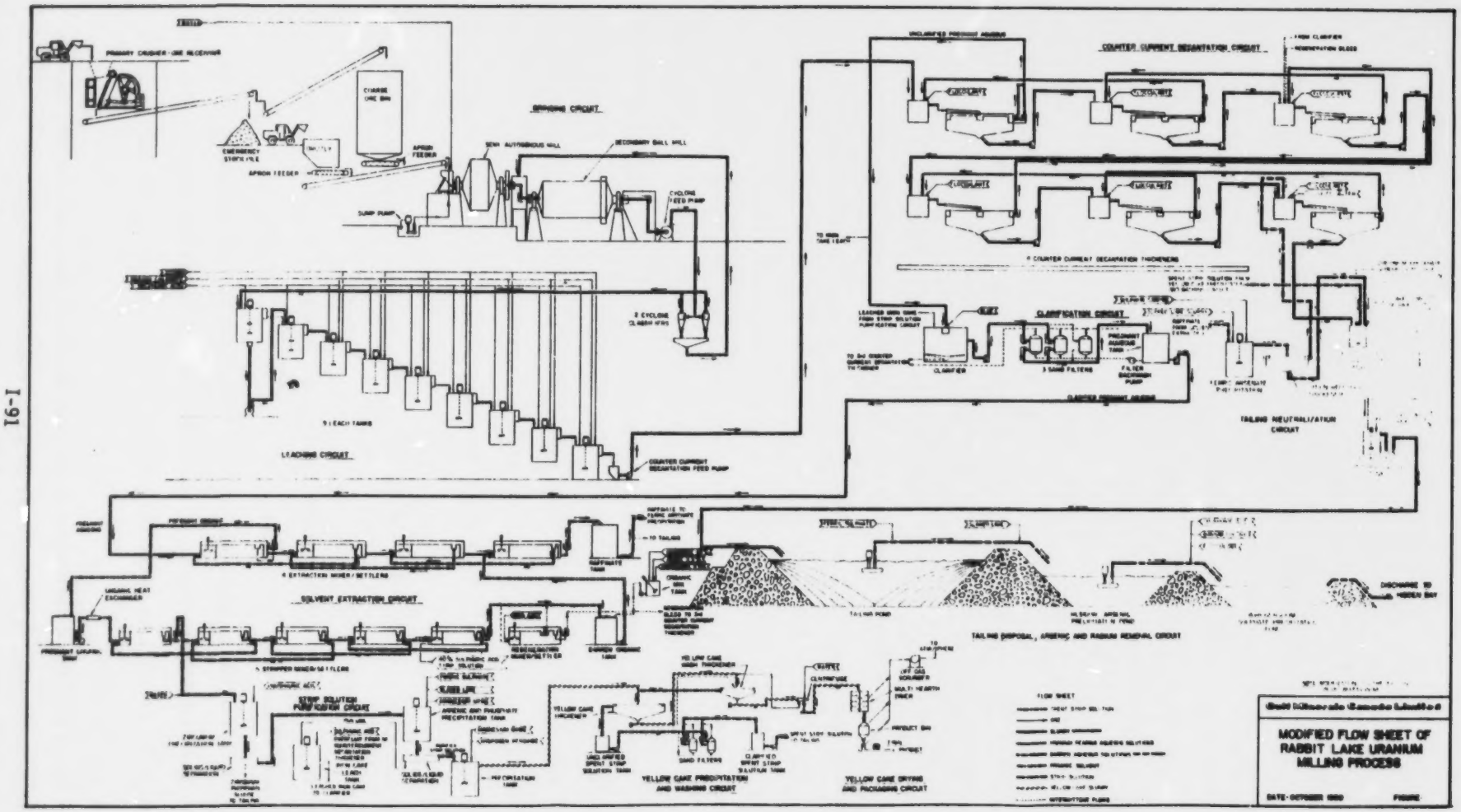
   - SO_2 to convert Fe^{++} to Fe^{+++} for ferric arsenate precipitation.

   - High pH nickel precipitation to pH 12.5-12.7 with lime to precipitate nickel.

   - Radium removal by addition of $BaCl_2$.

   - Avoiding ammonia releases in effluents by selecting an alternative means of stripping loaded SX adsorbent and for pH adjustment.


FLOW SHEET OF EXISTING
RABBIT LAKE URANIUM
MILLING PROCESS
DATE - APRIL 1980
FIGURE -


PRIMARY CRUSHER - ORE BLENDING
EMERGENCY STOCKPILE
APRON FEEDER
CHARGE ORE BIN
APRON FEEDER
SEMI AUTOGENOUS MILL
SECONDARY BALL MILL
SUMP PUMP
CYCLONE FEED PUMP
GRINDING CIRCUIT
2 CYCLONE CLASSIFIERS
9 LEACH TANKS
LEACHING CIRCUIT
COUNTER CURRENT DECANTATION FEED PUMP
COUNTER CURRENT DECANTATION CIRCUIT
6 COUNTER CURRENT DECANTATION THICKENERS
CLARIFICATION CIRCUIT
CLARIFIER
3 SAND FILTERS
PRECIPITATE AGITATOR TANK
FILTER DISCHARGE PUMP
TAILING NEUTRALIZATION CIRCUIT
4 EXTRACTION MIXER/SETTLERS
SOLVENT EXTRACTION CIRCUIT
4 STRIPPER MIXER/SETTLERS
STRIP SOLUTION PURIFICATION CIRCUIT
ARSENIC AND PHOSPHATE PRECIPITATION TANK
TAILING POND
TAILING DISPOSAL, ARSENIC AND RADIUM REMOVAL CIRCUIT
DISCHARGE TO
YELLOW CAKE PRECIPITATION AND WASHING CIRCUIT
YELLOW CAKE DRYING AND PACKAGING CIRCUIT
CLARIFIER
SAND FILTERS
FLOW SHEET
MODIFIED FLOW SHEET OF RABBIT LAKE URANIUM MILLING PROCESS
DATE: OCTOBER 1980
FIGURE

Abstract

Gulf Minerals (Canada) Limited's Rabbit Lake Uranium Operation is located in the northern portion of Saskatchewan, 198 miles southeast of Uranium City and 134 miles northwest of Lynn Lake, Manitoba.

This paper describes flow sheet changes to solve operating problems and briefly describes future changes to accomodate the new "B" Zone ore.

The Rabbit Lake mill was designed to process 1600 dry tons per day of uranium ore, with an average grade of 0.370 percent U_3O_8. In 1981, the mill processed 2040 tons per day at a grade of 0.231 percent U_3O_8.

The process modifications and flow sheet changes that allowed this increase in tonnage will be discussed in relative chronological order.

Mill feed was introduced on June 10, 1975, the original equipment consisted of an Ingersoll Rand hydraulic breaker mounted over a 24" square grizzly. The - 24" ore was fed to a 20" X 6" semi autogenous grate discharge mill close circuited with 20" cyclones, the mill discharge was screened on a tyler double deck screen with the undersize (8 mesh) reporting to the cyclones, the screen oversize was returned by conveyor belt to the mill feed chute.

The cyclone overflow (28 mesh) was thickened in a 100' diameter thickener to obtain 55 percent solids for the leach circuit.

The leach circuit consisted of two slurry holding tanks and five leach tanks.

The leach discharge was washed in five 100' diameter thickeners to remove the soluble uranium.

The pregnant liquor was clarified in a 60' diameter clarifier and pumped to three 7' diameter sand filters.

The clarified pregnant aqueous was pumped to a solvent extraction circuit for concentration and removal of impurities, after the stripping phase the uranium was precipitated from the pregnant strip liquor by adding ammonia in two precipitation tanks.

The precipitated yellowcake slurry was thickened and washed in two counter-current thickeners, centrifuged and dried in a multi-hearth dryer.

The dried product was passed through a hammer mill before being packaged in 45 gallon steel drums.

The slurry from the last C.C.D. thickener was pumped to three neutralization tanks where milk of lime was added before discharging to the tailings pond.

As with most mill start ups, problems were encountered shortly after feed was introduced. In 1975, tonnage was limited due to several reasons. Wear on the S.A.G. mill liners was excessive due to uneven feed rates to the mill allowing the mill to run empty, at this time the mill was charged with 4" balls, these were removed and replaced with a charge of 1 1/2 and 2" balls.

The acid section of the mill, was lined with urethane rubber. These liners failed in 1975, shortly after start-up, all C.C.D. thickeners, associated tanks, solvent extraction cells, yellowcake area tanks and tailings line were affected.

The decision was made to replace all lining with fiberglass and to replace the tailings line with sclairpipe. This project would proceed into 1976 and proved to be an exercise in ingenuity as thickeners and tanks were bypassed to allow full mill operation during the relining process.

In 1975, the C.C.D. thickener diaphragm pumps were found to be an impractical design, necessitating major modifications.

In 1976, the mill tonnage reached 63.5 tons/hr.

The hydraulic rock breaker was abondoned as it was impossible to operate during the winter months. A used Kue Ken double toggle 42" X 48" crusher was purchased and temporarily installed during construction of a permanent crusher facility.

A new off gas scrubber was required for the yellowcake dryer and was purchased in 1976.

Considerable improvements to the mill ventilation system were required to control radon gas, venturi scrubbers were installed on the leach tanks, ventilation was steadily improved over the next three years.

In 1977, the tonnage increased dramatically to 80.5 T.P.M. due mainly to the completion of the crusher installation.

Major modifications were carried out in the grinding circuit.

The neutral thickener was removed from service when it was discovered that cyclone overflow could be maintained at 55 percent solids with no adverse effection on the grind.

A used 9'6" X 17' Nordberg ball mill was purchased and installed as a regrind mill. The Tyler screen and associated recycle belts were removed.

The S.A.G. mill discharges directly to the regrind which is close circuited with the 20" cyclones.

Mine drainage water was pumped to the mill for treatment and disposal to tails. A decant barge was installed at the tailings pond and a second precipitation pond was added.

Flocculant and Barium Chloride mixing stations were installed at the tailings area.

Pump capacities were increased in the solvent extraction area.

In 1978, tonnage increased to 86.8 tons/hr. the neutral thickener was converted to a sixth C.C.D. thickener.

In 1979, tonnage again increased to 105.9 tons/hr.

Two more leach tanks were installed and the acid plant capicity was increased to 200 T.P.D. from 150 T.P.D.

A test sandfilter was installed at the precipitation pond effluent discharge.

In 1980, tonnage was 117 tons/hr.

Four inch balls were added to the S.A.G. mill with a control system to prevent the mill running empty.

A mass flow system was insatlled from #1 slurry tank to the leach circuit to provide even feed.

A clutch was installed on the regrind mill drive, originally the synchronous motor was sufficient to start the mill when installed on a power grid in the south, but at Rabbit Lake the power factor could not be maintained to start the mill when it was heavily loaded.

A grate discharge was installed on the regrind and a trommel on the auto mill, the trommel undersize feeds the cyclone feed pump box.

A fourth sand filter was installed in the clarification circuit.

The lime screws feeding the lime mill were increased in size in order to neutralize the increased tonnage of tailings.

The Ingersol Rand Hobgoblin was recommissioned as an oversize rock breaker in the crusher building.

Extensive remodelling of floors and sump areas was carried out in 1980.

In 1981, tonnage was 124 tons/hr.

The diaphragm pumps in C.C.D. were recommissioned using a hydraulic drive system.

The grate discharge opening on the S.A.G. mill was increased allowing fully autogenous grinding.

<u>Slide</u> - Flow Sheet of Existing process.

The end of the Rabbit Lake orebody is in sight. Mining operations in the Rabbit Lake pit will cease in 1983. Enough ore will remain in stockpile to provide feed to the mill until 1985. The remaining years will see a marked reduction in the production of yellowcake as ore grades drop.

In order to insure continuity of operation, Gulf Minerals Canada Limited is presently attemting to obtain regulatory approval to develop a nearby orebody named the Collins Bay B-Zone, to provide ore for processing the existing mill.

If the planned mine development schedule becomes a reality, the first ore from the Collins Bay B-Zone deposit will be delivered to the mill in 1985.

The orebody contains approximately 3.5 million tons of ore grading 0.453 percent U_3O_8. The total reserve contains 31.3 million pounds of U_3O_8.

The Rabbit Lake and Collins Bay B-Zone orebodies have major mineralogical differences. A comparison of the analysis of typical samples of ore from Rabbit Lake and the Collins Bay B-Zone is given in Overhead 1.

Typical Rabbit Lake Ore Sample Analysis

		Rabbit Lake Sample (%)
U_3O_8		0.31
Arsenic		0.003
Nickel		0.014
Molybedenum	Approximately	0.002
Iron		-----
Vanadium		0.021
Thorium dioxide		-----
Sulphur		-----
Phosphate		0.16
Carbonate expressed as Carbon dioxide	Typically	2.0 - 3.0 %

Typical Collins Bay B-Zone Ore Samples Analysis

	H.R.I. Average Grade Uranium Sample (%)	L.R.C. High Grade Uranium Composite Sample (%)	L.R.C. Low Grade Uranium Composite Sample (%)
U_3O_8	0.62	15.0	0.28
Arsenic	0.47	10.2	0.49
Nickel	0.35	8.27	0.36
Molybdenum	0.01	0.12	0.015
Iron	3.11	1.94	1.20
Vanadium	0.021	0.12	0.047
Thorium dioxide	----	0.040	0.003
Sulphur	0.07	0.56	0.10
Phosphate	0.02	----	----
[illegible]nate expressed as [illegible]bon dioxide	0.20	0.29	0.04

Metallurgically, the greatest difference is a higher concentration of nickel, molybdenum, zirconium and arsenic bearing minerals in the latter.

Nickel and arsenic are presently generally in combination as niccolite, a nickel arsenide mineral which is often found massive, in combination with pitchblende. Some minor sulphides have also been recognized including millerite (nickel sulphide), galena (lead sulphide), chalcopyrite (copper iron sulphide), pyrite (iron sulphide) and ankerite (a dolomitic limestone, containing iron), although the sulphur content is low.

Gangue materials include serecite and kaolinite rich graphic clays, chlorite, and carbonaceous material, generally in a host sandstone.

Uranium is present as uraninite, pitchblende and coffinite, the former often found massive or in fracture fillings, usually in association with niccolite.

From these and other analysis, there is an apparent, though not absolute, relationship between uranium, nickel, and arsenic concentrations in the orebody.

In designing modifications to the mill so that it can accept the Collins Bay B-Zone ore, there are a number of environmental constraints, which affect the selection of the specific processes to be used.

The present Rabbit Lake mill consumes approximately 0.70 pounds of anhydrous ammonia for every pound of U_3O_8 produced. While some of the ammonia added is removed in the tailing neutralization and precipitation processes, a significant percentage reports with the effluent at the final point of discharge. Regulatory authorities have directed this company to reduce ammonia levels in the effluent to a target level of 15 mg/l. This represents a reduction, of present levels, of the order of 95 to 97 percent. In addition, the significant quantities of arsenic and nickel in the Collins Bay B-Zone ore require special consideration, to ensure that their concentrations in the final effluent were less than 0.5 mg/l in each case.

Process Selection Description

Introduction

Early leaching tests confirmed that both arsenic and nickel would solubilize under leaching conditions which are favourable for uranium, and that extraction of both of these elements would be in excess of 80 percent. A series of physical tests was therefore conducted, to determine wheather the minerals of nickel or arsenic could be effectively separated from the uranium minerals, before the leaching stage of the process. Gravity separation and flotation were both evaluted, but no reasonable degree of separation of arsenic and nickel from uranium was achieved. These techniques were therefore abandoned in favor of chemical removal

of dissolved nickel and arsenic, from effluent solutions, prior to discharge.

The process, as it is conceived today, is as shown on Slide of Flow Sheet.

Test work confirmed that, with minor modifications, the crushing, grinding, leaching and countercurrent decantation processes, in existence, were suitable for beneficiation of the Collins Bay B-Zone ore. Major modifications will, however, be required to the solvent extraction process, to the precipitation process, and to the tailing disposal and effluent treatment processes.

The existing grinding circuit is satisfactory for Collins Bay B-Zone ore. No changes are required to the equipment or equipment layout. The ore is basically a sandstone which is readily amenable to grinding. It is significantly easier to grind than the existing Rabbit Lake ore, having a Bond work index of 10.3 to 10.7, as compared to 14 to 16 for the Rabbit Lake ore.

During actual grinding operations, some adjustments of the circuit operating parameters may be expected, to ensure production of a suitable grind.

Test work has indicated that satisfactory extraction of uranium can be realized with the available retention time of 7.5 to 10.5 hours. Sulphuric acid consumtion will be approximately 100 pounds per ton, which is 50 to 60 percent of the Rabbit Lake consumption. The major change in leaching conditions is the significant increase in sodium chlorate consumption which will be approximately 16.5 pounds per ton, or 300 percent of the present consumption. The projected average leaching conditions will therefore be:

- Grind	Nominal minus 35 mesh.
- Feed slurry density	50% solids by weight.
- Retention time	Six hours minimum
- Leach temperature	50 to 55° C.
- Free acid	15 to 30 g/l.
- Terminal emf	Minus 400 to 450 millivolts.

The countercurrent decantation and clasification ciruits will remain essentially unchanged. Although process economics may justify an additional seventh stage of C.C.D. thickening, that addition is not an essential modification to enhance the existing circuit's capability for processing the Collins Bay B-Zone ore.

Initial test work, with leach liquors from the Collins Bay B-Zone ore, was directed towards the application of the existing solvent extraction circuit, with ammonium sulphate stripping, to the purification and concentration of those liquors. Two major disadvantages were identified:

- Rates of sludge formation at the interface between the organic and aqueous phases in the stipping circuit, were several orders of magnitude higher than presently experienced.

- To continue to use an amonium sulphate strip would involve the design onstruction of a process for removing ammonia from the effluent, to achieve the objective of 15 mg/l of ammonia in the effluent.

Sludge formation rates would be effectively reduced by various techniques, which involved pretreatment of the solvent extraction feed solution, but not eliminated entirely. In addition, although a process for removing ammonia from the effluent does exist, its ability to extract at the required efficiency is questionable. As a result, the existing tertiary amine, amonium sulphate solvent extraction process was abandoned.

Test work was then directed at a solvent extraction circuit which would use existing equipment and could be operated with an alternative stripping reagent. Sodium chloride and sodium carbonate were both evaluated and sodium chloride, in particular, was found to be ideal.

Although sodium chloride stripped the uranium efficiently from the loaded organic solvent, with a minimum rate of sludge formation, estimates indicated

that the ammonia in the effluent would be replaced by 12,800 pounds per day of sodium and 16,300 pounds per day of chloride, originating from the stripping circuit. Sodium chloride was therefore environmentally unacceptable.

One solvent extraction process then remained, which would allow continued use of the existing process equipment. It would require a change from use of the tertiary amine presently employed, to a quaternary amine named Aliquat 336. The major advantage of the quaternary amine is that it may be stripped of its uranium using a sulphuric acid solution, thereby eliminating ammonia and avoiding the use of sodium chloride. Laboratory testing of the solvent again showed, however, that sludging at organic aqueous interfaces, in a modification of the Rabbit Lake solvent extraction plant, would be severe. Chemically, the amine was also less selective, with the result that arsenic in particular loaded onto the solvent and would have to be scrubbed in a significant plant addition. Both the kinetics raction and stripping were significantly slower than the tertiary amine, so that additional solvent extraction cells would be required. While the quaternary amine therefore was environmentally acceptable, it was less than satisfactory as a possible alternative to the existing process.

One laboratory test work programme, in its inital stages, however, held some promise of success. It involved solvent extraction using the existing solvent, but stripping with a strong sulphuric acid solution. Although initial results were encouraging, the approach was unconventional. Between June and October 1980, a considerable amount of test work was completed at Hazen Research Incorporated, which eventually established the viability of the process. It is now intended to make the minor modifications which will be required to convert to a strong sulphuric acid stripping circuit.

The operating conditions for the extraction section of the solvent extraction ion exchange circuit will remain unchanged.

The sulphuric acid stripping solution will have a concentration of 400 g/l sulphuric acid and will be advanced through the stripping circuit at about 17 igpm, approximately one third of the flow rate required for ammonium sulphate stripping. Five mixer settler stripping cells are required, so that one extra cell must be constructed in the solvent extraction area.

Pregnant strip solution presently contains approximately 15 to 20 g/l of U_3O_8. Strong sulphuric acid stripping will produce a pregnant strip solution which will contain 100 to 125 g/l of U_3O_8. That solution will be diluted with water to approximately 25 g/l as feed to the strip solution purification circuit.

See Overhead 3 (next page).

Table 4

Distribution of U, As, Mo, Zr, Si, and Bi in Alamine 336/H_2SO_4 Strip SX at 57 Organic Cycles - Collins Bay Liquor

	Assay, g/l							
	SX Feed	Raffinate	Pregnant Strip	Loaded Organic	Stripped Organic	% Extracted	% Stipped	Pregnant Strip Ratio Impurities/100 U
U_3O_8	2.15	0.00069	112	4.26	0.065	99.97	98.5	
As	1.78	1.79	0.35	±0.02	<0.01	0.4	>50	0.37
Mo	0.029	0.0056	0.68	0.14	0.087	81	38	0.71
Zr	0.0037	0.0017	0.059	±0.002	<0.002	≈ 54	>50	0.06
SiO_2	0.46	0.45	0.037	<0.01	<0.01	< 5	>50	0.04
Bi	0.0032	0.0024	0.007		<0.02			
H_2SO_4	10.0	12.0	293					
Cl	1.52	1.40	2.55					

Overhead 3 shows a typical distribution of major dissolved ions throughout the various products of a continuous laboratory solvent extractive. It demonstrates good selectivity for uranium, but poor rejection of, in particular, arsenic and Molybdenum. If allowed to pass to the precipitation stage, they would precipitate to some degree with the uranium, producing the maxima specified by our refinery. A strip purification stage is therefore included in the modified flow sheet. The first stage in the purification process will be the precipitation of zirconium, as zirconium phosphate, by the addition of phosphoric acid to a concentration of 0.5 g/l. The zirconium phosphate precipitate will be filtered from the eluate and pumped to tailing neutralization.

The filtered elute will then pass into a system of agitated tanks, where arsenic will be precipitated as ferric arsenate, by the addition of ferric sulphate, followed by the pH controlled addition of slaked lime to an approximate pH of 3.5 and magnesium hydroxide to an apporxinate pH of 3.8. The solution and precipitated solids (or iron cake) will pass to a thickener, from which the underflow solids will be removed. Since the iron cake will contain a minor amount of precipitated uranium, it will be leached with pregnant aqueous solution from the overflow of the first C.C.D. thickener, for uranium recovery. The leach iron cake will then be pumped to the clarifier, as show on the flow diagram, so that the solubilized uranium may be recycled to the solvent extraction circuit for recovery. The ferric arsenate eventually leaves the circuit, in the tailing stream from the C.C.D. circuit.

In the present circuit, anhydrous ammonia is used, not only as a reagent for stripping but also for precipitation. In order to entirely eliminate its use in the Rabbit Lake mill, and to avoid precipitating molybdenum and silica, it will be replaced by the precipitant, hydrogen peroxide. Magnesium hydroxide will also be used to maintain the pH in the range 3.5 to 3.8 throughout the precipitation. Because a continuous hydrogen peroxide precipitation system has not been developed to date, the new system will be a batch process. When

precipitation is complete, the solution and precipitated solids will be pumped to the yellow cake thickener, from where washing and drying of the product will be carried out as currently practiced. The spent eluate, from the yellow cake thickener, will be pumped through the existing sand filters, for the recovery of any entrained product solids, and then to tailing neutralization.

Almost five years of operation of the existing tailing disposal and effluent treatment at the Rabbit Lake mill has demonstrated its efficiency to produce an environmentally acceptable effluent in every respect except, for its ammonia content in the future, circuit modifications will eliminate the ammonia completely.

Two additional soluble contaminants must, however, be removed from the effluent, when processing ore from the Collins Bay B-Zone. They are arsenic and nickel and their maximum allowable concentrations in the final effluent are 0.5 mg/l in each case. The effluent neutralization has been examined, to modify it so that it will effect that removal.

Arsenic may be precipitated from tailing slurries and from the ion exchange barren solution as either ferric arsenate or calcium arsenate. Tests, which have been completed to determine the potential for redissoltuion of each of those precipitates, have indicated that the former is less soluble than the latter. The modified process, therefore, will precipitate the majority of the arsenic in that form. The barren solution, which contains the majority of the arsenic, will be treated separately. The equipment will consist of a number of tanks, where a one percent mixture of sulphur dioxide from the existing sulphuric acid manufacturing plant, in air, will be sparged into the agitated solution, to ensure that all iron present in the solution is oxidised to the ferric state. Lime will also be added to maintain the pH at approximately 1.3. The pH will then be raised to 4.5, at which point the arsenic will precipitate as ferric

arsenate. The resulting slurry will pass to a solution recovery thickener, from where the solids will be pumped to a first stage neutralization circuit. The thickener overflow, if acceptable for reuse as wash in the C.C.D. circuit, will be recycled. Otherwise it also will be pumped to the first stage of the neutralization circuit.

In the first stage neutralization circuit, the discharge or discharges from the solution recovery thickener, will be combined with the underflow tailing slurry from the last C.C.D. thickener, and the pH will be adjusted to 4.5 with slaked lime. The slurry will be held at that pH for approximately one hour, to precipitate as much arsenic as possible as ferric arsenate. The slurry will then pass to the second stage neutralization circuit where the pH will be raised to 12.5 to 12.7 with slaked lime and retain for approximately two hours. Although no residual soluble arsenic is expected after the first neutralization stage, any arsenic which may be present will be precipitated by the pH adjustment. Nickel will also precipitate as a nickel hydrate, and achieve the required specifications for both dissolved arsenic and nickel. After two hours, the slurry will be pumped to the tailing impoundment area.

OPERATION	RÖSSING URANIUM MINE PRIVATE BAG 5005 SWAKOPMUND 9000 SOUTH WEST AFRICA/NAMIBIA
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TELEX	56-053 WK
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INTRODUCTION

Rössing Uranium Mine is one of the world's great mines and also a most interesting uranium recovery operation, first because of the large size of the operation, secondly because of the remoteness and aridity of the location, and because operating costs are comparatively low, despite the very low grade of the ore.

As in any other desert, water is a scarce and valuable commodity in the Namib desert where Rössing is situated. Water is supplied to Rössing from two underground rivers, both over 100 miles from the mine. Rössing's policy is to minimize water consumption as much as possible both on the basis of cost saving and in the national interest. This case study is an excellent opportunity to see what happens in an acid leach uranium plant when it is necessary to recycle a large proportion of the water.

Of particular interest at this operation are the following aspects:

1. Rössing Uranium milling operations consume about 30% of the amount of fresh water per ton ore milled that is consumed at comparable uranium operations where water is not in short supply.

2. The degree to which tailings reclaim water and seepage are recycled to the process and its effect on TDS buildup, scaling, and corrosion.

3. Water quality effects at every stage of the process are interrelated, sometimes yielding unexpected results.

4. Natural attenuation of contaminants in seepage from the tailings dam.

5. Control of scaling.

6. Control of corrosion.

7. Effect of recycling on the uranium recovery process.

8. Water/salt balance modelling.

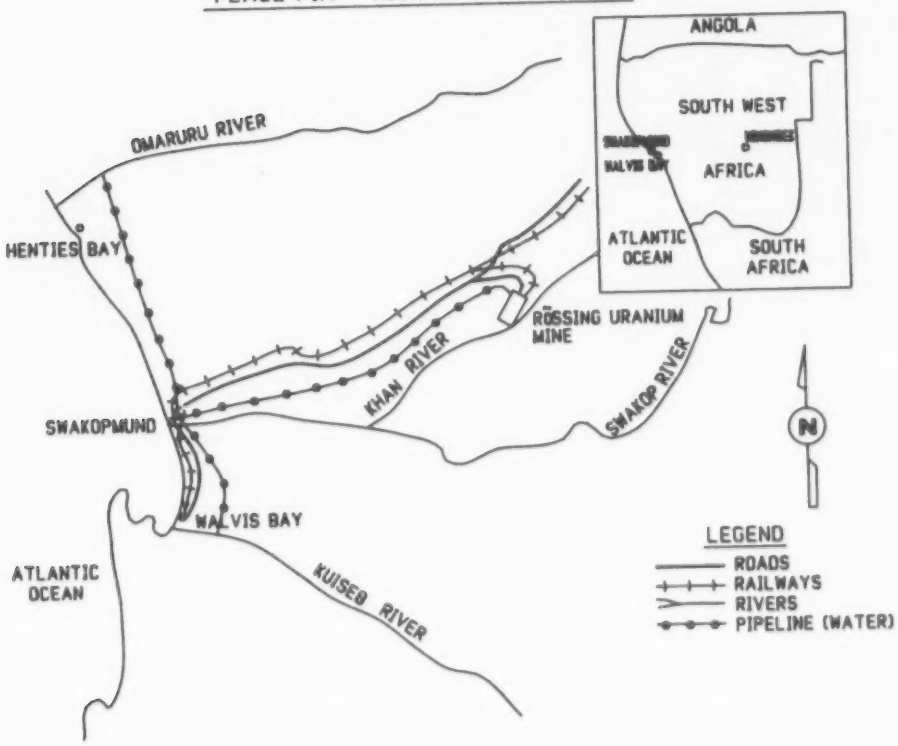
CLIMATE

20mm rainfall per year. Hot summers with occasional 60 knot bergwinds; up to 3.0 m evaporation per year.

WATER CONSERVATION PROGRAM

The Rössing Uranium Mine and Mill are located in the extremely arid Namib Desert where fresh water is scarce. The establishment of the mine and the mill which required up to 30,000 m^3/d of water was a significant additional demand, for the area had to be supplied from wellfields in two subterranean rivers, the Omaruru to the north and the Kuiseb River to the south. To supply this amount of water, the South West African Department of Water Affairs constructed major pipelines and pumpstations across the desert and supplied the water on a toll basis. Well water from the Kuiseb and Omaruru rivers is also supplied to the towns of Walvis Bay and Swakopmund, as well as minor rural consumers.

PLACE FIX - RÖSSING URANIUM MINE



After overcoming initial plant problems, Rössing was, by 1981, in a position to expand its efforts to reduce water consumption, and a program was put into effect to find all possible ways to achieve what, at the time, must have looked like an impossible dream. The first step was to measure and analyze the water balance and to examine where recycle water could be used without seriously affecting the process. Since then, the main thrust of the water management plan has been:

1) To recycle as much water as possible.

2) To reduce and control resulting corrosion and metallurgical effects of recycling.

Before 1981, the only use made of recycled tailings dam water was to dilute tailings before pumping them to the dam to maintain velocity in the tailings line.

One major use of fresh water was in pump glands. All the pumpstations except one are now converted to use acidic tailings return water for this purpose.

At the tailings dam area two reservoirs were built, one for acidic tailings water and one for nearly neutral collected seepage. These dams are at an elevation from which water flows by gravity to the plant. Rubber lined and high density polyethylene pipes were installed for this purpose.

A major savings was found to be possible if 12-13,000 m^3/d tailings return water could be used to replace that much fresh water in the rod mills. RDS and seepage water were recycled to the rod mills. The water saving benefits were immediate. Apart from using less fresh water in the mills, the water level in the tailings dam has dropped, thereby reducing the surface area and conserving more water because of reduced evaporation.

DESCRIPTION OF RÖSSING URANIUM OPERATION

NUMBER OF EMPLOYEES 2,600

TONS MINED Approximately 1 million tons per week (including wasterock).

STRIP RATIO 2.5 to 1

MILLS Four Open Circuit 14'Ø x 20' Marcy Rod Mills

TONS MILLED

1984 Est.	38,000 Metric tpd
1983	37,800 Metric tpd
1982	39,000 Metric tpd

NET FRESH WATER CONSUMPTION AT MILL

	Ore Milled, t/d	Fresh Water Consumption, m^3/d	m^3/t Ore Mined
1984	33,000	15,000 m^3/d	0.39 m^3/t
1983	37,800	20,600 m^3/d	0.54 m^3/t
1982	39,000	25,700 m^3/d	0.66 m^3/t
1981	46,000	29,850 m^3/d	0.65 m^3/t

This compares with 1.3 - 1.5 t new water consumed per ton ore milled at a typical mill using a comparable process (acid leach + SX) near Grants, New Mexico, where there are no water supply constraints.

ANNUAL URANIUM PRODUCTION About 5,000 tons per year U_3O_8.

CAPITAL R350 million in 1976.

MINING METHOD

Open pit, drilling, blasting, and face shovel loading to 170 t haul trucks.

ORE TYPE

Alaskite intrusions in metamorphosed sedimentary ocks. Some of the metasediments are high in carbonate.

METALLURGICAL PROCESS

The process is schematically shown below: crushing, grinding, leaching in sulfuric acid with MnO_2 oxidant, and cyclone removal of sand which is washed by rotoscoops. Slimes are washed by CCD followed by ion exchange, primary U_3O_8 recovery, and purification concentration by SX. Uranium is precipitated as ammonium diuranite and $(NH_4)_2SO_4$ recycled to the SX strip circuit.

PRODUCTION REQUIREMENT

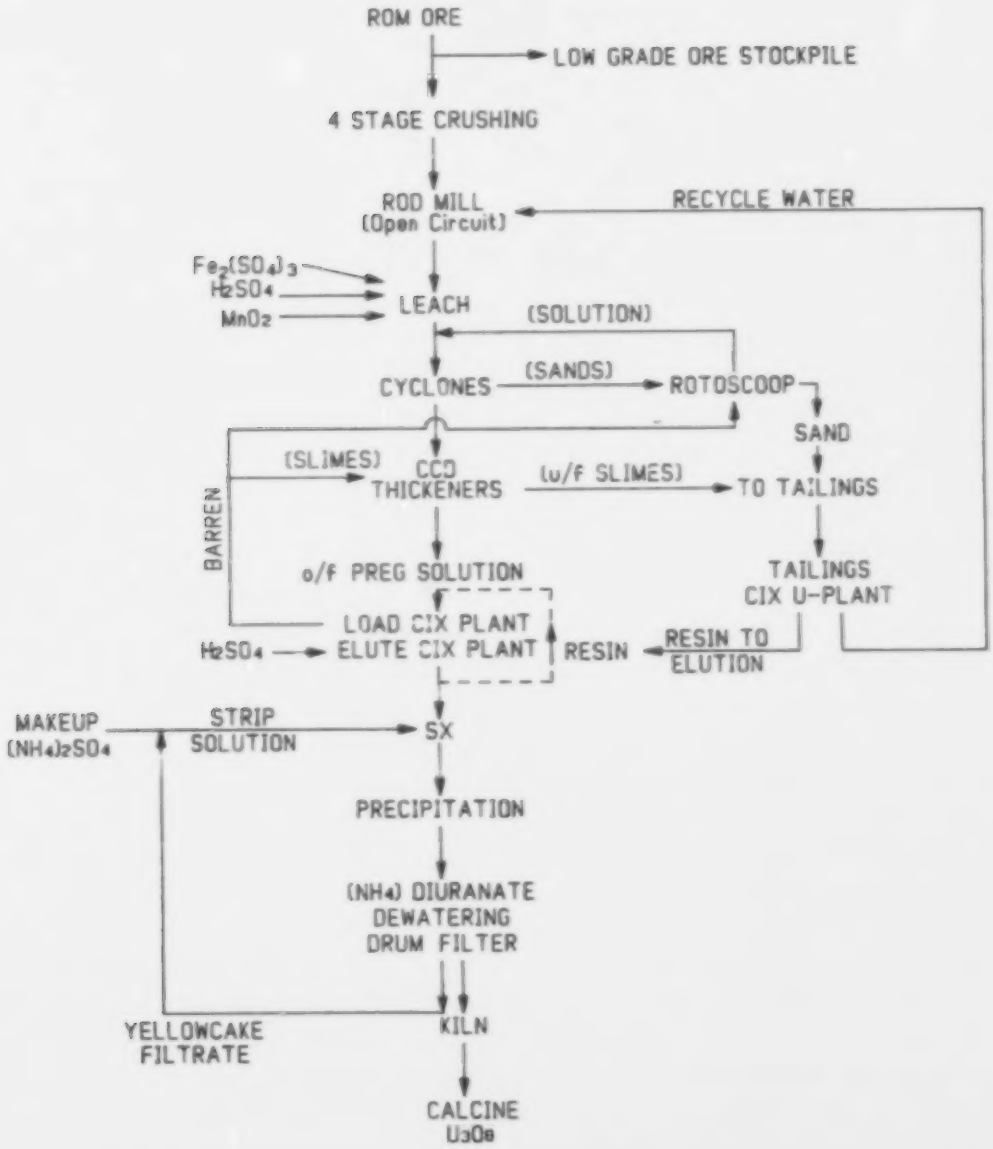
With the current state of the uranium market, it is no longer necessary for Rössing to achieve the maximum production of which the plant is capable. Minimizing costs is the dominant management objective.

DAILY PULP TO TAILINGS	40,000 m^3/d
ORE DENISTY	2/7-2.7
MILLS	Four Rodmills on 2 Modules

GRIND

Grinding at 76-78% solids, residence time 4½ minutes, yields a course grind: 100% - munus 6 mesh, 30% plus - 20 mesh, mean size - ±0.7 mm.

RÖSSING URANIUM MINE



LEACH TANKS

On each module there are six mechanically agitated leach tanks in series, each fitted with 350 HP Lightnin gearboxes and motors. Initial solids settling in the tanks was overcome by extending the impeller blades to 5.1 m dia. and changing to a peripheral speed of 254 m/min. The impellers are rubber covered, and pulp is transferred via upcomers.

LEACH EXTRACTION 90%

LEACH CONDITIONS

Leach at 72% solids; average retention time - 8.6 hours. Leach time is regulated by bringing leach tanks on or off line. There is an economic balance between additional recovery and extra acid consumption with increased residence time. Leach temperature has dropped from 48-49°C to 38-39°C as a result of recycle water use. Here, too, there is a tradeoff in terms of reduced acid consumption.

ACID CONSUMPTION

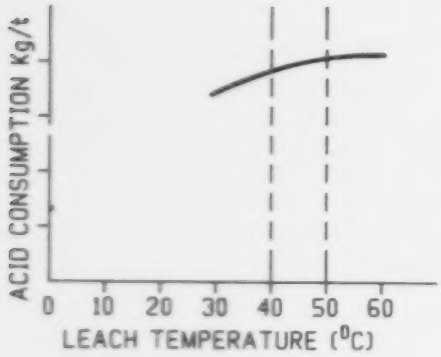
Actual acid consumption is currently about 20 kg H_2SO_4/metric ton of ore. Rossing manufactures most of its own acid requirements on site from local pyrite.

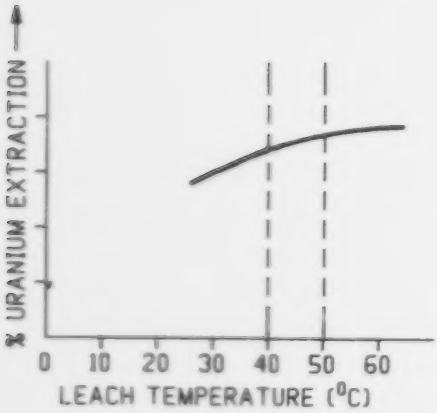
The acid consumed depends on several factors but mainly on the acid consuming minerals present in the ore. This property of the ore is expressed in terms of an empirical factor known as 'Calc Index.' To determine calc index, an ore sample is crushed and ground, and an aliquot agitated in a beaker of acid. By back titrating the residual acid, an index which relates to the acid comsumption of the ore is determined.

The acid consumption of the ore is an important factor in considering the quality of recycled solutions since for every ton of ore leached, 40-50 lbs. of sulphate is introduced into the solution. Excessive acid addition may also have an effect on metal ions other than uranium that are leached--certainly more calcium is dissolved.

Small scale heap leaching tests were carried out on ores with calc indexes of 50-60 kg/t which indicated an acid consumption of less than 30 kg H_3SO_4/t. In one test, an ore with a calc index of 45 gave 40% extraction over 1½ months at an acid consumption of 7 kg/t using return dam dolution. Test work on the subject is continuing.

AFFECT OF TEMPERATURE ON LEACHING





Note: Not to Scale; qualitative data only.

EFFECT OF RECYCLING ON LEACH

There are three advantages in using return dam solution for milling and leaching:

1) Reduced overall acid consumption.
2) Recovery of some uranium values from RDS
3) Reduced water consumption.

Because RDS cannot be passed through heat exchanges, it is added directly to the mills without preheating. One effect has been a drop in temperature in the leaching step from the original 48-49°C. The result has been a drop in acid consumption. The effect on uranium extraction is negligible.

Solar heating of RDS using black plastic pipes and also solar brine ponds have been considered but in little detail.

SAND-SLIME SPLIT

Sand and slime are split using cyclones with two stages of rotoscoops to wash U_3O_8 values and residual slime from the sand in the cyclone underflow.

SOLID-LIQUID SEPARATION

The CCD train consists of four 42.67 mØ Envirotech thickeners in parallel as first stage thickeners followed by four 68.6 mØ Dorr-Oliver thickeners to provide 5 stages of CCD using the eight thickeners. After washing the slimes by CCD, final underflow is diluted with RDS, recombined with the sand fraction, and pumped to tailings. CIX Barrens are recycled to the tail end of the CCD circuit and rotoscoop circuits for use as wash solution. Feed density of pulp to the CCD is at SG 1.2-1.3. The ore has SG 2.6-2.7. Underflows have 45-47% solids, and the CCD overflow solution runs 1,200 ppm suspended solids.

CIX ADSORPTION

The Porter CIX System installed at the main plant at Rössing treats over 80,000 m^3/day of pregnant solution fed with a tenor of approximately 160/180 ppm U_3O_8. The pregnant solution flow is split equally between four CIX lines.

Barrens from the CIX plant in 1979 were reported as 8 ppm. Details of the design and operation of this circuit with its rectangular adsorption tanks were provided by P.

Vernon in a paper presented in 1979 at a conference in South Africa which can be made available to sponsors on request by RANDOL INTERNATIONAL LTD. In recent months, barrens have been up to 15 ppm, but much of this is recovered ultimately through RDS recycling.

Feed to the CIX plant in 1984 contained some 800 ppm solids. These solids tend to carry over via the preg eluate to the SX plant where they cause a problem.

Loaded resin in 1979 contained about 27 g U_3O_8/l.

During the 1984 visit, it was found that a regular cleanout of solids from the CIX adsorption system is needed to maintain uniform solution flow.

Solution enters each CIX contactor via a fiberglass distributor.

CIX adsorption performance has deteriorated as shown by the average preformance data provided below with recovery across the CIX plant dropping from 97% to 92.5%.

	Preg Feed (ppm U_3O_8)	CIX Tails Solution (ppm U_3O_8)
1980-81	190	5 ppm
1982	200	About 9 ppm
1983	160	8.5 ppm
1984	160	5-12 ppm

This data should, however, be viewed in conjunction with volume of solution throughput, resin type, and inventory changes, frequency of elution, frequency of acid washing, resin consumption, and changed water quality due to RDS recycling.

RESIN TRANSFER

Resin is airlifted from the lead CIX adsorption tank to the resin transfer sump and pumped via a WEMCO centrifugal vortex pump to the loaded resin storage cone located above the three elution vessels. The storage cone is fitted with a Dorr Oliver 60 mesh wedgewire DSM screen and a water spray. Screen underflow is returned to the No. 1 adsorption contactor.

CIX ELUTION

Loaded resin is gravity fed to one of three elution columns, each being totally independent of the other. A six-step elution cycle is employed as illustrated by the elution curves provided in P. Vernon's (1979) paper.

RDS INFLUENCE ON CIX PLANT

Recycling acid, sulphate, and chloride-rich RDS to the mill results in five main influences on the CIX plant.

- Competition with U_3O_8 for loading on IX resins by $SO_4^{=}$, Fe^{+3}, Cl^- and other dissolved species.
- Reduced solution volume throughput through the CIX unit due to jarosite scale buildup in the barrens lines (now controlled by the use of pigs).
- Risk of enhanced corrosion due to jarosite buildup where metal is unprotected by rubber or polyurethane.
- $[Cl^-]$ has risen in the eluate, too, and could be expected to result in enhanced corrosion of screens in the adsorption and elution sections.

There is not much that can be done to counteract the competition effect for adsorption sites on the resin. Slight alleviation might be possible by optimizing resin selection for use under the changed set of circumstances and more frequent elutions. This means having to live with lower U_3O_8 adsorption loadings on the resin, lower tenor eluates, and a generally reduced capacity of the IX plant, which is not a major concern while operating at reduced throughput.

The Rössing pregnant solution has, since 1980, had a fairly constant zinc content of about 37 ppm. The most probable source of this zinc is thought to be the calcine arising from roasting of pyrite for acid production. There was a concern that this might have a detrimental effect on CIX performance, but as yet no evidence of this has become apparent.

The CIX barren solution uranium tenor of 5-15 ppm U_3O_8 and a current recovery into eluate of only a little over 92% is poor by comparison with most plants around the world. The performance of the IX plant has been under scrutiny ever since the operation started and with greater intensity of late. Some of the factors that have been examined are TDS buildup in preg solution, SiO_2 fouling, ore type, and manganese levels in solutions.

- SiO_2 in the preg solution has increased steadily since 1980.

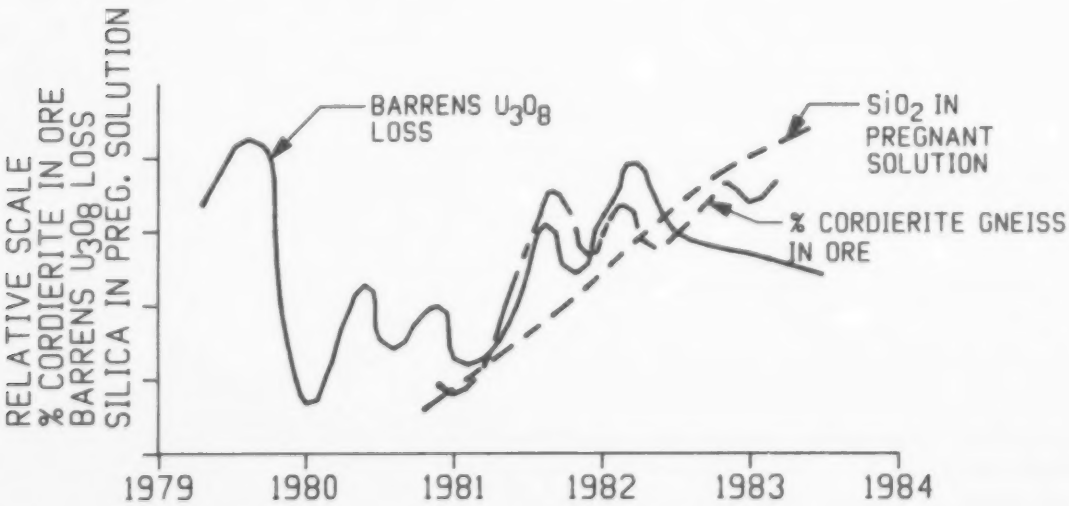
	March, 1979	February, 1984
SiO_2 (ppm) in Preg Solution	427	950

Resin regeneration frequency has been adjusted to keep resin SiO_2 levels below 2,000 ppm. However, the cost of regeneration with 4% and 1% NaOH solution is high and lately, regeneration frequency has been cut back without adverse effects on silica loading on resin. The cost of regenerating the resin has been cut by 40% since 1983 by optimizing frequency and procedure.

After increasing the frequency of elutions, the SiO_2 buildup rate on the resin has dropped noticeably and considering the higher levels of SiO_2 in the pregnant solutions, it is likely that the SiO_2 passes through with eluate to the SX plant and may end up in CRUD.

Rössing ore contains variable amounts of cordierite gneiss containing pyrrhotite which seems to be directly related to barrens loss and SiO_2 levels in the pregnant solution. Certainly the recycling of RDS has an influence on SiO_2 in the pregnant solution and, therefore, also on the relative merits and costs associated with different resin types.

AFFECT OF ORE CHARACTERISTICS ON SiO_2 BUILDUP ON RESIN AND BARRENS LOSS



(Qualitative Data based on freehand sketch)

RESIN LOSS

The CIX plant has a resin inventory of 750-800 m^3. Resin losses amount to ±17 m^3/month, i.e., 25% of inventory per year, i.e., 8 parts resin per million parts solution treated.

RESIN SELECTION

In March ,1984, Dowex XFS resin was the predominant resin in use; it cost R5800/m^3 at that time (U.S. $0.82 = R1.00).

Sentrachem-KOP resins had been tested in the laboratory and had a lower price of R4,800/m^3. This resin was found to have a comparable uranium loading capacity and a better resistance to osmotic shock, but its attrition properties proved poorer than the Dow resin.

Current thinking has been that the major contribution to resin loss is attrition rather than osmotic shock.

SX PLANT

The SX plant at Rössing was originally intended for operation with the organic phase continuous in extraction. Experience was, however, that the continuity flipped to aqueous very readily and for ease of operation, it has been allowed to run that way for the past six years.

A model of the SX system was built for laboratory improvement development aimed to:

- Improve Phase Separation
- Reduce Organic Entrainment

A crud treatment tank is installed in the system.

Crud is treated with acid.

Rössing looked at centrifuging crud but at a cost of R70,000 a centrifuge could not at the time be justified. .

Most organic losses are lost via raffinate to fresh eluant to resin to barrens to CCD wash to tailings dam.

The ion exchange eluate at 100 g H_2SO_4/l has a high chloride level as well and would be expected to corrode stainless 316L steel. However, due to some passivation mechanism that is not yet understood, this does not occur in the elution system or the SX plant. The phenomenom has been reproduced in lab corrosion tests.

CORROSION

Recycle of RDS to the process results in several points where corrosion has been enhanced, due mainly to higher chloride levels in an acid pH and to corrosion associated with jarosite scale associated with bacterial processes.

Another factor that may affect corrosion is the high level of fluoride in the RDS and seepage at 98 and 42 ppm respectively. At these levels, fluoride-related corrosion deserves some attention, especially where elevated temperatures are employed. A consultant who is interested in fluoride induced corrosion is:

JIM MAVIS
CH2M Hill
1500 114th Avenue, S.E.
Bellevue, WA 98004
(206) 453-5000

This factor could become more important if a way is found to heat the RDS solution prior to addition to the rod mills. There are ways to remove fluoride from water which could be considered if this was found to be a factor.

The following general observations on corrosion risks and preventive actions have been accumulated by Rössing engineers:

ROD MILLS

In early 1984, 81% of the water needs in the grinding circuit were provided by recycled water of which 58% was RDS (return dam solution), and 23% was recovered tailings dam seepage water. One deleterious effect is the increased risk of corrosion of the rod mill shells and actual corrosion of the linings and rods. These effects were still under investigation to determine their precise cost and to find alternative ways to reduce the impact.

ROD MILL SHELL

The use of acidic high TDS recycle dam solution in the rod mills was anticipated to be a cause of corrosion. The neutralizing characteristics of the ore raise the mill solution pH from 2 to 4.5, but there is, nonetheless, a pH profile along the 20' lengths of the mills.

Experiments were carried out with mill shell coatings eventually settling on an epoxy tar layer on the inside of the mill shell. The product used is an amine-cured cold tar modified epoxy material sold by Plascon Paints (Pty) Ltd. in South Africa under the product code EPD-100 which was applied by Rossing's protective coatings department.

The epoxy tar coating was spark tested to be pinhole free; then tested at 30% and 60% RDS recycle usage followed by inspections. All four mills have been coated.

A physical ultrasonic inspection procedure to test coatings is offered by two companies in Johannesburg, including Engineering Inspection Company (Pty) Ltd. Inspection is now done in-house.

ROD MILL RODS

Consumption of rods has increased by about 20% when 1984 consumption is compared to 1980. 50-60% of the water used in the mills is now acidic RDS, but this is not the only factor involved. In particular, the milling rate has decreased somewhat which certainly contributed to the increased consumption. The Rössing estimate is that about half of the increase can be directly attributed to RDS.

Tests have been carried out with heat treated steel rods which are imported. Although a reduction in steel consumption of some 19% was observed with the heat treated rods, their high cost at present renders them unattractive economically.

MILL LINERS

In the early years of the life of the mine, the standard mill shell liners used at Rössing were two-piece, forged liners. The life of a set of these liners was of the order of two million tons milled.

In 1981, a test was started with heat treated high chrome, cast liners supplied by Foundaries Magotteaux. These test liners ran a mill fed with 100% fresh water. The test set of liners gave a life of 5.6 million tons, and all mills were progressively changed over to these liners.

The installation of the second set of Magotteaux liners coincided with the introduction of a significant quantity of RDS into the grinding circuit and with a slight reductionin milling rate. Liner life experienced today is variable but well below the 5.6 million tons shown by the first set of Magotteaux liners. As with rods, it is difficult to attribute the proportion of this reduction to RDS and to other causes, but Foundaries Magotteaux metallurgists are convinced that corrosion does play a part.

CCD RAKES AND MECHANISM

The leached pulp at about 3.5 g/l H_2SO_4 comes in contact with the CCD thickeners with rakes and mechanisms constructed of stainless steel 316L. RDS recycle contains high Cl^-, and ferric concentrations would accelerate corrosion of these components. Numerous corrosion tests were performed based on advice by the Resource Conservation Company International of Seattle, Washington. These tests are discussed elsewhere in this report, but it was found that stress corrosion did not occur and at very high chloride levels, pitting and crevice corrosion would occur at about 3.5 g H_2SO_4/l.

Cost estimates of replacing the CCD thickener rakes and mechanisms with superior corrosion-resistant stainless steels were obtained from Envirotech and Dorr Oliver, but these were very expensive.

Experiments were conducted successfully on coating exposed stainless 316L surfaces with abrasion-resistant polyurethane foam coatings. These experiments were extended to the actual plant with encouraging results.

Polyurethane coating applied as a mixture of two components manufactured by Bayer Leverkusen, West Germany, has been used for coating the rakes. This step was taken with consultant guidance from:

MICHAEL A. BRETT AND PARTNERS
Post Office Box 61872
Marshalltown 2107
South Africa
(011) 803-2273
Dr. Colin E. Alvey, Partner

The polyurethane coatings were applied on different rakes by two different contractors who specialize in polyurethane corrosion protection. The first two thickener rakes were coated by:

RÖSSING

ATLAS FOAM (PTY) LTD.
Post Office Box 2268
Trekker 1547
Brakpan, South Africa
(011) 558-504
Graham Pole

ATLAS FOAM uses a non-solvent method of applying foam through a nozzle that mixes the components at 4-5 l/minute. The two components are polyether and Isocyanate mixed 100 parts:75 parts.

The electronic mixer can apply to any thickness. e.g., 3 or 4 mm in sequential layers without waiting for the solvent to dry. Because of the configuration of the thickener rake, there is a high wastage of material during the application. ATLAS FOAM took six days to complete the job on the second thickener job, including spark testing. The cost of these coatings is normally R20 per m^2 per mm thickness ($1.30/$ft^2$ per 4 mil thickness) which is comparable to rubber coating in price, but much quicker to apply and more appropriate for the application (according to the vendors).

Specifications of the Polyurethane coating are:

Shore A Hardness	65-70	W. German DIN 53505
Density	0.9	W. German DIN 53479
Strain	100%	DIN 53504 MPa 4
Strain	300%	DIN 53504 MPa 7
Tensile Strength		DIN 53504 MPa 10
Elongation		DIN 53504 600%
Tear Propagation Resistance		DIN 53515 16
Impact Elasticity		DIN 53512 45%
Abrasion Resistance		DIN 53516 mG 130

The product expert at Bayer Leverkusen is Mr. Vogel who has advised ATLAS that the coating is good for use up to 80°C with temperature surges to 130/140°C, but he would be nervous about continuous service at 120°C.

ATLAS FOAM (PTY) Ltd. claims that their coatings are pinhole free because of the solvent-free application. Sometimes thin spots in the corners and nooks are difficult to avoid using spray application, but the material is also trowlable.

According to ATLAS FOAM, there may have been isolated pitting corrosion the first rake; however, there has been no corrosion on the second because they were more experienced for their second rake job.

ATLAS FOAM (PTY) Ltd. claims that their BAYER polyurethane material is cheaper than the UNIROYAL polyurethane system which costs R18-19/kg compared with the BAYER product at R13/kg (prior to the recent devaluation of the Rand).

The second two thickener rakes were polyurethane coated by an Australian company:

WEAR RESISTANT MATERIALS (PTY) LTD.
2 Kelsey Place
Asquith NSW 2078
(02) 476-5655
Telex: c/o Chatswood Public Telex Office
WRM POL AA 70410
Ian Lyon, Managing Director

WEAR RESISTANT MATERIALS (PTY) LTD. use a solvent based polyurethane application using standard spray equipment and polyurethane imported from Australia.

The Rössing Uranium Mine subsequently coated the fourth thickener themselves.

CIX PLANT

Apart from the ion exchange effects, the higher Cl^- levels can be expected to [illegible] .ce corrosion of stainless steel.

Elution columns were rubber lined. SX solvents loosened the rubber steel bond. Now the mild steel shell is being coated with FRP as needed--so far, 5 out of 12 columns have been lined in FRP, of which one has been in service for two years without attention.

PUMPS

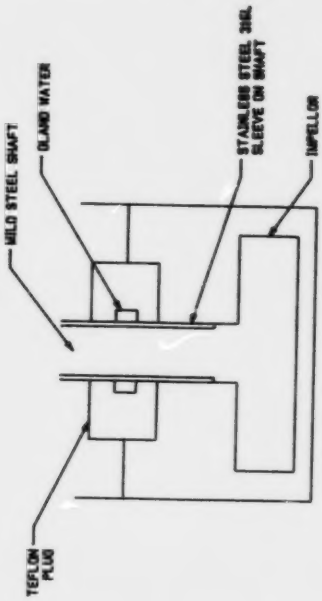
Tailings and solution pumps for an operation this size require a large amount of gland water. For example, the tailings pumps each require 1.2 l/sec of gland water, and there are 10 of them in each pump station--i.e., 160 gpm per pumpstation is required.

Rossing has converted to RDS water for pump glands which is not recommended by pump manufacturers. RDS with its low pH and high chloride level also contains about 1,000 ppm suspended solids which caused increased abrasion on the pumpshafts and sleeves.

To overcome this, Rössing has fitted stainless 316L steel sleeves over the mild steel shafts of the pumps. A major cause [illegible] ...ure resulted from abrasion through the gland

seal due to the high solids. Before using RDS for pump shaft lubrication, the shaft sleeve lasted 1,600 hours between replacements. After RDS, life was reduced to 1,200 hours, at a cost of R1060 each plus labor. This is a possible application for plastics.

PUMP MODIFICATION FOR RDS AS GLANDWATER



An innovative water filter was installed on an experimental basis; This was a Filtomat filter unit manufactured and offered by:

BATEMAN EQUIPMENT LTD.
Post Office Box 565
Boksburg 1460
South Africa
(011)899-9111

The Filtomat unit installed at the time of the visit was a rubber lined mild steel unit fitted with a 20 micron screen. A second unit fabricated from stainless steel was on order to test as a means of removing solids from pump gland water. The stainless steel Filtomat unit sells for R12-13,000. In the Rossing application, the units were not satisfactory as a high pressure, not available on the system, is required for efficient filtration and backwashing.

SCALE

Leaching Tanks

Jarosite Scale has built up on the bottom of the large leaching vessels particularly where the walls meet the floor. This did not occur until after tailings solution was recycled, and is still not a serious problem.

BARREN LINES

Following the introduction of return dam and seepage recycling, iron silicate jarosite started to build up in the barren lines, particularly remote from the pumps.

Several workers link jarosite formation with bacterial action, and a literature survey suggested that this was a likely cause at Rossing. Dr. E. Liversley-Goldblatt and the Gencor Group Laboratory identified a thriving bacterial community in the recycled solutions, including thiobacillus ferroxidons which is associated in the literature with jarosite formation.

Jarosite buildup in the barren lines restricts solution flow significantly. Rössing's response is to remove the buildup periodically by mechanical means. Experiments with sandblasting the interior of the pipes were unsuccessful due to damage to the rubber lining of the pipes. Polymer pigs with abrasive surfaces have, however, been successful, and these are put through the lines whenever the flow is observed to have decreased.

RANDOL IDEAS/COMMENTS FOR JAROSITE CONTROL

- Jarosite scale creates a highly corrosive environment when in close proximity to steel. Metal concentrations in the jarosite create electrolytic cells with steel as the other electrode resulting in its corrosion.

- One possible way to kill the bugs may be through sterilization of the return solution with ultraviolet light. There are innovative transparent plastic tube devices for this.

- A major water treatment company pointed out that biocides are essential ingredients in many scale control and corrosion inhibitors. Possibly, dosing the RDS dam or return line with biocide could prove helpful.

OTHER WATER USES AT RÖSSING URANIUM MINE

1) Water for Environmental Control
   - Water sprays to control dust at the primary crusher. 250 m^3/day water is used for this purpose.
   - 3,000 m^3 water is used for dust control in the mine on roads and muck piles.

2) Treated Water used as Boiler Feed Water

3) The Rössing Uranium Mill water consumption is:
   - 0.39 m^3 fresh water per ton milled (1984) = 87 U.S. g/st = present.
   - 0.54 m^3 fresh water per ton milled (1983) = 108 U.S. g/st.
   - 0.66 m^3 fresh water per ton milled (1982) = 132 U.S. g/st = historical.

WATER CONSERVATION STEPS

4) Water use was originally 30,000 m^3/day when fresh water was applied to every use except tailing transport. Since then, it has been cut down to 14-15,000 m^3/day.

5) Seepage water collected from below the tailings dam has an improved quality compared with the dam water itself, it is relatively low in particulates and is used for gland seal water for the pumps.

6) Seepage and return dam solution is used in the rod mills. This has required acid proofing of the mill shells.

7) Return dam solution is used for gland seal lubrication in some pumps after acid proofing pumps, glands, and seals.

8) Since July, 1983, the rodmills were converted so that 80% of their water needs are met by tailings dam reclaim solution.

9) Late in 1984, seepage water was to be used for general washdown.

10) A water manager is employed to keep detailed track of water usage. Every operator is monitored, based on the size of his pipes and pumps. The water manager alerts operators when their water consumption is high. This is an essential measure as unless operators are constantly watched and the importance of saving water impressed on them, this remains a low priority item to them.

WATER BALANCE MODEL

A water balance model for a metallurgical plant must also compute the salts balances. Dames and Moore, Denver, Colorado, has assisted in the water model for the complete mine, mill, tailings dam system. The Rössing staff includes several who are adept at computer applications, and the water-salt balance model now seems to be capable of accurate predictions of water quality.

CLHORIDE BALANCE

Chloride levels in the RDS are one of the major causes of corrosion and a competitive ion in the CIX adsorption circuit.

CHANGING [Cl^-] LEVELS IN PROCESS SOLUTION

1979	500 ppm in Preg Solution
March, 1984	1,400 ppm
[1] December, 1984	1,500 ppm
[2] Ultimate	1,100 ppm

[1] Evaporation of tailings result in higher concentration.
[2] As the tailings dam gets smaller, evaporative losses will be smaller compared with fresh water intake.

The dam water balance model has been programmed into Rössing's mainframe and DRS 50 Computers. To date, the model has been able to give a good prediction of water quality. The engineer working on this model is Brian Olver.

One assumption is that as the chloride concentration in solution increases, a smaller percentage of the Cl^- in the ore will be leached. The main input of chloride is, however, in the fresh water which contains 200-300 ppm chloride.

FRESH WATER REQUIREMENT

Historically (Max.)	28-30,000 m^3/d	0.7 m^3/t Ore
1984	15,000 m^3/d	0.4 m^3/t Ore

COST OF WATER

The unit price of water supplied to Rössing has increased since 1978 by 86%. However, due to the economy measures, the actual gross cost of water to the company has increased by only 16%. To bring about these savings, substantial capital expenditure has been justified.

WATER QUALITY

Fresh water quality, as delivered for December 1981/82/83, is shown below:

WATER QUALITY - FRESH WATER DELIVERED TO OPERATIONS

	December 1981 (ppm)	December 1982 (ppm)	Decmber 1983 (00m)
pH	8.3	7.9	8.4
Conductivity (Micromhos)	1,200	1,250	1,200
Total Dissolved Solids	888	828	750
Suspended Solids	8	2	
Total Hardness, ($CaCO_3$)	279	286	
Calcium Hardness, ($CaCO_3$)	180	187	
Magnesium Hardness, ($CaCO_3$)	99	99	
Total Alkalinity, ($CaCO_3$)	195	194	196
Chloride, (Cl^-)	280	250	240
Sulphate, ($SO_4^=$)	99	81	54
Fluoride, (F^-)	0.53	0.5	0.4
Nitrate, (NO_3^-)	24	12	15
Ammonia, (NH_3)	-	1	1
Iron, (Fe)	0	0	
Manganese, (Mn)	0	0.1	0
Potassium, (K)	16	14	11
Sodium, (Na)	136	150	140
Silica, (SiO_2)	20	23	
Arsenic, (As)	0.003	0.003	
Uranium, (U)	-	-	-
Calcium, (Ca)	72	75	80
Magnesium, (Mg)	24	24	21
Aluminium, (Al)	0	0	
Radium, (Ra^{226})	-	-	-

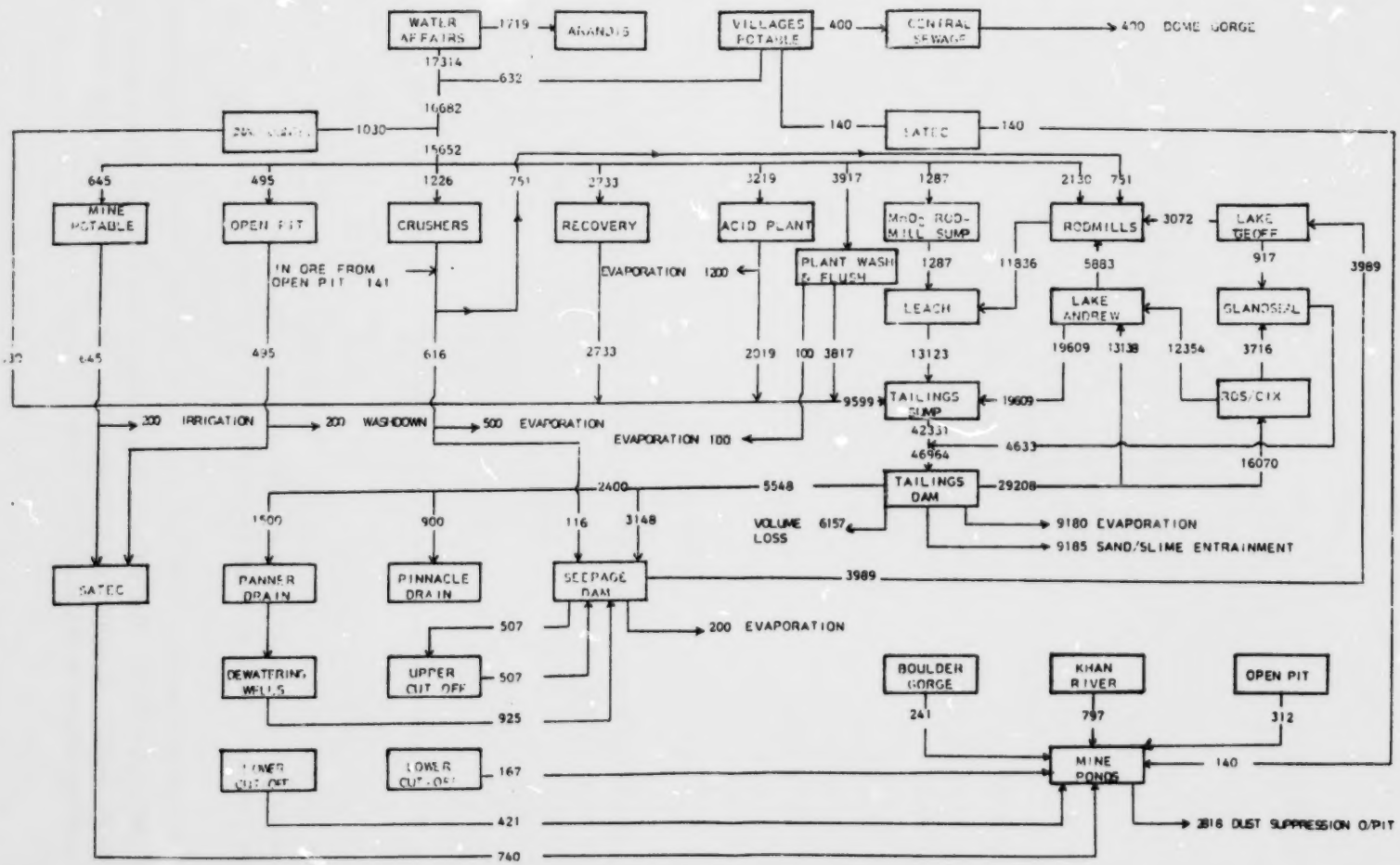
FRESH WATER CONCLUSIONS

- Based on the estimated cost of fresh water consumption, there appears to be a significant cost incentive in reducing fresh water consumption.

- Rössing is fortunate in that the price of their water is not structured to reflect the fixed costs of the pipeline and pumps and so does not increase as consumption drops.

DAILY WATER BALANCE — UNITS IN m³

APPENDIX 7.33



FRESH WATER USAGE

A typical 1983 daily water consumption distribution is shown below.

645 m^3/d	Potable Water to Mine - Potable and Toilets
495 m^3/d	to Open Pit Mine Toilets and Potable
1,226 m^3/d	to Crushers
2,733 m^3/d	to U Recovery Plant
3,219 m^3/d	to H_2SO_4 plant
3,917 m^3/d	to Plant Wash and Flush
1,287 m^3/d	to MnO_2 Rodmill
2,130 m^3/d	to Rodmills (731 m^3/d with Ore from Crusher)
15,652 m^3/d	to U-Plant
632 m^3/d	to Daily Paid Housing
1,719 m^3/d	to Arandis Village
1,030 m^3/d	Unaccounted for
19,033 m^3/d	TOTAL

A current and detailed water balance is maintained which is essential in order to improve and monitor water conservation management.

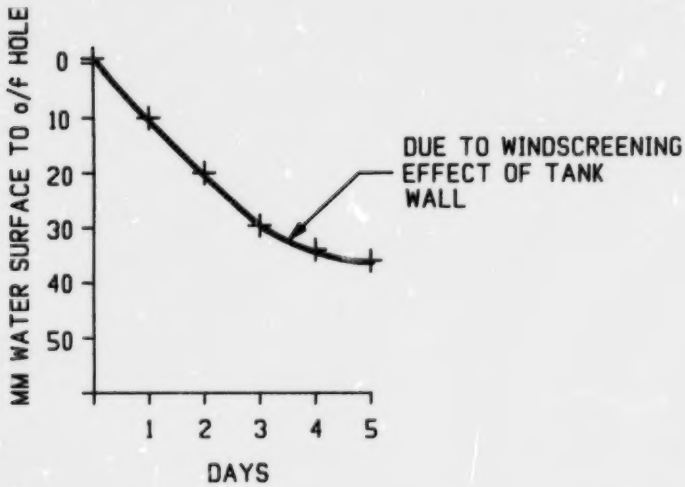
WATER TREATMENT

The only active water treatment plant used at Rössing is for desalination of boiler feed water.

In 1981, a study was undertaken by the Resource Conservation Company International which reviewed ion exchange, reverse osmosis, evaporation, neutralization, and EDR at the Rössing Complex. None of these has been found to be cost effective to date.

Rössing loses approximately 9,600 m^3 water/day to evaporation. It is found in evaporation pan experiments that effluent evaporation rate decreases with time as shown in the following graph. Rössing has concluded that the reduced evaporation rate is due to wind sheltering effects of the wall of the tank.

TANK EVAPORATION EXPERIMENT



In experiments at North American, operators found the same effect but concluded that the increasing salinity was responsible for the reduced evaporation rate.

The tails dam water level has dropped due to recycling and evaporation losses reduced.

Evaporation losses at Rössing are on occasions very high. The evaporation rate typically runs 8-9 mm per day (120 inches/year). Over 9,600 m^3 per day of water is lost to evaporation. The water surface in the tailings as of early 1984 was 120 hectares--1.2 million m^2 in extent.

A literature search was undertaken on evaporation. Several experiments were undertaken to cover the tailings pond including the installation of 12 hectares of floated plastic sheeting. Somehow, water was blown on top of the sheeting.

The tentative conclusion so far is that the best way to reduce evaporation is to make the water pond deeper with a smaller surface area. The area has been reduced slightly because of the bigger water off take and increased recycle which has reduced the water inventory in the tailings impoundment. Research is continuing in this area. Tailings deposition is so directed as to minimize surface area.

SEWAGE

There are four sewage plants located at Rössing:

Mine Changehouses
Village Housing
Day Rate Employee Housing
Rössing Country Club

The sewage treatment areas are monitored to determine that treated sewage water meets effluent standards.

GROUND WATER QUALITY PROTECTION

At any mining operation today, protection of the quality of the local ground and surface water is of major importance. Rössing is no exception. However, the scale of operations required to achieve this is unusually great.

The prime source of potential impact on ground water quality is the heavy metals and radionuclides contained in the acid solution within the tailings dam. The tailings disposal area is situated upon calcereous sediments, and the sands with which the tailings dam walls are constructed are also acid consuming. Seepage of acid solution through the wall and through the underlying sediments is, therefore, permissible as the radionuclides and heavy metals precipitate virtually completely. The same is not, of course, true of the anions, and it is necessary to recover seepage water from the sediments and from the alluvium of the (normally dry) water courses of the area. A complex of more than 80 monitoring and recovery boreholes are located around the tailings dam. One of the seepage recovery installations, that in the Pinnacle Gorge, is illustrated in the accompanying figure.

The groundwater of the area is extremely brack, typically with a chloride content of over 2,000 ppm and a TDS in the range 4-8,000 ppm. Sulphate content is variable but relatively low, in the range 1,000-2,500 ppm. Tailings dam water, however, contains some 30,000 ppm sulphate and less than 1,500 ppm chloride. Any increase in the sulphate:chloride ratio in the groundwater quality monitoring boreholes is, therefore, a sensitive indicator of infiltration of seepage from the tailings dam and provides early warning of the need to install recovery pumps. Rössing, with assistance from Dames and Moore, has, during 1984, been developing a computerized model of the movement and quality of groundwater in the various geological structures of the area. Use of this in a predictive role will, in the future, permit even better groundwater quality protection and greater recovery of recycleable water.

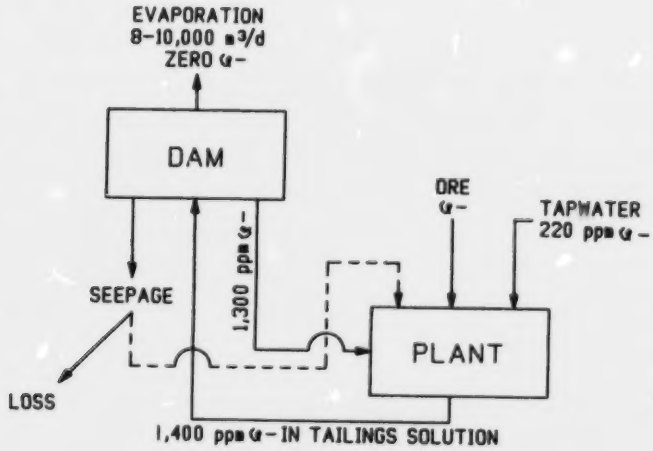
By these methods, Rössing has been entirely successful in protecting the environment off its own property. This has been done to the satisfaction of the regulatory authority, the Department of Water Affairs, to whom comprehensive and regular returns are made.

Responsibility for the functions of environmental control and all aspects of water economy is vested in the Superintendent, Environmental Control and Water Management. He reports to the Assistant General Manager and has a staff of 15 dealing with a wide range of environmental concerns including dust, radiation, and noise monitoring as well as water quality and economy.

EFFECT OF RECYCLING ON WATER QUALITY

TDS in the tailings dam water has built up steadily. According to a computer model, this will increase to a point at which it will stabilize at 40,000 ppm TDS and 1,600 ppm Cl^-.

The water management plan called for a drastic drop in water consumption from 26,000 m^3/day to 14-15,000 m^3/d. This is resulting in a shrinkage in surface area of the tailings pond water surface. When this reaches a small size, it is likely that fresh water intake will have to be increased somewhat.



The change in concentration of various species as a result of recycling is shown below:

	Mn (ppm)	Cl^- (ppm)	$SO_4^=$ (ppm)	SiO_2 (ppm)	F^- (ppm)
July, 1981	1,890	820	20,264	324	115
December, 1981	1,925	880	20,647	320	98
July, 1982	2,450	930	20,903	340	52
January, 1984	2,550	1,220	30,273	No Data	102

AFFECT OF RECYCLING ON CORROSION: SUMMARY

ROD MILLS

Water recycling effects on corrosion of rod mill shells is likely to have been prevented by applying a special protective coating. Additional rod and lining steel consumption or conversion to more costly steels is an added cost resulting from water recycling.

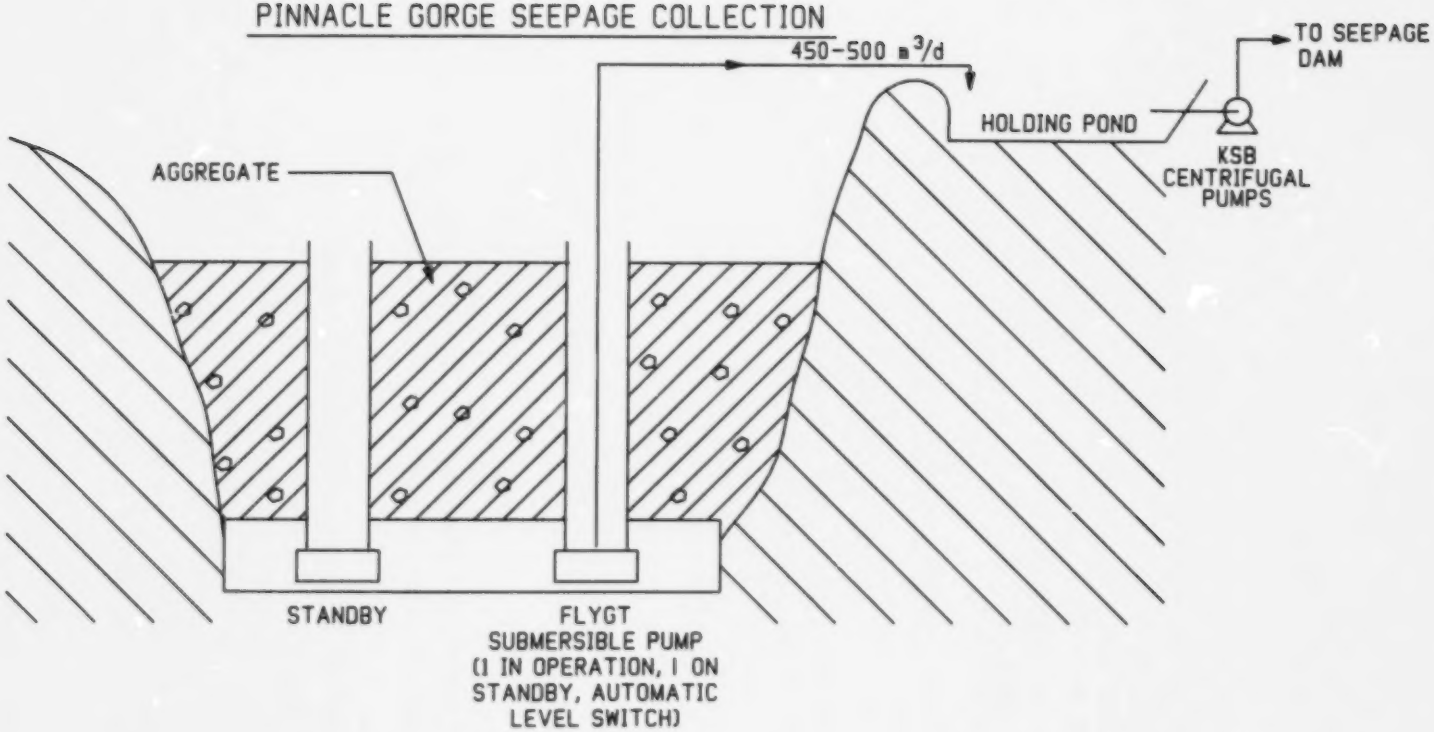
CCD RAKES AND MECHANISM

Another area of concern is corrosion of stainless steel 316L components of the CCD thickeners which would be more susceptible to corrosion in the very low pH environment as chloride levels build up due to use of RDS. These components included the rakes and the central mechanism. Replacement of the rakes and mechanisms with ones fabricated from more corrosion-resistant stainless steels has been evaluated but would be expensive. Prior to this alternative, an attempt is being made to prevent corrosion of rakes by applying a protective abrasion-resistant coating of polyurethane discussed above which, to date, has after trial and error evolved to an effective measure.

ION EXCHANGE PIPING AND ELUTION CIRCUIT

The piping on the elution columns employed in the CIX circuit are fabricated from stainless steel. The elution components come in contact with solutions that have 100 g H_2SO_4/l. Recycling of RDS solutions results in an increase in $Fe^{3=}$ and Cl^- in the system which carries through to the IX eluates, and should result in enhanced corrosion, but this has not yet been observed. Repeated inspections have shown that the 316L stainless has not been corroded at all, contrary to expectation. Some kind of passivation mechanism must be occurring which has not yet been explained.

PINNACLE GORGE SEEPAGE COLLECTION



RDS AND SEEPAGE RETICULATION

Return dam solution and seepage are stored in separate reservoirs situated on an elevated point about one half kilometer from the plant. These reservoirs are built in tailings sand and plastic lined.

RDS is pumped from a station on the edge of the tailings lake to the reservoir via dense polyethylene pipes from whence it gravitates through pipes of the same material to its points of use in the plant.

Seepage is pumped from the various collection points to its own reservoir using a variety of pipeline materials.

Experiments are underway to use a spun polyurethane pipe coating. Two test sections of pipe have been installed, supplied by:

BOSWORTH PARABRASON (PTY) LTD.
Post Office Box 3705
Airode 1451
South Africa
(011)864-164318
Telex: 4-21208SA
Gerald Bosworth, General Manager

TAILINGS LINE

Tailings are pumped against a significant head so a high pressure line is needed. Steel pipes are used. These are protected against abrasion and corrosion by rubber lining.

PUMPSHAFTS AND SEALS

Pump Manufacturers do not recommend the use of low pH RDS water with high chloride levels for gland lubrication water. Increased abrasion on the sleeves and shafts of the pumps would be expected due to high suspended solids. Rössing built stainless steel 316L sleeves onto the pump shafts. Filtomat grit removal filters were installed on a test basis to screen RDS water for gland use at 50 and 20 microns.

The pumps require 1.2 l/second glandwater each, and there are up to 10 pumps at each pump station, which works out to 160 U.S. gpm per station.

Further protection had to be provided to protect pumps and concrete pads from RDS splashes which would also be corrosive.

CALCINE THICKENERS

The thickener rakes used on a calcine slurry after discharge from the acid plant at pH 2-3 are made of exotic stainless steel 704 or its Sandvik equivalents 2RD65, SAF2205, or Cronifer 1925 steel. This steel stands up adequately.

CALCINE REACTORS

Calcine is reacted in an acid brick-lined vessel, also with a lead lining using PTFE and stainless components and air agitation. Again, no impact due to recycling RDS in the U-plant would be anticipated.

CIX ELUATE AND SX PLANT

The CIX eluate which becomes feed for the SX plant and later raffinate contains 100 g H_2SO_4/l. This solution is high in chlorides too, yet no attack of stainless steel 316L is observed. The phenomenon was borne out by laboratory tests which indicate some passivation mechanism at work.

TAILINGS DAM

35,000 m^3/day of tailings pulp are transferred to the tailings impoundment via a rubber lined steel pipe. A flowrate velocity of 4.5 m/sec is needed to keep the coarser particles from settling in the line. Experiments are in hand to reduce velocity and pumps required.

A moving slurry at this velocity is certainly abrasive. The rubber pipe lining serves to protect as much against abrasion as corrosion. The entrained solution is likely to be very scaling as well as corrosive.

The tailings dam represents a large surface area for evaporation, especially in the arid, hot desert climate with not infrequent high velocity wind. Before RDS recycling was started, the tailings dam contained 14 million m^3 of solution which by March, 1984, had dropped to 8 million m^3, thereby reducing the surface area of the pond exposed to evaporation. The tailings dam water serves as a host to a bacterial culture believed to enhance scaling and corrosion phenomena in the U-plant when the RDS water is recycled.

The water balance around the tailings dam has not been completely defined as yet. DAMES AMD MOORE has been retained to help develop the model.

DAMES AND MOORE
Advance Study Group
1626 Cole Blvd.
Golden, CO 80401
U.S.A.
(303) 232-6262
Dr. Devra Sharma
Mike Keifer, Project Manager

SUMMARY

RDS RECYCLE EFFECT ON PROCESS

Advantages

1) Reduction of acid consumption.

2) Recycled ferric ions.

3) Reduced water consumption cost which is significant.

4) U in RDS recycles to plant and is recovered.

Disadvantages

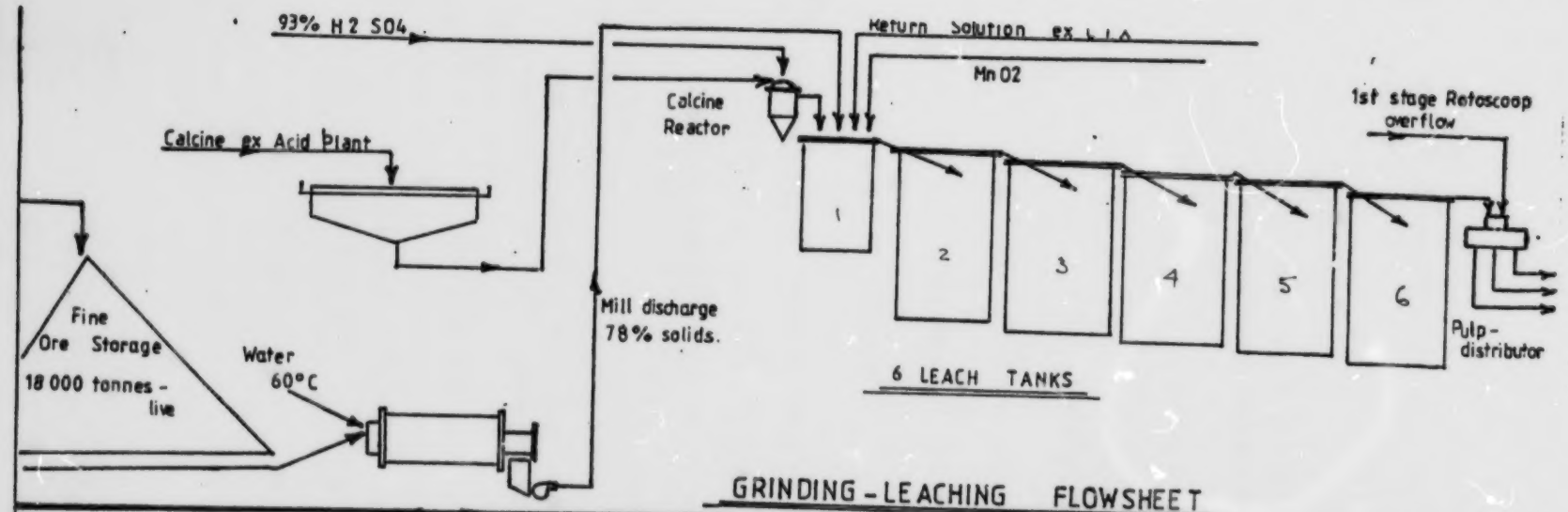
1) Higher TDS, $SO_4^{=}$, and Cl^- in preg solution reduces CIX adsorption plant capacity and increases operating costs.

   Possible answer: find a more selective resin or one that has a higher loading capacity or has improved kinetics.

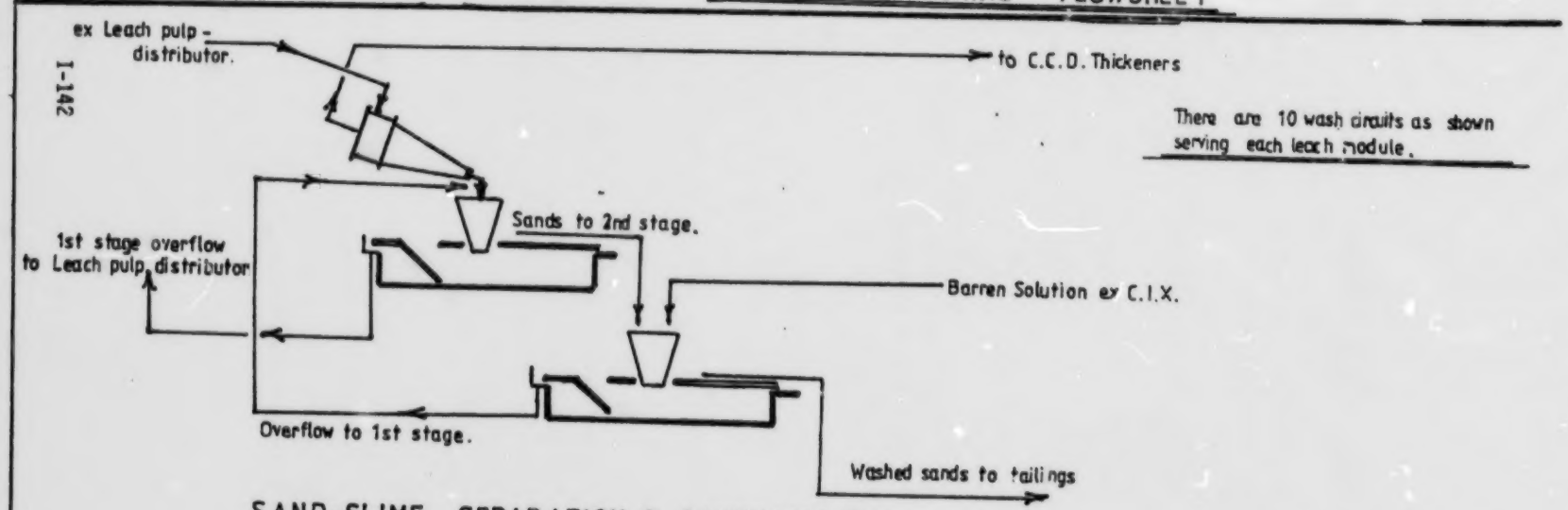
2) Requires more frequent elution cycles.

RDS EFFECT ON PLANT OPERATION

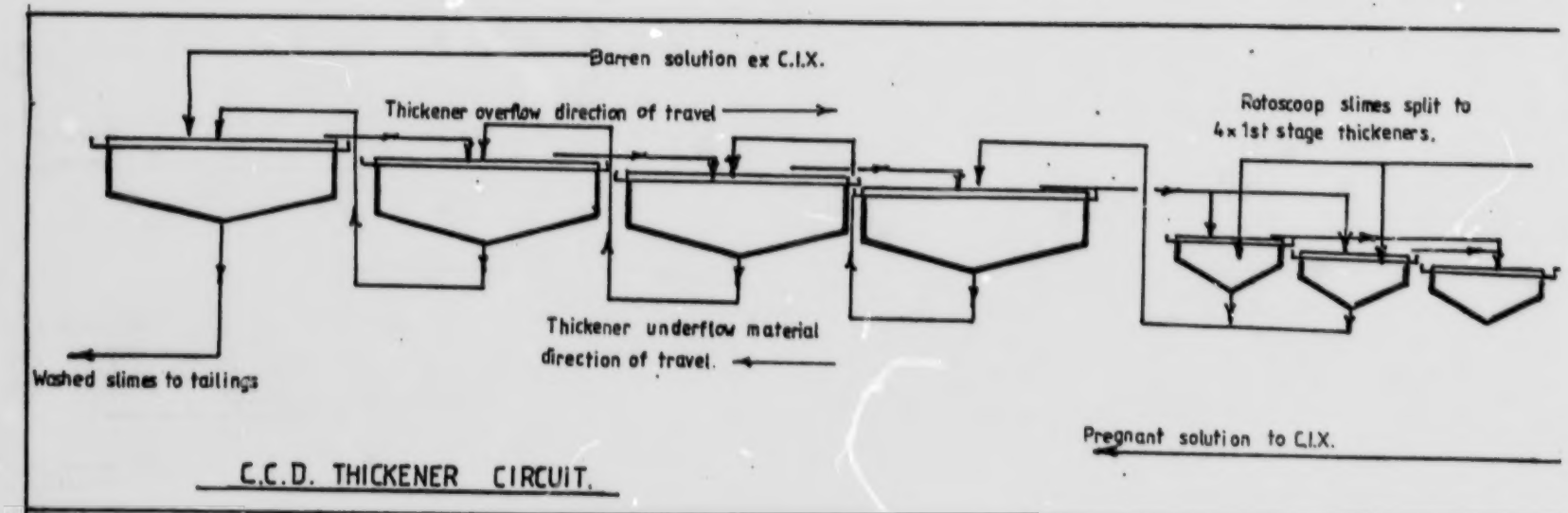
1)	Pump Shaft Corrosion and Gland Seal Abrasion	Fit stainless steel sleeves to pumps. Filter particulate material from gland seal RDS water.
2)	Rod Mill Shell Corrosion	Epoxy tar shell coatings.
3)	Rod Mill Liner Corrosion	Live with increased liner cost or try out more expensive liner materials.
4)	Rod Corrosion	Enhanced rod steel consumption cost.
5)	Scale Buildup in Leach Tanks Reduced Capacity (Minor Effect)	Isolate tanks for regular cleanouts.
6)	CCD Rake Corrosion	Polyurethane coating application or very expensive rake replacement.
7)	CIX Adsorption Plant Scale Formation	More downtime plus labor costs to clean.
8)	Jarosite Scaling on Barrens Line; Reduced Capacity of CIX Adsorption Plant - Corrosion	Use abrasive polymer pigs to clean out the rubber lined pipe. Examine ways to clean bacteria in RDS which cause jarosite scale.
9)	Higher Cl^- in the Eluate Should Enhance Corrosion in Elution Plant and SX Plant Stainless Parts	Does not happen in practice. Some kind of passivation.



GRINDING - LEACHING FLOWSHEET

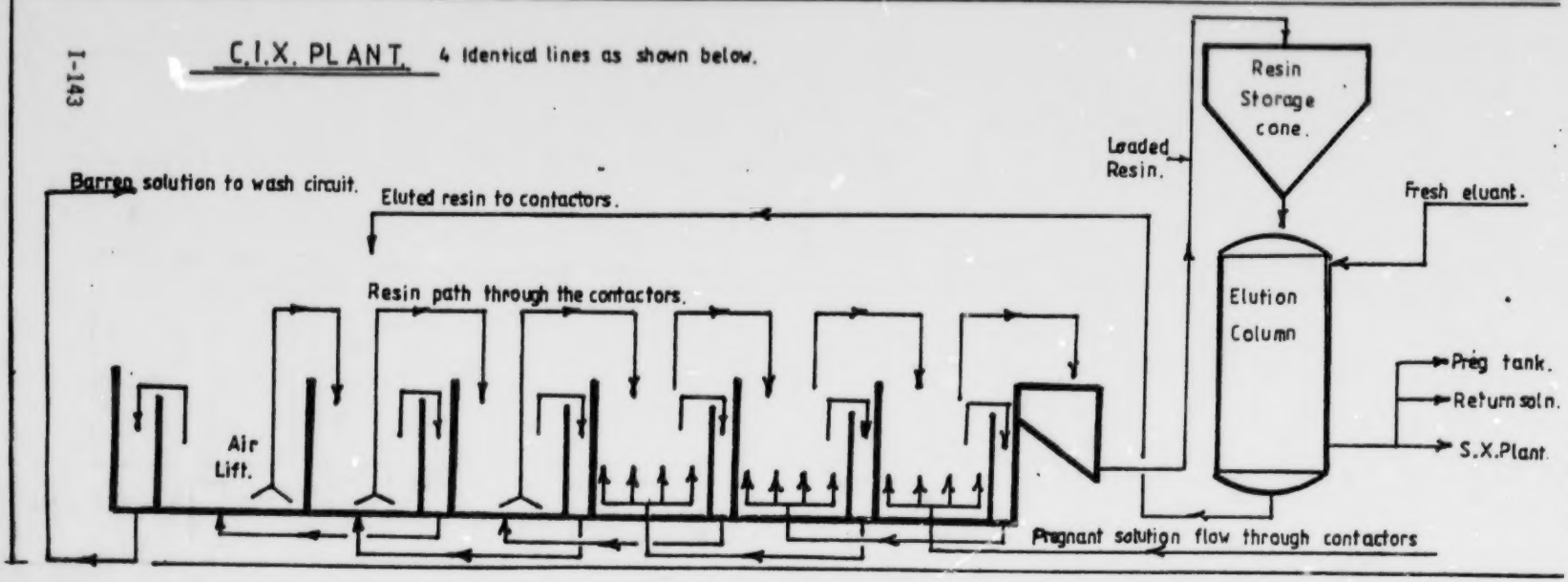


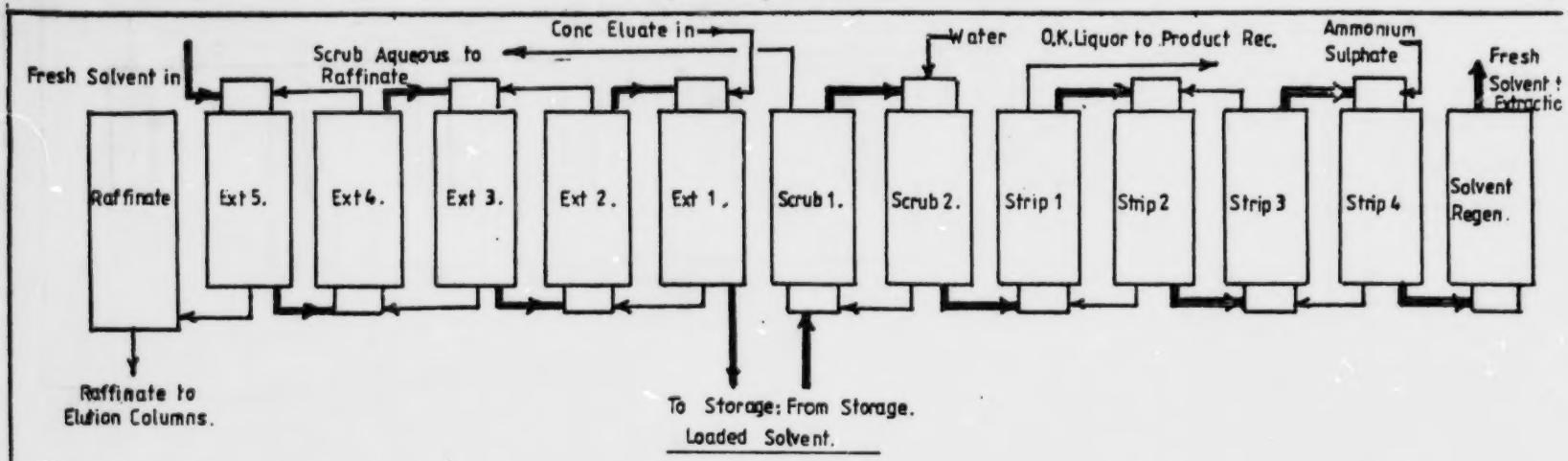
SAND-SLIME SEPARATION & SANDS WASHING



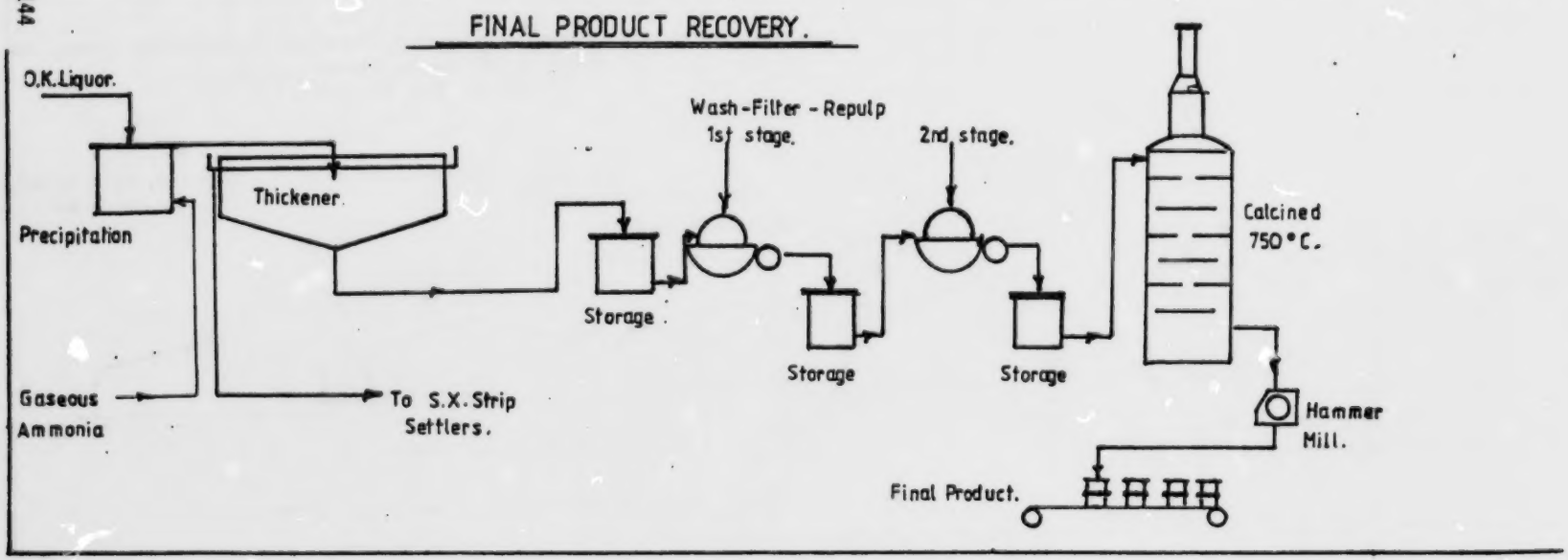
C.C.D. THICKENER CIRCUIT.

C.I.X. PLANT. 4 identical lines as shown below.





S.X. PLANT. 2 identical lines as shown above.



OPERATION	COMINCO LTD. CON MINE P. O. BOX 2000 YELLOWKNIFE NWT CANADA XIA 2R3	
TELEPHONE	(403) 873-2783	
CONTACTS	John Van Brunt	Manager (1984)
	Jim Gowans	Mill Superintendent
	Holger Krutzelmann	Mill Superintendent
	Bob Smithies	Mill Foreman
COMPANY	COMINCO LTD. Northern Group P. O. Box 2000 Yellowknife, NWT Canada XIA 2R3	
	Dave Johnson	Vice President
DATE OF VISIT	9 August 1984 At the time of the visit most of the experienced mill staff were away on vacation.	

INTRODUCTION

The Con Mine started operations at 50 tpd in 1938 and initially treated an arsenical sulfide gold ore by roasting and calcine leach. The operation expanded in stages. Since 1972 when the refractory arsenical ore was exhausted, a non-refractory ore has been treated by direct cyanidation.

The arsenic dusts collected from the original roaster were impounded in unlined ponds, and ultimately became recognized as an environmental liability. Cominco recently developed and implemented what appears to be a simple arsenic recovery process yielding a gold bearing residue for cyanidation.

Also, the Con mill now operating at 750 stpd is housed in the cramped original mill building and still uses several pieces of original equipment. Several innovative new items of equipment are being or have been installed and are of interest to determine how well they will perform in a commercial operation.

Items of particular interest at the Con Mine and Mill are:

GOLD RECOVERY

- Performance of a Japanese Tower Mill for ore grinding.
- Performance of Atara Air Cannon Mixers being retrofitted into obsolete existing agitators.
- Recovery of gold from arsenic plant residues.
- MnO_2 and fluorspar in the smelting flux.

WATER TREATMENT

- Decomposition of cyanide and arsenic plus base metal precipitation in the tailings pond effluent.

ARSENIC PLANT

- A process that is extremely simple on paper ends up requiring an investment of C$14 million to treat less than 30 stpd arsenic feed.

PLANT CAPACITY

750 stpd ore plus 5 tons per day arsenic plant residue. Average annual throughput is 650 stpd ore.

GRADE

0.4 oz Au/st (13.6 g Au/t).

RECOVERY

90-91% to yield 200-250 oz Au/day.

MINES

Ore is mined at the C shaft and the Robertson shaft. Workings currently extend to 5300 ft. below surface and are likely to be deepened to 5500 ft.

MILL DESCRIPTION

Mill throughput has grown in stages:

1938	40 tpd
1955	400 tpd
1965	450 tpd
1983	750 tpd

The latest expansion to 750 tpd came about with conversion of the mill to treat oxide ore.

Because of the cold climate all conveyers are completely enclosed and the mill building is weatherproofed and insulated.

Mill facilities are very cramped and the plant includes several old equipment items some of which have stood up to much wear.

The mill flowsheet is shown on the diagram inserted below with some changes: The Akins Classifier has been replaced by two 10" Ø cyclones and the 5' Ø x 9' AC secondary Ball Mill has been replaced by a Japanese Tower Mill.

Cyanide is added to the ball mill and the tower mill to allow grinding in cyanide, and the No. 2 and 3 thickeners have been removed to make room for a large leach tank that is to be fitted with ATARA Air Cannon Mixers. Cyanide is added in increments throughout the plant to maintain 0.6 lb CN per ton solution in all the leaching steps.

Minewater is used to mix the cyclone recovered sand fraction of tailings with cement for transport back underground at 60% solids.

Apart from the application of the tower mill and ATARA mixers for leaching, the circuit is a conventional crush - grind - leach - filter - Merrill-Crowe system. Another unusual feature seen more in Canada than elsewhere is the sequence grind in cyanide (leach) - decant of Preg 1 - agitation leach - filter for Preg 2 - repulp and leach - filter for Preg 3 - repulp and leach - filter for Preg 4. This is shown on the flow chart.

WATER BALANCE

The Con Mine is permitted to draw 1,600,000 m^2 water per year from the lake, which is 4,822 short tons water per day or 670 lgpm.

Based on fragments of information and the 1977 flowsheet an estimate of water balance is as follows:

Water Intake	Minewater	± 230 stpd	35 lgpm
	Fresh lake water to mill	1300 stpd	180 lgpm
	Fresh water to non milling		
	Total Permitted Water	4822 stpd	670 lgpm
Water Use in Mill	Barrens recycle to grind	540 stpd	
	Barrens to filter wash	1138 stpd	
	Minewater for sand backfill	230 stpd	
	Freshwater filter wash	330 stpd	
	Freshwater tailings repulp	1270 stpd	
Discharge	Barrens Bleed	90 stpd water	
	400 stpd slimes @ 25% solids	1200 stpd water	
	350 stpd sand @ 60% solids	230 stpd minewater	
	750 stpd	1520 stpd	

Total allowable consumption of water would work out to about 6 tons water per ton ore milled, but how much is actually used is not clear - possibly about 2 tons water per ton ore.

At Yellowknife water is not in short supply at all, the only limitations would be the cost of pumping it and the permit to use it.

JAPANESE TOWER MILL

A Japanese Tower Mill has been installed at the Con Mine for grinding cyclone underflow from the secondary cyclones as a secondary grind.

The Con Mine had historically milled to 75% minus 200#. It is hoped to improve recovery slightly, and to expand throughput by adding the tower mill to grind to 80% minus 200#.

The tower mill was working well generally but had experienced some gearbox trouble. Some of the abrasion resistant flights on the tower mill lifting helix had worn out within a year of its being installed.

Cyanide is added to the tower mill to grind in cyanide.

The mill was certainly silent and compact. It is claimed to be energy efficient and all three factors would be advantageous in the cramped mill building of the Con Mines. The mill was so silent there was some question as to whether it was running at the time of the visit.

The Japanese Tower Mill is supplied in North America by:

Mineral Processing Systems Inc.
211 Consumers Rd., Suite 107
Willowdale Ont.
Canada M2J 4G8

Telex: 06-986946
Telephone: (416) 492-7433
Contact: Gordon A. Griffiths
General Manager

Koppers Mineral Processing Systems Division
Koppers Company Inc.
P. O. Box 312
York, PA 17405
USA

Telephone: (717) 843-8671
Telex: 840446
Contact: Dale M. McLane Product Manager

RANDOL did not have an opportunity to discuss the tower mill with the plant superintendent who was away.

ATARA AIR CANNON MIXERS

The ATARA Air Cannon Mixers had not yet been installed. Three had been purchased together with two more agitators to provide better agitation at a lower energy consumption.

ENERGY

Cominco Ltd. own and operate a hydropower plant not far from Yellowknife, believed to be at Churchill Falls. This provides part of the power required by the Con Mine. Incremental power is likely to be very expensive, hence it is logical to find the Con mill installing energy efficient process equipment. Furthermore, considering space heating costs in winter, the compactness of the Japanese tower mill is an added energy saving feature.

PRECIPITATION

If the arsenic content is over 2% in the 5 tons per day residue from the arsenic plant, then it is found that several problems occur in the gold plant. One of them is difficulty in precipitating gold from solution with zinc.

ENVIRONMENTAL

The Con Mine is regulated by the:

Northwest Territories Water Board
P. O. Box 1500
Yellowknife NWT X1A 2R3

Telephone: (403) 920-8191
Telex: 034-45622
Contact: Glen B. Warner, Chairman

WATER QUALITY

No data was provided on mine, mill tailings or final effluent quality. It is known that the effluent is high in chlorides, containing 2-3% Cl^-/l introduced with the ore that contains pockets of halite.

USE OF $FeSO_4$

In arsenic precipitation using ferric sulfate, Cominco tests showed that vigorous agitation is essential to bring the arsenic in contact with ferric ions before it precipitates as ferric hydroxide. When adding ferrous sulfate there is more time available because the ferrous ions take awhile to oxidize and precipitate as ferric hydroxide, so allowing coprecipitation of arsenic without such drastic agitation needs. Other advantages of ferrous sulfate are its lower price and the much easier handling than ferric sulfate which is highly corrosive.

EFFLUENT LIMITS

The regulated effluent limits for the gold mill and the arsenic plant in their permit valid from June 1, 1980 - May 31, 1986:

	Max. Average for Discharge (ppm)	Maximum Grab sample (ppm)
As_T	0.50	1.00
CN_T	1.50	3.00
CN Available	0.40	0.80
Cu_T	0.30	0.60
Pb_T	0.20	0.40
Ni_T	0.50	1.00
Zn_T	0.50	1.00
Suspended Solids	15.00	30.00
Oil and grease	-	5.00
pH	6.0-9.5	6.0-9.5

Comment: The above apply to the discharge from the tailings pond decant basin at the far end of the tailings pond from the mill, where effluent is discharged via the lake system to Great Slave Lake.

TAILINGS DISPOSAL

Tailings after repulping the filtercake with freshwater are cycloned to make a sand slime split approximately in the ratio 400 tpd slimes : 350 tpd sand.

Sand is pumped underground as a 60% solids slurry using minewater. Slimes are pumped from the cyclone overflow at 25% solids to the tailings dam where they are discharged at the end closest to the mill. Barren bleed is blended back into the slimes pulp as it leaves the plant and before $FeSO_4$ and Na_2S are added to detoxify cyanide and precipitate metals.

The Con Mine tailings dam is a large shallow segmented basin which appears to have originally been a lake. As it has filled up with tailings, a dam wall has been constructed at the downgrade end of the dam.

Because of the long freezing winters tailings solutions are accumulated during the winter months. During 1983/4 there appeared to have been a tailings dam breach which had been repaired and the dam height was being raised using a steel pile curtain.

The large shallow surface area of the tailings dam is believed to result in polishing of solution by natural degradation of residual cyanide in the effluent solution. During winter months the cyanide level and liquid volumes in the tailings increase.

TAILS & EFFLUENT TREATMENT

The tailings solution treatment is carried out in two steps:

1) Ferrous sulfate and sodium sulfide are added at the point of pulp discharge to the tailings dam. At this point the pH is 10.5-11.0.

2) Ferrous sulfate and lime are spread into the tailings pond at the discharge end close to the overflow ahead of the decant as a means of dropping more arsenic as a safety measure after connecting the arsenic plant sewer to the tailings pond.

CONSUMABLES

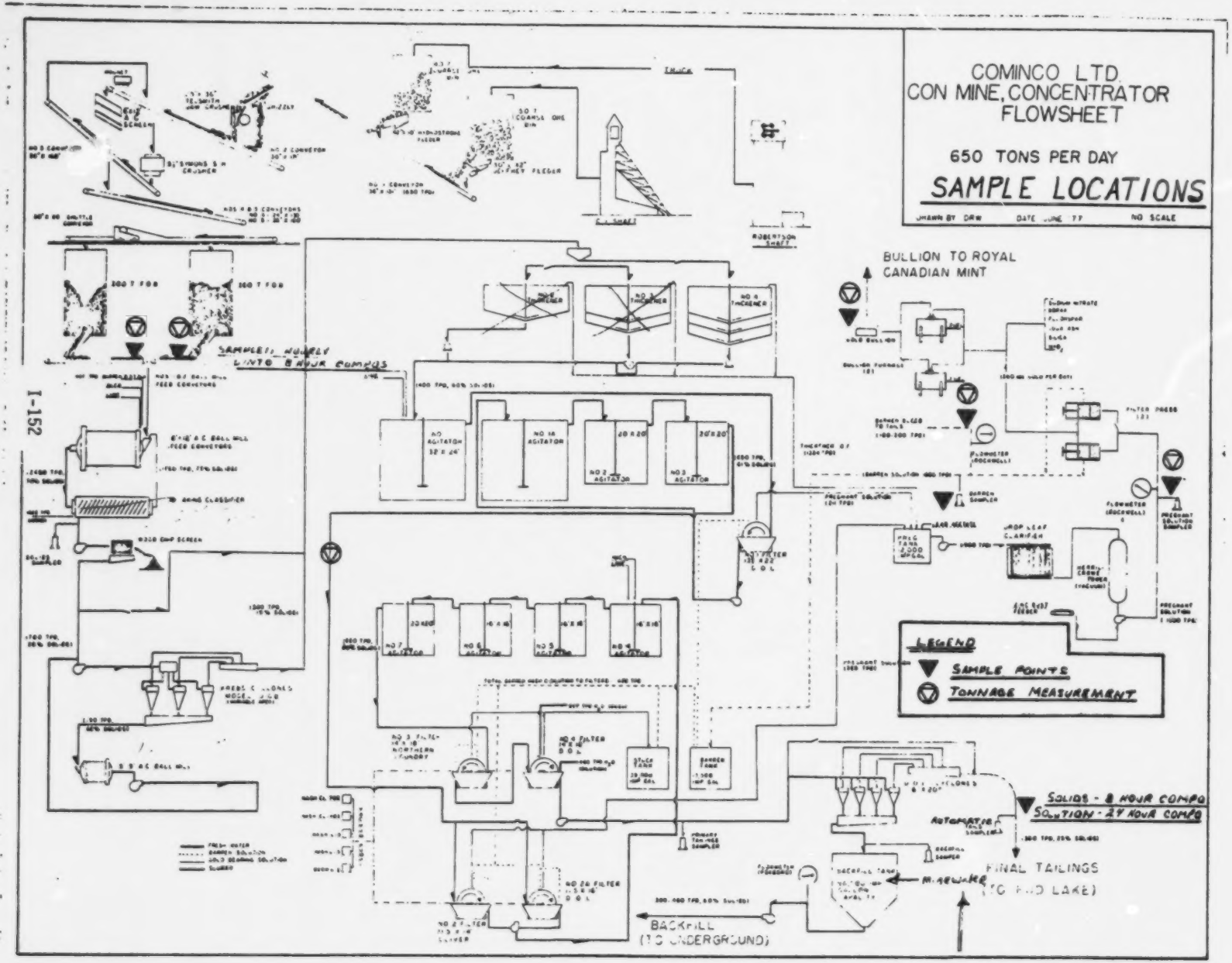
Cyanide	:	Averages 1000 lbs NaCN/day	
Lime	:	Average 21.3 bags @ 50 lbs/day	= 1065 lbs/day
$FeSO_4$	:	Average 18.4 bags @ 50 lbs/day	= 920 lbs/day
Na_2S	:	Average 3.6 bags @ 50 lbs/day	= 179 lbs/day
Zn dust	:	Average 56.4 lbs/day	
Pb Acetate	:	Average 14.0 lbs/day	
3" steel balls	:	570 lbs/day	
1½" steel balls	:	300 lbs/day	

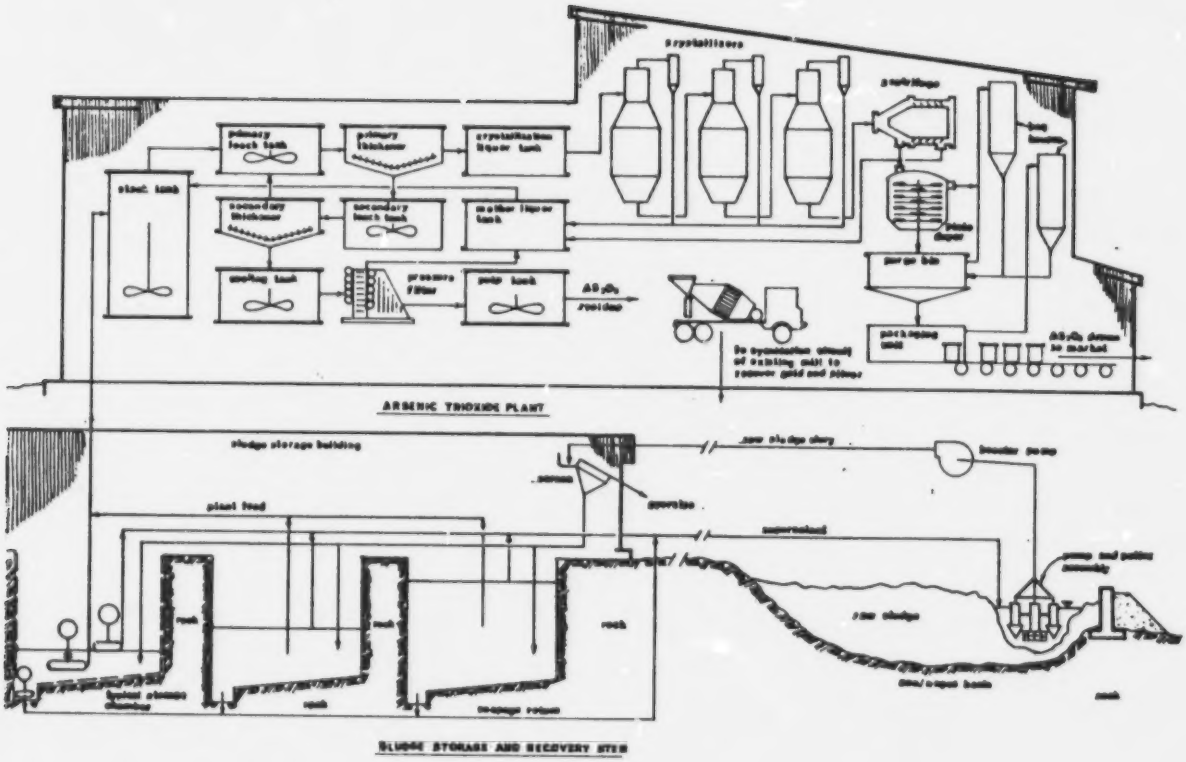
DISCUSSION

Based on the reagents used and the sequence of their addition it appears that the addition of Na_2S + FeS with the tailings at discharge (pH 10.5-11.0) will react with complexed metal cyanides to precipitate the metals and remove cyanide according to the patent by Walter J. Kuit and Alan R. Babcock assigned to Cominco.

Addition of ferrous sulfate and lime downstream seems to be a step to remove any excess arsenic added with effluents from the arsenic plant.

What is curious about the procedure is that in the Kuit and Babcock patent, pH is adjusted to pH 7.5-8.5 to make the process work. It is not clear how/if pH is adjusted at CON tailings dam or whether this occurs naturally.


COMINCO LTD.
CON MINE, CONCENTRATOR
FLOWSHEET
650 TONS PER DAY
SAMPLE LOCATIONS
DRAWN BY DRW
DATE JUNE 77
NO SCALE
BULLION TO ROYAL
CANADIAN MINT
SAMPLED HOURLY
INTO 8 HOUR COMPOS
LEGEND
SAMPLE POINTS
TONNAGE MEASUREMENT
SOLIDS - 8 HOUR COMPO
SOLUTION - 24 HOUR COMPO
FINAL TAILINGS
(TO FIND LAKE)
BACKFILL
(TO UNDERGROUND)
FRESH WATER
BARREN SOLUTION
GOLD BEARING SOLUTION
SLURRY



ARSENIC TRIOXIDE PLANT

SLUDGE STORAGE AND RECOVERY SITE

ARSENIC RECOVERY PLANT

INTRODUCTION

The arsenic plant is an example of how an environmental liability was to be converted to a profitable byproduct by a simple process. This turned into a larger investment with more process headaches than anticipated. Arsenic has been an emotional issue at Yellowknife despite no confirmation of it ever having harmed anyone.

PROCESS DESIGN

The arsenic recovery process was developed by COMINCO. One person particularly knowledgeable in the process is:

Dr. Lorne Ball
Group Leader - Chemical Metallurgical Research
Cominco Ltd.
Trail, BC

Telephone: (604) 364-4419

CAPITAL COST

Capital cost was budgeted at C$12 million for a 15 stpd As_2O_3 production. The actual plant cost C$14 million.

PLANT STARTUP November 1982

FEED MATERIAL

Arsenic oxide dusts were collected by wet Doyle Impinger scrubbers on the Edwards Roaster gasstream treating arsenical goldbearing sulfide flotation concentrates from the Con Mine from 1938 to 1972. About 30,000 tons of the dusts containing about 85% As_2O_3 and 0.3 oz Au/t was accumulated in the two small open ponds at the Con minesite. The material also contains dust, antimony, lead, iron and some sulfide. The leached arsenic residue contains about 0.69 oz Au/t and 2% As_2O_3.

PLANT CAPACITY

The plant was designed to treat a maximum of 30 tpd feed for about 15 stpd As_2O_3 product. This throughput has not yet been achieved.

MOTIVATION

The arsenic ponds at Con Mine, although small in size, contain a considerable amount of arsenic in a soluble form contained in ponds that are not isolated from groundwater.

Located near the environmentally sensitive Great Slave Lake the arsenic ponds were a cause of concern to both Cominco and the Canadian Government. Something would have to be done to fix the arsenic in these wastes in a permanent and safe manner.

Economic incentives to treat the arsenic pond materials were:

1) Recovery of a salable arsenic product
2) Recovery of an incremental gold raw material
3) Alternative means of disposing of the arsenic and restoring the ponds would require capital and operating expense anyway.

The potential gross value of the arsenic and gold in the arsenic ponds appears roughly to be:

Arsenic	:	30,000 x 85% As_2O_3 x C$800/t	C$20,400,000
Gold	:	30,000 x 0.3 oz Au/t x C$430/t	3,870,000
		TOTAL	C$24,247,000

Assumption: 10% of the solids in the feed to the plant remain insoluble after arsenic has been leached.

PROCESS

The feed material is leached in hot water at 95°C at pH 3-5. Reagents such as H_2O_2 or H_3PO_4 are added to the leach vessel to precipitate impurities such as Sb, Pb, S, Fe etc. which are settled and removed. This is done as a two stage leach each stage followed by decantation of solids.

Supernatant leach liquor from stage 1 leach advances as pregnant liquor to the 4 stage crystallizer circuit. Supernatant solution from the second thickener after leaching the solids a second time advances to become leach liquor to the first stage leach.

The pregnant solution is concentrated in a three stage multi-effect crystallizer to drop coarse arsenic oxide crystals. The crystals are dewatered on a Dorr-Oliver horizontal pan filter and the filtrate pumped to the mother liquor tank for return to the leach tank.

Insoluble residue that did not leach is cooled, thickened and dewatered in a Larox pressure filter before being transported in a cement truck to the gold recovery plant. The crystallized arsenic product is dried in a plate drier and packaged for shipment.

FEED HANDLING

Arsenic sludges are reclaimed from the outdoor pond in the summer months using 3" Ø Toyo pumps. This pump can transport material with up to 60% solids and has worked well in this application. The slurry is boosted by a centrifugal pump which moves the material to one of three indoor storage pits after first screening it to remove trash. The capacity of these impoundments is adequate to store feed for the plant through the frozen months, estimated therefore as 25 weeks x 7 days x 30 tpd = 5200 short tons solids.

Toyo sludge pumps are available from:

Toyo Denki Industrial Company
1-7-10 Norimatsu Yahatanishi-ku
Kitakyushu City
Japan

Toyo Pumps North America Corporation
Esplanade Centre
119-255 West 1st Street
North Vancouver, BC
Canada V7M 3G8

Telephone: (604) 988-7187
Telex: Waterfront 0435-2841

Contact: Richard Binning

There were some initial problems with wood particles clogging of the system and with corrosion of the pump motor seals which allowed the arsenic to get into the motor. The stainless 304 seals were replaced by stainless 316L steel to solve the pump problem.

The building that houses the indoor sludge stockpile is heated just enough to prevent the material from freezing. The necessity for indoor storage has added significantly to the capital cost of the operation.

Seepage from the three indoor sludge storage pits is intercepted and pumped back to the system.

During summer the storage impoundments are decanted and water is returned to the outdoor sludge pond.

LEACHING

Solution returning from the crystallizer and filtrate from the arsenic crystal dewatering step is returned to the mother liquor tank where it is heated to become leach solution at 95°C. The arsenic level in the leach liquor reaches 53g As/l.

H_2O_2 and/or H_3PO_4 are added in the leach tank to precipitate unwanted impurities and apparently to enhance arsenic dissolution.

Solution is heated by heat exchangers which in turn are heated by steam coils.

Arsenic in the leach residue must be reduced to below 2% As or problems are in Merrill-Crowe gold precipitation.

INSOLUBLE RESIDUE

5 - 15 tons per day of leach residue is returned from the arsenic plant to the gold plant at 0.69 oz Au/t. The residue is dewatered in a Larox pressure filter to remove as much soluble arsenic as possible. The cake is repulped to 60% solids for transport to the gold plant in a cement truck. It runs 0.6-1.0 oz Au/t.

ARSENIC PRODUCT

The arsenic is crystallized in large crystals to satisfy market demand. Product quality typically is:

As_2O_3	99.5%	
Sb	0.3%	max
S	0.1%	max
Pb	0.02%	max
Fe	0.016%	max

Large arsenic crystals make it possible to reduce dusting in handling the product.

OPERATING STARTUP PROBLEMS

1. There have been startup problems with the multi-effect crystallizers which have yet to achieve design capacity of 15 stpd As_2O_3.

2. The centrifuge originally installed to dewater the arsenic crystals did not work. It has been replaced by a Dorr-Oliver horizontal pan filter.

3. Seals on the Toyo pump for reclamation of sludges from the pond and from the indoor storage pits were corroded by the arsenic to the extent that arsenic sludge got into the motors. This was overcome by replacing the stainless 304 steel seals with 316L seals.

4. The plant is fitted with stainless steel 304 piping. Some of these lasted 2 weeks before being corroded through by the arsenic solution.

5. The antimony level in the lab tested solutions was reduced by H_2O_2 or H_3PO_4 addition. In the plant however antimony did not get depressed to the same extent.

6. The complexity of the counter current leaching by hot water seems to be easily underestimated.

ENVIRONMENTAL

Arsenic vapor gets into the working atmosphere in the plant. To prevent loss of arsenic to the environment as dust, the plant is completely enclosed which results in a hot, humid working environment.

Any antimony in the feed ends up leaving the plant in the undissolved gold-bearing residue or in the arsenic oxide product.

No water is discharged from the arsenic plant. It is operated as designed on a zero discharge basis, except for a sewer to the tailings pond.

Arsenic rashes are experienced by some workers. In some areas workers were asking for "space suit" type protective clothing, but it is questionable whether these would provide the protection hoped for. It appears that the hot, perspiration prone environment inside space suits might well result in a greater likelihood of arsenic rash than without the space suit.

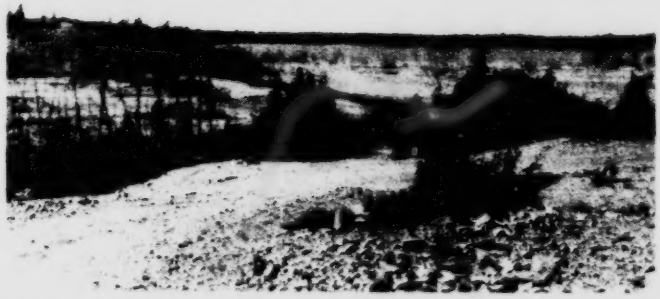
All personnel are limited to 5 hour shifts in the arsenic plant. Urine samples are taken for analysis in and out of each shift.

No TLV has been decided on yet for arsenic. If the urine analysis level is below 500 micrograms As per liter then it has been decided in the interim that a worker may work in the plant. An arbitrary level of 50 ug As/m^3 air limit in the plant has been set. The plant air is around 20 ug As/m^3except around the arsenic feed pits where it is higher.

Workers are issued with special overalls and boots for working in the arsenic environment. Before leaving the plant they shower in the changehouse and then cross to the other side of it to change back into street clothes.

Con Minesite with Yellowknife in background.

Large Shallow Tailings Pond



$FeSO_4$ and Na_2S ready for distribution over pond surface.

OPERATION	EAST RAND GOLD & URANIUM COMPANY LIMITED P. O. BOX 980 BRAKPAN 1540	
TELEPHONE	(011) 55 9050	
CONTACTS	A. G. Webster	General Manager
	Ken Henderson	Metallurgical Manager
	Dave Grimsby	Plant Superintendent - CIL
	Rob Ingles	Plant Production Superintendent (R&D)
COMPANY	Anglo American Corporation of South Africa Ltd. P. O. Box 61587 Marshalltown 2107 South Africa	
TELEPHONE	(011) 638-0111	
CONTACT	A. D. Deuchar	Deputy Technical Director
	Harry Brown	Project Manager

INTRODUCTION

ERGO recovers gold, uranium and pyrite (sulfuric acid) by re-processing 1.6 million tons of slimes per month from the tailings dams left by the previous gold mining operations on the East Rand.

Large amounts of water are used by this undertaking and several items of particular interest from a water management standpoint were identified:

1. Water Saving measures through increased recycling of effluents.

2. High TDS underground minewater used as a major water source for the plant.

3. Gypsum scale problems, monitoring and counter measures.

4. An innovative process for the removal of arsenic and cyanide from existing effluents.

5. TDS levels in the effluents that are relatively high, but still within statutory limits.

6. The possible future need for desalination to reduce TDS levels in these effluents.

7. A new CIL installation for the recovery of additional gold from flotation tailings, that utilizes the last seven out of a total of eleven carbon contacting stages for cyanide removal. The tailings from this plant are pumped to a new disposal dam.

DESCRIPTION OF PROCESS

The ERGO process and plant is described in the attached document made available by the company.

MAJOR WATER SUPPLIES AND USES

ERGO uses the following water supplies.

1. Rand Water Board (Potable) Water - 563m³/hour

In response to water savings measures necessitated by the prevailing drought conditions, ERGO has cut back its Rand Water Board water consumption to essential applications only. This includes, in most cases, the conversion of gland service requirements to process water. Some thought might be given to the use of engineered plastic sleeves to reduce abrasion of pump shafts when this low quality water is employed for gland service. A company that could possibly make useful suggestions is:

Virginia Engineering Services (Pty) Ltd.
P. O. Box 47
VIRGINIA O F S

Contact: Alan Leger

2. Underground Mine Water from Grootvlei Pumping Operations - 1517m³/hour

The neutralized mine water is pumped up from underground by Grootvlei Mines (Pty) Ltd. via the old S A Lands and Exploration Company pumping installation and shaft. It arrives at ERGO at 29°C and is cooled to 21 - 23°C by evaporation sprays in the process water reservoirs. In 1983 a further R60,000 was spent on improving the cooling spray system.

This water is mainly used in the Acid Plant in both the calcine quench tanks requiring a total of 150m³ water/hour and in the Peabody Scrubbers requiring 1650m³ water/hour to scrub calcine dust particles out of the roaster gases prior to drying and conversion to SO_3 for acid production. The calcine solids are removed from the quench and scrub waters in two thickeners.

The thickener overflow at pH 1 is pumped to the Flotation Plant where a 1000m³/hour is used for dilution and acidification of the flotation feed pulp and the balance, 900m³/hour, is sent to a two stage effluent treatment plant fitted with Envirotech

surface aerators. 50m³/hour raffinate and sufficient lime to adjust the pH to 7, are introduced into the first stage. Additional lime is added to the second stage to produce a pH of 8.5.

The overneutralized product (solution and sludge) of the effluent plant is delivered into the flotation tailings thickener distribution box, where it is used for the neutralization of the pH 3.8 flotation tailings. Small amounts of lime are also added to the thickener feed launders for final pH control. This method of neutralizing the excess calcine thickener overflow and flotation tailings has been found to give the most effective use of lime and better pH control. Total lime consumption for this purpose is 2.4 kg/ton of solids in the flotation feed.

Raffinate containing 6,400 ppm iron is added to the effluent plant to boost the overall iron concentration thereby ensuring that sufficient ferric hydroxide is formed by the high pH and vigorous aeration, to co-precipitate the 32 ppm arsenic typically found in the calcine thickener overflow. The arsenic is removed to below 0.5 ppm.

A typical analysis of the underground water as received at ERGO is:

Conductivity		237	mS/m
pH		7.9	
TDS		1939	ppm
Suspended Solids		7	ppm
Total hardness	(as $CaCO_3$)	984	ppm
Sulfates	(as SO_4)	984	ppm
Chlorides		170	ppm
Fluorine		1	ppm
Potassium		9	ppm
Phosphates	(as PO_4)	1	ppm

Out of necessity, ERGO uses more underground water in the Acid Plant than is required to make up the total water losses in the circuit. For this reason, ERGO has to dispose of its excess water by way of effluents at both the Complex and the tailings dam.

3. Water Associated with S A Lands Gold Plant Tailings - 553m³/hour

The S A Lands and Exploration Company currently disposes of its Gold Plant tailings by pumping them into ERGO's tailings thickener distribution box. Some of the water associated with these tailings is recovered in the thickener overflows, while most of the remaining water is decanted from the solids at the ERGO tailings dam.

4. Water Associated with Simmergo Plant Tailings - 292m³/hour

The Simmergo tailings are scheduled shortly to be pumped via a 38 kilometer pipe-line directly to the ERGO tailings dam, where the bulk of the water associated with these tailings will be removed.

WATER BALANCE

A generalized water balance is shown in the attached drawing. The balance includes the new CIL Plant and the scheduled pumping of Simmergo tailings to the ERGO tailings dam. Seepage and evaporation losses are also given.

EFFLUENTS

1. Complex Effluents

The clear water reservoir is the collection point for the overflows from the four 138m tailings thickeners plus 504m³/hour of the ERGO tailings dam return water. A total of 2 580m³/hour of water from this reservoir is pumped via high pressure Allis Chalmers pumps to the reclamation sites for slimes recovery. The excess water (540m³/hour) is allowed to overflow from the reservoir, gravitating to a primary and secondary settling pond system.

The primary system consists of two parallel ponds. When one becomes full of settled sludge, the flow is switched to the second so that the sludges can be removed by hosing from the first.

The second system is made up of two large reed-filled ponds which remove the remaining suspended solids to below 25ppm. The reeds and associated ecosystems are also known to reduce sulphate levels.

The total overflow from the second settling pond system was until July 1983 discharged into the Rietspruit with the Vaal River as the ultimate destination. Now approximately 40% of this effluent is recycled to the process water reservoirs at the ERGO complex.

2. Tailings Dam Effluent

The underflow from the four flotation tailings thickeners is pumped to the tailings dam and discharged via a ringmain with cyclones around the periphery of the 791 hectare (+ 1750 acres) dam. The cyclone underflows are used for wall building and the overflows migrate to the central area, forming gently sloping beaches. The walls of the tailings dam are constructed with a 1:3 slope.

The water run-off collects in a central pond from where it is removed by a mobile decant system consisting of a barge fitted with large Flygt pumps that deliver via flexible hoses into Allis Chalmers pumps mounted on a moveable land-based platform. This system pumps the decanted water to activated carbon columns for soluble gold adsorption. The water then gravitates to a decant station and thence via a cement enclosed pipe under the dam wall into the toe trench which runs parallel to the walls around the outer periphery of the dam. All seepage gathered by the toe drain network from the dam walls also enters this trench.

The lowest point of the toe trench acts as a collection point from which an average of 938m^3/hour of tailings dam water is returned via four 200HP APE Sangus multistage vertical spindle pumps to the ERGO complex, where 434m^3/hour enters the process water reservoirs and the balance of 504m^3/hour is delivered to the clear water reservoirs (see Section 1 above). The actual amount of return water pumped is controlled by the number of APE Sangus pumps on line.

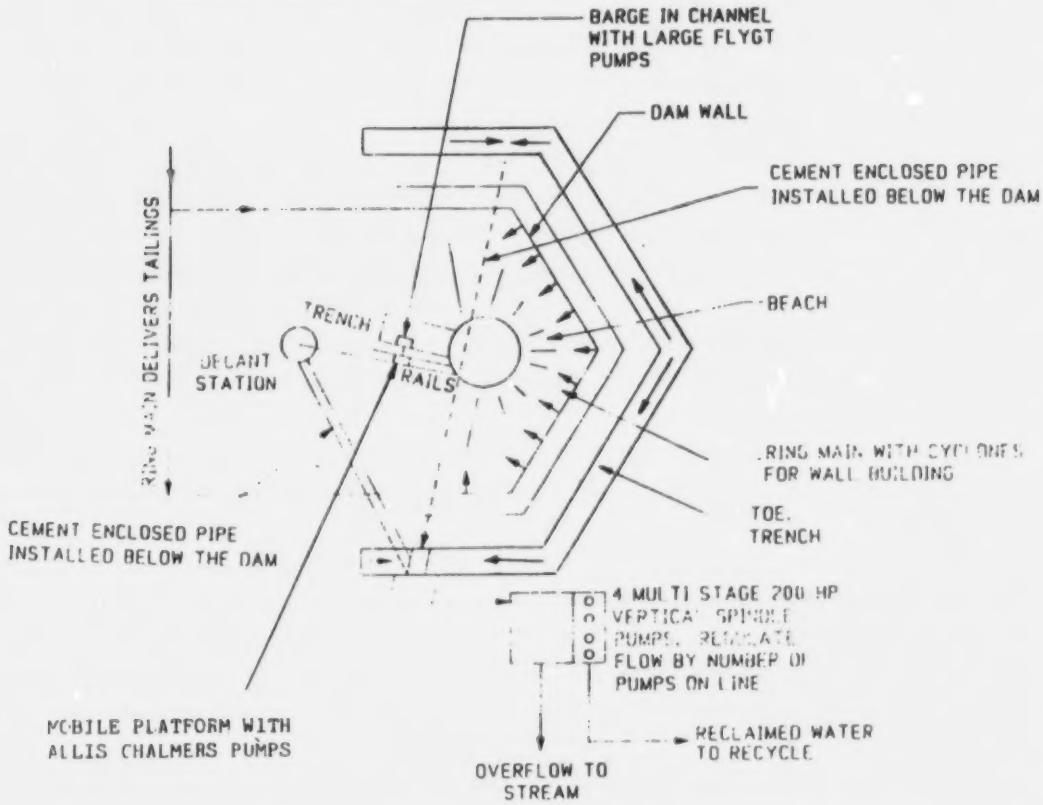
Excess tailings dam water (697m^3/hour) is discharged as an effluent from the same toe trench collection point, eventually joining the Complex effluent in the Rietspruit.

Immediately the new R56 million Carbon in Leach (CIL) Plant comes on line, ERGO's tailings will be pumped to a new dam currently under construction adjacent to the existing tailings dam site, at a cost of R31 million. The latter amount is being funded as part of the Daggafontein slimes dam treatment project, which also provides for the future retreatment of the existing tailings dam in the ERGO CIL Plant.

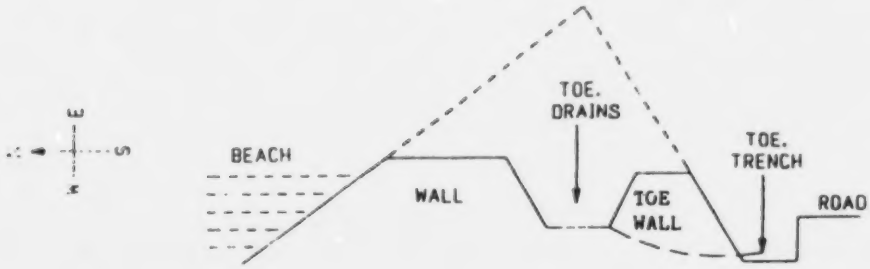
Water run-off from the new tailings dam will be handled in six collection area each with its own mobile decant system. These decants will deliver into a central holding pond, from where the water will be pumped initially into the existing tailings dam for disposal via the present pumping systems and carbon columns. Eventually the new dam will have its own decant station and return water pumps.

ERGO TAILINGS DAM

MOBILE DECANT SYSTEM - ORIGINAL CONFIGURATION



PROFILE OF WALL AREA



3. Effluent Analysis

The composition of the Complex and tailings dam effluents are as follows:

		Complex	Tailings Dam
Total effluent generated	m^3/h	583	1635
Amount recycled	m^3/h	220	938
Amount discharges	m^3/h	363	697
Conductivity	mS/m	363	375
pH		6.8	7.3
TDS	ppm	3408	3581
Suspended Solids	ppm	20	45
Total Hardness (as $CaCO_3$)	ppm	2168	2271
Sulfates (as SO_4)	ppm	1993	2101
Chlorides	ppm	154	162
Fluorine	ppm	1	1
Sodium	ppm	171	187
Potassium	ppm	40	49
Phosphates (as PO_4)	ppm	1	1
Cyanide (as CN)	ppm	0.5	0.5

4. Calcine Dam Effluent

$50m^3$/hour raffinate is added to the Gold Plant residue pachuca containing repulped calcine which has been leached at pH 10.5 with cyanide and filtered for pregnant gold solution recovery. The raffinate drops the pH of the calcine residue to $^+$ 7.5. The low pH and the air agitation in the pachuca destroy most of the free cyanide and the balance is converted by the high iron concentration in the raffinate to stable iron-cyanide complexes.

The raffinate-treated Gold Plant residue was until recently pumped to a separate calcine tailings dam, with the decanted water as effluent being injected into the tailings dam feed pipe-lines. Currently the cyanide-free calcine residue is deposited directly with the flotation tailings on the ERGO tailings dam.

CAUSES OF TDS BUILD-UP IN THE ERGO WATER CIRCUIT

Salts are introduced into the ERGO water circuit from the following sources:

1. Soluble oxidation products of pyrite in slimes feed material add Fe^{2+}, Fe^{3+}, $SO_4^{=}$, H^+ and undoubtedly dissolved Al^{3+} and silica.

2. Reagents added for pH control are by far the greatest contributers to TDS build-up. These are:

   a. Calcine thickener overflow ($^{+}$ 1.5g/l sulphuric acid) and concentrated sulphuric acid used for dilution and acidification (pH 3.5 - 4.0) of the incoming pulp prior to pyrite/gold/uranium flotation;

   b. Lime addition for neutralizing the acidic flotation tailings and the excess calcine thickener overflow solution, and for protective alkalinity during cyanide leaching of the calcine.

3. 100m^3/hour of raffinate is generated in the Uranium Plant, and can contain from 30,000 to 40,000 ppm TDS. Half of the raffinate (50m^3/hour) is used to assist in co-precipitating arsenic from the excess calcine thickener overflow in the effluent treatment plant and the balance, for cyanide destruction/complexing in the Gold Pant residue. Some of the salts associated with the raffinate and other high TDS solutions obviously precipitate out of solution when contacted with lime to pH 7 and above.

CALCIUM SULPHATE SCALE PROBLEMS AND COUNTER MEASURES

ERGO's water circuit is saturated with calcium sulphate. This has led to severe scaling problems in the past. When it first occurred in the major pipe-lines, high pressure water cleaning was used on the slurry lines because the scaling was relatively soft, but this proved ineffective on the monitor water lines where the scale formation was extremely hard. The only cost effective method of removal in this case proved to be blasting using long lengths of detonating fuse on the outside of the pipe, covered by a mud pack. This method could not be repeated because of partial pipe deformation.

By 1980 antiscalant reagents were being used to prevent calcium sulphate precipitation, the first reagent being Antiprex supplied by Allied Colloids S A (Pty) Ltd.

Allied Colloids (S A) (Pty) Ltd.
P. O. Box 48775
Roosevelt Park 2129

Telephone: 782-5335
Telex: 4-24410 SA
Contact: Robert M. Page

The reagent in use at the time of the visit was Anikem 4393 supplied by Anikem (Pty) Ltd, a South African subsidiary of Nalco.

Anikem (Pty) Ltd.
P. O. Box 67817
Bryanston 2021
Telephone: (011) 706-6106
Telex: 422256 SA
Contact: Merwyn S. C. Wilson

The total dosage rate was 6g/ton of feed to the Flotation Plant, added to the monitor water circuit.

Other antiscalants tested include CL4000 supplied by Floccotan (Pty) Ltd (for address see below) and PC 40 from Ferste Chemicals (Pty) Ltd.

Ferste Chemicals (Pty) Ltd.
P. O. Box 41109
Craighall 2020
South Africa

Telephone: (011) 787-8857
Contact: Stuart Ferguson

ERGO is currently developing a modified NACE method that will give a reliable performance comparison between the different antiscalant products and allow addition rate optimization.

Coupons are suspended at various points in the ERGI water circuit to monitor scale build-up on a monthly basis and pipe-lines are opened for regular inspections. Tests are being conducted on a dynamic scale-monitoring device developed by Calgon and available in South Africa from:

Floccotan (Pty) Ltd.
P. O. Box 4578
Randburg 2125
South Africa

Telephone: (011) 789-3823
Telex: 4-26994
Contact: John Hallows

The Dynamic Scale Monitor device is also available from:

Calgon Corp.
P. O. Box 1346
Pittsburgh, PA 15230

Telephone: (412) 777-8000
Contact: Frank Daniher

The monitor water and slurry pipe-lines, plus certain critical lines in the plants are now 'pigged' on a regular basis with plastic pigs to clean out any scale build-up that occurs. The flotation tailings thickeners and the effluent treatment plant are also taken off line on a scheduled basis for descaling.

There has not been much of a scale problem in the tailings dam return water line even though the TDS levels are usually in excess of 3,500 ppm, with 2,059 ppm sulphates which is at or over saturation.

WATER SAVINGS THROUGH RECYCLING OF EFFLUENTS

In the past, Rand Water Board (RWB) water was used to make up any shortfalls in underground water from Grootvlei pumping operations, required by the Acid Plant for calcine quenching and dust scrubbing. Since July 1983, recirculation of a portion of ERGO's effluents into the process water reservoir has reduced RWB water make-up to emergency situations only, resulting in a 18% drop in consumption.

The recycled effluents have also compensated for the underground water required to replace RWB water in other applications.

EFFECT OF RECYCLING ON EFFLUENTS

No noticeable effect on metallurgical performance, scale build-up or effluent quality has been encountered with the increased recycling of effluents to date. The effects of further increases in effluent recycling are unknown at this stage, but more precipitation and an increase in the level of soluble salts could be expected.

SALT BALANCE MODELLING

The ERGO complex plant represents an excellent example where a good salt balance model could be helpful in predicting the cost and effect of various alternative strategies for water management. Names of a few consultants who are learning how to model salt balances are provided in Chapter 10.

ENVIRONMENTAL ASPECTS

The slimes dams left over from the previous gold/uranium mining operations that contain pyrite, are expected to be AMD generators and can lead to seepage of AMD to contaminate aquifiers. ERGO by reclaiming these dams and removing pyrite by flotation, is reducing the long term acid generating capacity of the slimes and thereby helping in the long term reduction of TDS build-up in the local regional water supply.

ERGO's effluents also meet the current quality standards set by the Department of Environment affairs.

The ERGO pollution officer follows the potential pollution route daily, sampling all effluents and the local stream for laboratory analysis. Various additional control points in the Complex are also sampled. Principle items of interest in the daily analysis are suspended solids, cyanide, arsenic and pH.

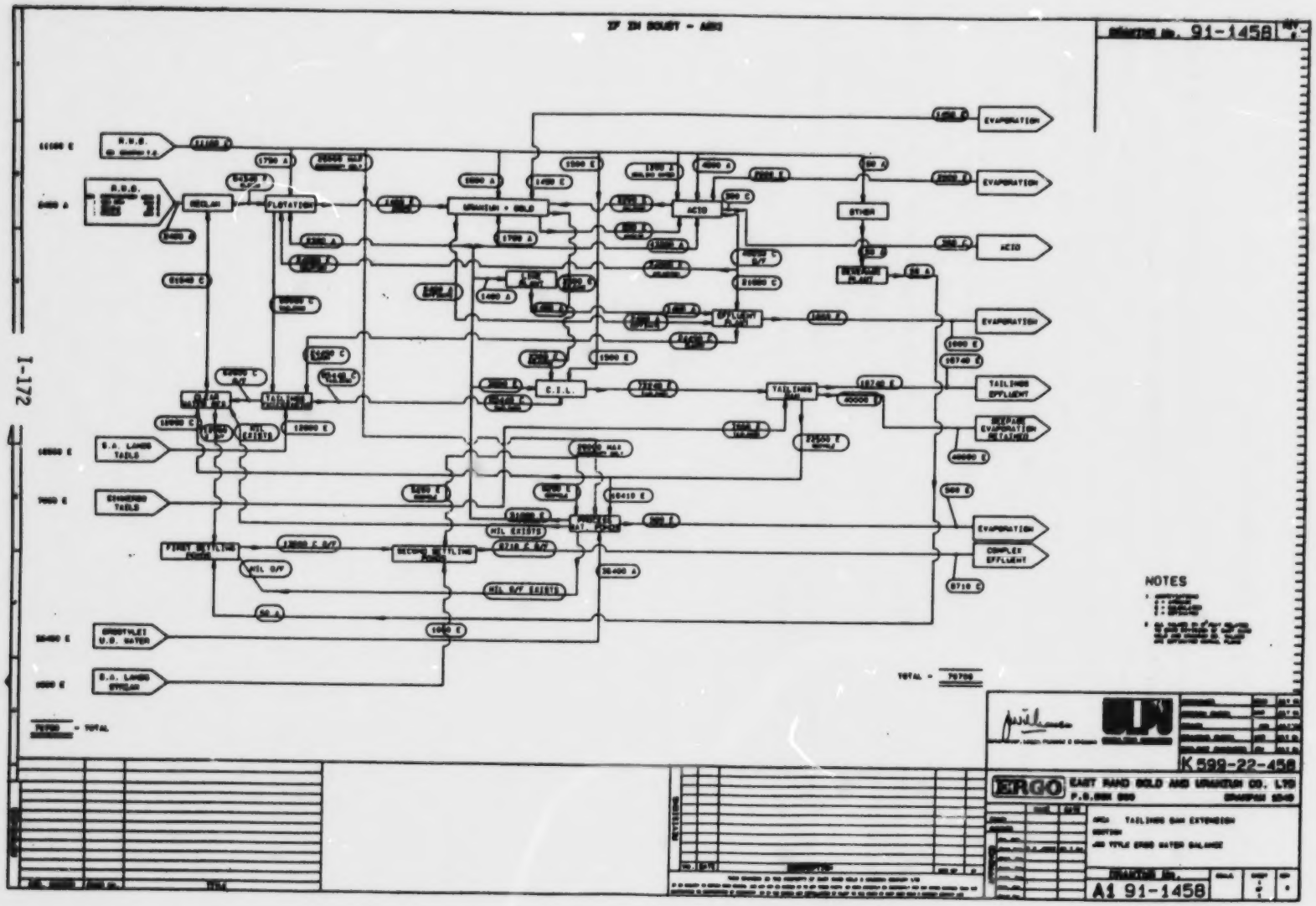
POSSIBLE FUTURE NEEDS FOR DESALINATION

Considering the scaling nature of the recycled solutions and effluents from ERGO, any processes considered for desalination of effluents would have to take this into account. Two approaches might be considered - one is to treat all the effluent to the conductivity level of 250 mS/m, i.e., about 1900 ppm TDS or to treat half the flow all the way and blend it back. Seeded reverse osmosis (SRO) is the only method that would drop the TDS level while avoiding serious membrane fouling problems.

ERGO is currently running a SRO pilot plant in conjunction with RCCI.

A rough estimate of the capital costs for a full scale SRO plant to treat ERGO's effluents would be R12 - 18 million, with an operating cost in order of R0.45/m^3.

Other area being considered for improving effluent quality include sulphate level reduction by bacteria in either natural or controlled environments.


DRAWING No. 91-1458
R.O.D.
R.O.D.
REGRIND
FLOTATION
URANIUM + GOLD
ACID
ETHER
EVAPORATION
EVAPORATION
ACID
EVAPORATION
TAILINGS EFFLUENT
DEEPDRE EVAPORATION RETAINER
EVAPORATION
COMPLEX EFFLUENT
C.I.L.
TAILINGS DAM
EFFLUENT PLANT
S.A. LANDS TAILS
EVANDERSON TAILS
FIRST RETILING
SECOND RETILING
GROSVLEI U.D. WATER
S.A. LANDS SPIGAN
NOTES
K 599-22-458
ERGO
EAST RAND GOLD AND URANIUM CO. LTD
TAILINGS DAM EXTENSION
A1 91-1458

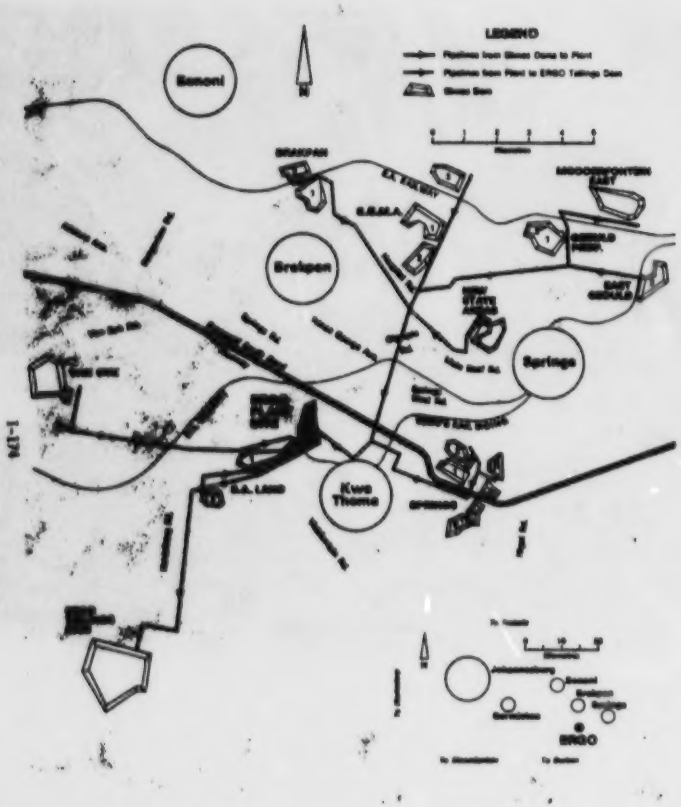
An aerial view of the complete treatment plant

How it all began

For more than 20 years Anglo American had been building up valuable experience in the treatment of gold plant tailings, both from dumps stockpiled for their uranium content, and through the recovery of pyrite for sulphuric acid manufacture. The improvement in the gold price and the increased demand for sulphuric acid regenerated enthusiasm for a major independent slimes reclamation project. About 1 000 test holes were drilled in several slimes dams on the East Rand and the results were sufficiently interesting to justify a full scale testing programme.

In the meantime, scientists at the Anglo American Research Laboratories had developed a flotation technique to produce a concentrate of three per cent of the mass of the slimes which contain sufficient gold and uranium to enable a conventional extraction process to be applied.

A pilot flotation plant with a capacity of one ton an hour was erected in 1974 and results confirmed the findings of the laboratory test work. Feasibility studies indicated that flotation would have to be conducted on a very large scale indeed if it were to be viable and the plant would need to treat a minimum of one million tons of slime a month. This posed several crucial questions. For example, what was the best method of transporting the material for treatment? Should there be a very large single flotation plant or three separate flotation plants established closer to the slimes dams destined for treatment? Various means of transportation, including road and rail, were examined and it was eventually concluded that the most economic method was to pump the slimes in slurry form by pipeline to a central processing site. A subsequent investigation carried out by the Council for Scientific and Industrial Research confirmed Anglo American's own conclusions. The CSIR's report also formed the basis of the engineering design of the pipelines and the pumping systems. Test work undertaken at the Group's Vaal Reefs gold mine showed that by 'hosing' slimes with high pressure water cannons an acceptable slurry could be obtained which could then be pumped through large diameter pipes to the central treatment plant complex.

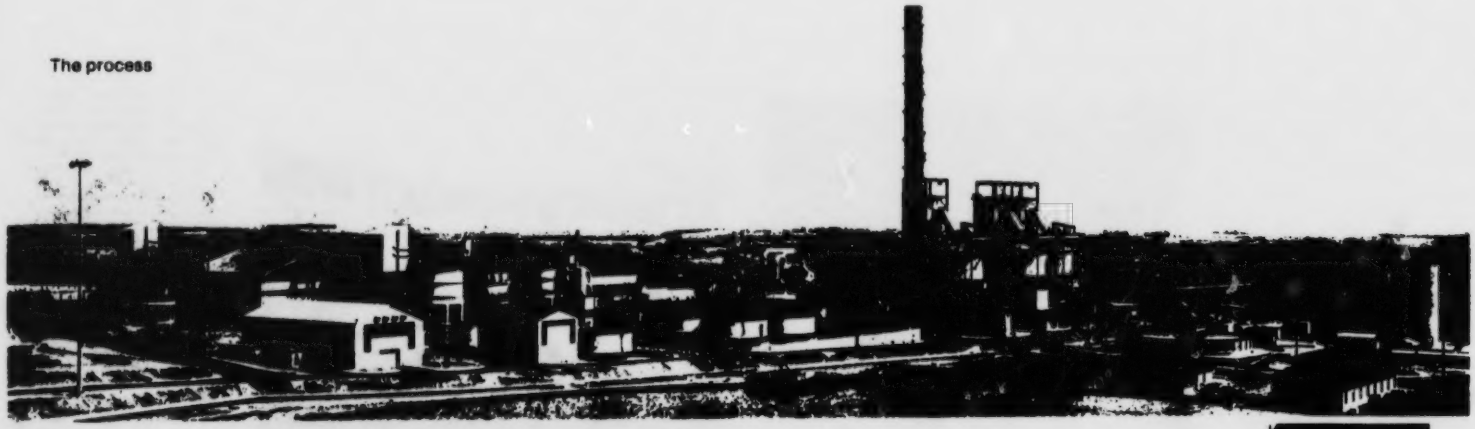


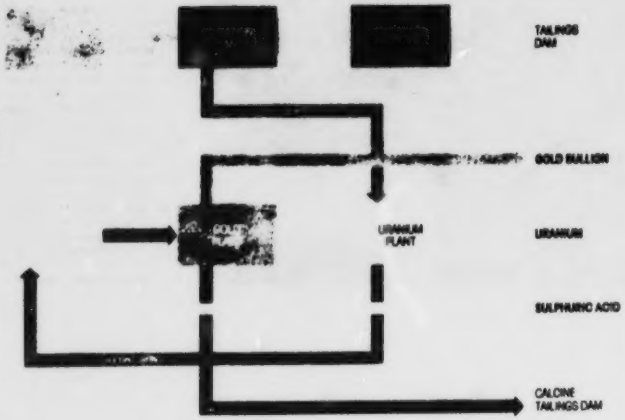
Financing arrangements

In 1975 the Anglo American Corporation Group began providing the main finance for Ergo's expenditure, through a series of interest free loans. By June 30, 1977 these loans totalled about R52 million. The following month Ergo made an offer of 16 million shares at R3,50 a share, of which 12 250 000 shares were firm subscriptions by certain companies and financial institutions. When the offer closed on July 29, applications totalling R286 million had been received, a record for a South African share issue, and the 3 750 000 shares offered to the public were subscribed eighteen-and-a-half times. Since the inception of the company, the net proceeds available from the issue of equity capital amounted to R114,8 million with the balance of funds for Ergo's capital expenditure being provided by revolving credit facilities and short-term borrowings. In November 1977 Ergo received the Rand Daily Mail's Business Achievement Award in recognition of its pioneering technical accomplishments and its outstanding contribution to the development of the South African economy.

Tailings disposal and return water pipelines with acid plant and storage tanks in the background

The process





Dam reclaiming

Specially built remote controlled, and hydraulically operated water cannons direct jets of water under high pressure – 2.5 MPa – at the dam walls. A battery of three cannons 'monitor' each of the three dams being worked and every hour the combined cannons use 2 500 cubic metres of water to slurry 2 100 tons of solids which are gravity-fed to the adjacent pumping station. After screening the slurry is pumped through large pipes to the flotation plant at the Ergo complex some 10 or more kilometres away. Three slimes dams are monitored simultaneously, with two main pipes servicing each dam: one pipe carrying water for the monitoring guns and the other carrying the slurry.

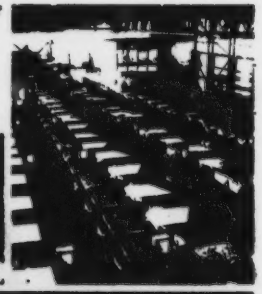
Flotation plant

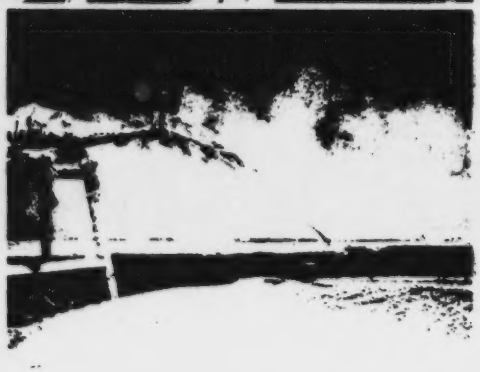
The slurry is processed in the flotation plant to recover gold, uranium and sulphur in the form of a pyrite concentrate. Treatment is in three separate streams each of

Left: The pachuca area of the flotation plant
Right: Processing of the slurry through the flotation plant
Bottom: A cyclone in operation at the tailings dam

The uranium plant with the repulper in the foreground
Bottom: The 500 tons a day acid plant

approximately 500 000 tons a month, to accommodate any difference in metallurgical characteristics that may exist in the respective dams. The slurry is diluted before sulphuric acid and various chemical reagents are added, to prepare the pulp for froth flotation. The low value mineral content of the pulp requires large tonnages to be processed to ensure profitable recovery of these minerals. By passing through a series of flotation cells the pulp yields valuable minerals which are floated in a froth from the waste, and the pyrite is then passed through two thickeners before delivery to the uranium plant. The process is supervised from the main control room.



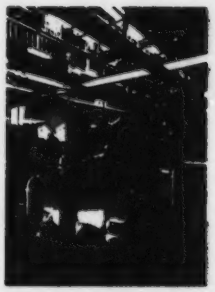


Tailings disposal

In the meantime, the residual slurry from the flotation plant cells is delivered to three 138 metre diameter thickeners before being pumped to a tailings dam far removed from built-up areas. Here the solids in the slurry are separated from the water and remain at the tailings dam site, while most of the water is pumped back to the Ergo complex for re-use by the monitors at the slimes dam reclamation sites. Additional water is obtained from the underground workings at SA Land gold mine or from the Rand Water Board. The pollution-free tailings will be systematically dumped over the years into a 750 hectare disposal area, and research into suitable vegetation cover is currently being undertaken.

Uranium plant

The pyrite concentrate is pumped as a pulp from the flotation plant to the uranium plant, where it is heated by steam and sulphuric acid is added to dissolve the uranium oxide. The pregnant solution (containing uranium) is removed from the pyrite by rotary filters and the pyrite residue is pumped as a pulp to the sulphuric acid plant. Any fine solids remaining in the solution are removed by settling tanks and filters in order to prevent problems in the solvent extraction plant. The solution is then mixed with a solvent consisting of a special reagent (amine) dissolved in paraffin. This absorbs the uranium into the solvent leaving behind all the impurities in a solution which is returned to the flotation plant. After a further purification stage of the solvent, the chemical conditions are changed forcing the uranium out of the paraffin into a water solution. The solvent is then re-used for the uranium extraction step. The final product called ADU (Ammonium Di Uranate) is then precipitated as a solid by adding ammonia to the solution. The ADU is despatched in slurry form by road tanker to Nuclear Fuels Corporation of South Africa.



Sulphuric acid plant

The leached pyrite concentrate is pumped to the sulphuric acid plant from the uranium plant. It is then fed into the roasters where in the presence of air the sulphur burns to form sulphur dioxide, and a residue called calcine. The sulphur dioxide gas is cleaned, cooled and dried and then reacts with oxygen in the presence of a catalyst to form sulphur trioxide, which is dissolved in strong (99%) sulphuric acid, and its concentration is maintained at this level by the addition of water. The hot calcine residue, containing gold, is discharged from the roaster, cooled and after mixing with water, pumped to a calcine thickener. The overflow is reclaimed and pumped to the flotation plant, and the calcine underflow is sent to the gold plant.

OPERATION EAST RAND PROPRIETORY MINES LTD.
BOKSBURG, TRANSVAAL

GROUP RAND MINES (MINING & SERVICES) LTD.
P. O. BOX 62370
MARSHALLTOWN 2107

TELEPHONE (011) 833-0611

CONTACTS Johann Wagner Consulting Civil Engineer

INTRODUCTION

The ERPM Mine is an underground drainage point for the mines on the east Rand from which water is pumped to the surface at 64,600 m^3/d (average).

Since 1970 ERPM has operated a large high density sludge process, designed under license from the Bethlehem Steel Corp., which does an excellent job of removing iron and adjusting pH while yielding manageable volumes of sludge.

During the 1982-4 drought an immense amount of attention has focused on South Africa's water supply situation and it has been concluded that non-precipitatable dissolved solids in the regional water supply will continue to rise unless something is done to limit the amounts that flow into the Vaal Dam with drainage from the area. A major study for the Water Research Commission by a local firm of civil engineers, Stewart Sviridon & Oliver, concluded that about one third of the point source TDS in effluents was derived from mining and milling in only 12% of the volume of effluent. These point sources accounted for 129,000 tons per year of dissolved solids in 43 million m^3/year of effluent with an average TDS of 3000 ppm.

Based on the above data, the Department of the Environment has started to exert government pressure on mines that discharge effluent into the Vaal catchment, to find ways to reduce the dissolved solids level of their effluents. In a joint test program funded by the Chamber of Mines of South Africa, the Water Research Commission and Rand Mines Ltd., several desalination processes have been evaluated and tested at ERPM. These tests were still in pilot stages during the RANDOL visit to South Africa in March, 1984.

The results of the pilot tests were considered confidential at that stage, however several observations could be made. Details of the HDS treatment were assembled from several published sources including VAN STADEN (1979).

WATER VOLUME

ERPM used to pump 6,800 m^3/d to the surface which was neutralized conventionally to achieve about 4 g/l solids in the underflow density. When a number of mines in an area measuring 40 Km E-W and 10 Km N-S stopped operating, the underground flow of water to ERPM increased to about 50,000 m^3/d. ERPM collected this water at the 29 level by plugging shafts etc. preventing it from reaching lower workings. Th s enabled the water to be pumped to the surface by single stage pumping.

UNDERGROUND NEUTRALIZATION

Underground neutralization of acid mine drainage collected in the mineworkings is necessary to prevent excessive corrosion of equipment and to meet legal requirements prior to disposal. This application was said to be a major part of the total lime consumption in the South African Mining Industry. Acid mine drainage is neutralized to pH5-5.5 underground before being pumped to the surface.

HIGH DENSITY SLUDGE PROCESS

After neutralization to pH 5-5.5 underground, the water is pumped to the surface where it must be aerated to oxidize ferrous ions to ferric. The treated water flows to a settler in the conventional process, to settle $Fe(OH)_3$.

In the conventional process, the 45,000 m^3/d water with 5000 precipitatable solids would generate 250 tpd solids. At a sludge density of only 4% solids, this would generate 6250 m^3d sludge. The logical way to dispose of this would be by mixing it with the gold plant tailings pulp for disposal to the tailings dam. The maximum that could be disposed of in this way was 2727 m^3/d.

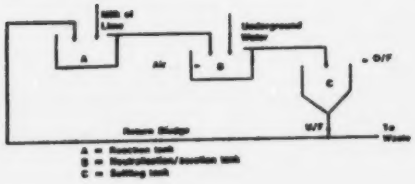
The HDS process, developed by Bethlehem Steel, proved to be a practical solution to the problem by producing a high density sludge with a correspondingly lower volume to be disposed of.

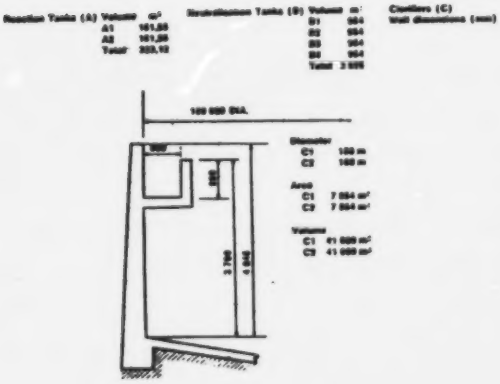
An important aspect of the HDS process is the recirculation of a large percentage of the sludge which is mixed with lime and then mixed back into new feed water. Precipitation of metals takes place in layers which yield large particles in a dense sludge. One aspect of concern initially was whether the preneutralization of water underground to pH 5-5.5 would interfere with the HDS process - it did not.

UNDERGROUND NEUTRALIZATION

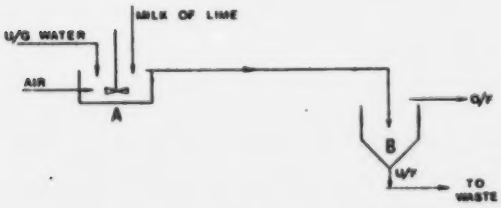
Four stainless steel pipes feed water from the plug in the shaft to a common mixing chamber. Lime slurry is added by gravity to pre-neutralize the water to pH5-5.5. Very little iron is precipitated at this stage. Four pumps move the preneutralized water from

H.D.S. FLOW DIAGRAM





CONVENTIONAL LIME NEUTRALISATION METHOD



A = NEUTRALISATION / AERATION TANK
B = SETTLING TANK

Source: VAN STADEN (1979)

the mixing chamber via two 356 mm Ø mild steel pipes to the surface. Each pump is driven by a 4000 KW motor and can pump 17,000 m^3/d against the 1050 m^3 head. In each case two pumps serve one of the two vertical lines.

HDS Plant Description

On the surface two mixing tanks A and four aeration tanks B were designed to treat a total flow of 90,000 m^3/d providing a 100% standby capacity.

Two clarifiers C were designed from settling curve data. Considerable flow flexibility is built into the design.

Ground, unslaked lime (-2 mm) is supplied by the Northern Lime Co. Ltd. from a plant at Lime Acres, Cape Province. Lime is delivered in rail tankcars and is pneumatically off-loaded into seven storage and one feed silo. Each silo has a capacity of 200 t.

Lime is slaked in two Omega slakers installed in parallel to give a milk of lime with SG=1.05 equivalent to 5 g CaO per 100 g suspension. The milk of lime is passed through a settler to eliminate coarse particles which may be carried over from the slakers and which would damage the multi-stage pumps underground. Settler overflow is piped underground for pre-neutralization.

The lime settler underflow is pumped to the HDS plant. About 10% of the total lime consumption is used for pre-neutralization underground, the remainder being consumed in the HDS plant.

Water level behind the plug in the shaft is monitored by measuring the water pressure and the pumping rate is varied accordingly.

HDS PLANT PERFORMANCE

According to VAN STADEN (1979) sludge densities as high as 50g solids per 100 ml are readily obtainable. By 1979 the plant had operated at an average rate of 34,000 m^3/d, the rate being determined by the amount of water that needed to be pumped from underground.

WATER QUALITY

	Underground Minewater	HDS Product	HDS Sludge
pH	3.6	7.3	
Fe^{2+}	650	Nil ppm	
Fe^{3+}	30	Nil ppm	
TDS	7,500	5,600 ppm	
Solids	(1) 1,650	(2) 15 ppm	Up to 50g/100ml

(1) Precipitable Solids
(2) Suspended Solids

CAPITAL COST (1975 data)

Surface facilities	R3.2 million
Underground	R1.9 million
Plug in Shaft	R0.5 million
Total	R5.6 million

Additional discussion of the HDS plant at ERPM is provided in the chapter on Acid Mine Drainage Treatment. Until March 24, 1984 Rand Mines was bound by a secrecy agreement with Bethlehem Steel Corp.

More information on the ERPM HDS installation could now be requested via Mr. Johann Wagner at Rand Mines.

More information on the application of HDS for which there have been further more recent improvements can be obtained from:

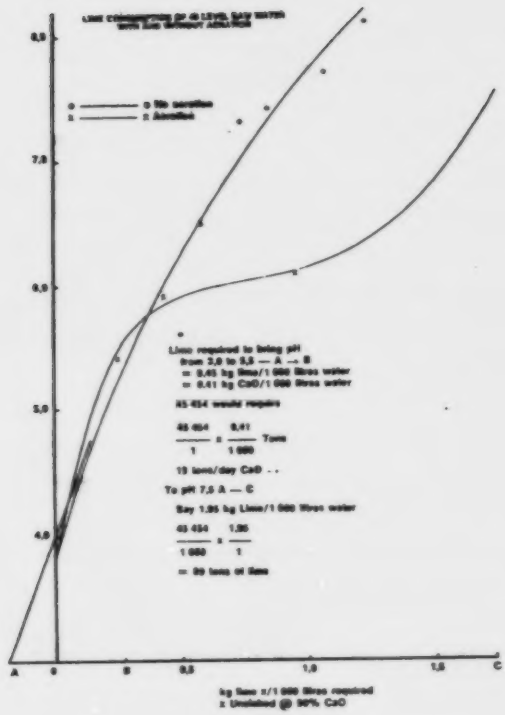
Bethlehem International Engineering Corp.
Bethlehem, PA 18106

Telephone: (215) 694-2424
Contact: Jim Forand, Vice President
Stewart T. Herman

LIME CONSUMPTION

VAN STADEN (1979) showed the following curve of lime consumption in Kg lime per m^3 of underground water versus pH to which the water is neutralized which shows that lime requirement to bring the AMD from pH 3.0 to 5.5 for 45,000 m^3/d is 19 tons/d CaO compared with 89 t to bring the pH from 3.0 to 7.5.

Consideration could be given to testing a pre-aeration step of the partially neutralized water pumped from underground to remove CO_2 before adding more lime in the surface



Source: VAN STADEN (1979)

HDS plant, which could possibly result in a lime savings at ERPM, depending on the level of bicarbonate in the water pumped from underground.

DESALINATION TEST PROGRAM

One of the difficulties in desalinating water with high gypsum levels in solution is that as water is recovered, the levels of TDS in the concentrate build up until gypsum and other species precipitate and foul the membrane or evaporating surface, depending on the desalination process employed.

At the Hercules shaft of ERPM a pilot facility was established to develop and test several desalination approaches including Electrodialysis Reversal (EDR) and Seeded Slurry Reverse Osmosis (SRO).

At ERPM an EDR unit and an SRO unit are installed side by side. The EDR plant is compact, but there is a string of pretreatment processing steps ahead of it that are far from compact.

The SRO test system is very compact and requires no pretreatment steps.

SRO is without question a major technology breakthrough in desalination of brackish water - mainly because of its simplicity.

Comparative data for the two desalination systems will ultimately be published either by the Water Research Commission or by the South African Chamber of Mines.

EDR Test Plant

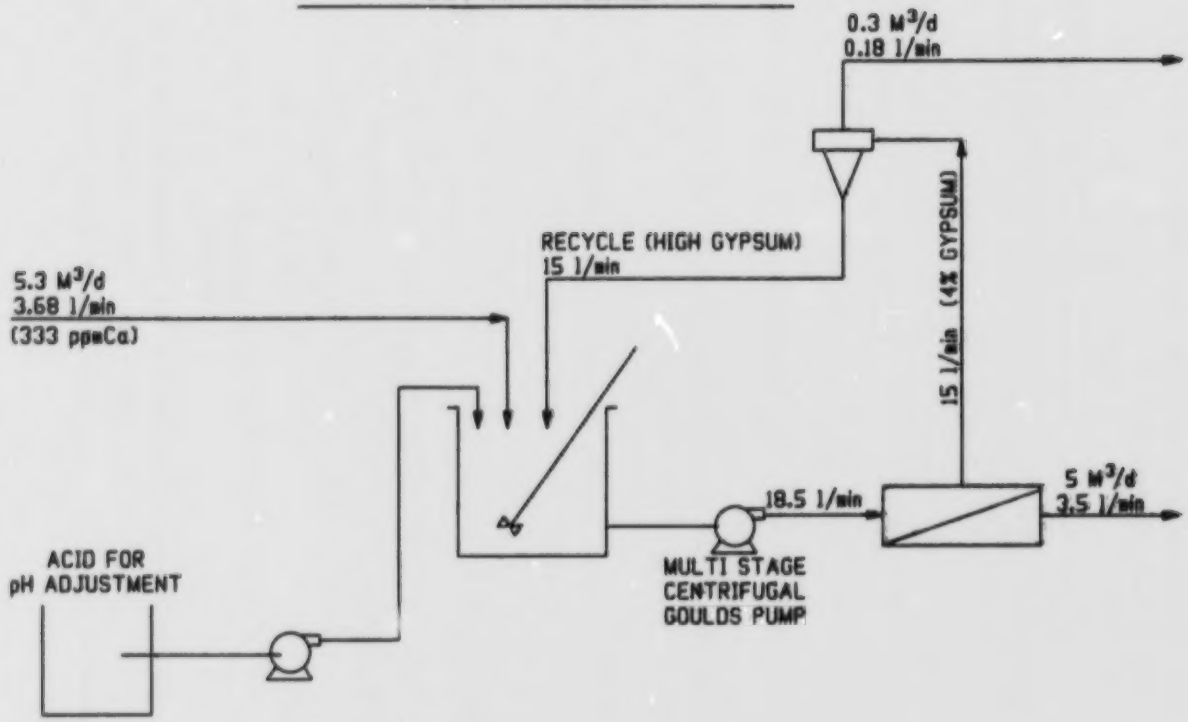
The EDR test unit with pretreatment was an IONICS unit installed by their South African representative:

Process Sytems (Pty) Ltd.
P. O. Box 10142
Johannesburg 2000

Telephone: (011) 802-4230
Contacts: Ralph Jones, Managing Director

Concentration of gypsum that can be tolerated in the reject from EDR is around 2 times saturation, e.g. around 4000 ppm. EDR vendors claim they can operate to 3½ times saturation levels but this must still be demonstrated as routinely applicable for general applications.

SEEDED SLURRY REVERSE OSMOSIS
TEST ARRANGEMENT



SRO Test Plant

The Seeded Slurry Reverse Osmosis plant was installed by RCCI:

Resources Conservation Company International
P. O. Box 47041
Parklands 2121
Telephone: (011) 788-5070

The SRO plant was designed to recover 5 m^3 desalinated water per day and to achieve a 95% recovery from gypsum bearing feedwater without any pretreatment. The R. O. module was installed in the arrangement illustrated below to allow for recycle of concentrate. The pilot unit was a single stage R. O. demonstration test.

A flow diagram for a conceptual 10,000 m^3/d seeded slurry R. O. system achieving 95% recovery is also shown below.

The seeded slurry R. O. system uses tubular R. O. modules. Currently these are available in units that yield 1 m^3/d of product. Consequently for a plant treating 10,000 m^3/d of feedwater, 10,000 R. O. modules would be required.

The R. O. modules installed in the test plant were operating at 4000 kPa or 600 psi.

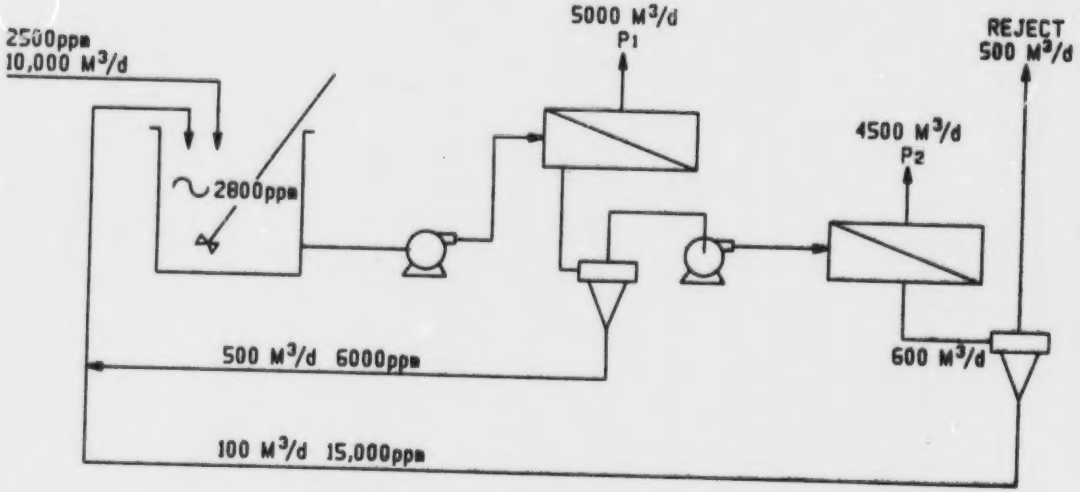
By employing a seeded slurry recycle concept, the applicability and water quality conditions have been shown to be dramatically extended, which allows for a greatly improved operating range. For example:

Operating Limits for R. O. Modules

Composition of Concentrate	Conventional R. O.	Seeded Slurry	
		Feed	Conc.
Mn	0.1 ppm max	8.4	69 ppm
Fe	0.1 ppm max	6.4	100 ppm
Al	low	280	
Heavy Metals	very low for metals that precipitate e.g. Co, Ni, Sr, Ba		
Sr	very low	40	
Ni	very low	8.0	
Co	very low	2.0	
Silica	160 ppm in reject	No limit	
$CaSO_4$ in reject	1.5-2 times solubility (around 3000 ppm)	No limit	

An interesting set of data was obtained for one application of SRO. It is believed that the data reflects acid mine drainage water treatment by SRO in a situation analagous to ERPM.

CONCEPTUAL SEEDED SLURRY
REVERSE OSMOSIS ARRANGEMENT



SEEDED SLURRY R. O. TEST DATA REFLECTING 93% RECOVERY FROM ACID MINE DRAINAGE CONTAINING GYPSUM

Sample labelled	Raw Mine Water	Recirculation Sump	Permeate
pH Value	4.00	4.50	5.00
Conductivity uS/cm at 25°C	2600	12,000	550
Suspended Solids Dried at 105°C	50	45,000	LT 1
Volatile Suspended Solids Ignited at 450°C	6		
Total Alkalinity ($CaCO_3$) to pH 4.5	Nil	Nil	2.0
pH 3.7	17.0	40 filtered	13.0
Total Hardness ($CaCO_3$)	1300.0	5500	70
Calcium (Ca)	350	450	10.0
Magnesium (Mg)	120	1000	10.0
Sodium (Na)	130	1500	60
Potassium (K)	15	60	4
Total Strontium (Sr)	3	40	0.1
Strontium in filtered (0.8 u) sample (Sr)		10	
Total Barium (Ba)	0.04	0.50	LT 0.02
Barium in filtered (0.9 u) sample (Ba)		LT 0.02	
Free Ammonia (N) (as received)	8.0	40	3.0
Nitrite Nitrogen (N)	0.10	0.08	0.10
Nitrate Nitrogen (N)	8.0	15.0	6.0
Chloride (Cl)	90	400	50
Fluoride (F)	1.0	8.0	LT 0.1
Sulphate (SO_4)	1600	8000	100
Total Phosphate (P)	0.2	0.8	0.1
ortho Phosphate (P)	LT 0.02	LT 0.02	LT 0.02
Reactive Silica (SiO_2)	40	90	10.0
Total Aluminium (Al)	25	300	0.5
Aluminium in filtered sample (Al)			
0.8 u	25	50	0.5
0.45 u	25	50	0.5
Total Iron (Fe)	6	100	0.06
Iron in filtered sample (Fe)			
0.8 u	0.25	0.7	LT 0.02
0.45 u	0.25	0.6	LT 0.02

ERPM

Sample labelled	Raw Mine Water	Recirculation Sump	Permeate
Total Manganese (Mn)	8.0	70	0.50
Manganese in filtered sample (Mn)			
0.8 u	8.0	70	0.50
0.45 u	8.0	70	0.50
Total Zinc (Zn)	2.0	18.0	0.10
Zinc in filtered sample (Zn)			
0.8 u	2.0	14.0	0.10
0.45 u	2.0	14.0	0.10
Total Lead (Pb)	0.1	1.2	LT 0.02
Lead in filtered sample (Pb)			
0.8 u	0.1	0.5	LT 0.02
0.45 u	0.1	0.5	LT 0.02
Total Copper (Cu)	0.3	3.04	LT 0.01
Copper in filtered sample (Cu)			
0.8 u	0.3	0.8	LT 0.01
0.45 u	0.3	0.3	LT 0.01
Total Cobalt (Co)	2.0	17.0	0.10
Cobalt in filtered sample (Co)			
0.8 u	2.0	15	0.10
0.45 u	2.0	15	0.10
Total Chromium (Cr)	0.08	0.90	LT 0.02
Chromium in filtered sample (Cr)			
0.8 u	0.05	0.09	LT 0.02
0.45 u	0.04	0.07	LT 0.02
Total Nickel (Ni)	8.0	70	0.30
Nickel in filtered sample (Ni)			
0.8 u	8.0	50	0.30
0.45 u	8.0	50	0.30
Total Cadmium (Cd)	0.02	0.12	LT 0.005
Cadmium in filtered sample (Cd)			
0.8 u	0.02	0.06	LT 0.005
0.45 u	0.02	0.06	LT 0.005
Absorbance at 275 nm	0.05	0.246	0.011

Chemical results in mg/l

LT = Less than

Samples filtered through 0.45 microns unless otherwise specified.

Analysis of sump deposit material

A sample of the sump deposit slurry was filtered on a 0.45 u filter and the sediment dried at 105°C prior to analysis.

Loss on ignition - % loss on drying to 180°C		5.00
	180 - 450°C	2.00
	450 - 600°C	3.00
	600 - 1000°C	2.00

Acid insoluble (siliceous material) 5.00%

Analysis of dried materials in mg/kg

Copper (Cu)	30
Iron (Fe)	2300
Manganese (Mn)	20
Cobalt (Co)	30
Chromium Cr)	30
Cadmium (Cd)	2
Nickel (Ni)	200
Lead (Pb)	30
Zinc (Zn)	30
Aluminium (Al)	6200
Barium (Ba)	200
Strontium (Sr)	750
Calcium (Ca)	250,000
Magnesium (Mg)	500
Sulphate (SO_4)	550,000

The 5 R. O. modules installed in series at the ERPM seeded slurry desalination test plant were supplied by a South African firm:

Bakke Industries (Pty) Ltd.
P. O. Box 344
Paarl, Cape
South Africa

Telephone: (02211) 23031
Contacts: D. B. Smit
Johan Barnard

More information can be obtained on the results of other seeded Reverse Osmosis tests that have been performed from the patent holders of the concept.

Resources Conservation Company
3101 NE Northrup Way
Bellevue, WA 98004

Telephone: (206) 824-2400
Telex: 350166 RCC SEA
Contacts: Russell Vandenberg
Tom Wolfe
Reams Goodloe

DISCUSSION SRO

1. Seeded slurry R. O. as demonstrated by RCC represents a major breakthrough in desalination technology in that membrane fouling is avoided even when recovery is increased to a point where the concentration levels of species in the reject rise to many times saturation which would result in fouling in the conventional application of R. O.

2. Slurry seed is kept in the dihydrate gypsum form for recycling. This is controlled by temperature.

3. A second major advantage of seeded slurry R. O. is that the compact concentrate slurry has a high solids content, i.e., it is compact and less costly to dispose of safely. One way would be to take the SRO reject and recover more water by evaporation resulting in a dry solid waste for disposal. Another would be to mix the reject with a pozzolin to make a pozzolinic dry waste for landfill disposal. Typical pozzolins would be cement, or power plant flyash.

4. In the recycle flow the concentration of calcium reaches about 440 ppm which is not much more than the level of 330 ppm Ca in the feed solution. This is because calcium is removed from solution by the seed crystals.

5. Silica and alumina levels are also effectively controlled by the seed slurry. A typical slurry seed contains 5% SiO_2. Levels of trace elements; e.g., Co, Ni, Zn, etc. are all very effectively reduced as well in the permeate.

6. Because the seed slurry contains solids, it would be expected that there could be abrasion damage to the membrane surfaces. This does not, however, appear to occur.

7. Abrasion of pump impellers etc. could be expected but has not been apparent. In the ERPM test unit, however, some abrasion of the choke valve at the end of the pressure system is believed to have occurred. In a full scale system a different pressure maintaining system would be used: e.g., an orifice plate. It is not known to what extent abrasion will be a problem here.

8. It is expected and hoped that the ERPM tests will proceed using larger scale plants and that their data and experience will be released to industry for general use.

Others involved in the desalination test program joint effort include:

Chamber of Mines Research Laboratories
P. O. Box 91230
Auckland Park 2006
(011) 726-3020

Contact: Dr. Brian Protheroe
Dr. Don Hebden, Project Coordinator

Water Research Commission
P. O. Box 824
Pretoria 0001
South Africa

Telephone: (012) 28-5461
Telex: 30464 SA
Contact: Dr. M. E. Henzon, Chairman
Piet E. Odendaal, Senior Advisor

REFERENCE

VAN STADEN, C. M. (1979) How ERPM uses Lime to Solve Unique Underground Water Problem. Coal, Gold and Base Metals of South Africa, May 1979, pp. 100-110.

OPERATION GIANT MINE
CHEGUTU
ZIMBABWE

COMPANY Cambrai Mining Company
P. O. Box HG 499
Highlands
Harare
Zimbabwe

TELEPHONE Harare 460884

CONTACT Ron I. Edington Managing Director

INTRODUCTION

Cambrai Mining Company has attempted to recover gold from an old tailings dump from a former operation that recovered gold in a sulfide flotation concentrate.

Based on promising laboratory tests (presumably using tapwater from Harare) a CIP plant was installed. Results have been extremely disappointing. Although a reasonable percentage of the gold could be cyanide leached, recovery by carbon adsorption has been very poor (25-60%).

This description of results from the plant and in various laboratory experiments shows the following:

1) The complex nature of the gold leaching and CIP adsorption problems. When a process does not perform well, finding the reasons means considering a very wide range of parameters.

2) Water quality effects either because of the quality of available water or because of oxidation products in the sulfide containing feed material appear to be adversely affecting gold adsorption onto activated carbon.

3) The need to test a CIP process on pilot scale using the same water and conditions as planned for commercial scale is indicated.

LOCATION At Gadzema 112 kilometers south of Harare, 12 kilometers west of Harare

RESERVES AND GRADE 928,000 tons of tailings overall
528,000 tons have a grade of 1.4 g Au/t
400,000 tons at a grade of 0.7 g Au/t

RECOVERY Laboratory tests showed that 80% of the 1.4 g in the 528,000 ton section of dump could be cyanide leached in 5.5 hours.

NATURE OF MATERIAL

The Giant tailings have an average SG of 3.1 (dry) and the material contains up to 30% pyrrhotite. Sizing is

4%	+	450 microns
66%	-	450 microns + 44 microns
30%	-	40 microns

PROCESS DESCRIPTION

The dump surface is cemented and has to be ripped and dozed prior to hydraulicing with home-made monitor pumps. The dump material is very acid and the pH of water source being 7, NaOH is added to the main reservoir to raise the pH of water used for hydraulicing to 10.

From a water management standpoint an interesting method of controlling pulp density is employed. This is done by changing the number of monitors in operation at any one time (More monitors reduce pulp density) and by changing the aperture of the water cannon nozzles (these are glass bottle necks). Changing nozzle sizes makes it possible to change water volume and pressures. 1 to 3 water cannons operate at any one time delivering 24 - 30 m^3 water per hour.

The pulp is run along launders, puddled by mechanical puddlers to break clods and then screened over a polyurethane sievebend to remove oversize grass and woodchips.

The minus 450 micron material passes through the sievebend and is discharged into the first 130 m^3 pre-aeration/conditioning tank into which 450 m^3/h air is sparged at 0.6 bars. pH is maintained at 9.5 by lime addition which requires about 10 Kg per ton feed. Pulp in the tank is agitated by a Flygt SR 4500 submersible mixer.

Pulp flows by gravity to the next 130 m^3 leach tank which is also agitated by a Flygt mixer. Cyanide as $Ca(CN)_2$ is added at the rate of 1.5 Kg/t of dry solids to maintain a cyanide strength of 0.03% - 0.04% in solution. Pulp is pumped by Warman rubber lined pump to the first of three 30 m^3 CIP adsorption tanks which are mechanically agitated and 6 x 8 m^3 air agitated CIP tanks and finally over a sievebend to scavenge abraded carbon particles before being pumped to tailings.

Carbon is loaded to 1200-4450 g Au/t depending on carbon fouling. Loaded carbon is acid washed in hot 5% HCl solution for 10-15 minutes to get rid of sulfates and carbonates prior to elution, then tabled to remove coarse grit and to rinse acid, before being placed in perforated containers to drain prior to elution.

1,250 Kg carbon is eluted at a time in a 2500 l mild steel vessel with 3% NaCN, 2% NaOH and 15% ethanol eluant at 65°C pumped via the bottom of the elution column. Pregnant eluate overflows to the electrowinning cell where gold and silver are recovered allowing for 80% recovery per pass. Eluant solution is pumped at 500 l/hour to give a bed volume every 3.5 hours through the carbon. After 60 hours the solution head value drops from 155 g Au/t to 8 g Au/t at which point a further 10% ethanol is added to the eluate which strips a further 200 g Au/t from the carbon over another 60 hours. 1,250 Kg of carbon are eluted in 5 days reducing gold loading from 1200 g to 60-150 g Au/t.

Eluate flows by gravity at 250 l/h through two rows of three plastic electrowinning cells in parallel. Cells are 250 mm wide, 600 mm long and 100 mm deep. 500 g wire wool is layered loosely onto a stainless steel sheet which serves as the cathode. The steel wool cathode is separated from the 3 mm thick stainless steel anode by a 3 mm thick plastic sheet insulator. Current is maintained at 4 V and 20 amps per cell. Steel wool cathodes are treated with 33% HCl then water washed to get rid of iron solution, oven dried, fluxed and smelted.

PROBLEMS ENCOUNTERED

1) The high pyrrhotite content consumes large amounts of oxygen.

2) Fouling of the carbon by sulfates, carbonates and clays seems to inhibit gold adsorption on the carbon.

3) Gold losses to CIP tails increased steadily from 0.15 to 0.4 g Au/t gold in tailings, at which point the CIP operation was suspended.

WATER QUALITY CONSIDERATIONS

Several factors could cause the metallurgical problems experienced:

1. The tailings dump material contains up to 30% pyrrhotite. A typical sample of dump assayed as follows:

Sb	0.14%
Pb	0.04%
As	0.19%
Bi	0.01%

Ni	0.04%
Cu	0.04%
Zn	0.05%
Au	1.6 g/t
Ag	1.8 g/t

The dump also contains weathered mica which is high in soluble magnesium.

2. During aeration of the pulp considerable amounts of calcium and magnesium go into solution. RANDOL questions whether a one-stage pre-aeration tank will be adequate expecially when installed on a flow through overflow basis. Short circuiting will let enough unreacted pyrrhotite through to cause metallurgical problems. These would be expected to inhibit cyanide leaching of gold to consume excessive amounts of cyanide. It is therefore surprising that 0.03-0.04% KCN can be maintained by addition of only 1.5 Kg KCN/t (added as $Ca(CN)_2$), one would have expected a higher cyanide consumption if there was a significant level of pyrrhotite in the feed. Even if all the pyrrhotite was oxidized to sulfate and ferric ions, cyanide would be tied up as ferric cyanate complex.

3. When loaded carbon is acid washed, it fizzes. This indicates that at least some of the scale on the carbon is carbonate. Where does this carbonate come from? Possibilities are :

   - $CO_3^{=}$ could be introduced as HCO_3^- in the water used which is drawn from an old mineshaft, at pH 7.0.

   - The sulfide-rich tailings contain nutrients for bacteria and clearly there is bacterial oxidation of sulfides taking place in the dump. It is possible that CO_2 is generated as a byproduct which is absorbed into moisture in the tailings material. Carbon source could also be flotation reagent degradation products or sewage dumped with the tailings when they were first laid down.

4. Water analysis for the Giant Mine Shaft water is compared with that for the Sherwood Starn project. The Sherwood Starn operation had no difficulty loading gold onto carbon, yet the Giant project experienced very poor loading.

		Giant Mineshaft Water	Sherwood Starn Water	Giant Pulp Solution
Total Hardness	(as $CaCO_3$)	1872	1740	6000
Calcium	(as $CaCO_3$)	486	792	2080
Magnesium	(as $CaCO_3$)	1386	-	3920
P Alkalinity	(as $CaCO_3$)	0	0	0
M Alkalinity	(as $CaCO_3$)	364	426	48
Chloride as Cl^-		24.5	22.5	34.0
TDS		2050	1900	7000
pH		7.1	7.5	7.7
Fe (ppm)		Nil	1.6	-
Silica		26.1	28.7	1.25

From the above analyses it is clear that a large amount of calcium and magnesium is added to the pulp solution due to contact with the feed material.

5. In another analysis of tailings from the pulp after CIP no calcium was found in solution which was construed to mean that the calcium was adsorbed onto the carbon.

6. In a test where soda ash was used to adjust pH pulp samples before and after carbon adsorption indicated that no calcium was adsorbed on the carbon. How this affected gold adsorption is not known although it is assumed that this did not solve the problem either, or else the plant would not have shut down.

7. The dump material varies in color from pale to red-yellow, brown to purple indicating significant amounts of iron in various degrees of oxidation.

8. Tests of the slimes dam material showed that cyanidation of gold in the magnetic fraction was much higher than in the non-magnetic. Adsorption of gold onto carbon from the non-magnetic fraction is poorest. Adsorption from the magnetic fraction can be improved significantly if it is roasted before leaching.

	Extraction to Cyanide Solution %	Adsorption to Carbon %	Overall Gold Recovery
Magnetics	73.2	41.7	30.6
Non-Magnetics	31.5	15.7	4.9
Roasted Magnetics	74.8	89.6	67.0

The poor adsorption from the non-magnetic fraction has been interpreted as due to adsorption of clay-like particles on the carbon which block the pores.

9. Solutions from the cyanided pulp in the tailings dam carry a considerable amount of a suspension of Prussian Blue. Prussian Blue is a complex of ferric and ferrous cyanide indicating that ferrous ions in the pulp were inadequately oxidized. This indicates that the pre-aeration step is inadequate. It is possible that some of the partly oxidized pyrrhotite in the tailings may take a long time to oxidize as the tailings contain a considerable quantity of coarse particles which could take longer to oxidize.

   Prussian blue adsorbs readily onto carbon and could well be responsible for blinding of the carbon and interfering with gold adsorption.

   It is not completely clear what can be done to remove Prussian blue from the pulp once it has formed. Very thorough oxidation of the pulp is one way to prevent its formation in the first place.

   The suggestion has been made to remove the magnetic pyrrhotite from the pulp for separate treatment to oxidize it ahead of cyanidation, possible by allowing it to weather outdoors.

10. In cyanide leach - CIP tests it was found in one test that about 900 g Mg^{2+} per ton solids went into solution and adsorbed onto carbon. Calcium dissolution from the solids amounted to 750 g CA^{2+}/t before the carbon adsorption and 1500 Ca^{2+}/t in CIP tails.

    It appears that under certain conditions magnesium and calcium in the pulp will cause carbon fouling.

11. Gold can be more efficiently precipitated by zinc than adsorbed onto carbon from solutions derived from this pulp. Reasons for this are not completely clear. Since the tailings contain a large percentage of very fine slimes, filtration is unlikely to be feasible - CCD solid-liquid separation followed by zinc precipitation is one possible solution to the problems observed above.

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	Ken Blower	Manager
	Tim Riordon	General Superintendent
	Kent Morton	Mill Superintendent
	Bryan Cross	Environmental Technologist
	Gary Halverson	Mill Metallurgist
	Al Hall	Plant Foreman
GROUP	FALCONBRIDGE LTD. Box 40, Commerce Court West Toronto Canada M5L 1B4	
TELEPHONE	(416) 863-7000	
TELEX	065-24211	
CONTACTS	Frank Pickard	VP Metallurgy & Research (416) 863-7030
	Simon O. Fekete	Chief Metallurgical Engineer (416) 863-7216
	Lynn S. Price	Environmental Advisor

INTRODUCTION

Giant Yellowknife Mines Ltd. is located 62° north of the equator - just 5° south of the Arctic Circle on the northern shore of the Great Slave Lake on the outskirts of Yellowknife. Its remote location and long frozen winters are two interesting features of this gold mining operation. Giant Yellowknife Mines started this operation in 1948 and is of interest from both a gold recovery standpoint and for several aspects of how water is managed and treated in this sparse but sensitive part of the world. Because this mine has taught the industry so much about roasting and leaching of calcines from arsenopyrite concentrates it is valuable to examine the operation in as much detail as possible.

GOLD RECOVERY FEATURES

- Treatment of a low grade refractory arsenical gold ore.
- The use of roasting. Much of today's state of the art on roasting auriferous concentrates was developed at this operation. Efficient removal of arsenic from roaster gas stream is achieved.
- Gold recovery from calcines at Giant is higher than average at 92-94%. The latest leaching and solid liquid separation of the calcine is particularly interesting. It combines CCD washing with belt filtration.
- Gold recovery from precipitator dust by carbon-in-leach.
- Incremental gold recovery from the treated effluent discharge stream.
- The very low arsenic release to the environment now achieved at Giant Yellowknife would support the idea that roasting should not be ruled out in North America if a market for the sulfuric acid or SO_2 can be found.

WATER MANAGEMENT & TREATMENT

- Managing water and effluent treatment in a location where everything is frozen for over half the year.
- Removal of arsenic, base metals and destruction of cyanide in the effluent stream.
- Incremental gold recovery integrated with effluent treatment for environmental reasons.

DATE OF VISIT 7 - 8 August 1984

LOCATION 600 air miles north of Edmonton, Alberta

MINE The underground C mine and an open pit (40%) produce 1215 st ore per day for five days per week.

GRADE 0.24 oz Au/st (5.6 g Au/t) is nowadays much lower than the original operation which as long ago as 1963 processed 0.78 oz Au/t.

OVERALL RECOVERY 84 percent

ORE TYPE

Giant ore consists of sericite and chlorite schist containing a high level of free quartz, variable amounts of calcium and iron carbonates and sulfides - mainly fine-grained arsenopyrite and pyrite, with smaller amounts of stibnite, and sulfosalts of lead, iron and copper. The gold is very finely divided. Flotation concentrates would give about 30% gold recovery if leached without prior roasting.

ORE TREATMENT

Ore is crushed and ground in ball mills. Grinding is in closed circuit and after primary flotation is followed by a regrind of the tailings and a secondary flotation followed by a scavenging step. Cyanidation of tailings was discontinued years ago. 80% of the gold is recovered by a primary flotation step employing a Maxwell cell. The aim is to produce a reasonably coarse flotation concentrate at a satisfactory sulfide level while getting the best gold recovery. Overall flotation recovery is 92% down from 94%. 2-4% more gold could be recovered but not if the required 18% sulfide grade for roasting is to be maintained.

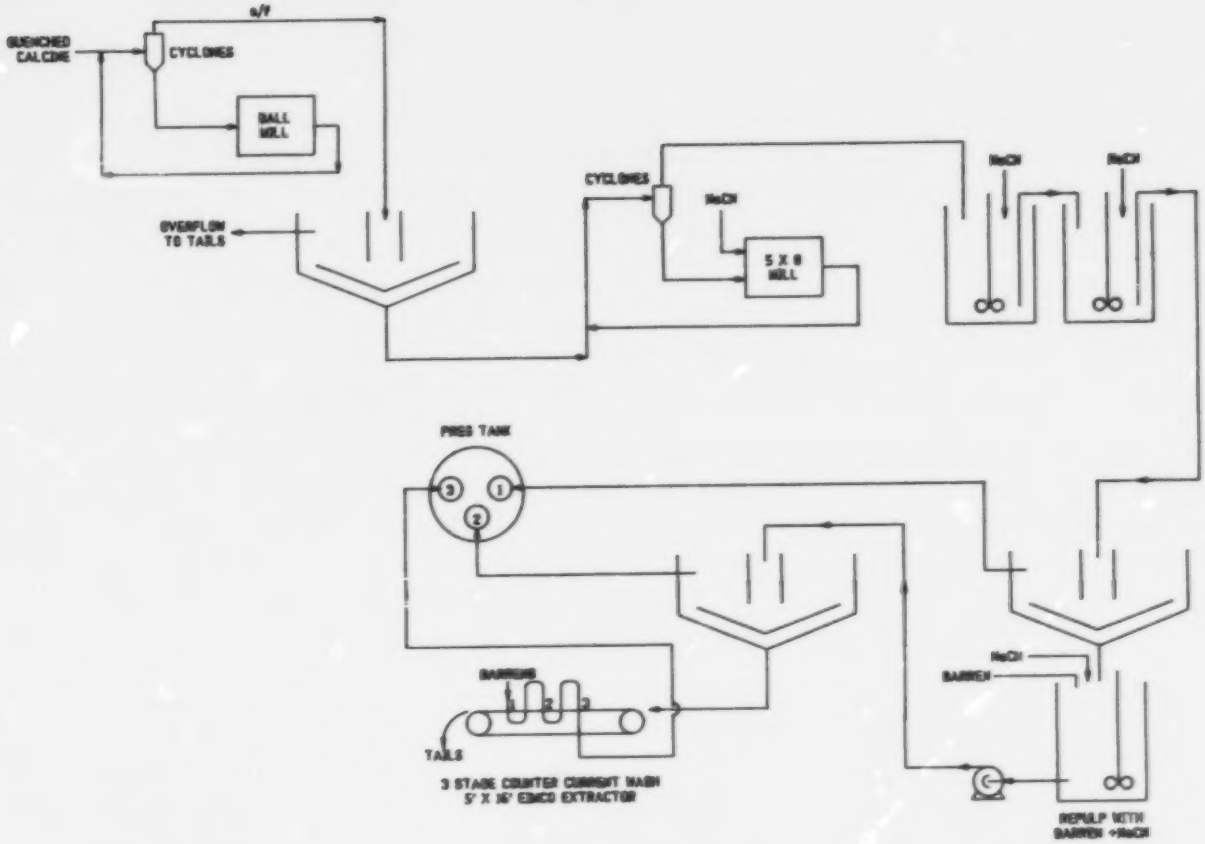
CONCENTRATE PROCESSING

About 106 st per day of concentrate at slightly below 2 oz Au/t are produced. After thickening and filtering these are blended and fed to a two-stage fluid bed roaster designed and installed by Dorr Oliver. Calcine and the coarsest dust particles are captured by cyclones from the roaster gases, quenched, reground then washed once in a thickener to remove soluble arsenic and metals, prior to leaching in cyanide after regrinding in a second 5'Ø 8' ballmill where initial cyanide and lime additions are made. According to MORTIMER & TAIT (1959) the earlier operation cyanided the flotation tailings and calcined the leached calcine for a second time in a rotary kiln, but these steps have been discontinued.

Currently a barren bleed of about 45-54% of the recirculating barren cyanide stream permits control of the undesirable buildup of copper and zinc in the calcine leach circuit. This barren bleed would have to be much greater were it not for the calcine washing step ahead of leaching.

There have been process changes since the plant was described by MORTIMER & TAIT (1959) and by FOSTER (1963). One of these is the calcine washing, leaching and flotation circuit which is now arranged as follows.

GIANT YELLOWKNIFE MINES LTD.
CALCINE LEACHING



Leached calcine still contains around 0.15 oz Au/t and represents a loss of about 15 oz Au/day. The calcine was reacted with concentrated sulfuric acid on rolls and in one test was reduced to 0.08 oz Au/t, after subsequent neutralization and cyanidation. This result however could not be duplicated in a follow up test nor when sulfurous acid was used. This incremental recovery is not considered economically attractive enough to justify additional investment.

GOLD METALLURGICAL LOSSES

MILL LOSSES

	DAY		MONTH		YEAR	
	TONS	Ounces	TONS	Ounces	TONS	Ounces
FLOTATION TAILS	1116.0	37.9	21471.6	567.3	44243.1	1092.3
CARBON TAILS SOLID	21.7	4.8	436.0	81.7	692.9	129.4
CARBON BARREN SOLN	39.2	0.3	802.0	12.0	1341.7	19.3
BAGHOUSE DUST	16.1	3.9	338.8	67.9	683.9	148.3
WASH THICK O/F	591.0	0.3	15365.7	24.4	32180.4	40.6
BARREN BLEED	626.5	0.3	13728.0	77.3	26068.4	122.4
CALCINE RESIDUE	86.9	11.3	2164.8	299.2	4283.3	554.6
CALCINE RES. SOLN	23.8	0.3	632.2	19.1	1495.5	42.8
TOTAL Ounces LOST		59.0		1149.0		2149.7

COST PARAMETERS The cost of reagents reflects the distant location of Giant and the impact of expensive freight costs.

LIME : C$241.80/st C$0.121/lb delivered

CYANIDE : C$0.86/lb NaCN delivered

CARBON : C$1.68/lb Coconut carbon from Calgon

MILL SOLUTION BALANCE - CALCINE LEACH
(2 August 1984)

Product		Tonnage	Au Assay	Au(oz)	% Distrib
Calcine Wash Thickener o/f	527.382	0.0016	0.844	0.46	
Calcine Wash Thickener u/f	89.153	2.060	183.65	99.54	
Assayed Roaster Calcine	89.153	-	184.49	100.00	
Preg Solution	981.000	0.1400	137.340	98.88	
Calcine Residue	89.153	0.1200	10.698	7.16	
Calcine Residue Solution	31.487	0.0107	0.337	0.23	
Barren Soln.	283.650	0.0009	0.255	0.17	
Calculated Roaster Calcine	89.153	1.6766	149.474	100.00	
Press Ounces Gold Recovered			136.457		

Cyanide Extraction Efficiency Calculated by	Solution Vol	94.17%
	Month to date	93.98%
Cyanide Extraction Efficiency Calculated by	Solids Balance	93.85%
	Month to date	93.67%
Average Gold Extraction Efficiency		94.01%

Cummulative Monthly Balance (for 1st 2 days of August 1984)

Product	Tonnage	Au Assay	Au(oz)	% Distrib
Calcine Wash Thickener o/f	1,036.500	0.0018	1.862	0.50
Calcine Wash Thickener u/f	177.095	2.0750	367.454	99.50

MILL SOLUTION BALANCE - CALCINE LEACH (cont.)

(2 August 1984)

Product	Tonnage	Au Assay	Au(oz)	% Distrib
Assay Roaster Calcine	177.095	-	369.316	100.00
Preg Solution	1,857.000	0.1510	279.252	91.75
Calcine Residue	177.095	0.1250	22.131	7.27
Calcine Residue Solution	61.272	0.0103	0.632	0.21
Barren Solution	576.200	0.0009	0.489	0.16
	177.095	1.7189	304.366	100.00

CALCINE LEACH RECOVERY : 92-94%

ROASTING

Giant Yellowknife Mines achieves an excellent gold recovery from a refractory concentrate containing arsenic and antimony. Roasting practice reflects decades of effort to optimize recovery of gold. Roasting at Yellowknife has been described by MORTIMER & TAIT (1959), FOSTER (1963), CONNELL & CROSS (1981) and in general by ROSTRON (1982) three of which were included in the Randol Phase II study on "Innovations in Gold and Silver Recovery." The CONNELL & CROSS (1981) description is inserted at the end of this report.

Nevertheless, several observations were made which reflect Giant operating practice which could be of practical value: Factors of importance seem to be:

1. Feed Control
2. Roaster Condition Monitoring & Control
3. Gas Cleaning System

1) ROASTER FEED CONTROL

Maintaining Feed Uniformity

Flotation concentrate is transferred as a slurry and is screened to remove debris across a chip screen on arrival at the roaster section. Screen underflow is cycloned in an 8"Ø cyclone primarily as a dewatering measure. The overflow from the cyclone is clarified and the thickener overflow returned to the flotation plant.

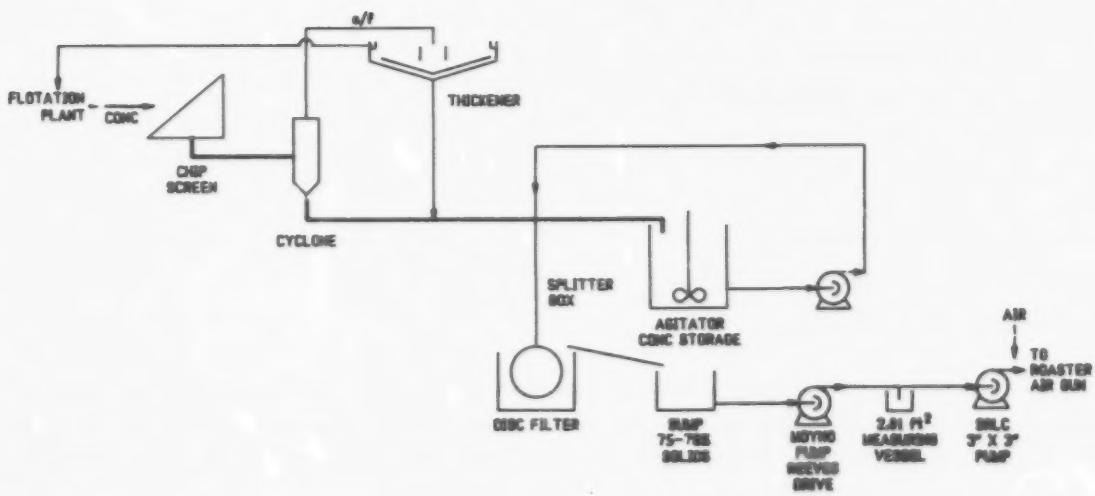
Cyclone underflow and the thickener underflow are combined and split in a splitter box into three streams. The major stream goes to a concentrate storage agitator where it is constantly mixed. One stream is filtered across a disc filter and the cake pumped by a Moyno Pump (Reeves-drive) at 75-78% solids from the disc filter cake discharge to an SRL pump. The SRLC 3" x 3" rubber lined pump advances the concentrate slurry at a uniform rate to the airgun injectors to the roaster No. 1 bed.

The flow of concentrate feed to the roaster is regularly measured as the time in seconds it takes to fill a 2.01 ft^3 measuring vessel. Density is measured to compute the flow rate of concentrate feed. The feed rate in tons per hour is read off a chart, recorded and adjusted. The specific gravity of the concentrate is 3.6 dry and around 2.2 for the 78% solids slurry. A third split of concentrate is fed with the filter discharge to the Moyno pump.

The purpose of the recirculating flow of concentrate through the storage agitator is to smooth out the temporary changes in concentrate grade particularly with respect to sulfur level. By drawing roaster feed from the recirculating flow, the feed is always well mixed and changes are slow.

In the flotation plant conditions are controlled to be sure to maintain 18% S in the concentrate. Slightly higher gold recovery in the flotation step could be achieved at the expense of sulfide grade which would result in greater losses in the roasting-calcine leach end of the process. Every attempt is made to keep antimony in the concentrate at 1% Sb or less.

GIANT YELLOWKNIFE MINES LTD
ROASTER FEED ARRANGEMENT



CONCENTRATE FEED PUMPS

The Moyno pump meters the flow of concentrate whereas the soft rubber lined 3 x 3 pump provides the velocity into the airgun to the roaster.

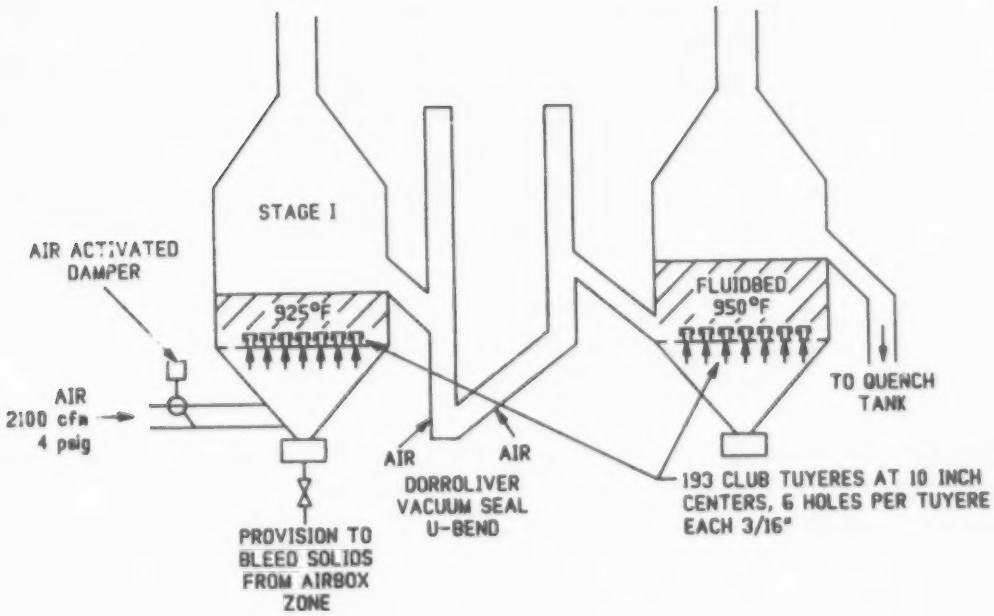
Giant has tried several pumps to feed concentrate into the roaster. The uniform pumping rate of the Moyno pump was found to be a very good feature.

ODS pumps (air-driven diaphram pumps) were tried out but flow surges caused problems in the roaster bed.

The SRLC pump inlet is fitted with a machined high density plastic insert to prevent the inlet from rapid abrasion. The 3" inlet pipe is lined by a 1" wall tube leaving a 1"Ø inner aperture which projects right up to the SRLC pump impeller. The liner life is 2 months and it is easily replaced compared with a life of 2 weeks for the steel inlet without it.

The feed concentrate is sprayed via the air lances into the freeboard above the roaster bed.

GIANT YELLOWKNIFE MINES LTD.
ROASTING CONDITIONS



Feed rate at the time of the Randol visit was 6.11 tph solids. Roaster conditions were recorded as follows:

Stage 1

Airflow 2150 cfm at 35°F at inlet and	936° F in the bed
Freeboard temperature	757° F
Water Spray to freeboard	0.4 lgpm
Transfer Air at 413°F	

Stage 2

Airflow to bed	900 cfm
Bed temperature (NE thermocouple)	956° F
Freeboard temperarature	866° F
Water Spray	2.8 lgpm
Windbox Pressure	4.10 psi
CALCINE QUENCH WATER	75 lgpm
Water pressure	64 psi
Baghouse temperature	225° F

Specified Standard Operating Conditions are:

Feed Rate	: 6.4 tph
Slurry density	: 2.250
1st Stage Temperature	: 925° F
1st Stage Air	: 2150 cfm
2nd Stage Temperature	: 950° F
2nd Stage Air	: 900° F

Bed Density Control

Should the bed start to clinker or become non-uniform in density, gas flow will be reduced in some parts and increased in others resulting in non-uniform roasting conditions and excessive particulate flowover.

Conditions in the bed can be monitored by comparing the temperature readings from four thermocouples installed one in each quadrant of the bed. The important aspect is the spread in readings at any given time.

These are recorded, and an example of the temperature range between the four quadrants in each bed on 8 August 1984 is shown here:

ROASTER BED TEMPERATURE

Time	Roaster Bed I (Range in 4 Readings)	Roaster Bed II (Range in 4 Readings)
8 am	927-940°F	951-956°F
10 am	925-936°F	938-941°F
12 am	922-935°F	940-944°F
2 pm	928-940°F	949-953°F

Calcine Transfer

Calcine from Stage I bed is transferred to the freeboard zone of Stage II fluid bed via a Dorr Oliver vacuum Seal U-bend shown in the diagram above.

Calcine Leach Recovery

Concentrate feed to the roaster is maintained as close as possible to 18% S to allow autogenous combustion.

Antimony must be kept as low as possible, exceeding 1% as seldom as possible to avoid roaster problems.

If the ore is ground too finely then the particles are prone to be blown out of the roaster without being roasted adequately.

The roaster is operated to avoid generating pentavalent arsenic in Stage I. Oxygen concentration is kept at around 0.2% in Stage I and 1.2% in Stage II to keep the arsenic in the trivalent form. It has been speculated that if pentavalent arsenic is generated in the first stage of roast it forms ferrous arsenate which does not volatilize.

The concentrate is roasted down to 3% sulfur. If roasted beyond this, the calcine turns from chocolate brown to black as more magnetite is formed, and gold recovery by cyanidation is reduced.

The roaster controlled by varying the air, concentrate feed rate and water addition (with concentrate and as control water added as air spray to the bed). Control used to visual by on the color of the calcine, but now it is also through observing bed temperatures. Independent temperature measurement in four quadrants of each roaster bed allow hot spots to be detected early and controlled.

Corrosiveness of Roaster Gas

A gold-platinum electrode which was installed in the fluegas for O_2 analysis completely volatilized in less than a day. This observation led to the as yet unanswered question as to whether some gold is lost by volatilization to the Cottrell dust.

3) GAS CLEANING

The roaster gas train serves two main purposes. Firstly, it recovers arsenic for safe storage underground with minimal release to the atmosphere. Secondly, the gas train recovers a significant value of recoverable gold.

30,000 cfm of hot roaster gases are released up the stack at about 200° F. Gas first passes through two hot cyclones to drop any coarse particles into the quench tank with the calcine.

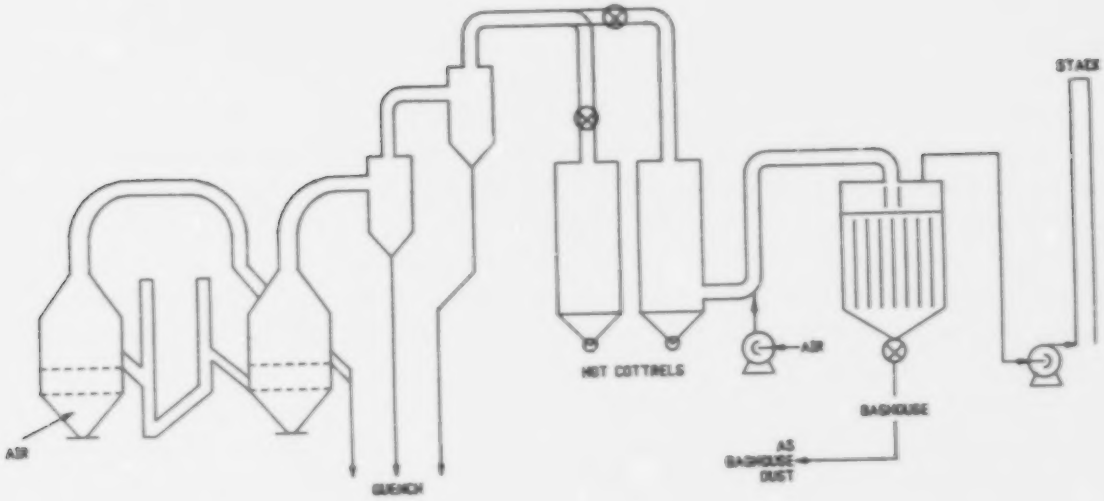
The gases next pass through a hot electrostatic precipitator at around 700°F at which solid particulates including gold values are dropped out. This yields about 14.5 tons per day of dust at an average of 1.21 oz Au/st, containing around 2.53% arsenic and 1.36% antimony, and thereby recovering over 90% of the gold that enters the roaster gas entrainment system. This requires careful control of the Cottrel precipitators, however.

After leaving the hot Cottrell electrostatic precipitator the gases are cooled by mixing with ambient air and at 220°F enter a baghouse where condensed arsenic trioxide is collected.

About 14 tons per day As_2O_3 is produced in this way, while only 10-20 lbs arsenic escape up the stack daily, most of the time. The arsenic dust is pneumatically transported to specially selected areas in the underground workings which are kept in permafrost condition and closed off by 12 ft concrete bulkheads from the other mine workings. The arsenic is transported to the disposal chambers via a 4"Ø feedline in and a 6"Ø return line.

The roaster gas entrainment system is driven by fans providing cooling air between the hot Cottrells and the baghouse, and by a fan at the base of the stack. SO_2 is nor removed from the roaster gases and is vented to the atmosphere. The method of condensing the arsenic dilutes the SO_2 strength to about 1%, well below the concentration of economic acid plant feed.

GIANT YELLOWKNIFE MINES LTD.
ROASTER GAS ENTRAINMENT SYSTEM



Synthetic polymer Draylon bags are used in the baghouse. The As_2O_3 recovered in the baghouse currently has an average 85-95% purity with occasional levels reaching 98% during periods of long steady state operation.

Arsenic emissions from the stack were found to occur mainly when the bags were being shaken. These emissions were dramatically reduced by converting the shake cycle from one that was timer controlled to one that was pressure drop activated. By setting a 2 inch water gauge pressure drop the bags are now shaken four times a day - a reduction from 16 cycles when the system was timer controled.

The arsenic oxide baghouse dust is transported to the permafrost stopes pneumatically using a Fuller-Kenyon pump.

Fuller Corporation
County Line Road
Bethlehem, PA

(215) 264-6011

A large truck-mounted vacuum cleaner for dust collection is maintained on the site for use in the event of a dust spill. Provision is made for the vacuum truck to unload to the arsenic storage bins.

COSTS

Labor base rate at Giant Yellowknife is C$16/hour. When workers are exposed to high arsenic areas they get paid 250% of their normal wage. However, they have available the latest protection equipment as this mine was the location for a National Task Force in Arsenic Exposure in 1976.

Because of the location most items are more expensive at Yellowknife than in the main industrial centers. For example lime costs C$241.80/ton or C$0.121/lb, and NaCN C$0.86/lb.

COTTRELL DUST TREATMENT

Cottrell dust is slurried, screened and leached with cyanide for about 6 days in the presence of carbon. Carbon-in-leach results in a better recovery than conventional leaching. The use of carbon is also necessary as the dusts are ultra-finely divided and neither settle nor filter well. This circuit recovers 85% of the gold contained in the Cottrell dust feed.

FOSTER (1963) showed that recovery of gold from this dust is sensitive to the type of alkali used and that with no alkali addition at all, gold recovery was actually the best but cyanide consumption went up to 53.5 lbs NaCN/ton.

The dusts are discharged from the Cottrell hoppers by screw conveyors into enclosed agitators, and pulped with water to 10% solids by weight before being pumped to a 30ft diameter storage thickener. The dust slurry has a pH of 5.0, is highly viscous and almost impossible to filter. It settles overnight to 50% solids however.

Each day a measured volume of pulp from the storage thickener is pumped to a conditioner where it is sampled for assaying and neutralized to pH 9.8 by addition of NaOH, Na_2CO_3 and Armac HT. After conditioning this goes to 2 (20'Ø x 25' h) agitators for pre-carbon cyanide-leaching for about 6 days. This has not significantly changed overall recovery.

An equal quantity of cyanided pulp is added to the first of two carbon in leach agitators in series which are operated on a batch basis. Residence in the CIL tanks is 72 hours.

Barren pulp is discarded from the second CIL tank after recovering carbon by screening which is returned to the leading CIL agitator. 120 lbs. fresh carbon is added daily to the tail agitator to scavenge gold from the pulp.

Discarded pulp contains 0.0002 oz/t Au (0.006g Au/t) in solution and 0.23 oz Au/t in the solids.

When carbon in the leading CIL agitator reaches the desired gold loading which normally occurs bi-monthly, it is removed by screening the pulp and washed to remove slime before being dried in a steam drier to 2 percent moisture for shipment to a smelter.

Parameters of the 1984 Cottrell dust processing are:

SOLIDS TONNAGE	: 14.50 stpd
PULP DENSITY	: 50% solids SG 1.518
PULP TONNAGE	: 29.7 stpd
LEACHING pH	: 9.8
LEACH RECOVERY	: 85%
CARBON TYPE	: CALGON CARBON (delivered cost $1.68/lb)
CARBON CONSUMPTION	: 18t in 1983
CARBON COST	: $1.68/lb delivered (estimate)

	Tonnage Stpd	Au (oz/t)	As (%)	Sb (%)	Au (distribution)
Dust Feed	14.50	1.21	2.20	1.36	100.00
Solids in Tails	11.34	0.23			14.86
Barren Solution	19.46	0.0002	983ppm		0.22

REAGENT CONSUMPTION	lbs/day	average lbs/ton
NaOH	14.50	1.00
Na_2CO_3	72.00	5.00
NaCN	180.00	12.82
Amine Acetate	11.60	0.80
Carbon	120.00	7.96

Amine acetate is added as it seems to improve gold leaching, possibly by reducing the surface tension allowing cyanide to penetrate pores better. The mechanism for this is not clear.

HCN MONITORING

The CIP plant building is enclosed to conserve heat in the cold climate so it is important to monitor HCN levels in the air. This is done with a Draeger sampling tube. Only on one occasion in the last 8 years has the HCN level reached the threshold level value for safe exposure of $10mg/m^3$. This occurred when the emission duct from a tank fume hood fan ruptured at an elbow joint.

HISTORICAL DATA

Data from FOSTER (1963) showed that the leaching and carbon adsorption recovery of gold from the Cottrell precipitator dusts is sensitive to the type of alkali used.

EFFECT OF VARIOUS ALKALIS ON GOLD EXTRACTION

		(1963 data)				(current)
		Nil	CaO	NaOH	Na_2CO_3	
Dust Au	(oz/st)	3.85	3.85	3.85	3.85	1.21
Residue Au	(oz/st)	0.5	1.41	1.13	0.72	0.23
Barren Solution	(oz/st)	0.005	0.016	0.021	0.009	0.0017
Gold Extraction	(%)	87.01	63.37	70.65	81.29	85%
Reagent Consumption						
NaCN	lb/t solids	53.5	7.5	9.3	12.5	12.4
Alkali	lb/t solids	-	9.5	8.1	40.5	6.0
Carbon		10.0	10.0	10.0	10.0	8.3

INCREMENTAL GOLD RECOVERY : TAILINGS EFFLUENT

After the tailings dam is decanted and the water treated by alkaline chlorination and ferric flocculation for cyanide destruction and arsenic precipitation, the decant pond overflow is gravity fed to carbon adsorption columns for incremental gold recovery. It was not determined whether the full flow of effluent is treated in the carbon adsorption columns. Fragments of information on the carbon columns are summarized as follows:

Number of Columns: 3 stages

Design of Columns: Upflow Cortez type columns with 2 % open area in plate distributors. (unconfirmed open area)

Feed Solution Tenor: pH 7.5
Au concentration 0.0008-0.002 oz Au/t

Carbon Loading: Adsorption Stage I 60 oz Au/t

Carbon Consumption: 20 tons for 1984

Tailings Solution Flow Rate: In 1983 a total of 312,000,000 lg (1,415,223 m^3/a) of effluent were treated and discharged, which had a gold content of around 3000 oz per year and is clearly a worthwhile target.

Carbon Elution: Formerly loaded carbon was shipped to a smelter by road in 2-3 ton shipments. In 1983 18 tons of carbon were shipped to ASARCO in 10-11 shipments packed in steel drums. Carbon freight costs at C$344/t and the additional cost of the carbon smelted, 5 month wait for payment and a recovery charges work out to over $5000/ton carbon making this an expensive route. Giant is currently evaluating an elution and regeneration system, and in the meantime is shipping their loaded carbon to a custom elution plant:

N.A. Degerstrom Inc.
N. 3303 Sullivan Road
Spokane, WA 99216
(509) 928-2987
James A. Bradbury
Chief Metallurgical Engineer

DISCUSSION

(1) Gold adsorption to 65.85 oz/st carbon from solutions with tenor as low as 0.0008-0.002 oz Au/st is evidence of the positive influence on adsorption of reducing the pH, removing most free and complexed cyanide and removing the base metals from the feed solution. These factors were discussed in the RANDOL (1983).

(2) The Giant tailings are frozen for much of the year. Even in summer only the upper layers thaw so the decanted solution drained from tailings is relatively cold. At low solution temperatures the density is higher and must be taken into account when designing fluidized bed adsorption units.

(3) Giant has experimented with several adsorption systems and has found that unless the carbon is fluidized correctly adsorption recovery is poor.

(4) Economics of elution and regeneration of carbon on a small scale is poor considering the capital costs involved and labor factor. For a conventional elution plant and regeneration kiln to treat 1 ton carbon per week, the Falconbridge preliminary capital cost estimate was around C$400,000. Meanwhile, a simpler elution system design has been found with indications that regeneration may not be essential.

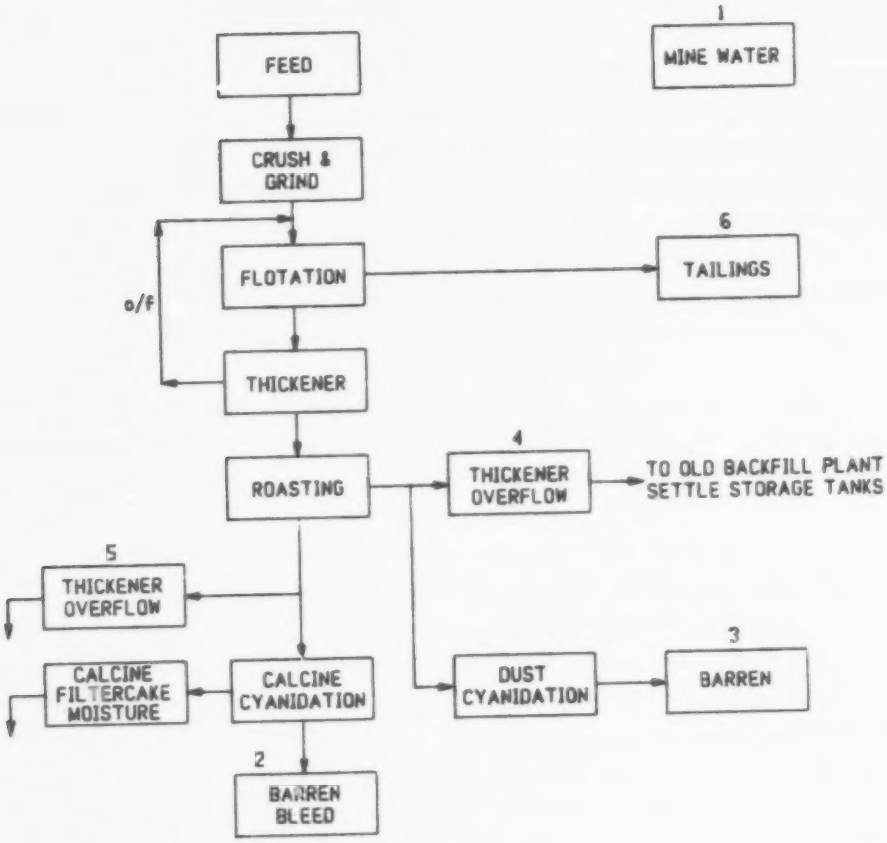
WATER LOST TO EFFLUENT IN GIANT CIRCUITS

Tons Ore Treated	1250	stpd	325,000 stpa
Tons Concentrate	125	stpd	
Tons Calcine	120		
Tons Fluedust (baghouse)	14	stpd	
Tons Precipitator dust	14.5	stpd	
Tons Flotation Tails	1125	stpd	

Flow	Rate Igpd	Rate Stpd	Flow per Ton Ore M^3/t	Flow per ton solids in circuit
Flotation Tailings	655,000	3275	2.62	2.91 ton Water/ton tailings (approximate)
Calcine Wash Thickener o/f	109,086	545	0.55	6.09 tons Washwater/ton Calcine
Calcine Barren Bleed	88,367	442	0.28	2.96 tons Bleed per ton Calcine
Precipitator	4,548	22.7	0.02	1.93 tons Water/tons Dust

Water Licence Maximum Consumption 1,950,000 m^3/year 6.60 st/ton Ore

GIANT YELLOWKNIFE MINES LIMITED
FLOWDIAGRAM AND EFFLUENT LOCATIONS



Typical Analysis of Giant Yellowknife Mines Limited Effluents

	Flow (IGPD)	pH	As	CN	TSS	Fe	Cu	Zn	Ni
1	220,000	7.7	5.1	1.3	840.	1.5	0.1	0.2	0.05
2	71,000	10.1	11.0	400.0	12.2	16.7	130.	84.6	5.1
3	4,000	8.2	1,500.	600.	244,000.	50,600.	680.	564.	104.
4	11,500	6.7	552.	0.7	670.	270.	1.1	8.4	1.3
5	138,500	4.8	100.	0.	150.	115.	0.5	8.	0.5
6	655,000	8.2	0.5	0.5	24,000.	18.7	0.8	0.7	0.2
Pond	1,100,000	8.8	12.1	8.6	-	-	6.87	0.10	1.23
Tailings Decant	1,100,000	7.7	0.14	0.20	1.2	-	0.08	0.05	0.11

(estimate)

TAILINGS DAM

The 200 acre tailings dam at Giant Yellowknife was originally a lake into which tailings were pumped and solutions decanted via Baker Lake to Great Slave Lake. The pond has been in use since the mine started up in 1948, and dam walls have been built to expand its capacity since then.

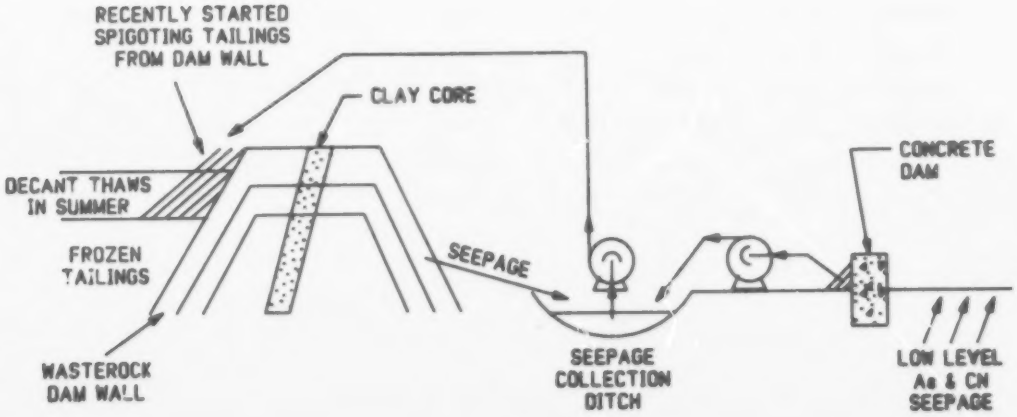
Dam walls are built of wasterock with a clay core and wasterock riprap. The lower levels of the waste pond are frozen yearround and only the top 3 or so feet thaw in summer.

Initially the tailings entered the dam at the end closest to the mine so the pond was at the far end against a relatively porous wasterock wall. The tailings site in 1945 was selected and used without geotechnical surveying. Seepage remains less than 5 gpm.

Since 1979 seepage has been collected from cutoff trenches and pumped back to the dam in the summer months. In 1983/4 tailings were discharged to the pond at the far end by spiggoting at the dam wall. The result has been a noticeable drop in seepage rate. It requires an extra mile of tailings line. Sclair pipe is used. In winter the tailings are discharged at the plant end of the dam also through a sclair pipe line. Below the dam wall there are two seepage collection points including a collection trench and beyond that a concrete dam to bedrock to trap seepage. Still there is evidence of some low level seepages from the ground beyond these two protective devices, but these are intercepted.

Tailings include all flotation waste, calcine washings, calcine leach tails, precipitator dust washings, precipitator dust CIP tails and the Barren bleed.

GIANT YELLOWKNIFE MINES LTD.
TAILINGS DAM WALL AND SEEPAGE CONTROL



WATER MANAGEMENT AT GIANT

Water is abundant in the Northwest Territories and Giant being located almost on the Great Slave Lake is close to an abundant supply. The only limitations on fresh water use are:

1) The cost of pumping it from the lake
2) The cost of treating it prior to discharge
3) The Northwest Territories Water Board license limitations on total fresh water use which currently allows 1,950,000 m^3 per year including mine drainage water.

Giant's overall water consumption is close to the limit re 1,950,000 m^3/year for 325,000 short tons ore/year mined, works out to 6.6 tons of water per ton ore mined.

HALVERSON & CROSS (1984) outlined a flow diagram of water and typical analyses of effluents as shown above. PRICE (1981) described the pilot treatment plant results and the rationale behind the process solution and the location of the treatment plant.

From this data and from the point in the flow of water that the treatment plant was inserted it is possible to conclude that:

1) The main water management objective came about in 1980 when within a year the arsenic, cyanide and base metals had to be significantly reduced in the tailings dam effluent to meet operating permits.

2) Although the most serious contribution to arsenic, cyanide and base metals are relatively small flows, their isolation for separate treatment in a small plant could do little in the short term to treat the water already in the large 200 acre pond which was well in excess of the limits that had been set.

3) The gold price was projected to remain high.

4) Consequently Giant Yellowknife installed a process for high pH chlorination followed by ferric flocculation which were the only proven technologies available at the time.

5) The plant is designed to treat the full annual flow of tailings decant solution over a six month operating season.

6) Tailings dam water containing 8.6 ppm CN^- is not suitable for recycle to the mill for the main water consuming step, namely flotation, because cyanide depresses pyrite which the plant tries hard to float.

7) Use of minewater in the flotation plant has been found for as yet undefined reasons to result in unsatisfactory results. Use of minewater in the flotation plant was tested to result in a 1% drop in gold recovery values at $30,000/month. Possibly the small cyanide values or oil and grease in the minewater are the problem.

8) Water is used to wash calcines and precipitator dusts prior to cyanidation to remove cyanicides and elements that interfere with gold precipitation.

9) Copper and Zinc are bled from the calcine leach circuit by discarding a 10% barren bleed to tailings.

10) In the existing arrangement, all contaminants are directed to the tailings dam and the whole volume of effluent treated. Since the tailings effluent must be treated anyway, the economics of separately treating a small segregated stream of the more concentrated effluents would have been impractical.

11) If one was to have an opportunity to design the whole mine-mill complex over from grass roots in today's environmental climate, it might well prove possible to keep the flotation tailings separate and cyanide-free allowing water recycle to the mill a very much reduced effluent treatment plant. However, then additional capital would be required for separate storage reservoirs.

12) In the past minewater averaged 1.72 ppm CN_T implying it gets there either with sand backfill or via seepage from the tailings dam. Minewater today no longer has a detectable cyanide level.

INFLUENCE OF COLD CLIMATE

1) Because the tailings pond is covered in snow and ice and because the water treatment plant would be too expensive to heat, it is operated only for the six warmer months from late spring to fall. This means that the tailings dam must be large enough to contain the tailings and precipitation plus spring thaw runoff. The latter is controlled to be very small.

2) During cool weather the oxidation reactions, precipitation and flocculation of precipitates is likely to be slowed down.

3) Because of the cool climate natural degradation of cyanide in the tailings pond will be slower than in a warm climate which means that there will be more cyanide in the final effluent to destroy. The large surface area of the tailings and decant ponds and plenty of wind makes up for this to a degree, however.

4) At the very cold water temperatures in the Giant tailings effluents, solution densities will be higher than at warmer temperatures. This must be taken into account in the design of fluidized bed adsorption columns.

5) The tailings are discharged to the tailings pond at the end nearest the plant i.e,, furthest from the dam wall, in winter to avoid problems of freezing in the extra mile of tailings line to the dam wall. This was true prior to the installation of a new "South" tailings dam.

MINE DRAINAGE WATER

In the late 1970's prior to installation of the Effluent treatment plant, Mine water had the following composition. (Listed for interest sake.)

pH	7.86	
Specific Conductivity	2.96	millisiemens/cm
Suspended Solids	45	ppm
AS_T*		8.92
CN_T	1.72	(0.6 -2.4)
Cu_T	1.31	(0.15-1.94)
Ni_T	0.55	(0.10-0.99)
Fe_T	3.63	(0.43-8.6)
Zn_T	0.18	(0.09-0.46)
Pb_T	0.10	(0.06-0.31)
Oil & Grease	1.03	
SO_4 ppm	734	
Cl^- ppm	706	
Hardness ($CaCO_3$)	960	
Alkalinity ($CaCO_3$)	136.9	

* The mine is located under Baker Creek and with workings adjacent to and under the final effluent pond. Since effluent has been treated however, minewater cyanide content has dropped to less than 0.01 mg/l.

Prior to 1980 effluents to Baker Creek which accounted for about 30% of its total flow to Yellow Knife Bay contained 20 - 35 mg/l CN^-.

WATER BALANCE DATA

A typical summer and winter water balance for the Giant Mine-Mill is as follows:

		July 1984 Summer (lgpd)	Jan 1984 Winter (lgpd)
A.	Yellowknife Bay Main Pumphouse to "C" area	722,610	926,803
B.	To Underground "A" Shaft 43-10	Ø	Ø
C.	To "A" Boiler	Ø	5,293
D.	To Diesel Plant	Ø	Ø
E.	To "C" Boiler	10	[illegible],610
F.	Total from Yellowknife Bay Main Pumphouse	722,610	926,803
G.	To Underground "C" Shaft 43-3	38,387	37,252
H.	From "C" Shaft Mine Discharge 43-2	420,490	295,071
I.	From Yellowknife River (domestic water)	81,539	121,616
J.	Wastewater Campsite to Mill Tails Box	79,908	Ø
K.	To Mill Process (+T)	Ø	Ø
L.	Estimated Seepage into Mine [H-(B+G+D)]	382,103	257,819
M.	Total Water Used A + L + I	1,186,252	1,307,239
N.	"C" Compressor Water Mill Process	110,935	138,652
O.	Tons Milled per month	26,529t	21,992t
P.	Arsenic Pumped u/g (lb/mo)	504,090	530,294
Q.	Tails Decant to Baker Creek (lgpd)	2,108,119	Ø

CARBON LOADING

	Analysis of Gold Laden Carbon (1963 data)		
Gold	Au	466.0	oz/st
Silver	Ag	95.0	oz/st
Arsenic	As	3.80%	
Antimony	Sb	2.75%	
Moisture	H2O	7.00%	

CARBON SELECTION

Various carbons have been used for gold adsorption in this plant over the years. FOSTER (1963) indicated that NORIT 8 X 20 mesh carbon made in Florida from pine wood was preferred. In recent years several varieties of coconut shell carbon have been tested and the current favorite is a Calgon carbon.

EFFLUENT DISCHARGE TO BAKER CREEK BEFORE TREATMENT PLANT

	CN^-	As	Cu	Pb	Ni	Zn	S/S
Tons/Year Discharge	23.1	17.04	13.47	0.083	1.75	0.54	4.31

WATER QUALITY AT BAKER CREEK BEFORE WATER TREATMENT

	1978 Tails Discharge to Creek	1978 Creek Discharge to Lake
pH	7.86	8.04 (ave)
Specific Conductance	1.07	1.14 mS/cm
Suspended Solids	4.78	11.59 ppm
AS_T	21.25	7.42 ppm
CN_T	27.52	1.61 ppm
Cu_T	15.55	2.97 ppm
Ni_T	1.88	0.80 ppm
Fe_T	1.08	1.43 ppm
Zn_T	0.65	0.24 ppm
Pb_T	0.10	0.05 ppm
Oil & Grease	1.77	1.38 ppm
$SO_4^=$		766. ppm
Cl^-	112.8	215. ppm
Hardness (as $CaCO_3$)	438.7	400. ppm
Alkalinity (as $CaCO_3$)	37.14	90.4 ppm

REGULATORY AUTHORITY

The Northern Inland Waters Act came into effect in 1976 and required a water use license for mining operators. The regulating authority is controlled by the Federal Government and is:

Northwest Water Board
P. O. Box 1500
Yellowknife NWT XIA 2R3

(403) 920-8191
Telex: 034-45623

Glen B. Warner, Chairman

PERMIT DETAILS

The permit specifies progressively strict limits for the main contaminants in the tailings effluent. After May 1, 1982 the following limits have been in effect:

	Max Average Concentration	Max Conc of Any Grab Sample
Total CN	1.5 ppm	3.0 ppm
Total As	0.8 ppm	1.6 ppm
Total Cu	0.8 ppm	1.6 ppm
Total Pb	0.2 ppm	0.4 ppm
Total Ni	0.5 ppm	1.0 ppm
Total Zn	0.2 ppm	0.4 ppm
Suspended Solids	15.0 ppm	30.0 ppm
pH	6.0 ppm min	6.0 ppm min

No floating solids, no visible oil or grease.

After May 1, 1984 the following additional limits have been added

Total Residual Cl_2	0.1 ppm	0.2 ppm
Ammonia (NH_3-N)	1.0 ppm	2.0 ppm

This average limit for ammonia of 1 ppm as N is relatively low and likely to be difficult to meet. Ammonia is probably added through minewater as a result of underground use of explosives and may also be added through release of sewage waters to tailings.

A 1 ppm N standard for NH_3 is a lot lower than most sewage treatment plant discharges in Canada. This is the only parameter of their license that is not met at present.

Residual chlorine at 0.2 mg/l is also a low level. Cl_2 is however toxic to fish down to 10 ppb which is a factor of 20 lower than the effluent limit, but a means of measuring Cl_2 below 0.1 mg/l are not readily available.

Environment Protection Service of Canada performed bioassay tests on Giant treated effluents in 1983. The rainbow trout test fish were killed until thiosulphate was added to consume the excess Cl_2.

It is noted that Giant has installed carbon columns at the overflow of the decant pond to recover incremental gold values. Activated carbon at the pH range of decant pond water should reduce chlorine to chloride, although this effect has not been monitored.

A bond of $150,000 has been deposited with the NWT Water Board to guarantee performance of the water effluent treatment.

ANALYSIS METHODS

Chlorine

A disposable rapid method for Cl_2 level analysis is available from:

Park Davis & Co.
11471 Vanowen Street
P. O. Box 9338
North Hollywood, CA 91609

(213) 765-7830

The test is known as the Water-Chex color comparison test for chlorine at 0 - 11 ppm. It is an aseptic-Thermo indicator which changes color proportionately to the Cl_2 level in the test solution.

The Water-Chex chlorine test kit is available in Canada from:

Miller Williams Hydronics Ltd.
4060 Fairview Sreet, Unit 12
Burlington, Ontario L7L 4Y8

(Catalog No. 00200)

This test is good only down to 1 ppm which is useful only for spot checking solutions and effluents for very high levels of Cl_2.

Giant Yellowknife Mines determines Cl_2 down to 0.1 ppm using a Hach Kit, available from:

Hach Company
P. O. Box 389
Loveland, CO 80539
USA

(303) 669-3050
Telex 910-930-9038

Arsenic

Arsenic is determined down to the parts per billion level using the AWWA color reaction with silver diethyl dithio carbamate to measure As in a spectrometer. This method is available (U.S. $60) in "Standard Methods for Wastewater Analysis," 15th Edition from:

American Public Health Association
1015 15th Street NW
Washington, DC 2005

(202) 789-5600

American Water Works Association
Vermont Avenue NW
Washington, DC
(202) 628-8303

$60.00

WATER TREATMENT PLANT

The selection of the water treatment process was made on the basis of pilot and laboratory testwork of available processses at the time when a final decision had to be made. The point at which it was inserted was due to the immediate need to improve effluent quality and because the existing tailings dam contained a large inventory of contaminated water which did not meet the new effluent standards. These factors are discussed by PRICE (1981), who also predicted capital and operating costs for the new plant. At the time it was expected that $400,000/year was a conservative estimate. Compare actual costs with projected:

	Plant Throughput	$[CN_T]$ ppm	[As] ppm	Capital Cost	Operating Cost Annual	C$ per 1000 gal.
1980 Estimate	1,476,000 lgpd	25.53	10.55	C$1,500,000	C$400,000 max	C$1.50
1983 Actual	312,000,000 lg in 6 months 1,750,000 lgpd	8.6	12.1	C$2,000,000	C$780,500	C$2.45

A detailed description of the design and performance of the actual water treatment plant by HALVERSON & CROSS (1984) is inserted below. This provides an excellent insight into how performance varies as operating parameters are changed. It shows in particular how reagent consumptions need to be considerably more than the theoretical requirement to achieve the design results.

Here are a few additional observations.

1) A Sulfuric acid tank is installed at the water treatment plant, the plan had been to use sulfuric acid to drop the pH of solutions to 8.5 after ferric sulfate addition to aid arsenic precipitation which requires this pH for optimum precipitation.

   In fact it is found that the ferric sulfate additon is itself adequate to drop the pH to 8.5.

   In the pilot plant which was tested at higher arsenic levels, so much ferric sulfate had to be added that the pH dropped below the optimum pH 8.5 - down to pH 4 in fact, and lime had to be added to bring the pH up. The full scale plant did not have a lime system for the second reactor so ferric addition is added only until the pH is brought down to 8.5.

   In the plant since As levels are lower and less ferric sulfate needed, pH does not drop too far.

2) The plant achieves As removal to 0.14 ppm at a ferric sulfate addition of 7:1. This is considerably lower than the limit called for of 0.8 ppm As in the license. Consequently $Fe_2(SO_4)_3$ addition will be economized by cutting it back to 5 or 6:1 which is not adequate to bring the pH to 8.5. H_2SO_4 could be dosed to achieve this however.

3) The CN-As treatment plant precipitates copper, zinc, lead and arsenic. Much of the nickel goes through as [Ni(CN)n].

   Ferro and Ferri cyanides are difficult to destroy and in fact probably remain in the effluent. Ferro/Ferri cyanides report in the CN_T analysis, but not in the weak acid dissolvable analysis for cyanide.

4) Co, Ag, Au cyanides are not detected in the CN_T analysis.

5) Plastic PVC lines manufactured by Pacific Plastic Co. were installed to dose sulfuric acid. Up to 25% of the plastic turns out to be a $CaCO_3$ filler, which dissolves when acid is added. A viscous white sludge has fouled the lines when the acid has been dosed completely blocking acid flow. It is important to correctly check material specifications. The complete acid piping system at Giant needs to be replace because of this pitfall.

6) A Hypalon lining has been installed over an earthen berm as protection against an acid spill from the tank. After 4 years glue failure is observed on all the lining joints indicating that plastic lining installation technology is not yet perfect.

7) Grit in both the lime and ferric sulfate clogs the BIF pumps. The BIF (Basics in Flow) pumps work with a diaphram and a ball valve which is essential to the pumping action. Grit gets into the ball valve and prevents it from closing - rendering the ball valve inoperable. Ferric Sulfate is now dissolved in a batch tank to settle out grit which can be removed by periodic flushouts. Ferric sulfate is too corrosive to be easily screened across available metal screens.

8) Ferric Sulfate is difficult to work with. It is very corrosive to most metals. The ferric sulfate does not dissolve readily and the drains in the plant get clogged. Open trench drains are needed which can be easily cleaned out.

9) Grit traps are considered essential ahead of any pumps. These traps must be PVC or stainless steel screens able to withstand $Fe_2(SO_4)_3$ corrosion. Ferric Sulfate corroded a ½" steel strainer within one 8 hour shift.

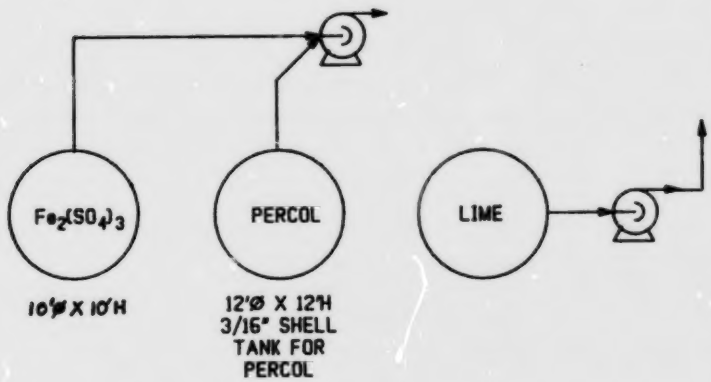
10) Three large reagent tanks are installed in the water treatment plant, each is about 10 ft Ø X 10 ft high made of 3/16" steel, one each for:

Ferric Sulfate Solution
Percol Solution
Lime Slurry

11) Allied Colloids PERCOL polymer flocculant is dosed with the ferric sulfate as a very dilute solution 4 lbs flocculant is added to 1000 gallons water in the mix solution. This is added to the third tank at a rate matching the ferric solution (dual head pumps); the mix strength is a function of flow.

12) The same BIF pump doses both ferric sulfate solution and flocculant, in separate delivery lines.

GIANT YELLOWKNIFE MINES LTD
EFFLUENT PLANT REAGENT DOSING



BIF: Basics In Flow
Division of General Signal Corporation
Division Road
West Warwick, RI
(401) 885-1000

13) The water treatment plant is located some distance from the main operations. To save need for fresh gland water for the lime solution pump, a grease seal has been installed. One cylinder of grease lasts 3 - 4 days.

14) The concentrated H_2SO_4 solution is dosed via BIF pumps which are installed in rubber lined concrete sumps as a protection measure. These pumps have yet to deliver one tank full of acid. The rubber lining has failed.

15) Cl_2 dosing is accomplished by a system supplied by:

Wallace & Tiernan
Division of Pennwalt Coporation
25 Main Street
Bellville, NJ
(201) 759-8000

This system has proven satisfactory. It has proved to be better than the Fisher-Porter Cl_2 dosing system installed at a Westmin Resources plant on Vancouver Island which reputedly has given poor service. Giant installed a W & T Cl_2 dosing unit after visiting Westmin Resources facility in 1980.

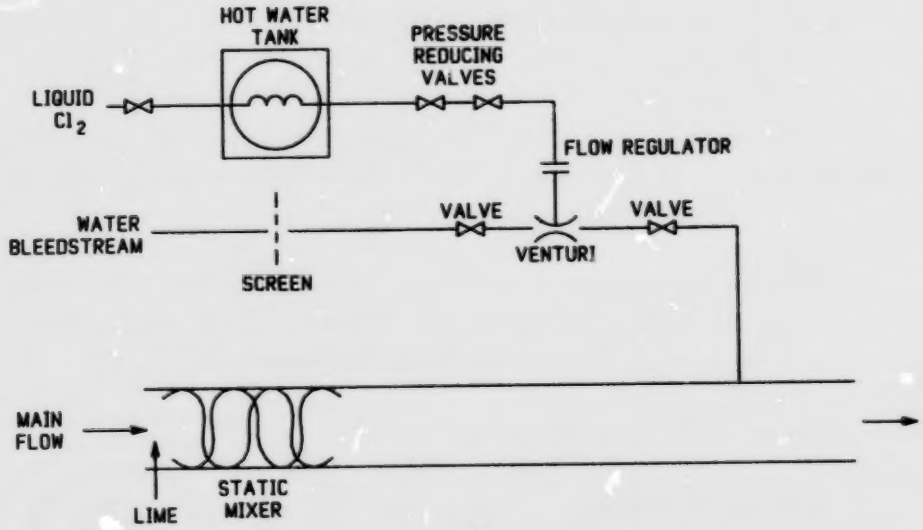
16) The Wallace & Tiernan chlorine dosing systems employs cathodic protection to prevent corrosion. Na_2SO_4 is dosed to increase conductivity for this purpose.

Electrodes prevent Cl_2 from oxidizing the pipeline. An automatic pressure sensing device allows the system to switch over from an empty Cl_2 cylinder to a new cylinder when empty (or if the gas pressure drops below a preset threshold for any reason.)

17) The welded steel pipelines for Cl_2 dosing must be replaced every 5 years. Also, one cannot weld a steel pipe with Cl_2 in it because this sets off an oxidation reaction inside the pipe, which being exothermic is self sustaining as long as the supply of iron and Cl_2 lasts.

18) 2500 lbs liquid Cl_2/day are consumed at the plant. It is delivered from liquid chlorine via a gasifier as shown schematically below.

GIANT YELLOWKNIFE MINES LTD.
EFFLUENT TREATMENT REAGENT ADDITION



19) The water treatment plant is operated for 6 months/year only. There is a problem hiring operators just for 6 months.

Three of the mill personnel have been trained in the operation of the water treatment plant. These are able to train the seasonal employees.

The plant requres 1 operator/shift, working two 12 hour shifts. Plant operators in the NWT receive C$14/hour with $0.75/hour extra for nights and afternoons or $1.50/hr extra for weekends. They work 4 days on, 4 days off.

Operators net about C$2000/month working 4 days on and 4 off alternating between day and night shift.

20) When the $Fe_2(SO_4)_3$ is first mixed it appears to be a milky suspension. After aging for a couple of hours it changes to a dark brown color. The $Fe_2(SO_4)_3$ supplier is in Tennessee and the product performance seems to vary from batch to batch.

1984:	Need 4 bags/day
1983:	Needed 6 bags/day

21) When $Fe_2(SO_4)_3$ is used it helps keep the pH probe clean. Operators clean the pH probes every second day with 25% HCl.

22) The plant was designed to be operated by only 1 dayshift operator. The enunceator system on the controls has not worked well and full time operator supervision has beer. required.

23) If the plant were to fail only for 1 hour in 24 it would result in a doubling of the As and CN^- level in the decant pond. Therefore it needs constant surveillance.

24) The three outdoor reaction tanks have drains connected to a sclairpipe header. Shrinkage and movement in winter breaks the line which is connected to the three tanks.

25) FRP walkways are used. These are expensive but have not corroded.

26) The Ferric Sulfate solution tank was made of steel lined with FRP. The lids of the tank corroded off and have been replaced by FRP. All in-plant piping uses PVC.

27) The pressure reducing relief valves in the plastic piping system clogged with grit after the plant was started up and has been useless.

28) The PVC piping throughout the plant is arranged along piperaces in such a way that it is extremely difficult to work on any one line. The pipes are too close together with too many fittings of glued joints. Threaded fittings could be replaced if one were to break at freezeup. In the present design, if one breaks 5 or 6 have to be replaced to get to the broken one.

29) Lime is fed via a rotary valve at the bottom of the lime silo which is operated for a timed period to add lime. The original volumetric feeder gave trouble and has been discarded. The lime silo and feeder was supplied by PEABODY ENGINEERS.

30) Numerous salts were tried out benchwork, leading to the pilot plant design, including:

Ferric chloride
Alum
Ferric Sulfate
Ferrous Sulfate
Lime

Ferric Sulfate addition gave the best results for arsenic oxidation.

Benchscale testwork over 2 years yielded valuable data but was not written up. It was carried out by Dr. Brian Leclair who left the Canada Centre for Inland Waters in Burlington for Ottawa then to Wolsous, Canada but has subsequently left there too and could not be traced.

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	William A. Humphrey	Executive Vice President
	Rex Guinivere	Vice President Engineering

INTRODUCTION

Homestake Mining Company in Lead, SD is still the largest gold producer in the USA and needs no introducing. It is also one of the oldest operations and is the only known example where percolation leaching of sand after a sand-slime split is still practiced. Flow diagrams are inserted below.

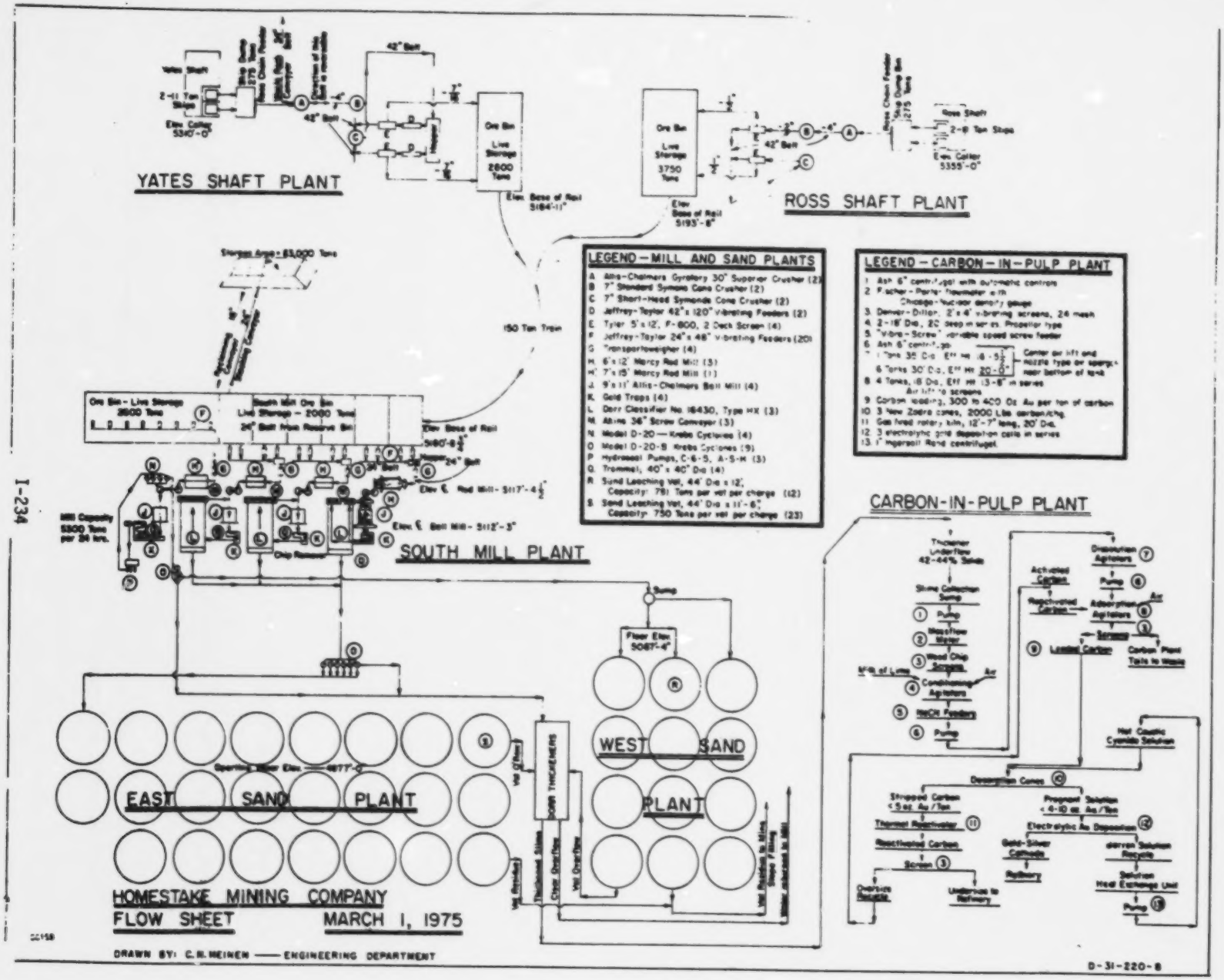
From a water management point of view, however, there are four main points of interest:

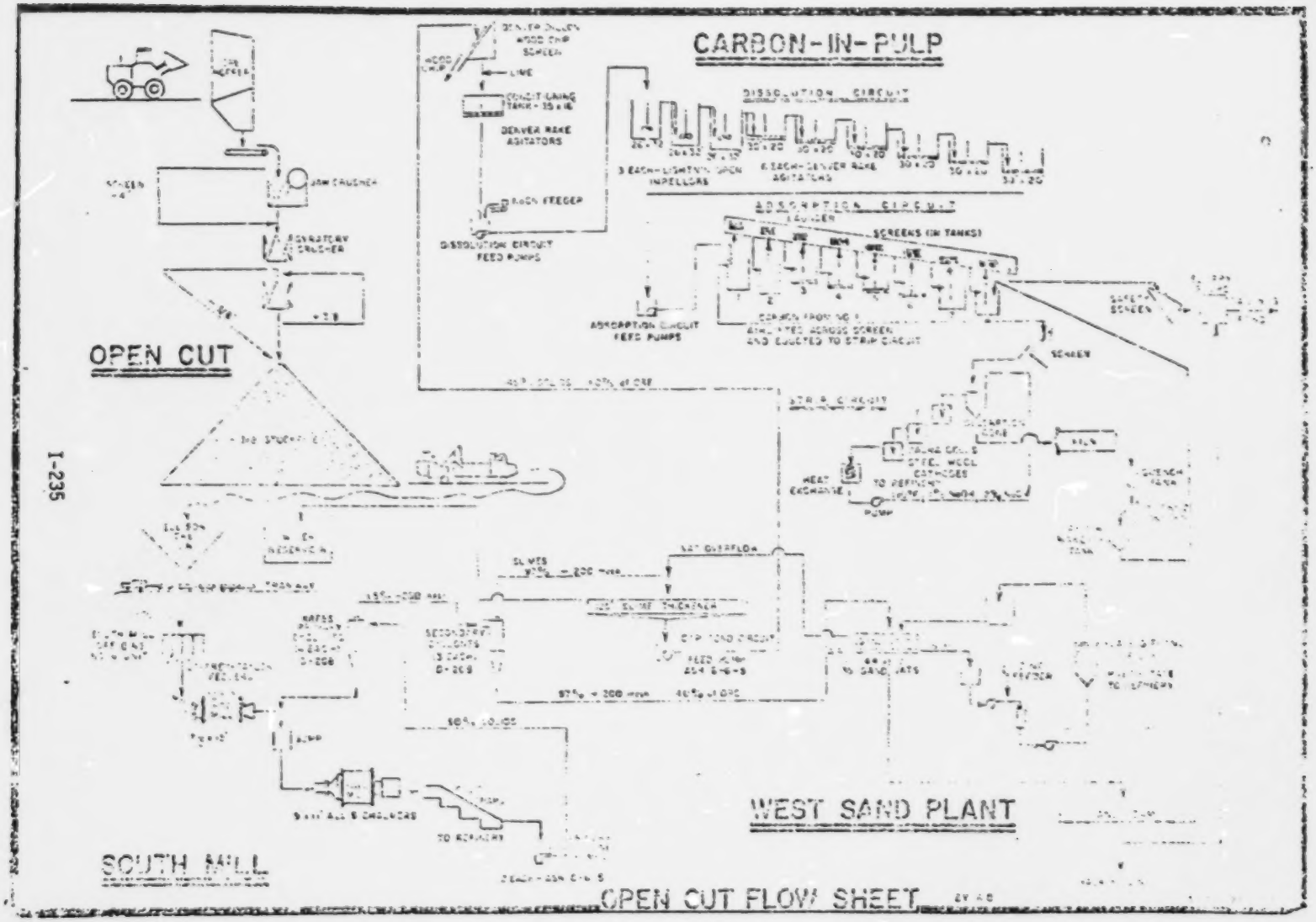
1. The pioneering use of engineered bacterial processes for detoxification of effluents.

2. The development of a quantitative in situ site specific bioassay technique to test the environmental compatibility of treated effluents.

3. The effect of new underground mining techniques on metallurgical processes due to an impact on water quality.

4. Development of effluent discharge regulatory limits for the Homestake operation, from the regulator's standpoint.


YATES SHAFT PLANT
ROSS SHAFT PLANT
SOUTH MILL PLANT
EAST SAND PLANT
WEST SAND PLANT
CARBON-IN-PULP PLANT
LEGEND — MILL AND SAND PLANTS
A Allis-Chalmers Gyratory 30" Superior Crusher (2)
B 7" Standard Symons Cone Crusher (2)
C 7" Short-Head Symons Cone Crusher (2)
D Jeffrey-Taylor 42" x 120" Vibrating Feeders (2)
E Tyler 5' x 12', F-800, 2 Deck Screen (4)
F Jeffrey-Taylor 24" x 48" Vibrating Feeders (20)
G Transportweigher (4)
H 6' x 12' Marcy Rod Mill (3)
H' 7' x 15' Marcy Rod Mill (1)
J 9' x 11' Allis-Chalmers Ball Mill (4)
K Gold Traps (4)
L Dorr Classifier No. 16430, Type HX (3)
M Atlas 36" Screw Conveyor (3)
N Model D-20 — Krebs Cyclones (4)
O Model D-20-B Krebs Cyclones (9)
P Hydroseal Pumps, C-6-S, A-S-H (3)
Q Trommel, 40" x 40" Dia (4)
R Sand Leaching Vat, 44' Dia x 12', Capacity: 781 Tons per vat per charge (12)
S Sand Leaching Vat, 44' Dia x 11'-6", Capacity: 750 Tons per vat per charge (23)
LEGEND — CARBON-IN-PULP PLANT
1 Ash 6" centrifugal with automatic controls
2 Fischer-Porter flowmeter with Chicago-Nuclear density gauge
3 Denver-Dillon, 2' x 4' vibrating screens, 24 mesh
4 2-18' Dia., 20' deep in series. Propeller type
5 "Vibra-Screw" variable speed screw feeder
6 Ash 6" centrifugal pump
7 1 Tank 35' Dia. Eff Ht 16'-5½"
6 Tanks 30' Dia. Eff Ht 20'-0"
Center air lift and nozzle type air sparger near bottom of tank
8 4 Tanks, 18' Dia., Eff Ht 13'-8" in series
Air lift to screens
9 Carbon loading, 300 to 400 Oz Au per ton of carbon
10 3 New Zadra cones, 2000 Lbs carbon/charge
11 Gas fired rotary kiln, 12'-7" long, 20" Dia.
12 3 electrolytic gold deposition cells in series
13 1" Ingersoll Rand centrifugal
HOMESTAKE MINING COMPANY
FLOW SHEET MARCH 1, 1975
DRAWN BY: C. H. HEINEN — ENGINEERING DEPARTMENT
D-31-220-8


CARBON-IN-PULP
DISSOLUTION CIRCUIT
DENVER RAKE AGITATORS
DISSOLUTION CIRCUIT FEED PUMPS
ADSORPTION CIRCUIT
SCREENS (IN TANKS)
ADSORPTION CIRCUIT FEED PUMPS
SCREEN
STRIP CIRCUIT
HEAT EXCHANGE
PUMP
OPEN CUT
JAW CRUSHER
GYRATORY CRUSHER
SCREEN
SLIMES
SAT OVERFLOW
SECONDARY CYCLONES
WEST SAND PLANT
TO SAND VATS
TO REFINERY
SOUTH MILL
OPEN CUT FLOW SHEET

1. EFFLUENT TREATMENT AT HOMESTAKE MINE, LEAD, SD

Homestake processes about 6000 tons per day of ore. After a sand-slime split the sand is percolation leached in vats and then after washing it is pumped back underground. About 2500 tons per day of slimes are agitation leached using cyanide, after being throughly pre-aerated to oxidize pyrrhotite. The leached pulp is then subjected to carbon in pulp to recover leached gold values. Finally the slime tailings are pumped to a tailings pond in Grizzly Gulch.

The Homestake Mine requires pumping and on account of residual cyanide in the sand fraction the underground minewater contains some cyanide and metals which exceed the levels that can legally be discharged. The tailings pond decant water also contains cyanide and metal values requiring treatment before they can be discharged. Typical analyses of Homestake's effluent flow streams are compared with their NPDES permit as documented by EDELMAN & WALLINE (1981).

The treatment plant must be able to treat up to a maximum of 21,000 m^3/d of combined effluent to render it suitable for discharge into Whitewood Creek which is a cold water marginal trout fishery.

In order to try and meet the NPDES permit requirements Homestake Mining Company has tested virtually every cyanide destruction method ever developed. In their case the minewater is warm and this has allowed them to consider the use of bacterial processes. The water from underground and the tailings decant is combined and has the following typical characteristics as reported by MUDDER & WHITLOCK (1984).

Parameter	Value*
CNS	45.0 - 75.0
CN_T	0.50 - 10.0
CN_C	0.50 - 5.00
Iron	0.50 - 2.00
Copper	0.10 - 1.50
Nickel	0.10 - 0.50
Zinc	0.10 - 0.50
Ammonia N	1.0 - 6.50
Phosphorous P	Trace
pH	5.5 - 10.0
Temperature	10 - 25

* All values in ppm except temperature and pH

	Effluent Analysis (1)		Permit Requirement (2)	HOMESTAKE LEAD Interim Permit
	Minewater	Tailings Decant	BPT Limits	
Total S/S	-	-	10	
Arsenic	-	-	0.38	
Cadmium	-	-	0.00025	
Chromium	-	-	0.85	
Copper	0.07-1.60	1.40-6.00	0.009	0.009
Lead	-	-	0.28	
Mercury	-	-	0.001	
Nickel	0.01-0.04	0.20-0.40	1.25	1.25
Silver	-	-	0.001	
Zinc	0.01-0.10	0.01-1.50	0.020	0.02
Cyanide Total	0.10-0.50	7.00-30.00	0.02	0.02
pH	5.0 -6.5	7.0-9.5	6-9	6-9
CNS	1.0 -16.0	110-240	-	
Method C Cyanide	0.02-0.10	4.00-20.00	-	
Iron	0.10-10.00	1.50-6.00	-	
Ammonia -N	5.0-6.0	less than 1.0	-	2-8 ppm
Phosphorous -P	trace	trace	-	
Temperature	70-85	34.70	-	

Sources: (1) WHITLOCK & MUDDER (1984), (2) EDELMAN & WALLINE (1981).

REQUIREMENTS OF PROCESS FOR CYANIDE TREATMENT

In comparing the characteristics of effluent streams with the required effluent limits it is clear that the levels of several species in addition to cyanide must be reduced, for example copper and zinc. In addition ammonia levels of 5.0-6.0 ppm and high CNS^- values indicate that possibly these species should also be reduced in order to improve the effluent quality with respect to its impact on aquatic life.

PROCESSES TESTED

MUDDER & WHITLOCK (1984) tested just about every cyanide treatment process available except the INCO SO_2 process, including:

- Ozonation
- Acidification/Volatilization
- Carbon Adsorption
- Ion Exchange
- Alkaline Chlorination
- Copper Catalyzed hydrogen peroxide with ferric chloride addition.

Alkaline chlorination failed on account of its inability to remove total cyanide, i.e., ferrocyanides. MUDDER & WHITLOCK (1984) indicate the reasons for rejection of all of the other processes. In addition they compared results achieved by various biological processes and describe the development of a two step biological process first to remove cyanides and metal and then to remove ammonia.

BIOLOGICAL PROCESS

The bacterial process employing Pseudomonas paucimobilis for cyanide oxidation is described by MUDDER & WHITLOCK (1984) and WHITLOCK & MUDDER (1984). Nutrient supplements of soda ash and phosphoric acid are added in a controlled dosage and the plant layout, as illustrated by MUDDER & WHITLOCK is shown below.

The biological process was shown in the laboratory and in a pilot scale operation employing a 2.0 m Ø biodisc to achieve excellent results for total and free (Method C) cyanide, thiocyanate removal, as well as removal of ammonia and copper. Test results shown by MUDDER & WHITLOCK are listed below as well as results of the commercial plant reported by SCOTT (1984):

	PILOT PLANT		COMMERCIAL PLANT	
		2M Ø RBC		12' Ø RBC
	INFLUENT	EFFLUENT*	INFLUENT	EFFLUENT*
	MUDDER & WHITLOCK (1984)		SCOTT (1984)	
Thiocyanate	60.0	1.0	50.0	0.3
Total Cyanide	6.5	0.35	2.0	0.02
Free Cyanide (Methoc C)	4.1	0.05		0.10
Ammonia N	6.0	0.50		0.5
Copper	1.0	0.06	1.0	0.05
Suspended Solids	-	-	-	10.0

* Values in ppm

The pilot RBC plants were furnished by ENVIREX. The original feasibility study was undertaken with the use of a 0.5 m Ø RBC pilot plant. The 2.0 m Ø pilot plant was operated with the first and second stages unbaffled. Supplemental aeration was fed to each stage of the pilot plant at an equivalent rate of 0.07 m^3/s (150 cfm). Stripping of biomass required 0.283 m^3/s (600 cfm). The total surface area of the pilot plant was 743 m^2 (8000 ft^2). The pilot plant was operated at flow rates of 0.13-0.50 l/s (2.0-8.0 gpm). Effluent values recorded above were obtained on clarified and sand filtered effluent by MUDDER & WHITLOCK (1984). Nitrification is the rate controlling step in the overall design.

The full scale biological treatment plant includes the following steps as shown schematically by SCOTT (1984).

1. Addition of phosphoric acid and soda ash
2. 48 rotating biological contactors with supplemental air
3. Ferric chloride and polymer addition
4. Clarification in a cylindrical clarifier
5. Emergency clarifier
6. Sand filtration
7. Discharge to stream

The full scale RBC's were supplied by:

Envirex Inc.
P. O. Box 1067
Waukesha, WI 53186

Telephone (414) 547-0141
Contact J. Witmann

At the time of writing this innovative new cyanide destruction plant - which should really be looked upon as an effluent treatment plant because it takes care of a spectrum of undesirable contaminants - was still in the commissioning stages and Homestake Mining Company has yet to release the final performance data.

It was found that calcium in the minewater which was introduced in part by cement addition in the mine backfill has resulted in an interfering scale on the biological contactors. As of December 1984, Homestake has embarked on a 90 day period during which no cement is added to the backfill as an experiment to see what effect this has on the biological effluent treatment plant results.

From the point of view of using bacterial processes, Homestake is fortunate in that minewater is heated underground so that the mixed mine and tailings effluent temperature is favorable for biological processes yearround despite the cold winters in South Dakota.

The capital cost of the 21,000 m^3/d (5.5 million gpd) biological treatment plant is around $10 million.

Design operating costs are around $500/day although at this point in time during the optimization program the costs are somewhat higher than this. This is a remarkably low cost which works out to less than $0.10/ton ore or $0.25/m^3$ effluent treated compared with other processes which have been reported to cost around $1.00/ton ore and more, as for example the Ok Tedi process using peroxide.

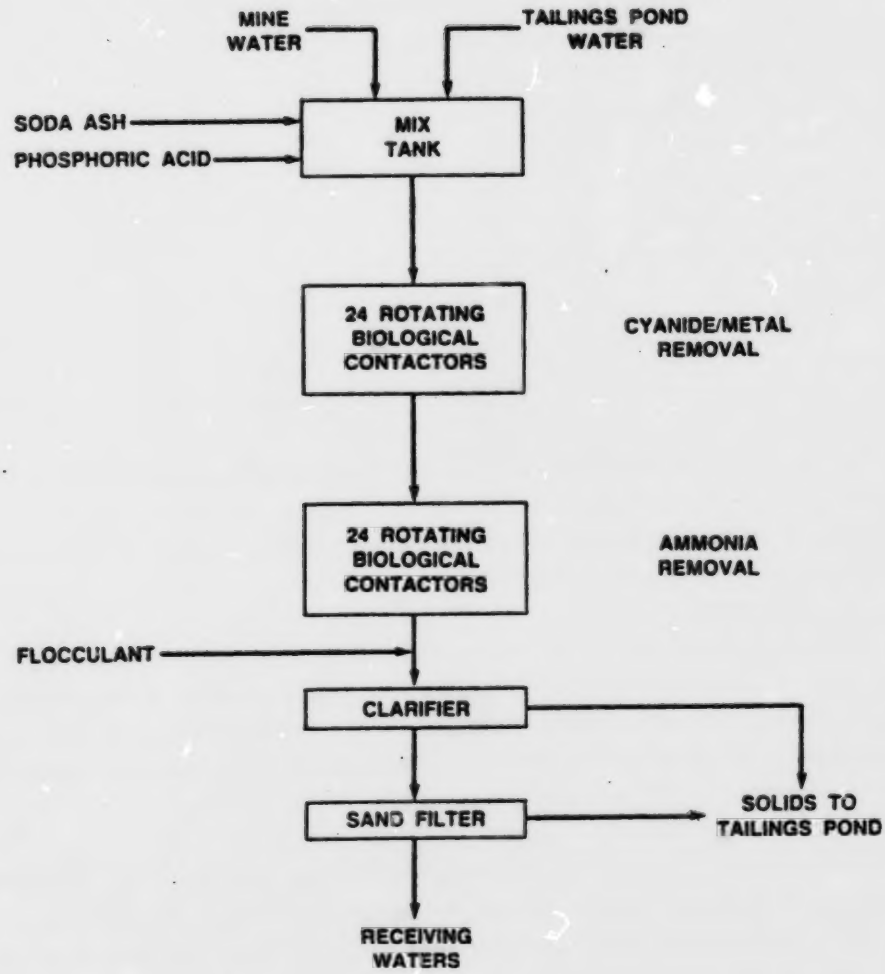


FIGURE 3 BIOLOGICAL TREATMENT PROCESS AT HOMESTAKE MINING COMPANY

CAPITAL COSTS OF CONSTRUCTION OF THE TOXICOLOGICAL TESTING FACILITY

EXPENDITURE PURPOSE	COST($)
Building	30,000.00
Internal piping	15,000.00
Aquaria	3,200.00
Pumps, dilutor system, metering system, tubing, glassware, etc.	6,000.00
Dilution water pumping system	
Pump house/pump	3,500.00
Stream modification for water source	5,000.00
4" buried water supply line to bioassay facility	12,000.00
TOTAL	74,700.00

TABLE 2

OPERATING COSTS OF THE BIOASSAY FACILITY

EXPENDITURE PURPOSE	TEST TYPE		
	48 HOUR STATIC	96 HOUR FLOW THROUGH	45 DAY FLOW THROUGH
Bioassay technician time ($11.50/hr)	$ 92.00	$ 276.00	$ 2,162.00
Chemical analysis ($5.00/analysis) (in house)	$390.00	$1,170.00	$ 8,190.00
Outside Chemical* Analyses	-----	-----	$ 1,500.00
Supervision ($20/hr)	$ 100.00	$ 100.00	$ 500.00
TOTALS	$ 582.00	$1,546.00	$12,352.00

*Outside chemical analysis of whole fish tissue for determination of bioaccumulation

SOURCE: MUDDER ET AL (1984)

2. SITE SPECIFIC BIOASSAY TOXICOLOGICAL TESTING

WHITLOCK & MUDDER (1984) describe an in situ site specific bioassay method that has been developed and demonstrated at Lead. MUDDER et al. (1984) have described how their technique is being used to develop site specific discharge criteria through toxicological testing.

Employment of aquatic toxicological testing for the selection of viable wastewater treatment alternatives and the development of site specific water quality criteria is increasing. The increase in its use is due to its cost effectiveness in solving environmental problems and it is proposed as a viable practical tool for use in commercial plants.

MUDDER et al. (1984) describe a new approach which follows flexible guidelines recently proposed in a new water quality development document published by the EPA. Discharge criteria based on general numerical standards often seem to include relatively broad safety margins. Site specific toxicological testing as developed at Homestake's Lead operations make it possible to demonstrate that an effluent is or is not compatible with the designated use classifications of Whitewood Creek which is the receiving stream. The need for this approach has been amply demonstrated at Homestake's Lead operation where no known processes are able to meet the original NPDES discharge criteria. However, biological effluent treatment using the new Homestake process yields an effluent that with the use of the site specific toxicological test demonstrated by MUDDER et al. (1984) can be shown conclusively to be environmentally compatible.

According to Consent Decree, Civil No. 78-5094 of United States of America, State of South Dakota vs. Homestake Mining Company, February 1980, if the treated effluent discharged by the mine can be shown not to interfere with the attainment and maintenance of the existing designated beneficial uses of Whitewood Creek under South Dakota water quality standards, the state will initiate proceedings to consider modification of its water quality criteria for Whitewood Creek.

Based on a $300,000 bioassessment of Whitewood Creek in accordance with proposed EPA guidelines and protocol, by a team of independent experts, a request was made to modify the use classification of Whitewood Creek from a "cold water permanent fishlife propogation" classification to "cold water marginal fishlife propogation." The new classification would allow survival of catchable size trout but not protect the stream for reproduction. In this case the study concluded that the habitat was limited due to low flows and excessive summer water temperatures. Also achieved was modification of South Dakota water quality regulation to allow for toxicological testing and its use in setting site specific water quality criteria.

MUDDER et al. (1984) describe the Homestake toxicological testing facility located adjacent to the site of the new biological wastewater treatment facility. The primary test

organisms include Daphnia magna, macroinvertibrates (stoneflies and caddisflies), and trout (rainbow and brown).

Dilution water is pumped continuously through the bioassay facility from a pumping station located along Whitewood Creek about one mile above Homestake's discharge. A bioassay facilities manual details the specific protocol employed in the laboratory and is utilized in training technicians, has been prepared by HOMESTAKE MINE (1981).

Capital and operating costs of the toxicological bioassay facility as reported by MUDDER et al. (1984) are shown below.

The two main conclusions drawn from discussion of Homestake's bioassay testwork is firstly that the use of such methods for site specific toxicological testing are most promising. Secondly, the Homestake program demonstrates that industry and regulatory agencies can work together effectively to solve complicated environmental problems.

3. EFFECT OF UNDERGROUND MINING TECHNIQUES ON WATER QUALITY/ METALLURGICAL RECOVERY

HAPTONSTALL (1984) describes the application of vertical crater retreat mining at Homestake's underground workings. This and other mining methods employ diesel and hydraulically powered equipment underground.

Servicing of diesel powered equipment underground is believed to be a potential source of grease, diesel fuel, lubricating oil and hydraulic fluids into the ore.

During a visit to Homestake's CIP plant in September 1984 it was noted that some dark colored oil was floating on top of some CIP adsorption tanks. This oil is likely to result in a reduction in adsorption efficiency of gold onto carbon because oil will coat the carbon with a hydrophobic surface. Pyrite and pyhrrhotite can float on the pulp surface and in some cases looks similar to oil, but several operators from other plants were convinced that the observed material was oil.

This is an example of the need to adopt a systems approach in all mine-mill-tailings systems. Mine operators need to know enough about downstream metallurgical processes that they will be cognizant of practices that could have both negative and positive effects on overall recovery. It is believed that Homestake mining staff are now becoming sensitive to this issue which is a common problem in gold mines all around the world. It is noted that at Homestake the mine has agreed to a 90 day experiment in which no cement will be used in backfill to test what effect this has on effluent treatment. This extent of interdepartmental cooperation is unusual in the industry.

4. DEVELOPING A COOPERATIVE APPROACH TO ENVIRONMENTAL REGULATIONS

A description of the development of the current regulatory limits and background for the huge effort by Homestake into seeking improved technology for cyanide destruction is provided by EDELMAN & WALLINE (1981).

Numerous exhaustive laboratory and pilot tests have been undertaken to find a way to meet the effluent discharge quality limitations that have been imposed.

It is interesting to note that the use of CIP at Homestake's Lead plant stems from their desire to avoid the use of mercury which formerly was used for gold recovery from the slimes fraction of their ore.

Next, a huge, expensive tailings dam was constructed to retain tailings that hitherto were discarded down Whitewood Creek.

The new biological effluent treatment plant is the end result of this cooperative approach.

The effluent limits imposed on Homestake in the 1976 standard shown above is onerous and appears to be arbitrary in some respects. The motivation of setting new regulatory effluent limits on an existing operation without providing the means to meet them is somewhat mystifying and it is hoped that the best interests of the American taxpayer and the nation as a whole are being served by the process of rulemaking that has evolved. Although this report is limited to discussion of technical aspects, the indication of some subsequent flexibility and pragmatism in the development of environmental regulations and the way they are applied is encouraging.

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Bulletin No. 315-13A1
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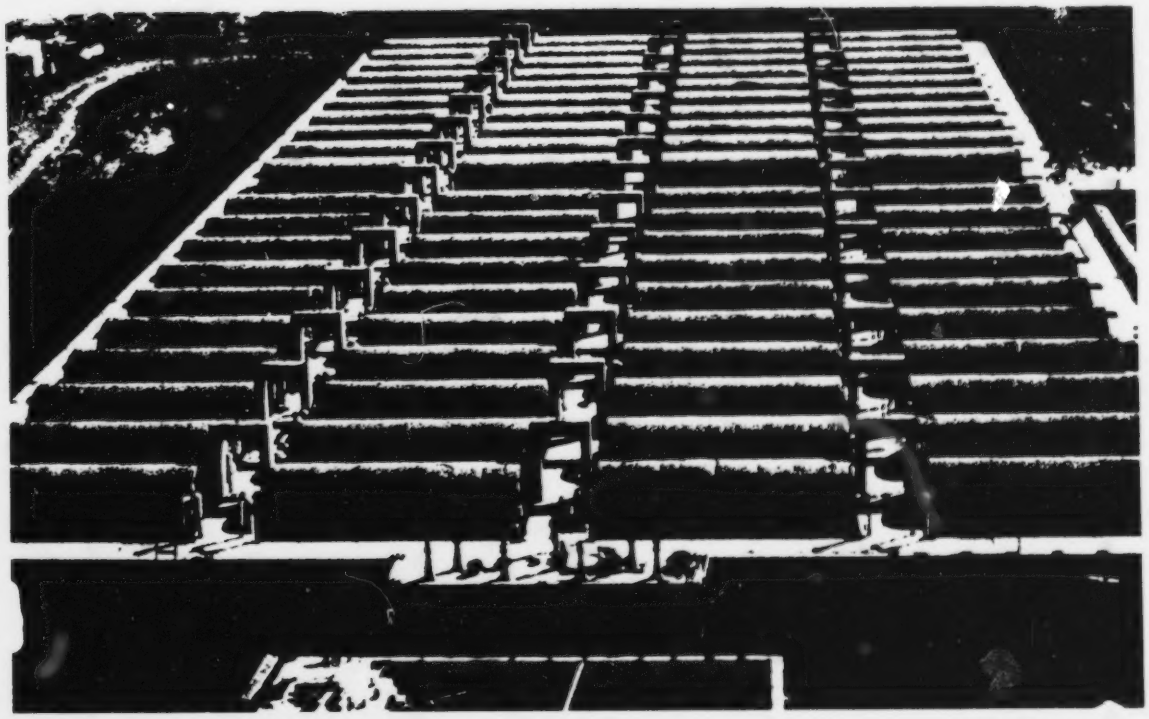

Rex Aero-Surf air-driven RBCs are now being started up at the rate of one nearly every day. Eighty units are shown in this photo taken during construction of the 20 MGD plant at Union Sanitary District in Union City, California.

rotating biological contactors

Aero-Surf
state of the art RBC's

I-246

Bio-Surf
proof of performance

AERO-SURF

process

In 1975, the most significant and cost-effective development in RBC process technology was introduced: the Aero-Surf process.

The Aero-Surf process evolved naturally from efforts to optimize RBC technology. The system offers substantial savings in capital as well as operating and maintenance costs, while enhancing the high treatment efficiency demonstrated by mechanically-driven Bio-Surf equipment.

An Aero-Surf assembly, Figure 1, consists of corrugated media with plastic cups attached around the outer perimeter and over the entire length of the contactor. The media assembly is installed in a tank in the same manner as a conventional unit with the addition of an air header placed below the media. Air is released from the header at a low pressure into the attached cups. The captured air exerts a buoyant force, which in turn exerts a torque on the shaft sufficient for rotation.

Because air cups are not placed over those portions of the media containing radial passage openings, Figure 2, approximately 20% of the released air escapes into the radial passages and flows upward into the corrugated sections. The additional aeration and increased turbulence achieved from this air flow permit a reduction in rotational velocity of the media while achieving an increased degree of treatment. Full-scale Aero-Surf units have been field tested side by side with mechanically-driven units and have demonstrated equal or better treatment efficiency at as little as half the normal rotational speed.

Increased turbulence reduces the biomass thickness, permitting an increased use of Hi-Density media. This results in as much as a 25% reduction in the number of assemblies required for a given application when compared to mechanically-driven units. Figure 3 shows a typical full-scale plant with an air-driven system. A blower delivers air at about 3 psi to a common air header. Approximately 50 to 200 cfm of air is withdrawn through a control valve for each shaft and distributed through the air header beneath the rotating media. Reducing or increasing air flow controls the speed of rotation. Speed of each Aero-Surf unit can be adjusted individually according to changing requirements, providing increased flexibility in the treatment process.

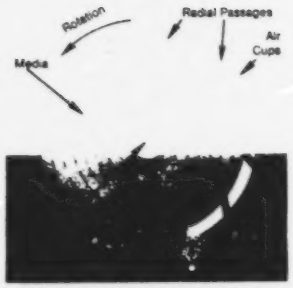

Figure 1. [illegible]

Figure 2. Spacing of air cups on media periphery permits the diffused air to flow through radial passage openings into the media.

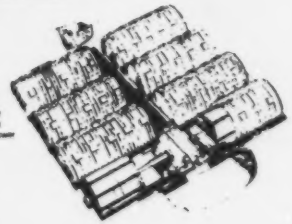

Figure 3. In typical Aero-Surf plant, air is piped to individual assemblies from a central blower.

process benefits

Full-scale field testing has demonstrated the process benefits of the Aero-Surf system:

Increased mixed liquor dissolved oxygen concentration is maintained in the Aero-Surf process due to the additional transfer of oxygen by the air diffuser system.

The increased dissolved oxygen level has two biological effects:

1. Maintenance of a completely aerobic biological culture on the media.
2. Increased oxidation-reduction potential (O.R.P.) within the Aero-Surf reactors. The development of undesirable microorganisms is thus reduced; treatment efficiency is increased.

Increased BOD removal. At high loads, or where oxygen-limiting conditions exist, the Aero-Surf process has demonstrated approximately 20% to 50% higher soluble BOD removal than a mechanically-driven RBC system.

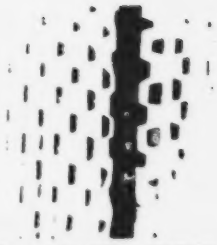

Figure 4. Hi-Density media provides 50% increased surface area.

Thinner biomass is achieved with the Aero-Surf process as a result of increased shearing action as air bubbles rise through the radial passages and corrugations in the media. This ability to control biomass thickness is a major advance in fixed-film technology which makes possible more complete optimization of the treatment process. Specifically the thinner biomass:

1. Reduces structural loads on the Aero-Surf shaft assembly.
2. Reduces hydraulic drag of the media, potentially reducing energy consumption.
3. Permits Hi-Density media, Figure 4, to be used at higher BOD concentration. This results in fewer media assemblies which significantly reduces construction and maintenance costs.

Process flexibility through variable speed control optimizes power consumption. The speed of each Aero-Surf assembly can be adjusted to changing wastewater flows and strengths, or effluent requirements.

design features

Aero-Surf media. Standard or Hi-Density Bio-Surf media with polyethylene air cups welded to the periphery captures air released from the air header.

Air Cups. Specially-designed air cups capture air which provides buoyancy to turn the media. Cups are 4 inches deep. Six-inch cups may be used where treatment requirements require increased torque.

Air control valve. Air supply to each Aero-Surf unit is controlled by a butterfly valve which permits variable speed operation.

Air Header. Air moves through the Aero-Surf system through lightweight headers, Figure 6, that run the length of the media assembly and are easily removed for cleaning. **Header mounting brackets** secure header to tank floor.

Air Diffuser. Air is distributed from the header into the air cups and media through coarse bubble air diffusers.

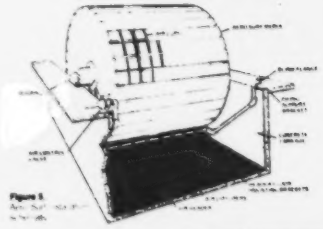

Figure 5. [illegible]

Figure 6. [illegible]

AERO-SURF

operating benefits

Simplicity is the key to Aero-Surf cost-effectiveness, particularly in very large treatment plants employing a substantial number of assemblies.

Maintenance. Many Aero-Surf media assemblies may be driven with a single source of air. Plants may be designed where one 5000 cfm blower can drive up to 50 assemblies. When compared to mechanical drives, the maintenance savings are obvious.

Aero-Surf maintenance manpower savings of up to 90% are not unusual in reports from municipal plants having experience with both air driven and mechanically-driven RBCs.

Optimized energy consumption is made easier by the system's variable speed capability, without the economic disadvantages and maintenance problems of mechanical or electrical variable speed drive systems.

Power factor improvement will further optimize energy consumption when a few large blowers replace a large number of motor-driven mechanical drives.

Operating flexibility. When Aero-Surf units are at less than design flow, during initial start-up years or due to seasonal variations, air flow can be reduced or units taken out of service, thus reducing energy consumption. Under the same low flow conditions, activated sludge and oxidation ditch systems usually require full power to maintain adequate mixing.

When an Aero-Surf system is operated at higher than design flows (due to temporary industrial discharge, for example), air to the units can be increased to maximize BOD removal and maintain control over biofilm conditions.

Provision for stand-by. Stand-by blower capability in an Aero-Surf system in effect provides a stand-by drive for each Aero-Surf unit. A back-up system is not economically feasible in mechanically-driven RBC plants.

Stand-by power generation capability in an Aero-Surf plant need only be sufficient to operate a single blower. All units can then operate at minimum speed until full power is restored. Since mechanically-driven RBC units operate at fixed speeds, stand-by power must duplicate full power demand.

Ventilation of buildings or enclosures is required in some applications. The air rates provided by Aero-Surf system blowers reduce, or even eliminate, the need for separate ventilation fans.

Operator safety is improved. Blower maintenance is performed away from the RBCs and does not expose personnel to chains, belts, gears, etc. In many Aero-Surf installations, all maintenance can be performed outside the RBC enclosures.

Figure 7. Full scale Aero-Surf media assemblies in an R & D facility at Milwaukee's South Shore treatment plant.

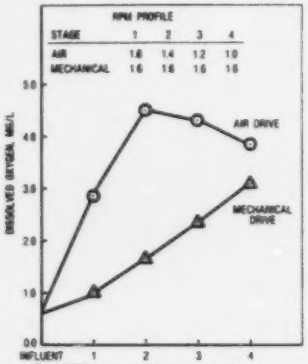

Figure 8. RBC speed and resulting dissolved oxygen profile, Aero-Surf vs. mechanically-driven systems.

process development

Extensive full-scale Aero-Surf process field testing has been performed at Milwaukee's South Shore wastewater treatment plant, Figure 7. A research and development facility, equipped with Aero-Surf and Bio-Surf process assemblies, has served as the basis for defining Aero-Surf process advantages.

As a result of research, a significant body of information on BOD removal, nitrification and sludge characteristics has been produced.

The data in Figures 8, 9, and 10 were developed from the full-scale tests conducted at the South Shore plant.

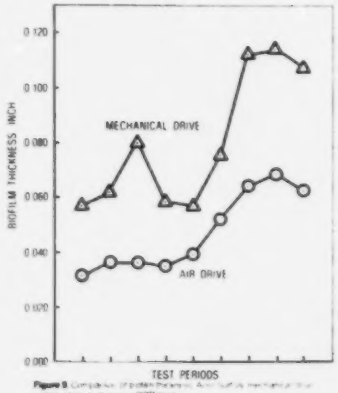

Figure 9. Comparison of biofilm thickness, Aero-Surf vs. mechanically-driven system, stage 1 at various BOD loads.

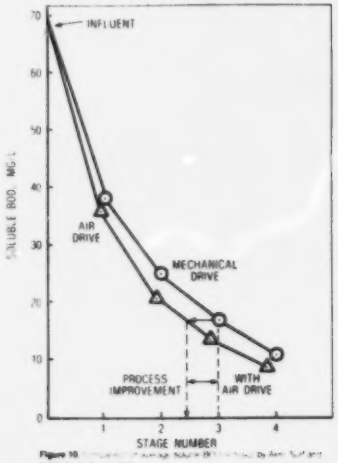

Figure 10. Comparison of average Aero-Surf vs. mechanically-driven systems.

Guelph. A Bio-Surf RBC in operation at Guelph, Ontario. Note the industrial size chains, sprocket and independent motor at Guelph report that the cost of installation and OMM including labor, power and maintenance was about 1/3 that of a comparable mechanically-driven system.

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US Department of Energy Report DOE/EIA - 0173(81)/3.

Biological Treatment of Cyanidation Waste Waters

T.I. Mudder and J.L. Whitlock

Abstract—*An attached growth aerobic biological treatment process has been developed at Homestake Mining Co.'s Lead operation which not only oxidizes free and complexed cyanides, including the stable iron complexed cyanides, but also thiocyanate, and the oxidation byproduct ammonia. Through the employment of a mutant strain of bacteria which has been gradually and specifically acclimated to the waste, these potential pollutants are mineralized to relatively harmless sulfates, carbonates, and nitrates. The resultant effluent, through toxicological testing, has been shown compatible with the receiving stream, which serves as a cold water marginal trout fishery.*

Introduction

Metal complexed cyanides in waste waters form as a result of interactions of free cyanide with metals present in the waste water and exhibit varying degrees of stability, toxicity, and treatability. Thiocyanate, a pollutant commonly found in cyanide-bearing waste waters, is formed through the interaction of free cyanide with sulfur containing species (i.e., pyrrhotite) both present in process and waste waters.

In certain industrial processes, such as the beneficiation of gold and silver, cyanide is an essential reagent. Since free cyanide, complexed cyanides, and thiocyanate are potentially toxic to humans and aquatic organisms, these compounds must be removed from waste waters prior to their discharge into surface or ground waters serving as potential potable water sources, marine or fresh water habitats.

Since 1977, personnel at Homestake Mining Co.'s Homestake gold mine in Lead, SD, have been engaged in research and development of a process to treat a maximum of 21,000 m^3d (5.5 million gpd) of combined mine and tailings impoundment waste waters (Table 1). The mine water is pumped continuously from underground and originates from several process and natural sources. The tailings impoundment waste water or decant water is separated from the tailings in a containment dam and flows to the treatment facility through pumping or by gravity. The treated waste water must be of high quality as it is discharged into Whitewood Creek, which serves as a cold water marginal trout fishery stocked seasonally with catchable-size brown trout.

Table 1—Chemical Characteristics of Combined Mine and Decant Waste Waters

Parameter	Value*
Thiocyanate	45.0-75.0
Total cyanide	0.50-10.00
Method-c cyanide	0.50-5.00
Iron	0.50-2.00
Copper	0.10-1.50
Nickel	0.10-.50
Zinc	0.10-.50
Ammonia-N	1.0-8.5
Phosphorous-P	trace
pH	5.5-10.0
Temperature (°C)	10-25

*All values in milligrams per liter except temperature and pH.

Various chemical and/or physical treatment processes were pilot plant tested and the effluents evaluated on both a numerical and toxicological basis in a flow-through bioassay facility to ensure effluent compatability with the receiving stream. However, construction of a treatment facility based upon chemical and/or physical processes never materialized due either to inadequate treatment performance, residual toxicological effects associated with the effluent, or prohibitive capital and/or operating costs.

As a result, beginning in early 1981, biological treatment was examined and evaluated on a pilot plant scale, yielding a simple cost effective process, the performance of which equaled or exceeded that of all other processes evaluated, while producing an environmentally compatible effluent. Actual construction of the facility was initiated in February 1983 with plant start up scheduled for the summer of 1984. The treatment plant design incorporated the use of flow equalization, 48 low- and high-density rotating biological contactors, and chemical addition for growth supplementation and residual metals/solids removal, secondary clarification, and pressure sand filtration (dual media).

T.I. Mudder and J.L. Whitlock, members SME, are chief environmental engineer and chief chemist, respectively, Homestake Mining Co., Lead, SD. SME preprint 84-37, SME-AIME Annual Meeting, Los Angeles, CA, Feb. 1984. MMP paper 84-607. Manuscript Nov. 1983. Discussion of this paper must be submitted, in duplicate, prior to Oct. 31, 1984.

Analytical and Toxicological Testing

Comparison and evaluation of the various treatment processes required accurate and interference free analytical procedures. Concurrently with the pilot plant testing of the chemical and physical treatment processes, research was conducted to evaluate and develop reliable methods for cyanide analysis. Two analytical methods with modification were found dependable and were used extensively in the laboratory during pilot plant evaluations. The modified ASTM procedures included the total cyanide reflux, substituting phosphoric acid for sulfuric acid, and the method-c cyanide reflux utilizing acetic acid, both methods allowing accurate and precise measurement of low levels of cyanide (0.02 mg/L ± 0.01 mg/L). The total cyanide reflux measured free and metal complexed cyanide, including cyanide bound to iron. The method-c cyanide measurement, considered the toxicologically significant cyanides, included free and metal complexed cyanides (i.e., copper, nickel, and zinc cyanides), except cyanide bound to iron. The biologically treated waste water provided additional accuracy and reliability in its analysis as potentially interfering substances were removed during treatment (i.e., thiocyanate) or were not required for treatment (i.e., chlorine, sulfur dioxide, copper, or hydrogen peroxide).

However, emphasis on specific parameter removal could have resulted in toxic effluents due to pollutants associated with or produced through breakdown of target pollutants that were not analyzed for and/or removed through further treatment. As a result, a toxicological testing facility was constructed with a twofold purpose. First to determine and compare the toxicological effects of the various treatment processes tested and second to utilize the data in the eventual development of site specific effluent discharge criteria. The organisms tested in acute (96 hr) and chronic long-term (greater than 21 days) flow-through bioassays included 5.1 cm (2 in.) fingerling rainbow trout and 15.2 cm (6 in.) stockable-size brown trout obtained from the local state fish hatchery. Other organisms tested in acute and long-term flow-through bioassays included the macroinvertebrates, stone flies, mayflies, and caddis flies. These organisms serve as the primary food source for the stocked trout populations, and therefore must be protected environmentally.

In addition, rapid measurement of relative process effluent toxicities was obtained with 48-hour static bioassays utilizing the microinvertebrate, *Daphnia magna*.

Evaluation of Chemical and Physical Treatment Processes

Several chemical and physical treatment processes were pilot plant evaluated either alone or in combination (Table 2). These processes included acidification/volatilization, ozonation, ion exchange, Prussian blue oxidation/precipitation, carbon adsorption, alkaline chlorination, and copper catalyzed hydrogen peroxide (DuPont Kastone process). The Inco sulfur dioxide oxidation/precipitation process was not pilot plant evaluated as estimates of chemical usage and sludge handling rendered the process cost prohibitive and impractical for this application. Prior to biological treatment, the pilot plant testing program indicated the Kastone process provided the best solution to Homestake's treatment problem, based upon numerical and toxicological evaluations. The patented copper catalyzed hydrogen peroxide process removed free and metal complexed cyanides, including the stable iron complexed cyanides, but it did not remove thiocyanate, the oxidation byproduct ammonia, or residual copper, all of which were potential toxicants requiring additional treatment for their removal. The process required large quantities of expensive chemicals resulting in expected high operating costs.

As a result, research was directed toward evaluation and development of a biological treatment that was theoretically capable of overcoming the limitations associated with other treatment processes, while producing a high-quality, low-toxicity effluent simply and cost effectively.

Development of the Biological Treatment Process

Although full-scale biodegradation of cyanidation waste water was not practiced in the mining industry, the literature indicated biological oxidation of free cyanide, metal complexed cyanides, thiocyanate, and their breakdown products was possible on a laboratory scale (Howe, 1965; Knowles, 1976; Murphy and Nesbitt, 1964; Pettet and Mills, 1954; Rael et al., 1977).

To test the effectiveness of biological treatment both suspended growth and attached growth processes were evaluated with and without supplemental carbon sources (raw sewage). The results indicated supplemental carbon sources were not required for the biological degradation of cyanide complexes and thiocyanate as these compounds themselves served as the sole carbon source for the bacteria. The biological processes tested included activated sludge, a suspended growth process, and several attached growth processes including trickling filters (rock and plastic media), biological towers, aerated biological filters (Eimco BAF process), and rotating biological contactors (RBCs) (Table 3).

The bacterial seed was obtained from several sources on Homestake property and was found indigenous to Homestake waste waters. During the pilot plant evaluations the bacteria were gradually and specifically acclimated to the waste water combination (mine/decant) to be treated. Although microbial seed was obtained from the local sewage treatment plant (activated sludge) to aid in inoculation of the various biological pilot units along with Homestake microbial seed, microbial characterization of the local sewage treatment plant (STP) activated sludge indicated the bacteria responsible for cyanide degradation were not present. Therefore, the use of microbial seed from the local STP was discontinued.

The only chemical requirements were an inorganic carbon source to aid nitrification (i.e., soda ash) and phosphorous as a trace nutrient (i.e., H_3PO_4). The biological treatment processes removed through oxidation and adsorption thiocyanate, free and metal complexed cyanides (including iron complexed cyanides), metals (principally copper), and ammonia, a byproduct of thiocyanate and cyanide degradation. The products of biological degradation included the relatively harmless anions sulfate, nitrate, and carbonate. The kinetics of thiocyanate, cyanide, and ammonia oxidation were generally zero order to levels of 1 mg/L for thiocyanate and cyanide, and 4-5 mg/L for ammonia. Below these levels the reaction kinetics shift to higher orders as substrate concentrations become limiting.

The activated sludge exhibited the highest degree of treatment efficiency with regards to total and method-c cyanide removal. However, due to slow microbial growth evidenced by long sludge ages (20 to 40 days) coupled with

accumulation of toxic metals within the biomass, the system failed at 60 days. Modification of the process to include pretreatment for metals removal would be required to yield a viable process, but was not tested as it was considered cost prohibitive and impractical in this application.

In general, all the attached growth processes mentioned yielded good to high-quality, low-toxicity effluents, but the RBC's superior performance coupled with its cost-effective design and low operating costs made it the process of choice for incorporation into the overall treatment plant design.

Biological Treatment Facility

In Figure 1 a schematic of the proposed biological treatment facility presently under construction is presented. Integral to the overall design was development of a steady flow system which allows precise control of the mine and tailings impoundment waste water flows and ratios. The ratio of the two waste waters is varied throughout the year and controlled either manually or automatically with the use of an on-line thiocyanate monitor developed by Homestake specifically for this application.

The rotating biological contactor design incorporated the use of low-density media in the first and second stages for thiocyanate and cyanide removal, and high-density media in the remaining stages for nitrification. To minimize structural problems and maximize process flexibility, several features were incorporated into the design. First, additional shafts were placed in the first and second stages to provide additional surface area to reduce biofilm thickness and biomass weight. Secondly, the fiberglass baffles between stages are removable, allowing plug flow or complete mix operation of the process. Thirdly, reversible variable speed drives were included on all RBC shafts. Lastly, supplemental air was made available to all stages to assure adequate dissolved oxygen and to provide for biomass stripping. The biomass weight was to be monitored with the aid of temperature-compensated electronic load cells with continuous readout capabilities. The RBCs are individually housed in insulated fiberglass covers.

Following the RBCs, ferric chloride and/or polymer can be added prior to secondary clarification to aid in residual metals and solids removal. The clarifier was constructed of concrete and was covered with a fiberglass dome. The clarifier underflow containing the settled solids was to be either discharged to the tailings impoundment or processed for metals recovery. Prior to discharge the waste water passes through three existing pressure sand filters which were retrofitted with dual media (sand and anthracite). The total hydraulic residence time through the RBCs, clarifier, and filters would be approximately five hours at 21,000 m^3/d (5.5 million gpd).

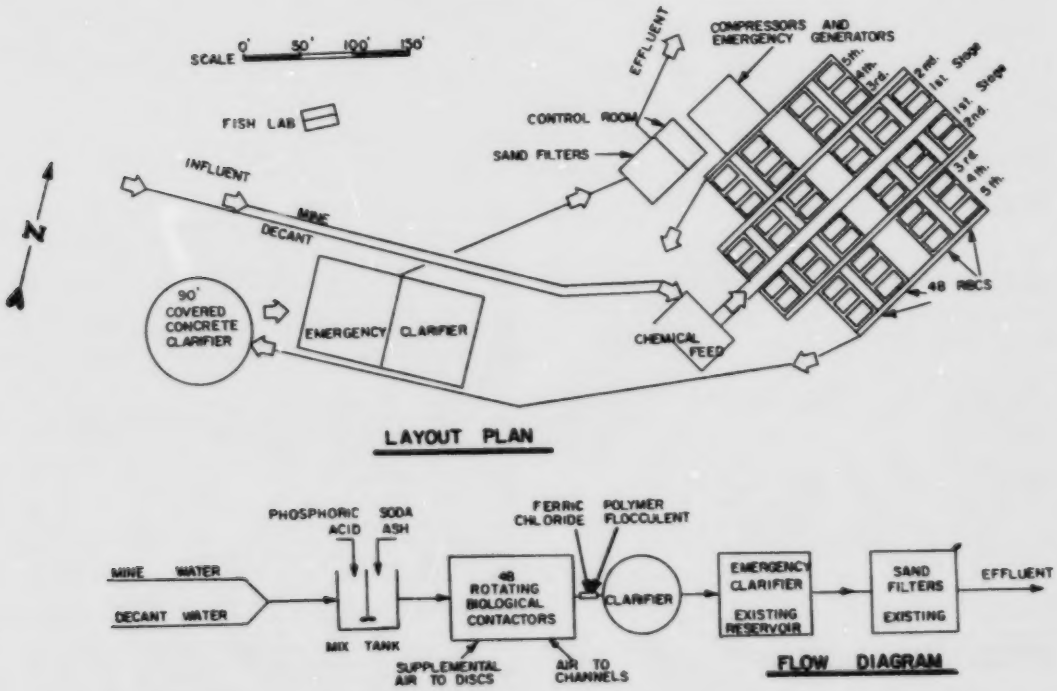

Fig. 1—Schematic of the biological treatment plant

Table 2 — Summary of Chemical/Physical Treatment Processes

Treatment Process	Summary of Parameter Removal					Comment
	Thiocyanate	Total Cyanide	Method-C Cyanide	Ammonia	Metals	
Ozonation	yes	no	yes	—	no	The pilot plant consisted of two 152-mm- (6-in.-) diam 5.5-mm (18-ft) plexiglass columns packed with 16-mm- (5/8-in.-) diam Pall rings. The columns were operated in series with the pilot plant flow, pH, and reaction time being 0.19 L/s (3.0 gpm), 8.0, and 2.5 hr, respectively. Excessive ozone demand if SCN is present (2.8gO_3/gCN^- and 4.2gO_3/g SCN^-). A staged sealed reactor with off-gas recycle would be required along with staged O_3 injection due to its low solubility. High capital and O/M costs if SCN^- is present as it is oxidized in preference to CN^-. Also a high level of operator expertise is required.
Acidification/ volatilization	—	yes	yes	no	no	The pilot plant consisted of a three-cell Denver flotation unit with the cells operated in series to achieve a 4.0-hr residence time at 0.05 L/s &0.80 gpm). The pH, air flow rates, and acid consumption were 3.0-4.0, 0.071 m^3/s (150 scfm), and 100 mg/L (0.0008 lb per gal) of H_2SO_4, respectively. Excessive air, power, acid, and base requirements rendered the process cost prohibitive.
Carbon adsorption	no	no	yes	—	no	The pilot plant consisted of two 152-mm- (6-in.-) diam plexiglass columns 2.4 m (8 ft) in length packed with 1.5 m (5 ft) of 12 mesh Westates GAC carbon. The two columns were operated in series of flow rates varying from 1.4-3.4 L/m^2/s (2-5 gpm/ft^2). SCN^-, total cyanide, and metals broke through quickly. Significant removal of method-c cyanide was realized. The carbon adsorption process was examined primarily as a polishing process for the biological treatment process. Regeneration of the carbon was not examined. Initial capital costs and projected operating costs were prohibitive.
Ion exchange	no	yes	yes	—	yes	The pilot plant consisted of 152-mm- (6-in.-) diam plexiglass columns 3.0 m (10 ft) in length containing a resin dept of 0.9-1.5 m (3-5 ft). The resins tested were all of the strong base type, such as A-101-D, as the metal cyanide complexes were negatively charged. An 8% NaOH solution was employed for backwash for 45 min at 3.4 L/m^2/s (5 gpm/ft^2). SCN^- breaks through quickly, irreversibly poisoning the resins. Ion exchange should be used only when SCN^- is not present and provides an acceptable polishing process in its absence. Other resins tested include A-102 and A-109. Flow rates of 1.4-3.4 L/m^2/s (2-5 gpm/ft^2) were examined. A-7 was also examined but lost its exchange capacity following successive regeneration.
Alkaline chlorination	yes	no	yes	yes	yes	The pilot plant consisted of three 200 L (55 gal) Nalgene barrels operated in series to produce a chlorine contact period of 45 min. The pilot plant flow was 0.19 L/s (3.0 gpm). Bleach was employed as the chlorine source and caustic was used for pH control (10.5-11.0). Following the oxidation sequence was clarification with polymer addition and pressure sand filtration. Sulfite and CO_2 were employed for residual Cl_2 destruction and pH adjustment, respectively. Ammonia could be destroyed if breakpoint Cl_2 was used. Excessive Cl demand if SCN^- is present (4.9gCl_2/g SCN^- and 2.8gCl_2/gCN^-). Process most viable for SCN^- and iron cyanide free waste waters.
Copper catalyzed hydrogen peroxide with ferric chloride addition for residual metals removal	no	yes	yes	no	yes	The pilot plant consisted of several 200 L (55 gal) Nalgene barrels operated in series to achieve a 2.5-hr contact period. The pilot plant flow rates varied from 0.13 to 0.20 L/s (2.0-3.0 gpm). 100 mg/L of H_2O_2, 10 mg/L of Cu, and 20.0 mg/L of $FeCl_3$ were employed. The pH was maintained at 9.0 with either caustic or lime. The process was operated at ambient temperatures. Following the oxidation sequence was a clarification step followed by pressure sand filtration. Excessive chemical requirements and costs rendered the process cost prohibitive for this application.

Table 3 — Summary of Biological Treatment Processes*

Parameter	Thiocyanate	Total Cyanide	Method-C Cyanide	Ammonia	Copper	Comment
Pilot plant influent	60.0 ± 10.0	6.50 ± 2.10	4.10 ± 1.30	6.0 ± 1.0	1.00 ± 0.40	The pilot plant influent is varied throughout the year from a ratio of 7/30 mine/decant (tailings impoundment) waste water in winter to 50/50 mine/decant waste water ratio in the summer. The pollutant concentrations are highest in the winter with temperatures falling to 10°C in the waste water.
2.0-m RBC pilot plant effluent	1.0	0.35 ± 0.10	0.05 ± 0.02	0.50	0.06 ± 0.02	The pilot plants were furnished by Envirex. The original feasibility study was undertaken with the use of a 0.5-m RBC pilot plant. The 2.0-m pilot plant was operated with the first and second stages unbaffled. Supplemental aeration was fed to each stage of the pilot plant at an equivalent rate of 0.07 m^3/s (150 scfm). Stripping of biomass required 0.283 m^3/s (600 scfm). The total surface area of the pilot plant was 743 m^2 (8000 ft^2). The pilot plant was operated at flow rates of 0.13-0.50 L/s (2.0-8.0 gpm). Effluent values recorded in this table were obtained on clarified and sand filtered effluent. The rate controlling oxidation in the overall design was nitrification.
Laboratory bench scale activated sludge	1.0	0.27 ± 0.27	0.06 ± 0.06	—	0.35 ± 0.12	The bench scale reactors consisted of 5-L (1.3-gal) plexiglass cylinders operated on a 24-hr draw and fill cycle. Sludge ages examined ranged from 10 to 40 days. Activated sludge from the local sewage treatment plant was utilized for the initial biomass along with microbial seed from Homestake sources. Eventually aeration periods from 2 to 24 hrs were examined. The system failed at 60 days due to metals accumulation and toxicity.
22-ft biotower	1.0	0.87 ± 0.30	0.08 ± 0.04	—	0.10 ± 0.04	The pilot plant consisted of a 0.6-m- (2-ft-) diam steel pipe 6.8 m (22 ft) in height packed with KORO-Z plastic media supplied by B.F. Goodrich Co. Maximum flow rate achieved was 0.17 L/m^2/s (0.25 gpm/ft^2) with 0.17 L/m^2/s (0.25 gpm/ft^2) recycle flow. Supplemental air was provided countercurrent to the gravity waste water flow. Nitrification data is not meaningful as soda ash was not added to the raw waste water feeding into the biotower. Trickling filters were also examined. The pilot plants consisted of two 1.8-m-/0.15-m-diam (6-ft-/6-in.-diam) plexiglass columns operated in series of flow rates similar to those of the biotower. The trickling filters were either packed with 16-mm- (5/8-in.-) diam Pall rings or crushed rock 13 mm (1/2 in.) in diam. The performance of the trickling filters was slightly less than the biotower.
Biological aerated filter (BAF process)	1.0	1.00 ± 0.60	0.06 ± 0.02	1.2 ± 0.7	0.03 ± 0.03	The pilot plant was supplied by Elmco. The pilot plant consisted of two 0.30-m- (1-ft-) diam plexiglass columns operated in series containing 1.8 m (6 ft) of their patented media. The columns were operated in parallel and in series. The data presented in this table was from the series operation. Hydraulic flow rates were varied from 0.27 to 1.0 L/m^2/s (0.40-1.50 gpm/ft^2). Supplemental aeration was added countercurrent to the gravity waste water flow.

**All values in milligrams per liter.*

Future Research and Development

Present research is directed at elucidation of the specific reaction orders and rates of thiocyanate, free cyanide, and metal complexed cyanide degradation. In addition, further research is required to determine the maximum levels of thiocyanate and cyanide degradation possible. Also, research continues to examine additional biological (algae) and chemical (ferric salts) treatment processes to aid in removal of residual copper in the effluent.

Toxicological testing continues with emphasis on developing site-specific discharge criteria and elucidation of the relationship of light intensity to the breakdown of iron complexed cyanides.

The full-scale facility will be in operation by August 1984, with two patents being received by the authors on behalf of Homestake covering the specific bacteria responsible for the thiocyanate and cyanide degradations and its use in the accompanying process. ■

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OPERATION	HOMESTAKE MINING COMPANY LOWER LAKE, CA 94557
TELEPHONE	(916) 446-1029
CONTACT	Jack E. Thompson, General Manager
COMPANY	HOMESTAKE MINING COMPANY 650 California Street San Francisco, CA 94108
TELEPHONE	(415) 981-8150

CONTACTS	Harry M. Conger	Chairman
	William A. Humphrey	Executive Vice President
	Rex Guinivere	Vice President, Engineering
	David B. Crouch	Manager - Environmental

METALLURGICAL SUPPORT

Homestake Mining Company
1726 Cole Blvd.
Golden, CO 80401

TELEPHONE (303) 277-0700

Robert D. Lear
Richard S. Kunter
John R. Turney

INTRODUCTION

The McLaughlin project is interesting in several respects:

1. It is the most expensive gold mine to be installed in North America to date, and the first to use pressure oxidation to treat refractory gold ore.

2. It is located in California in a high profile area above Lake Berryessa, overlapping three counties with different environmental regulations. The operating permits are more comprehensive than most.

3. Pressure oxidation will be used to treat the ore ahead of cyanidation, to liberate gold from an ore containing pyrite and sulfosalts.

4. A total of more than 280 permits had to be applied for in order to bring this project into operation.

From a water management standpoint there are several interesting features:

5. During the pressure oxidation step numerous metals are brought into acid solution. The pre-oxidized pulp is washed in two 55' Ø Enviroclear thickeners (6:1 wash ratio) ahead of leaching to remove as much of the dissolved metals and acid which are precipitated and neutralized using feed to the autoclaves which has a high carbonate level. Thereafter the separated solution is to be neutralized with lime to precipitate $Fe(OH)_3$ and $Mg(OH)_2$ as well as the metals that precipitate at higher pH. This will require 150-200 tpd lime depending on the amount of sulfide in the ore.

   Removal of the metals ahead of cyanidation reduces cyanide consumption and results in lower complex cyanides reaching the tailings pond.

   A general arrangement of the mine, mill, tailings, wasterock and metallurgical process is shown in the attached diagram from KUNTER et al. (1984).

6. As a result of autoclave oxidation, generally silver recovery in the subsequent cyanidation step will be poor as silver, along with heavy metals become tied up in jarosites. Modification of the pressure oxidation conditions is reported to improve silver recovery significantly (BULL et al. 1984; and WEIR, 1985), but raises new questions about the ultimate disposition of other metals in the circuit and tailings.

7. Tailings will be disposed of using a layered sub-aerial method similar to that used in South Africa and at Key Lake Mining in Saskatchewan. The tailings pond has a naturally impermeable clay base and will have a large gently sloping beach area and a large evaporation pond.

8. Because sulfides in the tailings have mostly been oxidized in the autoclave preoxidation step, the tailings will have a low sulfide content that one day could become a source of acid mine drainage. In this way McLaughlin will avoid the threat of serious future acid mine drainage problems.

9. Wasterock disposal sites will not be required to be lined because of the managed method in which the waste is disposed of.

10. The decision to proceed with this $250 million project was made at a time when gold prices were significantly higher than they are today. Ultimate process parameters and performance data as well as the economics of this fine new gold recovery

operation will be significant to many current projects under evaluation around the world that anticipate using pressure oxidation ahead of cyanidation.

11. Seldom, perhaps never, has a mining company gone to such lengths to make a mine-mill-tailings complex compatible with the environment and the community. This operation will hopefully be the one that swings public opinion around to favor responsible mining operations in their midst. The McLaughlin project is located at the site of an old mercury mine which did disfigure the landscape many years ago. Homestake will take this opportunity to leave the area in better condition than they found it.

12. The McLaughlin project is to be operated as a zero discharge site which is possible because of its net evaporation climate. Nonetheless careful water balance modelling on an annual and seasonal basis has been necessary. The generalized network flow computer model called Modsim used for the purpose was described by FERGUSON et al (1983).

13. The McLaughlin operation represents the current state of the art in mine-mill-tailings design from an environment protection standpoint.

LOCATION	Knoxville, California about 80 miles northeast of San Francisco, just north of Lake Berryessa.
CAPACITY	Mill 3000 stpd
STARTUP	June 1985 (projected)
STRIP RATIO	5 to 5½ : 1 Ultimately the pit will be 1 mile long, 0.5 miles wide and 700 feet deep.
ORE GRADE	20 million tons at 0.16 oz/t. Actual grade varies considerably as there are high grade ore zones.

ORE TYPE

The epithermal ore occurs in a major thrust zone. The orebody is complex and contains twelve distinct ore types nearly all with complex mineralogy which render the ore refractory. Gold is disseminated and fine grained (about 20 micron mean gold particle size), associated with fine grained sulfide minerals.

Sulfides are mainly pyrite, with minor marcasite, chalcopyrite, sphalerite and cinnabar. Gold occurs typically as gold silver electrum associated primarily with silver antimony sulfosalts, miargyrite, pyraginite, freibergite and polybasite, and also occurs locked in gangue.

Just about every base metal in the periodic table is associated with this ore including 1 oz Hg per ton ore.

The gold is refractory for three main reasons reported by KUNTER (1984).

1) Encapsulation in sulfides and sulfosalts.
2) Pressence of preg-robbing carbonaceous and clay materials.
3) Surface coatings of jarosite and hematite on weathered ore.

PROCESS SELECTED

The selected process according to KUNTER et al. (1984) and GUINIVERE (1984) is as follows:

- Contact the ore with acid to reduce $CO_3^{=}$ content
- Pressure oxidation in autoclave at 160-180°C
- Washing to remove soluble metals
- Cyanidation to leach gold
- CIP Gold recovery
- Sub-aerial tailings disposal

KUNTER et al. (1984) report the following conditions for the autoclave reaction:

Pressure	1300 kPa (188psig)
Temperature	160-180°C
Retention Time	1.5 - 2 hours
Pulp density	40 - 45%
Final Acidity	15 - 20 g/l H_2SO_4
Final emf	420 milliwatts (SCE)

The above conditions achieve oxidation of at least 90% of the sulfides present which is necessary to make the gold amenable to cyanidation. However, more than 92% of the silver and iron was found to report to the fines fraction of the oxidation residue which suggests that the silver is lost as an argentojarosite.

OPERATING COST

Estimated "cash costs" of around $240/oz. Autoclave preoxidation approximately doubles the operating cost to $25-35/t range.

RECOVERY

Recoveries of about 95% are indicated when the above process is used compared with direct cyanidation recoveries varying form 5% to 80% depending on the percentage of gold locked in the sulfides and the presence of carbonaceous materials, clays and surface coatings. Average recovery without oxidation is around 45%.

METALLURGICAL TESTING

The test and development results that went into the selection of pressure oxidation ahead of cyanide leaching are described by KUNTER et al. (1984).

Roasting and cyanidation of calcines was rejected because the ore contains mercury and insufficient sulfur for acid production. Flotation, roasting and calcine leaching results in lower recoveries.

Several other processes were tested and rejected on the grounds of inadequate recoveries:

- direct cyanidation
- direct leaching with non-cyanide reagents
- chemical oxidation by chlorine, ferric chloride, thiosulfate and sodium sulfide.

None of the above achieved a satisfactory recovery - invariably 0.05 Au/t or more was left in the leach residue solids.

ENVIRONMENTAL PERMITTING

The operation area is spread out over a 25 mile long project site which overlaps Yolo, Lake and Napa Counties, each of which has a different set of regulations. Napa County also falls in the Bay Area Air Quality District. Napa County became the lead county and was made responsible for data collection for the EIR. An environmental data aquisition committee was formed which involved Homestake Mining Comapny and 28 specialty subcontractors to gather environmental data. Homestake elected to proceed with development of the project in July 1982 and filed a draft EIR in August 1982 three years from the first step in evaluating the project. Preliminary permits were granted in September 1983 and construction commenced immediately. More than 285 permits were required and decisions were needed on 40 options. Under the regulations it is not

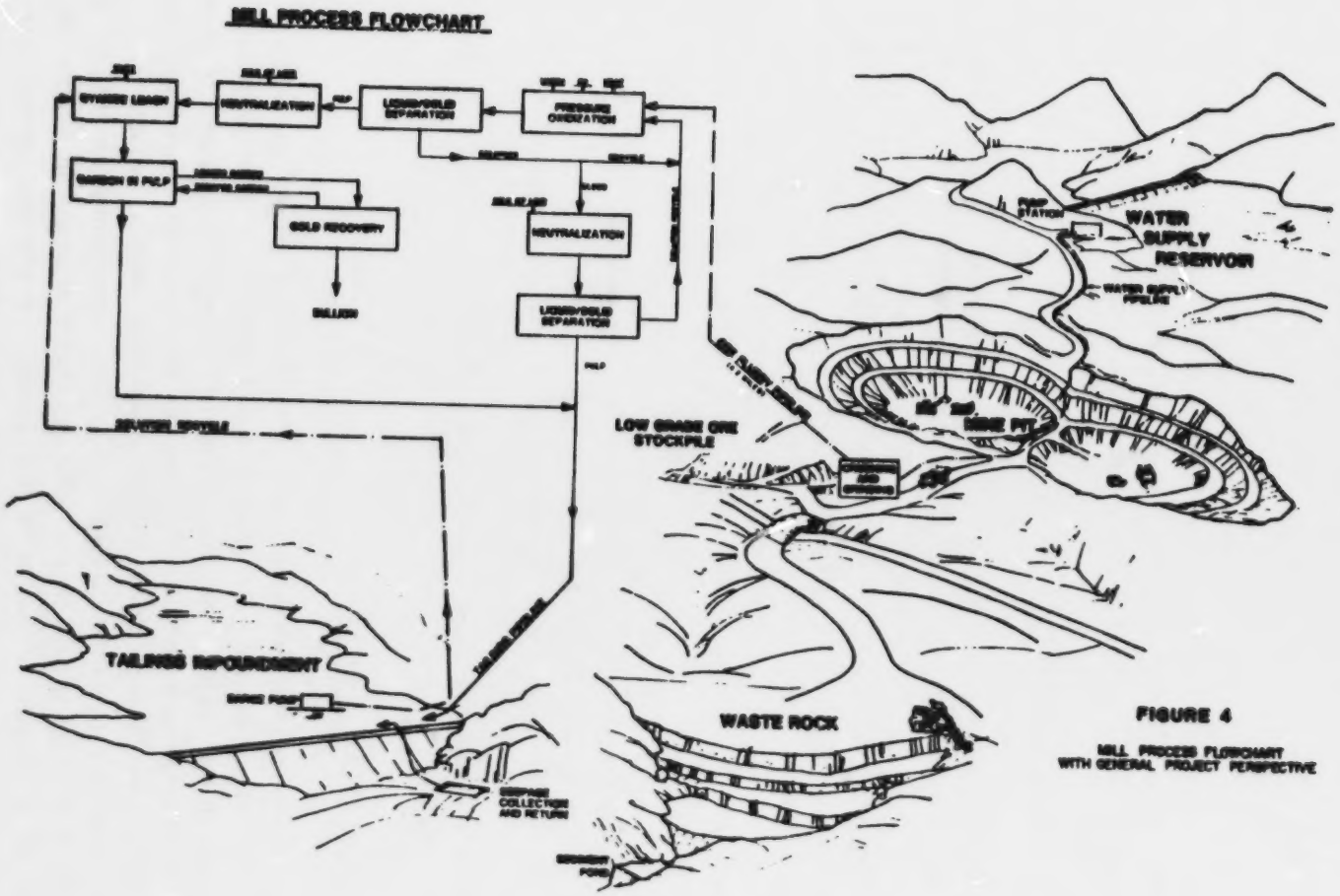


FIGURE 4

MILL PROCESS FLOWCHART WITH GENERAL PROJECT PERSPECTIVE

permissible even to store equipment on site that make dust until the Bay Area Air Quality permit has been granted. The new mine-mill operation required 13 million yd^3 earthwork and construction of a 6000 acre ft reservoir on site with 120 ft high wall and 1 million yd^3 earthworks.

Environmental problems encountered were overcome as follows:

1. Tailings pond was required to be zero discharge. The site selected for tailings disposal has a naturally low permeability of less than 10^{-7} cm/sec.

2. The tailings pond is installed down grade from the processing area so all spills will end up in the tailings pond.

3. Wasterock will be disposed of close to the mine on top of serpentenites. Drainage from the area is to Hunting Creek and ultimately to Lake Berryessa. Extensive cut-off trenches, rock drains and settlement ponds have been constructed to prevent pollution of the Berryessa system.

   Sulfide containing wasterock to be surrounded by high lime containing wasterock to neutralize any acid mine drainage generated.

4. Low grade ore stockpiles and waste liquor are placed over 10 ft wide 5 ft deep underdrains to collect seepage from both the low grade ore stockpiles and wasterock disposal site.

5. A study comparing haul vs. conveyors vs. pipeline conveying of crushed ore to the process area led to selection of pipeline transfer as being the most environmentally favorable.

Homestake Mining Company's Environmental Control Department supervised the permitting process with significant help from several carefully selected contractors:

EIS and Baseline studies:	D'Appolonia & Associates, now IT Corporation 17500 Red Hill Avenue Irvine, CA 92714 Telephone (714) 261-6441 Contact Ed Sirota
Air Quality Permits:	ERT Corporation
Socio-Economics:	Dames & Moore

Permitting, and quality assurance on all aspects of the project that could impact the environment from a water standpoint, including the water supply reservoir, wasterock disposal, tailings impoundment (including design), water balance management, runoff water collection and control were provided by:

Steffen Robertson & Kirsten
7510 West Mississippi Ave. # 210
Lakewood, CO 80226

Telephone (303) 936-8254
Contact Dr. Ian P. G. Hutchison
Dr. Phil DeDycker

COST OF ENVIRONMENTAL CONTROL MEASURES

The environmental impact report and data gathering backup cost $6 million. Dams for sediment control in runoff water cost $5 million. Overall $11 million has been spent on special design features for dust collection and water runoff control during construction and operation.

Just the quality assurance program for the water supply reservoir, wasterock disposal, tailings impoundment, water balance management and runoff collection and control, and associated permits cost around $2 million.

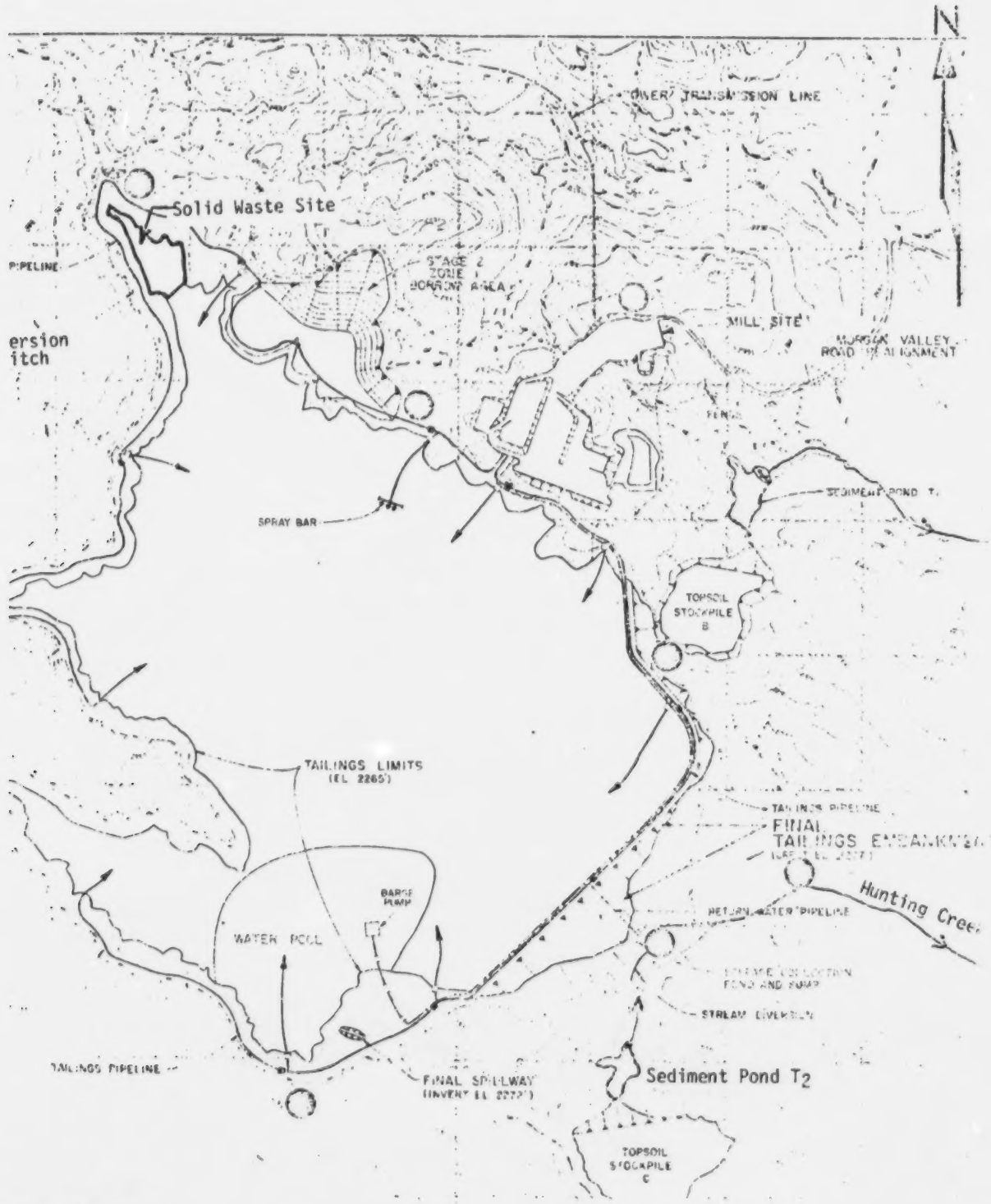
PERMITS

Of the 231 permits required to bring the McLaughlin project into production Randol International Ltd. found two of particular relevance to water management. These were the tentative California Regional Water Quality Control Board, Central Valley Region order for Waste Discharge Requirements, and the Federal NPDES Permit which is also administered by the California Regional Water Quality Control Board - Central Valley Region. Of these two permits, the NPDES permit is the shortest and simplest. It is inserted below to provide an idea of the kind of monitoring and reporting that is required for this operation in California.

OPERATOR TRAINING

An important aspect of water management, and environmental control is operator awareness and training. Homestake has established a training school on the property. Of the roughly 1200 people involved in the construction phase, about 250 will be kept on to operate the mine and the plant.

Detailed models of the complete project have been constructed as a design, construction and training aid. A computer model of the oxidation process provides input to an operator interface unit of the Bailey System 90 DCS to simulate this area for operator training.



Attachment " B "
McLaughlin Mine Tailings Disposal Reservoir

Potential Monitoring Well Locations

ENGINEERING CONTRACTOR

Engineering design for the McLaughlin plant was awarded to:

Davy McKee Corporation
P. O. Box 5500
San Ramon, CA 94583

Telephone (415) 838-1166
Telex 337635

REFERENCES

BULL, REX; SPOTTISWOOD, D.; TOURRE, JEAN MICHAEL (1985) Pre-Oxidation of Sulfides in Gold & Silver Ores - Control of Silver Lones. N.W. Mining Association, Spokane, 7 December 1984.

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KUNTER, R.S.; TURNEY, J.R. & LEAR R.D. (1984) McLaughlin Metallurgical Development, The Project, The Problems, The Process. International Precious Metals Symposium, Metallurgical Society of AIME and International Precious Metals Institute, Los Angeles, CA, February 26-March 1, 1984.

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Federal

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

ORDER NO. _____

NPDES NO. CA0081477

WASTE DISCHARGE REQUIREMENTS
FOR
McLAUGHLIN MINE
HOMESTAKE MINING COMPANY
AND
US BUREAU OF LAND MANAGEMENT
YOLO, LAKE AND NAPA COUNTIES

The California Regional Water Quality Control Board, Central Valley Region (hereafter Board), finds that:

1. Homestake Mining Company (hereafter Discharger) submitted a report of waste discharge, dated 15 April 1983, to discharge waste under the National Pollutant Discharge Elimination System.

2. The proposed mining operation will operate in part on public lands administered by the US Bureau of Land Management (hereafter Discharger).

3. The Discharger proposed to discharge water in contact with mine activities from five sedimentation ponds into Hunting Creek and Knoxville Creek, both tributary to Lake Berryessa, a water of the United States.

4. Homestake Mining Company proposes to develop a gold mine and mineral extraction facility (mill) to process about 4000 tons of ore per day. Units of the mine include: mine pit, waste rock site, grinding and crushing area, mill, low grade ore storage, slurry line, tailings disposal facility, water supply reservoir, interconnecting roadways and electrical transmission corridor.

5. The mining process will begin at an open pit mine which will ultimately be one mile long, one-half mile wide and 400 feet deep. Higher grade ore bearing rock will be crushed, ground and piped through a 4-1/2 mile slurry pipeline to the mill site. Waste rock from the mine pit will be disposed of on 342 acres some of which are public lands administered by the US Bureau of Land Management. The pipeline slurry will undergo a cyanide leach process to extract gold at the 35 acre mill site. Processed slurry will be discharged to the 546 acre tailings disposal facility.

6. The discharge to land of all mining activities, including the tailing disposal reservoir, is regulated through separate waste discharge requirements.

7. The report of waste discharge describes the water discharge as follows:

Pond	Discharge Point Serial Number	Description
T_1	001	Sediment trap for topsoil stockpile taken from the tailings reservoir. T_1 will function primarily during the first three years before the topsoil is revegetated and again towards the end of project during the reclamation phase. During most of the operating life of the project, the sediment yield to the pond is expected to be minimal. The pond will be maintained for the entire project and reclamation period.
T_2	002	Same as pond T_1.
W_1	003	Sediment trap for the waste rock disposal facility from stormwater runoff and waste rock subdrainage. This pond will be required for the life of the project.
W_2	- -	Sediment trap within the waste rock disposal facility. This pond may or may not be required. If constructed, it would flow only into pond W_1, and therefore would not be an NPDES discharge point.
M_1	004	Sediment trap for the grinding facility area during the mine construction period only (i.e., the first 1 to 2 years). Thereafter, the pond will be used as a water-recycling pond and will not be an NPDES discharge point.
M_2	005	Sediment trap for the early years of development at the south pit. This pond will be required for approximately the first 7 years of mining. Thereafter, all runoff from pit disturbance will be contained within the pit and the pond decommissioned.

8. The Board, on 25 July 1975, adopted a Water Quality Control Plan for the Sacramento River Basin (5A). These requirements are consistent with the Plan.

9. The beneficial uses of Lake Berryessa are municipal, industrial, and agricultural supply; recreation; esthetic enjoyment; navigation; ground water recharge; fresh water replenishment; hydroelectric power generation; and preservation and enhancement of fish, wildlife and other aquatic resources.

10. The beneficial uses of the ground water downstream of the project are municipal and agricultural supply.

11. The chemical quality of the ground and surface waters in the immediate vicinity of the tailings disposal facility and the waste rock disposal facility is generally poor, when compared to EPA Primary and Secondary Drinking Water Standards. Boron levels frequently exceed the recommended levels for continuous irrigation use.

12. Effluent limitation standards established pursuant to Sections 301, 302, and 304 of the Federal Water Pollution Contol Act and amendments thereto are applicable to the discharge.

13. On 6 July 1983, the Napa County Planning Commission certified the final Environmental Impact Report/Environmental Impact Statement (EIR/EIS) for the Homestake Mining Company McLaughlin Gold Project in accordance with the California Environmental Quality Act (CEQA) Public Resources Code Sections 21000, et seq. The EIR/EIS discloses that the project may have the following significant impacts on water quality:

    a. Increased erosion during construction.

    b. Landslides along the perimeter of the water reservoirs.

    c. Increased sedimentation to streams during construction.

    d. Increased TDS and heavy metals concentration to Hunting Creek downstream of the waste rock dump.

    e. Contamination of Hunting Creek from accidental spills of mill reagents or tailings disposal facility rupture.

14. The Board has reviewed the EIR/EIS. These waste discharge requirements provide protection to water quality equal to or more effective than the mitigation measures in the EIR/EIS relating to water quality. Compliance with these waste discharge requirements will mitigate or avoid the following significant impacts on water quality listed in Finding 13:

    a. Landslides along the perimeter of the water reservoir. Mitigation of this potential impact is required by turbidity, sedimentation and erosion controls contained in these requirements.

    b. Increased TDS and heavy metals concentration to Hunting Creek downstream of the waste rock dump. Mitigation of this potential impact is accomplished by receiving water limitations on heavy metals and the requirement to implement best available technology (BAT) to limit mineralization.

15. The following impacts will be mitigated to some extent by these requirements, but the EIR/EIS identifies these as unavoidable potentially significant environmental impacts:

    a. Increased erosion during construction.

b. Increased sedimentation to streams during construction.

c. Contamination of Hunting Creek from accidental spills of mill reagents or tailings disposal facility rupture.

While these significant detrimental impacts may occur, the Board finds these impacts are outweighed by the potential benefits of the project. This decision is based on the two potential benefits to water quality listed in the EIR/EIS:

a. Long-term improvement to Knoxville Creek water quality downstream of mine pit due to the ultimate elimination of poor quality runoff from the mine pit area.

b. Long-term reduction in sedimentation to Davis Creek downstream of the reservoir through dam releases of better-quality water than that presently existing.

16. Subsequent to the preparation of the final EIR/EIS, Discharger and the Solano Irrigation District (SID) entered into an Agreement (the SID Agreement) which provides for a comprehensive monitoring program and a series of response mechanisms designed to preclude any potential adverse environmental impacts on water quality which might otherwise occur in connection with the project. Pursuant to the SID Agreement, Discharger has agreed to comply with specified requirements in order to assure nondegradation of the water quality of any surface or subsurface waters flowing or draining into or through Hunting, Soda, Knoxville, Putah or Eticuera Creeks into Lake Berryessa.

17. The Board has notified the Discharger and interested agencies and persons of its intent to prescribe waste discharge requirements for this discharge and has provided them with an opportunity for a public hearing and an opportunity to submit their written views and recommendations.

18. The Board, in a public meeting, heard and considered all comments pertaining to the discharge.

19. This Order shall serve as a National Pollutant Discharge Elimination System permit pursuant to Section 402 of the Federal Water Pollution Control Act, or amendments thereto, and shall take effect ten days from the date of hearing, provided EPA has no objections.

IT IS HEREBY ORDERED, Homestake Mining Company and the property owner, in order to meet the provisions contained in Division 7 of the California Water Code and regulations adopted thereunder and the provisions of the Federal Water Pollution Control Act and regulations and guidelines adopted thereunder, shall comply with the following:

A. Prohibitions:

1. The discharge of domestic sewage, industrial wastes and runoff from ore stockpiles and process chemical storage/receiving areas, which is deleterious to fish, wildlife or other beneficial uses, is prohibited.

B. Effluent Limitations:

1. The discharge of an effluent in excess of the following limits is prohibited:

Constituents	Units	30-Day Average	Daily Maximum
Suspended Solids	mg/l	20	30
Settleable Solids	ml/l	1.0	5.0
Arsenic	mg/l	0.05	0.10
Cadmium	mg/l	0.01	0.02
Chromium	mg/l	0.05	0.10
Copper	mg/l	0.15	0.30
Mercury	mg/l	0.001	0.002
Lead	mg/l	0.05	0.10
Zinc	mg/l	0.75	1.5

Metals shall be analyzed and reported as totals.

2. The discharge shall not have a pH less than 6.5 nor greater than 9.0.

3. The Discharger shall use the best available technology to limit mineralization to no more than a reasonable increment.

4. Discharge to surface waters shall be limited to discharge from the sediment control ponds.

C. Receiving Water Limitations:

1. The Discharger shall not cause the dissolved oxygen concentration in Hunting or Knoxville Creek to fall below 5.0 mg/l.

2. The discharge shall not cause visible oil, grease, scum, foam, floating or suspended material in the receiving waters or watercourses.

3. The discharge shall not cause a measurable increase, over upstream levels of the receiving waters, of the following constituents: Arsenic, Lead.

4. The discharge shall not cause a statiscally significant, incremental increase of more than 10% (or, if greater than 10%, the minimum percentage increase that may be accurately measured) over upstream levels of the receiving waters, of the following constituents: Mercury, Chromium, Cadmium, Boron, Copper, Nickel.

5. The discharge shall not cause sedimentation or concentrations of any materials in the receiving waters which are deleterious to human, animal, aquatic, or plant life.

6. The discharge shall not cause esthetically undesirable discoloration of the receiving waters.

7. The discharge shall not cause fungus, slimes, or other objectionable growths in the receiving waters.

8. The discharge shall not cause bottom deposits in the receiving waters.

9. The discharge shall not increase the turbidity of the receiving waters by more than 10% over immediately upstream levels.

10. The discharge shall not alter the pH of the receiving water more than 0.5 units from immediately upstream levels.

11. The discharge shall not increase the temperature of the receiving water more than 5°F (3°C) from immediately upstream levels.

12. The discharge shall not cause a violation of any applicable water quality standard for receiving waters adopted by the Board or the State Water Resources Control Board as required by the Federal Water Pollution Control Act and regulations adopted thereunder. If more stringent applicable water quality standards are approved pursuant to Section 303 of the Federal Water Pollution Control Act, or amendments thereto, the Board will revise and modify this Order in accordance with such more stringent standards.

13 This permit shall be modified, or alternatively, revoked and reissued, to comply with any applicable effluent standard or limitation issued or approved under Sections 301(b)(2)(C), and (D), 304(b)(2), and 307(a)(2) of the Clean Water Act, if the effluent standard or limitation so issued or approved:

(a) Contains different conditions or is otherwise more stringent than any effluent limitation in the permit; or

(b) Controls any pollutant not limited in the permit.

The permit as modified or reissued under this paragraph shall also contain any other requirements of the Act then applicable.

D. Provisions:

1. Neither the discharge nor its treatment shall create a nuisance or pollution as defined in Section 13050 of the California Water Code.

2. The settling ponds shall be designed to contain the flow from the 10 year frequency storms in a 24 hour period.

   Annually, prior to the rainy season, the settling ponds shall be inspected and maintained to ensure the design capacity is provided.

3. The Discharger shall comply with all the items of the "Standard Provisions and Reporting Requirements (NPDES)", dated 1 January 1982, which are part of this Order.

4. The Discharger shall comply with the attached Monitoring and Reporting Program No. _____ as ordered by the Executive Officer.

5. This Order expires on 1 August 1988 and the Discharger must file a Report of Waste Discharge in accordance with Title 23, California Administrative Code, not later than 180 days in advance of such date as application for issuance of new waste discharge requirements.

6. In the event of any change in control or ownership of land or waste discharge facilities presently owned or controlled by the Discharger, the Discharger shall notify the succeeding owner or operator of the existence of this Order by letter, a copy of which shall be forwarded to this office.

7. The provisions of this Order are not intended to, and shall not limit or reduce any obligations or requirements which are additional to, or more stringent than, those created pursuant to this Order and which are imposed on the Discharger pursuant to (a) the terms of any agreement to which the Discharger is a party, including but not limited to, that certain agreement dated as of 30 June 1983, by and between the Discharger and the Solano Irrigation District, or (b) the requirements and controls imposed by any governmental agency or other authority having jurisdiction with respect to the Project. Nothing in this paragraph shall be construed to release or excuse the Discharger from full and timely compliance with the requirements of this Order or amendments or supplements hereto.

I, WILLIAM H. CROOKS, Executive Officer, do hereby certify the foregoing is a full, true, and correct copy of an Order adopted by the California Regional Water Quality Control Board, Central Valley Region, on _____.

_____
WILLIAM H. CROOKS, Executive Officer

GKV:dg
Revised 9/02/83

Attachments

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

MONITORING AND REPORTING PROGRAM NO. _____

NPDES NO. CA0081477

FOR
McLAUGHLIN MINE
HOMESTAKE MINING COMPANY
AND
US BUREAU OF LAND MANAGEMENT
YOLO, LAKE AND NAPA COUNTIES

Sample stations shall be established such that the samples are representative of the volume and nature of the discharge.

EFFLUENT MONITORING

During each discharge period, the discharge from each settling pond (discharges 001, 002, 003, 004, 005) shall be sampled and analyzed according to the following schedule:

Constituent	Units	Type of Sample	Frequency
Flow	Gallons per day	Estimate	Daily
Temperature	°C	Grab	Daily
TDS	mg/l	Grab	Daily
EC	umhos/cm	Grab	Daily
pH (field)	pH units	Grab	Daily
pH	pH units	Grab	Daily
Suspended Solids	mg/l	Grab	Daily
Settleable Solids	ml/l	Grab	Daily
Total Alkalinity	mg/l	Grab	Daily
Calcium	mg/l	Grab	Daily
Chloride	mg/l	Grab	Daily
Nitrate	mg/l	Grab	Daily
Sulfate	mg/l	Grab	Daily
Ammonia	mg/l	Grab	Daily
Boron	mg/l	Grab	Daily
Arsenic	mg/l	Grab	Daily
Barium	mg/l	Grab	Daily
Beryllium	mg/l	Grab	Daily
Cadmium	mg/l	Grab	Daily
Chromium	mg/l	Grab	Daily
Copper	mg/l	Grab	Daily

Constituent	Units	Type of Sample	Frequency
Iron	mg/l	Grab	Daily
Lead	mg/l	Grab	Daily
Magnesium	mg/l	Grab	Daily
Manganese	mg/l	Grab	Daily
Mercury	mg/l	Grab	Daily
Nickel	mg/l	Grab	Daily
Sodium	mg/l	Grab	Daily
Selenium	mg/l	Grab	Daily
Vanadium	mg/l	Grab	Daily
Zinc	mg/l	Grab	Daily

Metals shall be analyzed and reported as totals.

RECEIVING WATER MONITORING

Receiving water samples shall be collected daily during periods when discharge is occurring. All samples shall be grab samples taken near mid-stream, where safety permits. Samples shall be taken from each sampling station and analyzed for the following constituents:

Station	Description
R-1	Hunting Creek, upstream of tailings disposal pond or at the northern end of the tailings stormwater diversion ditch
R-2 (HC-9)	Hunting Creek, 1/2 mile downstream of tailings dam
R-3 (HC-5)	Hunting Creek, 1/2 mile upstream of Waste Rock Disposal area
R-4 (HC-10)	Hunting Creek, 1/2 mile downstream of Waste Rock Disposal area
R-5 (KC-3)	Knoxville Creek, 1/4 mile west of Knoxville

Constituent	Units
Flow	Gallons per day
Temperature	°C
TDS	mg/l
EC	umhos/cm
pH (field)	pH units
pH	pH units
Suspended Solids	mg/l
Settleable Solids	ml/l

Constituent	Units
Total Alkalinity	mg/l
Calcium	mg/l
Chloride	mg/l
Nitrate	mg/l
Sulfate	mg/l
Ammonia	mg/l
Boron	mg/l
Arsenic	mg/l
Barium	mg/l
Beryllium	mg/l
Cadmium	mg/l
Chromium	mg/l
Copper	mg/l
Iron	mg/l
Lead	mg/l
Magnesium	mg/l
Manganese	mg/l
Mercury	mg/l
Nickel	mg/l
Sodium	mg/l
Selenium	mg/l
Vanadium	mg/l
Zinc	mg/l
Turbidity	NTU

Metals shall be analyzed and reported as totals.

REPORTING

In reporting the monitoring data, the Discharger shall arrange the data in tabular form so that the date, the constituents, and the concentrations are readily discernible. The data shall be summarized in such a manner to illustrate clearly the compliance with waste discharge requirements.

Monthly monitoring reports shall be submitted to the Regional Board by the 15th day of the following month.

If the Discharger monitors any pollutant at the locations designated herein more frequently than is required by this Order, he shall include the results of such monitoring in the calculation and reporting of the values required in the Discharge Monitoring Reporting Form. Such increased frequency shall be indicated on the Discharge Monitoring Reporting Form.

The Discharger shall submit a report to the Board by 30 January of each year containing both tabular and graphical summaries of the monitoring data obtained during the previous year. In addition, the Discharger shall discuss the compliance record and the corrective actions taken or planned which may be needed to bring the discharges into full compliance with the waste discharge requirements.

The Discharger shall implement the above monitoring program on the effective date of this Order.

Ordered by _____
WILLIAM H. CROOKS, Executive Officer

_____
(Date)

GKV:dg
7/12/83

OPERATION	KLOOF GOLD MINING CO. LTD. P. O. BOX 190 WESTONARIA, TRANSVAAL
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CONTACTS	B. Schmitz, Consulting Mechanical & Electrical Engineer B. Sontar, Assistant Consulting Mechanical Engineer

INTRODUCTION

Gold Fields of South Africa have examined aspects of water conservation since 1978 when a Water Committee was formed.

Kloof is one of the Gold Fields of South Africa Ltd. Mine - Mill complexes which has been selected to test ways of reducing water purchases from the Rand Water Board through developing technology for increased recycle of water. A systems approach has been employed which involves the mine, mill, tailings dam and sewage reclaim water.

During this investigation it was still too early for detailed data from Kloof to be released. No visit was made to the property. However, some general information was gathered about some of the new approaches being tested at Kloof, including:

1) Treatment of reclaimed sewage water for use in cooling of underground workings.

2) Underground hydropower generation using the hydrostatic head from surface water.

3) Removal of algae, bacteria and other pollutants from sewage treatment plant effluent by dissolved air flotation after $FeCl_3$ addition.

4) Removal of PO_4^{3-} and NH_3 by activated sludge treatment - the Badenpho Process.

5) NH_3 removal by adsorption on clinoptilolite clays.

Most of the above work was in the development and testing stages and no firm decisions were believed to have been taken as to what route to go in the commercial installations.

DESCRIPTION OF OPERATION

Kloof is rated as one of the finest gold mines in the world, and is located 40 kilometers west of Johannesburg on the West Witwatersrand Line. Gold ore occurs down to 13,000 ft. below the surface and ore grades of about 21 g Au/t are typical over a reef thickness of 1.5 meters in the VCR reef. During 1984 2.08 million tons of ore were mined to produce 31.9 tons of gold. Published operating costs are around R72 (US$50.0) per ton milled, which worked out to about US $104/ounce gold.

Being a deep mine high temperatures are experienced and underground cooling using refrigerated water represents a major use of water.

WATER SUPPLY

Kloof has historically relied on water supplied by the Rand Water Board at a cost of around R0.21/m^3 in 1984.

WATER CONSERVATION

Due to the serious drought in the Transvaal from 1982-4 it became essential to cut back on water consumption. Kloof reduced RWB consumption by 33% in 1984 compared with 1983. Much of these savings were achieved by improved housekeeping.

Further savings were envisaged through:

1) Recycling of sewage reclaim water for use in underground cooling.

2) Use of underground fissure water.

Already Kloof reclaims about as much water from their gold plant tailings as is likely to be possible. RANDOL has no information on how much otherwise reclaimable water is lost through seepage from the tailings dam and water impoundments.

TREATMENT OF RECLAIMED SEWAGE WATER FOR USE IN COOLING OF UNDERGROUND WORKINGS

South African gold mines are labor intensive operations. Large numbers of workers live on mine hotels and townsites near the mine and generate a large volume of sewage. The large mine population also uses a lot of potable water - ranging from 0.4 - 0.8 m^3/man/day. A significant savings in purchased water could be achieved if reclaimed sewage water could be used in the mine and mill to replace RWB water.

Because semi-skilled mineworkers are accustomed to drinking water underground "where they find it," all minewater is disinfected by chlorination.

There are three factors that have to be overcome in using reclaimed sewage water for underground cooling.

- Ammonia if present in high concentrations in the reclaimed water, causes corrosion of Cu-Ni coils in the refrigeration plant.
- Ammonia consumes chlorine at the rate of 10 Cl_2 per 1 NH_3 which makes it potentially costly to disinfect reclaimed sewage water.
- The presence of organic compounds in the sewage water raises a possibilty of generating toxic organohalogen compounds during chlorination.

CORROSION OF REFRIGERATION TUBES

The Cu-Ni refrigeration tube corrosion problem was not found at Kloof because the treated sewage effluent contains only about 0.5 mg NH_3-N/l. This is a good testimonial to the type of sewage treatment process in use at Kloof which is believed to be the BADENPHO Process. Their sewage plant is shown below.

DISINFECTION

In order to disinfect water before it goes underground 10 parts chlorine are consumed per 1 part NH_3 to achieve breakpoint chlorination which is normally considered necessary to be effective. Since typical treated sewage water pumped from the Kloof treatment plant contains less than 25 ppm NH_3, this would mean an additional consumption of at most 250 ppm Cl_2.

The National Institute of Water Research, Pretoria pointed out that even when only small amounts of chlorine are added as HTH (hypochlorite), in amounts way below that needed for breakpoint chlorination no coliform bacteria are detected in the water. This suggests that the chloramines formed by reaction between ammonia and chlorine may be adequate for disinfection without the need to go to breakpoint.

Dissolved air flotation for phosphate removal was also found to result in an effective removal of phenols which on chlorination could form toxic chlorinated phenols in the treated water.

UNDERGROUND HYDROPOWER GENERATION

To make use of the potential energy being supplied from the surface, two types of hydropower are being developed for use underground in South African mines:

a) hydroelectric generation

b) hydraulic power for drills, etc.

The water is delivered underground via high pressure pipes designed to withstand the high hydrostatic head. This hydrostatic pressure can be used to drive a pelton wheel coupled to a generator or to a pump. SULZER BROS Pty Ltd., a South African company has already supplied several units to South African mines including the unit to be installed at Kloof.

Another benefit of this energy recovery is that the chilled water remains cold, the pelton wheel harnessing the energy which would otherwise be absorbed by the water.

The second way to use this hydrostatic head is to drive hydraulic tools such as drills etc. This development work has recently been announced by the Chamber of Mines Research Laboratories which claims significant successes.

The Chamber of Mines Research Laboratories declined to provide more information on the technology which is soon expected to become a common practice for deeper mines. One of the needs of such a system is a way to efficiently remove particulate matter from the water used in this way to avoid unnecessary abrasion.

Chamber of Mines Research Laboratories
P. O. Box 91230
Auckland Park 2006

Telephone: (011) 726-3020
Contact: Dr. Brian E. Protheroe

CONCLUSIONS

Numerous approaches are being investigated at Kloof Mine in conjunction with Gold Fields of South Africa Ltd. and the National Institute for Water Research, to water conservation through further recycling and reuse of sewage water, but it is still too soon to report any definite results.

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CONTACTS	Dennis W. Bosch	Consulting Metallurgist
	Reinhold J. Ortlepp	Consulting Metallurgist
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TELEX	8-9671	
DATE OF VISIT	1983	

INTRODUCTION

Rand Mines Milling and Mining Ltd. (RM3) reclaims old sand and slimes tailings dumps on the outskirts of Johannesburg. The dumps concerned have been prominent landmarks on the western edge of the City of Johannesburg and the operation is an excellent example of how a very large (over 15,000 tpd) gold and pyrite recovery plant, including cyanidation, can operate safely and compatibly in a built-up area.

RM3 uses as much recycled water and as little Rand Water Board water as possible. Considerable amounts of surface water from a stream on the property are used.

Poor water quality has been suspected for metallurgical results in the commercial scale plant that did not match the better results indicated in pilot plant tests, particularly in the CIP performance.

RM3 tries to segregate water used in the cyanidation and CIP circuit from that used in the flotation and classification steps which requires some careful water management considerations. Several water quality factors were identified by RM3 as having possible negative impact on gold recovery, and corrective measures could overcome some of these. However, in examining the flowsheet superficially from a water management viewpoint RANDOL is of the opinion that the potential exists to seek additional metallurgical improvement and perhaps some cost savings through further investigation of water quality factors relating firstly, to the extensive recycling of water in the front end of the plant including flotation and, secondly, due to the source of some of the water used.

These speculative expectations are based on preliminary and superficial information but are focused on here as an interesting illustration of some of the considerations that must be taken into account when water is recycled and as an example of the complexity and usefulness of adopting a systems approach to water management and also as an example of how viewing a metallurgical operation from a water and salt balance standpoint, a whole new perspective may be found of factors that can influence metallurgical performance.

Rand Mines and RM3 staff have not discussed metallurgical performance with RANDOL and gold recovery performance is not known for sure, but it is believed to be around 70% compared with 75% indicated in the pilot operation. Rand Mines Ltd. and RM3's forgiveness is asked for the following speculative discussion basen on only partial facts which must therefore be largely hypothetical, but which is offered in a constructive, helpful spirit.

DETAILS OF OPERATION

Capital Cost	R60 million (US$33 million)
Reserves of Feed	60 million tons
Recovery	0.5 g Au/t
Operating Costs	R11.60/g = R5.80/t ($5.60/g = $2.90/t)
Plant Throughput	4.4 million tpa sand plus slime
1983 Recovery of gold	About 70% at design capacity
Design Recovery	75%

ENVIRONMENTAL IMPACT OF RM3

Although the facts and conclusions are not yet available from a study of the subject, it is expected that Witwatersrand tailings do oxidize with time and are a source of acid mine drainage. This is believed to contribute to the diffuse source total dissolved salts that impacts the macro water supply system for the area.

Removal of pyrite from tailings by operations such as RM3 represents a reduction in the amount of pyrite left to oxidize and therefore can be expected to be beneficial in the national campaign to improve water quality.

In order to improve the grade of the pyrite concentrate RM3 has deliberately reduced flotation recovery efficiency which means that the amount of residual pyrite left in the tailings will be more than in the original design. It is not known to what extent the residual pyrite levels will possibly generate acid in the future.

It is interesting that when it was announced that the mine dumps around Johannesburg were to be reprocessed, a society was formed for the preservation of the dumps which had become a familiar landmark and wildlife refuge in the city limits.

DESCRIPTION OF PROCESS

RM3 processes sand and slimes tailings dump material to recover gold and a pyrite-gold flotation concentrate.

Sand tailings are classified into a coarse sand and a slime fraction. The coarse fraction is floated at pH 3.5-4.0 to recover a pyrite concentrate. The flotation tailings are ground to 50% minus 200 mesh and together with the slimes fraction are cyanided followed by gold recovery using CIP. The flotation concentrate consisting of a pyrite concentrate with higher gold values is ground to 95% minus 200 mesh, cyanide leached and gold recovered in a second CIP plant.

The main water management target is to use more tailings return water in the plant. At present water is managed in two separate circuits namely the low pH flotation circuit at pH 3.5-4.0 and a high pH gold leach, CIP, tailings and dam return water system.

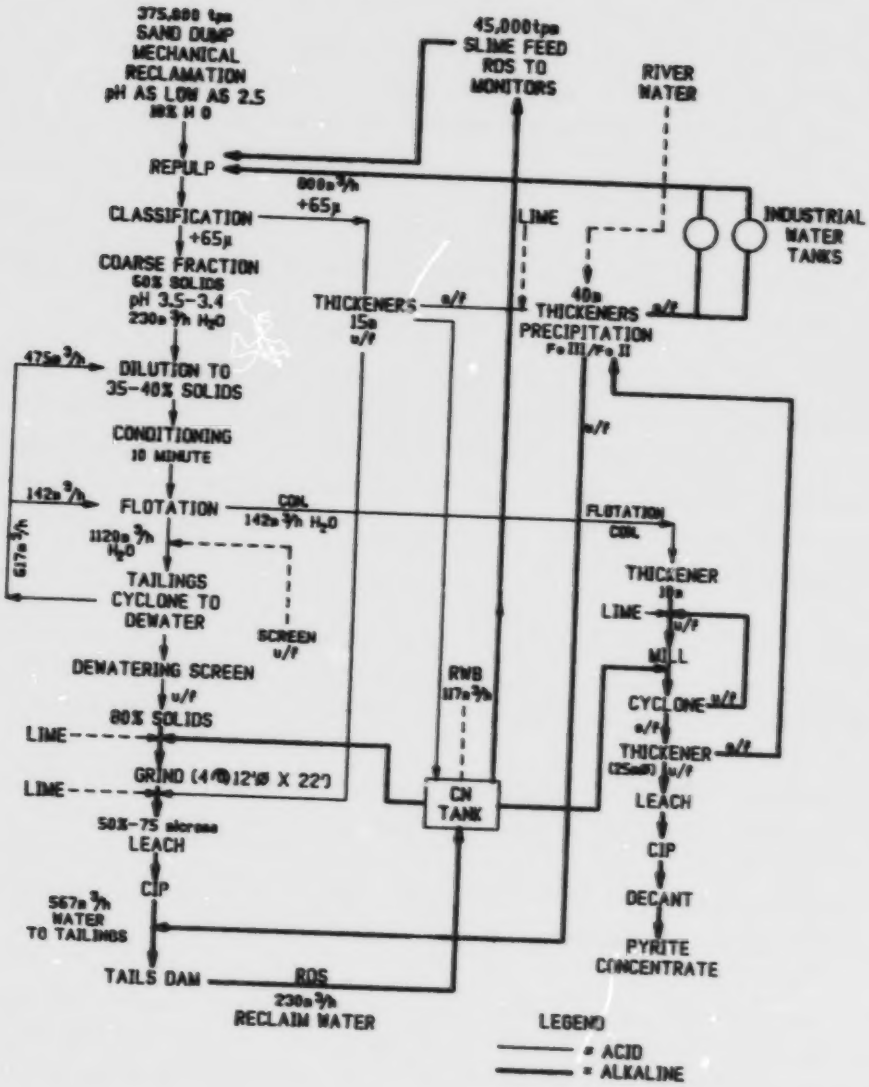
The principle flowsheet is illustrated overleaf showing the main operating units. The main internal water recycling pathways are shown by dashed lines.

Attrition of particles in the flotation step scrubs the particles ahead of milling and leaching and it is believed to result in enhanced leach recovery.

The concentrate leach was designed for a feed with 28% sulfide and 6 g Au/t. The plant was operating in 1984 at a feed of 40% sulfur and 15 g Au/t in the leach. It is suspected that possibly soluble sulfide in the pulp solution may deplete dissolved oxygen. RANDOL believes that this can be at least partially overcome by a preaeration step if inserted into the water recycling circuits around the flotation and/or repulping steps.

Originally the plant was designed to treat 325,000 tpm sand to yield 8600 tpm of concentrate at 28% S, i.e. 2410 tpm sulfur. In the 1984 operating arrangement 375,000 tpm sand was being treated to yield about the same amount of sulfide in only 6000 tons/month of concentrate with a grade of 40% S and 15 g Au/t.

RM3 FLOWSHEET



WATER RECYCLING

The RM3 process arrangement has several water recycling loops, e.g.,

1) Sand Repulping
   Classifier Cyclone overflow
   Thickeners $15m^2$ o/f
   $40m^2$ Thickener o/f
   "Industrial" water tanks
   Back to repulpers at 800 m^3/h

2) Dilution of Classifier Cyclone u/f — $475m^3/h$
   Flotation
   Flotation tailings dewatering Cyclone o/f recycle water — $617m^3/h$
   Flotation Tailings Dewatering Screen u/f — $1120m^3/h$

3) Flotation tailings dewatered
   Grind
   Add slimes
   Leach
   CIP
   Tailings dam
   RDS Recycle to CN tank — $230m^3/h$
   CN tank to slimes monitoring
   Slimes to mill outlet or direct to 1st stage leach

The water recycling and reticulation system is clearly complicated. Water used for repulping and classification of the feed is recycled in the first loop.

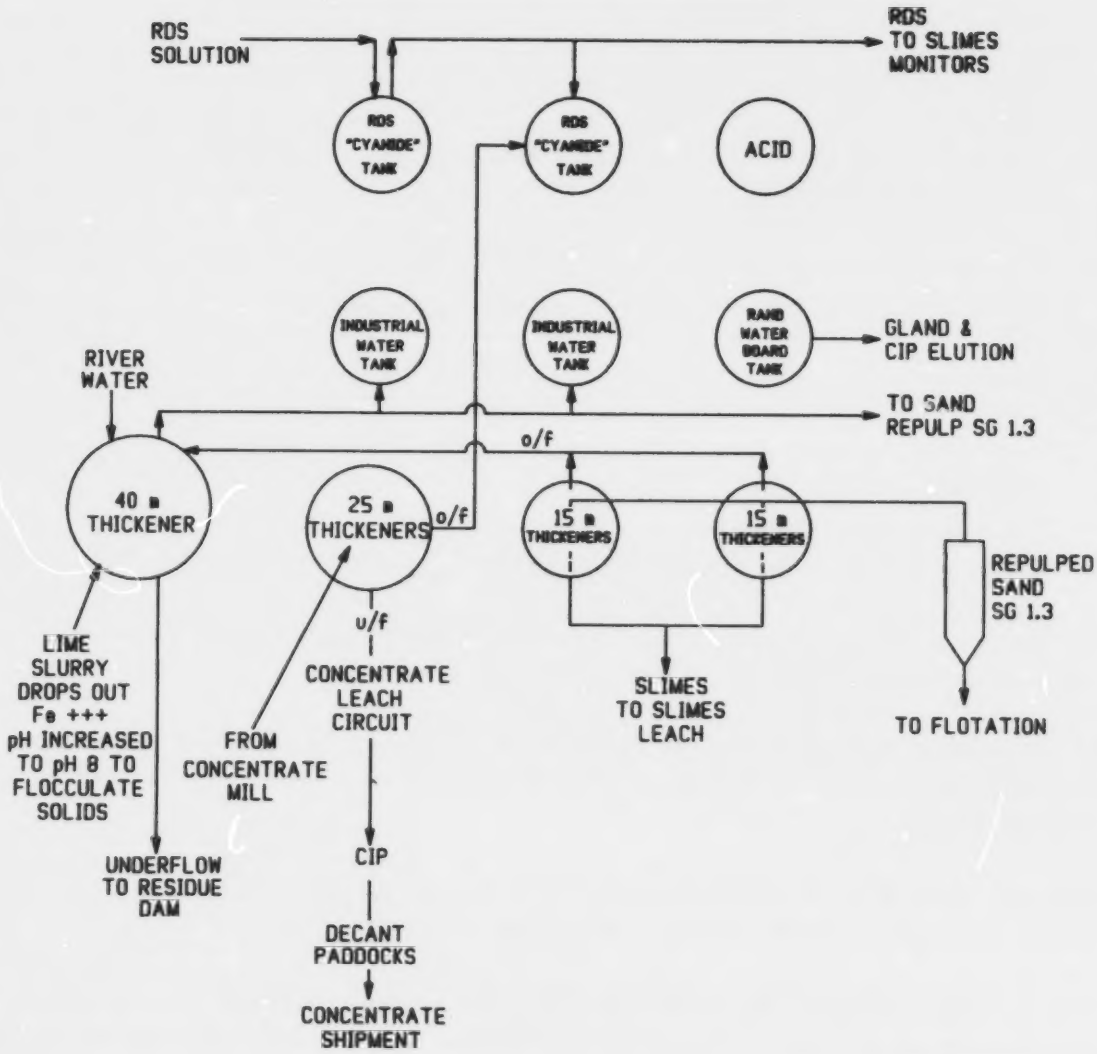
In the second loop acidic water used to dilute the sand fraction ahead of flotation is recovered to as great an extent as possible and recycled back to dilute feed to the flotation circuit.

High pH water used in the cyanidation - CIP circuit is recycled via the tailings dam reclaim dam solution via the "Cyanide" water tank.

Low pH water is kept in the flotation circuit which results in a better flotation recovery. Cyanide bearing solutions are kept from the flotation circuit where cyanide would depress pyrite recovery.

Use of tailings dam RDS in the slimes and ground sand cyanidation circuit has resulted in a drop in lime and cyanide consumption without noticeable adverse effects on gold recovery.

RM3 WATER RETICULATION



In order to increase the use of RDS, RM3 would like to treat it in a carbon column to recover residual gold and destroy cyanide before more of this water is used in the front end of the process. Treated RDS is also being considered for potential use as pump gland service water. These possibilities appear to be realistic.

Advantages of Using More RDS

1) Reduced requirement of Rand Water Board water
2) Allow the tailings dam water level to be dropped thereby reducing evaporation losses.
3) Save on lime and cyanide consumption.

Currently only about 33-34% of the water pumped to the tailings dam is recovered - amounting to some $230m^3/h$.

Water Quality Influences and Effects

1) RM3 dumps have a naturally low pH due to pyrite oxidation which result in pH levels down to 2.5 in repulped tailings. The low pH is claimed to be beneficial for gold/pyrite flotation recovery, e.g.,

   - Reduced tendency for fines agglomeration
   - Improved pyrite concentrate grade (A rougher concentrate with 40%S is achieved)
   - Reduced reagent consumption for flotation
   - Better leaching characteristics of flotation tailings - use of Xanthates is avoided
   - By operating the flotation at a low pH 3.5 - 4.0 it is possible to use flotation reagents such as merkaptothiazol and thiophosphate which are believed to be less stable at an alkaline pH, so once the flotation tailings are neutralized the reagents degrade rapidly to shorter chain molecules which have less adverse effect on leaching and CIP performance.

2) Local creek water is used in the process. Some metallurgical problems were ascribed to the use of this water which is generated by runoff from a local catchment including several tailings dams. This water proved to be contaminated by about 50 ppm organics which caused metallurgical problems. It was believed that an industry generating fats, located upstream was possibly responsible for the contamination.

3) Initially the startup of the flotation circuit had to be postponed because it was found that the original flotation reagents caused an interference with the CIP recovery of gold.

   The original frother used was a polyglycol supplied by Hoechst, called Flotinol C7 Polyglycol. Only 0.5 ppm of this reagent was added and the evidence of CIP interference caused by this reagent was not conclusive. However, the plant switched to a NCP (National Chemical Products) frother known as TEB.

4) Oils and greases in the feed may also have interfered with the CIP performance. Originally there was not an effective oil trap on the compressed air system and the compressors operated at a high temperature. It is known that carbon adsorption of gold can be impaired in this way.

5) In the concentrate regrind circuit lime and concentrate are added to the pumpbox ahead of the cyclone in the circuit. If milled in acid steel consumption would be excessive so the pulp is neutralized. In general, where possible, it is believed that better results would be achieved if the concentrate could be milled in an acid pH which would result in a lower viscosity. There might be some motivation to test stainless grinding media.

6) In examining the tailings sand and slimes repulping steps it is observed that there has been enough oxidation of pyrite in the feed to cause pH to drop as low as pH 2.5 at times. This undoubtedly introduces ferrous iron, sulfate and some soluble sulfides into the pulp solution. As this acid water is recycled it would be logical that Fe^{3+}, Fe^{2+}, $SO_4^{=}$, $S^{=}$, etc. would build up in concentration. Some will be dropped out by lime treatment in the 40m thickener, however not necessarily all. Also as water is recycled around the flotation step, undoubtedly more salts will build up in concentration in the solution. Some solution is always transferred with the pulp in thickener underflows.

It is suspected that as a result of this continuous recycling of water in contact with partially oxidized feed containing sulfides and iron, the oxygen level of the pulp is likely to be depleted. (The adverse effects of pyrrhotite in ores on leaching and CIP in other locations is well known.)

It is possible that aeration in the flotation step may partially oxidize soluble sulfides but residence time will be too short at the low pH to oxidize ferrous iron in the pulp.

RANDOL suggests that the oxygen, ferrous, sulfide, and thiocyanate levels in the recirculating water and in the pulp advancing from flotation to leaching be carefully checked as a possible contributor to metallurgical efficiency reduction in the subsequent steps.

In the event that there are residual sulfide and ferrous ions in the feed to the leaching and CIP plant, then the expected symptoms would be difficulty in effective elution of gold from activated carbon as was initially experienced at Homestake's CIP plant prior to insertion of an effective preaeration step. However, at RM3 no difficulty in eluting gold from carbon is experienced and levels of 10-50g Au/t are routinely achieved.

7) Water sources used and the recycled solutions at low pH should also be checked for $CO_3^{=}$ content. If carbonate has built up in these solutions then consideration should

be given to the economic advantages of removing CO_2 by vigorous aeration ahead of lime addition steps. This could reduce lime consumption and also the volume of sludge generated and possibly also reduce scaling of carbon in the CIP plants.

ELUTION AND REGENERATION OF CARBON

It is noted that as a result of higher gold levels in the concentrate feed and because of lower carbon loadings, carbon was being advanced through the elution and regeneration circuit at three times the original design rate of 4 tpd. All loaded carbon is acid treated ahead of elution.

The original design called for regeneration of carbon every cycle at 4 tpd. Since now 12 tpd are being eluted, the existing Bohler rotary regeneration kiln with a capacity of 210 kg C/hour is only able to handle 5 tpd. The Rintoul electric carbon regeneration unit can treat 4 tpd to give a total capacity of 9 tpd. This means that each day at least 3 tons of carbon must bypass the regeneration kilns.

Operating the carbon regeneration kiln continuously for 24 hours per day is believed to improve its operation.

The carbon dewatering step ahead of the regeneration kiln has been modified to allow less water to reach the kiln with the carbon which RM3 believes will improve CIP performance. RM3 was also experimenting with carbon drying techniques ahead of regeneration to make the existing regenerating equipment more effective. Even though some carbon is not regenerated each cycle it is not known whether the same applies to the acid washing step as well.

CONCLUSIONS

There remain questions and points to test to determine whether the float-leach-CIP sequence and recirculation of water to treat partially oxidized tailings containing pyrite has an impact on water quality which has a negative impact on cyanide leaching and/or recovery of gold by CIP.

Additional water treatment measures should be tested in the circuit. Some of these are simple and inexpensive. RM3 is presently persuing an investigation to identify the solution phase contaminants with a firm of water treatment suppliers.

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	William L. Jose	Mine Manager (former)
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TELEX	15-0033	

INTRODUCTION

This 3000 tpd heap leaching operation which shut down in the fall of 1984 is located in steep mountainous country alongside creeks that flow into important salmon spawning and fishing grounds. The value of the tourist industry attracted by the sport fishing makes it essential that the mining operation not contaminate the creek. The mine and metallurgical operations are on national forest land just 3 miles from the River of No Return Wilderness area. The project started up in July 1983. Topography consists of steep-sided canyons and swift- flowing streams. More information is available in STOTT (1984).

Main areas of concern are:

- Introduction of particulate material into the stream which could damage the riverbed.
- Introduction of heavy metals and/or cyanide which are toxic to fish.

DATE OF VISIT 16 October 1983

LOCATION 95 miles northeast of Boise, Idaho

OPERATION

400,000-500,000 tons per year ore is crushed to 1½" x O. 1.5 lbs of lime are added per ton of ore during the crushing step to neutralize the ore which is leached at pH 10-11.

The ore is clay rich but agglomeration tests did not indicate an improvement in recovery so the ore is not agglomerated.

The 10' high 30,000t heaps are subjected to a 50 day leach cycle:

10 days	build heaps
20 days	leach
10 days	wash and cyanide destruction
10 days	remove heaps

Solution is applied to the 250' x 350' heaps at a rate of 0.3 gph/ft^2 (0.005 gpm/ft) i.e., 2500 lb/minute per heap. The heaps are stacked on a specially prepared asphalt pad covered by 18" ore layer to protect the pad. The heaps are located only 300 ft from the Salmon River and one mine pit is situated on the banks of the West End Creek. Special environmental protection measures are adopted in the operation to protect water quality in the creeks and river:

Mining

The West End Creek has been diverted. It was impossible to work the lower levels of the mine without sidecasting into the creek. There was also no room for ponds to hold runoff water from the mine. Consideration must also be given to limiting the transfer of clay slimes from the mine area and haul roads to the rivers in runoff water - a problem not yet satisfactorily solved at the time of the Randol visit. Fish and Game trick: Use straw bales to dam and settle solids in runoff areas.

Metallurgical

A multiple layer pad has been prepared for the heaps together with a monitoring system to be doubly sure no cyanide solutions reach the groundwater.

Prepared surface covered with 1-2" layer of 100# tailings and compacted
30 mil PVC
Geotextile fabric layer
12" washed gravel to give compentency to pad
3" asphalt
Emulsion Seal SS11 or S11
18" ore layer over the asphalt protects it while heaps are placed or removed. A more detailed description is provided by STOTTS (1984) below.

Cyanide Detoxification

1) $Ca(OCl)_2$ generated at the site from lime and chlorine gas and the $CA(OCl)_2$ solution is sprayed over the heaps to destroy residual cyanide in the heaps.

   2 d drain after leaching
   6 d wash with $Ca(OCl)_2$ solution
   2 d drain after leaching

2) CN destruction uses the same sprinkler system that was used to apply the CN^- solution. This time, however, CN^- nutralization pond water is used at pH 12-13.

3) At all times 3.5 tons of $Ca(OCl)_2$ are kept on hand in case the $Ca(OCl)_2$ manufacturing system should fail.

4) Hydrogen peroxide was also tested for cyanide destruction in a test column by Heinen Lindstrom Associates in Reno, Nevada and was found to be less efficient.

5) The CN^- levels are monitored regularly in the "off" solution during chlorination.

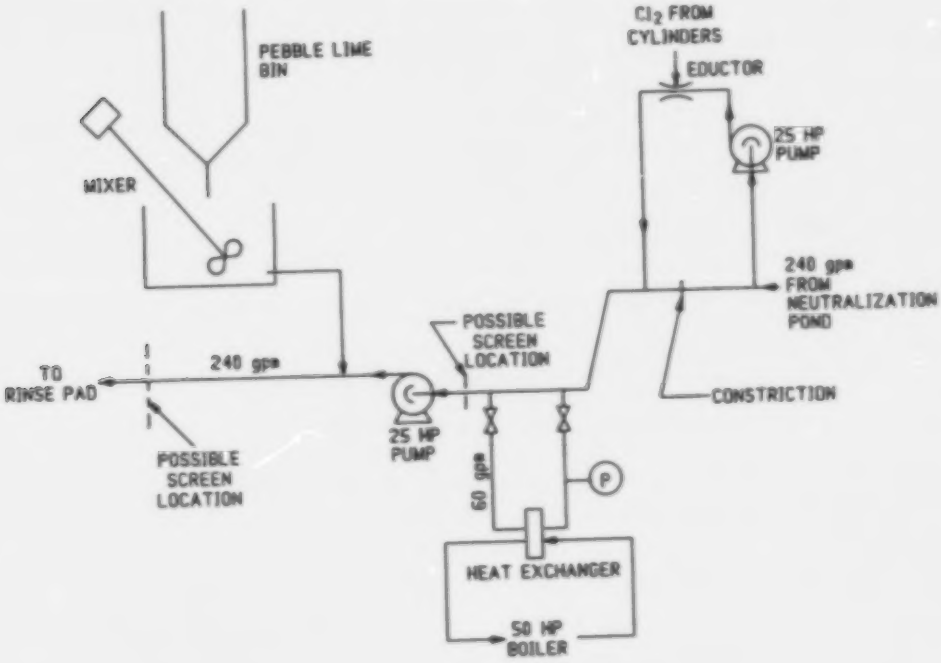
   CN^- is monitored at ppb levels in the 10 monitor wells using a Hachmeter Model DR100 calorimeter Model 41100

   Hach Co.
   Box 389
   Loveland, CO

   The heaps are chlorinated before the leached heaps are placed on the tailings dump. It is also required that any heap that may be being leached when it freezes should be neutralized. If left over winter CN^- could leak with spring runoff. In case a freeze occurs, the system is fitted with a 50 HP Boiler and heat exchanger to warm the solution which is applied at 240 gpm.

6) Pebble lime is used because slaked lime tends to blow around and is unsightly.

7) Chlorine is added via an eductor in the line which doses and mixes the chlorine solution. Pennwalt supplies Cl_2 @ \$360/t in cylinders. There are 10 cylinders hooked up to the Cl_2 system.



8) By converting from NaOH to $Ca(OH)_2$ for pH control on the heaps it was found that NaCN consumption dropped from 1½ lb/t ore to 0.2 lb NaCN/t ore. Suspected on the basis of lab tests that NaOH solubilizes Fe or other base metals which consume CN^-.

9) First heap neutralized at regular pH 10 took 22 days to bring CN^- in "off" solution to below 0.2 ppm CN^- by bringing pH up to 12-13 with $Ca(OH)_2$ the reaction is much faster (6 days).

10) When using pebble lime for $Ca(OCl)_2$ grit gets into the solution which clogs the sprinklers. This is overcome in practice by temporarily turning the lime supply off which allows the pH to drop due to reaction of Cl_2 with water to yield HCl.

11) A 1 mm gallon pond is used to contain neutralization solution.

Cost of Cyanide Detoxification

1¼ lb lime is consumed per lb Cl_2 added in the chlorination step. 4,000 lbs Cl_2 per day is added to solution which is applied at 240 gpm.

This works out to 12 tons Cl_2 consumption per heap of 30,000 t ore tailings or $4300/heap ($360/t Cl_2), which works out to $1.14/ton ore.

Monitoring and Environmental Aspects

Environmental consultants who supervise the groundwater monitoring - 10 monitor wells are:

James Montgomery Engineering
Boise, ID office
Headquarters in Los Angeles

Aug 1 - Sept 15 - No chemical reagents are hauled along the roadway to the plant in case of an accident which could spill reagent into the stream.

Before this operation started, old tailings of a former 1938 tungsten mine were getting into the river. These tailings were high in Fe, very fine and silted up the bed of the Salmon River. These tailings are now covered with minus 1½" HL material which now supports grass growth and prevents silt from getting into the River.

REFERENCES

STOTTS, William G. (1984) Handling Cyanide at Superior Mining Company's Stibnite Heap Leaching Operation. Conference on Cyanide and the Environment, Tuscon, AZ, 11-14 December, 1984.

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GROUP	Anglo American Corporation of South Africa Ltd. 44 Main Street Johannesburg 2000 South Africa
CONTACTS	A. D. Deuchar Deputy Technical Director, Metallurgy
TELEPHONE	(011) 638-9111
LOCATION	Vaal Reefs is located 170 km SW of Johannesburg, near Orkney
DATE OF VISIT	11 January 1984

INTRODUCTION

Vaal Reefs is one of the very largest gold producers in the world, with three gold and three uranium milling operations in the complex producing a total of 9.7 million tons/year ore at an average grade of around 8 g Au/t. Vaal Reefs is also responsible for operating the new Afrikander Lease plant which was originally designed as a pressure leaching uranium plant, but only the milling and gold recovery circuit is being used - conventional cyanidation followed by CIP.

Apart from being awe-inspiring on account of its size, Vaal Reefs is fascinating because of the variety of different metallurgical circuits employed. The complex is divided into East, West and South Divisions. The South has two gold plants and a uranium plant while the other two divisions each have a gold plant, a uranium plant, a flotation plant, an acid plant and a calcine plant. The complex covers many tens of square kilometers with hundreds of miles of water, solution and tailings lines linking the operations.

From a water management point of view Vaal Reefs represents an enormous challenge. Since water has historically been inexpensive (and still is) and since effluent disposal,

conservation of water, groundwater quality protection, etc. have been non-critical issues in South Africa until the recent 1982-4 drought, most South African mining and milling operations have had to adapt to a sudden need for change.

When there is just one mine and mill in a complex, water management can represent a challenge especially if it has to be "retrofitted." For an operation with numerous shafts and underground workings requiring cooling, five gold plants and three uranium plants and a huge labor force requiring large amounts of potable water and generating equally large amounts of sewage, establishing an integrated comprehensive water plan is very expensive and time consuming. Because of the complexity of the system, it has also taken longer to develop the plan.

As of January 1984 a quantitative water balance had yet to be drawn up. With such a complicated array of unit operations installed over many years, the establishment of a detailed water balance is no small undertaking. First, it is necessary to find the layout of all flows and then to measure them. The 1984 budget for instrumentation alone to measure flow rates and draw samples was R500,000 ($300,000).

With side-by-side uranium plants using a highly acidic process and gold plants using alkaline cyanidation, extreme caution is necessary to avoid acidification of cyanide streams which would generate toxic HCN.

In response to the national emergency brought on by the drought of 1982-4, Vaal Reefs was able to save 35% on water consumption in 1983 over 1982. Presumably much of this savings came about through improved housekeeping and by instilling in operators an awareness of the need to save water, e.g., closing taps, metering water use in hostels, etc.

Once a quantitative water balance has been established for each mine and each metallurgical operation, Vaal Reefs will be able to design a water conservation and effluent disposal plan. The company is acutely aware of the need and is responding diligently. Metallurgical staff are in charge of the water committee. At the time of the RANDOL visit it was possible to make only a few random observations. Once Vaal Reefs has completed their evaluation and implemented a plan which will probably take 12-24 months, it is likely that a most interesting water management story will emerge.

Vaal Reefs' annual new water consumption (plants only) amounts to 9.9 million m^3 to treat 9.2 million tons ore, i.e., 1.08 m^3 water/ton which is not excessive considering that this is for gold and uranium extraction. (These figures are for 1984 and have been projected to year end; they do not include Africander Lease.)

Vaal Reefs' annual water bill amounts to R1,000,000 (US $500,000) or R0.109/t ore (US $0.05/st) for water consumption costs which is relatively little. Cutting back on water consumption would make it possible to save on water costs, but these savings must be weighed against costs of scale inhibition and corrosion that may then arise as well as

possible impact on metallurgical recovery and reagent consumption which are likely to overshadow the actual water cost savings.

The current method of treating effluents at Vaal Reefs is rather unsophisticated but appears to be very effective - only expensive in terms of lime requirements. Comments made in this report as to ways that may make it possible to further improve water treatment and consumtion costs are purely hypothetical ideas.

MOTIVATION FOR WATER MANAGEMENT

Vaal Reefs has already achieved a significant water cost savings through implementing a water housekeeping and awareness program. Beyond cutting back on water wastage through operator carelessness, further water management improvements are unlikely to be motivated by savings in the cost of water at current price levels. The motivations are:

1) Anticipated stricter effluent discharge regulations including diffuse source discharge which may affect groundwater quality through seepage.

2) Uncertain future availability of regional water board supply and Vaal River water.

3) Likelihood of price hikes of regional water supplied to Vaal Reefs.

4) Possibility to recover additional incremental gold values from recycle solutions and effluent streams.

5) Reduction in cost of effluent treatment where lime is a major cost item.

CLIMATE

Temperate climate with 20" (500 mm) rainfall per year and an estimated evaporation of about 30" per year. Summer rainfall and dry cool winters.

PROCESSES

Gold is recovered primarily by conventional leaching followed by Merrill-Crowe. Uranium is recovered by sulfuric acid leaching followed by CCD, drum filtration and belt filtration in each of the three plants, followed by ion exchange and SX. At Afrikander Leases a pressure oxidation plant has been installed (but not commissioned) which leaches uranium followed by a CIP plant for gold. Heap leaching piles are under construction to recover residual gold from wasterock fines.

WATER CONSUMPTION (Latest figures include new gold plnat at No. 9 shaft being commissioned)

340,000 m^3/mo new water from the Water Board
535,000 m^3/mo river water from the Vaal
15,000 m^3/mo wellwater for Afrikander Leases
890,000 m^3/mo

Over 30 operating days/mo this works out to 30,000 m^3/d used to treat 29,000 tpd ore, or 1.03 m^3 new water per ton ore. (These figures include Afrikander Lease.)

COST OF WATER

Regional Water Board	R0.17/m^3	US \$0.09 /m^3
Vaal River water	R0.05/m^3	US \$0.024/m^3
Regional Water Board	R700,000/yr	US \$350,000
Vaal River water	R320,000/yr	US \$160,000
Total Annual Cost (1983)	R1,020,000	\$510,000

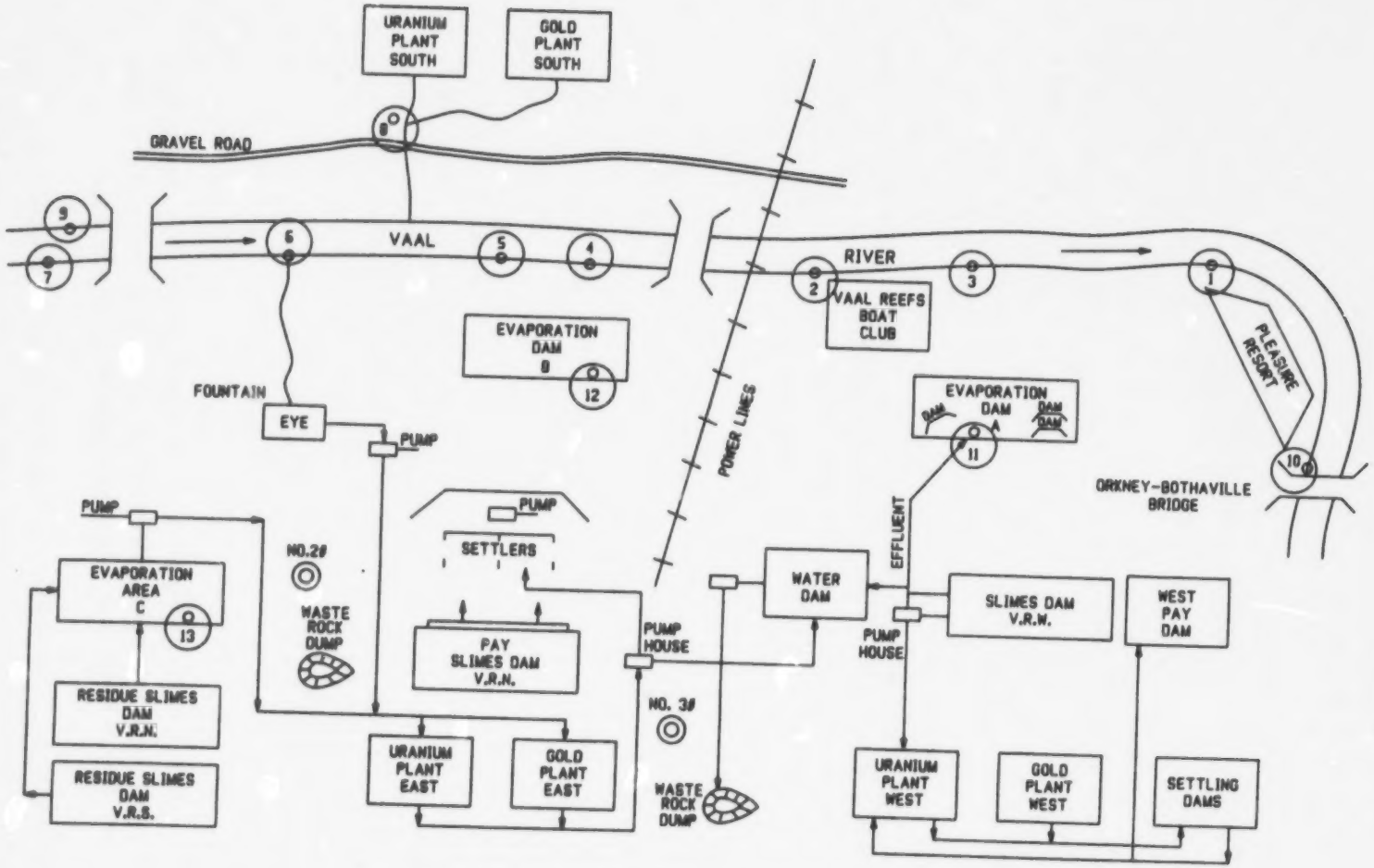
Considering the magnitude of the operation and the large amount of water used, this is a relatively low water bill, although further water savings would undoubtedly achieve a worthwhile additional cost savings. Note that these figures are for plants only. An additional 1,150,000 m^3/month is used for shafts, hostels and townships in the area and much of this water is recycled back to the plants via fridge plants and sewage plants.

WATER RECYCLING

Metallurgical managers indicated that at present all water that can possibly be reclaimed is recycled. Large amounts of water are currently recycled on a macro scale, and no effluents are deliberately discharged although, considering the design of most of the recycle water impoundments as evaporation dams, there are undoubtedly considerable losses of water through evaporation.

A general layout of the main ore processing units and how these are interconnected with respect to water flow is shown diagrammatically below. The diagram shows water reclamation for recycling as process water from the residue dams at Vaal Reefs North dam, Vaal Reefs South and Vaal Reefs West slimes and residue dams.

Water is reclaimed from areas marked as evaporation dams. Although aging of recycle solution is likely to result in some quality improvement the aims of evaporation and water recovery for reuse would appear to be contradictory. Sample 13 drawn from within evaporation area C appears to be saturated with gypsum which would be expected.



VAAL REEFS COMPLEX METALLURGICAL EFFLUENT DISPOSAL

Effluents from various unit operations are neutralized together with tailings pulps which results in the precipitation of gypsum onto tailings solids allowing solution to decant with no more than saturation levels of gypsum.

As much as possible of the reclaimable water from the tailings dams is recycled to the plant. The operators find that suspended solids is the only cause for concern about its quality.

Since the quality of reclaimed water seems to be excellent, the aims of the water management program are to recover more of it and to reduce the cost (lime consumption) of treating the effluents.

SEWAGE WATER RECYCLE

South African gold mining is labor intensive and large numbers of workers are accommodated, with correspondingly large sewage plants. Treated effluent from Vaal Reefs sewage plants is used as water in the gold plants. Sewage water use was tested on the West Plant for use in the gold and uranium processes and no ill effects were noted. In all there are five sewage plants on the Vaal Reefs complex, all of which employ biofilters.

REFRIGERATION PLANT BLEED WATER USE

A new gold recovery plant is to be commissioned in 1984 at 9 Shaft - at a cost of about R400 million including the 6000 ft shaft and plant. The 120,000 tpm gold plant capital cost was around R60 mm.

Chilled water is recirculated from the surface to the underground workings to cool the stopes. After being pumped back to the surface the water is cooled in a cooling tower and then refrigerated before going back underground. Each pass made by the water through the underground workings adds 1000 ppm TDS - including a considerable amount of nitrates. Water quality in the refrigeration loop is controlled by bleeding water which in the case of the new 9-shaft mine will be used in the gold plant.

WATER BALANCE STUDY

R500,000 had been allocated in the 1984 budget for sampling and flow measurement equipment to be installed to determine a detailed water balance at Vaal Reefs. Some innovative new sampling devices using solar power and batteries are being used.

Milltronics ultrasonic detectors are to be used for flow measurement. Portable solar power units are to be provided by Siemens. In house resources have been commissioned to provide computer services. ISCO samplers were installed; these are weatherproof and can

be operated from batteries or mains. A battery is good for 28 samples between recharging. The sampler with sample bottle casette costs R3000 and is manufactured by:

Instrument Specialties Co.
P. O. Box 82531
Lincoln, Nebraska 68501

Telephone: (402) 474-2233
(800) 228-4373

The sampler can be coupled to a flowmeter to take proportional samples if desired.

A firm of civil engineers had been hired as consultants to develop the detailed water flow diagram and water balance:

Jones and Wagener Pty Ltd.
Civil Engineers
P. O. Box 1438
Rivonia 2128

Contact: Fritz Wagener
John Wates

The objectives of the water balance study include a determination of whether or not to use sewage water in the metallurgical plants and to be able to predict and manage the seasonal availability of water that can be used for recycling.

WATER QUALITY

Contaminant levels in water sampled at various points in the water flow diagram and indicated by number, are shown in the table that follows the diagram.

From this table it is clear that:

1. There is virtually no increase in TDS in the Vaal River from the point of entry to the point of leaving the Vaal Reefs property: points 9 and 10. All other points measured close to the river are small seepage flows into the river: points 1 to 7.

2. Since manganese dioxide is used as an oxidant in all the uranium recovery operations, it is of interest that manganese in all the river water samples is less than 1 ppm. This is due to the effective removal of manganese by a lime treatment to pH 9.5 before tailings and effluents are discharged to the tailings dams. At the East and West divisions all the raffinate is neutralized together with the final residue and discarded on the slimes dams.

3. In April 1980 samples of effluent entering the river were measured at 5.5 ppm Mn and 65 ppm Mn. A uranium plant effluent was measured at 1300 ppm Mn which is not atypical of uranium plants that use manganese as an oxidant. Clearly the effluent treatment steps now employed have brought manganese levels in effluents under control.

4. Treated effluent composition is:

CN	less than	1	ppm
Cu	less than	1	ppm
Pb	less than	1	ppm
Zn	less than	1	ppm
Mg		150	ppm
Mn	less than	1	ppm
NO_3		30	ppm
$SO_4^{=}$		1000	ppm
Ca		550	ppm
Suspended Solids		20	ppm

This is a remarkably good water quality considering that it it reclaimed from a mixture of highly acidic uranium tailings, very high TDS raffinate and alkaline cyanidation gold barren solutions.

U Plant Effluents - Raffinate

Pregnant solution from the uranium plants is generated at the rate of 9000 m^3/d from the two Vaal Reefs East Plants and 9000 m^3/d from the three Vaal Reefs West plants for a total of 18,000 m^3/d from which uranium is extracted by SX. The resulting raffinate contains 25-30,000 ppm TDS at a very low pH.

Since the raffinate is a major consumer of lime in the effluent treatment system, consideration is being given to possibly treat and recycle this stream separately. Typical composition of U-plant raffinates on the Witwatersrand is:

Typical U-Plant Raffinate Composition

pH	1.5				
Na	300	ppm	CNS	Ø	ppm
K	70	ppm	Fe^{2+}	730	ppm
Ca	600	ppm	Fe^{3+}	500	ppm
Mg	130	ppm	NO_3^-	160	ppm
Cl	250	ppm	NH_3	0.1	ppm
HCO_3^-	Ø	ppm	F^-	0.1	ppm
$CO_3^{=}$	Ø	ppm	Mn	1670	ppm
$SO_4^{=}$	17,500	ppm	Heavy Metals	110	ppm
SiO_2	380	ppm	TDS	24,480	ppm
CN^-	33	ppm	Suspended Solids	750	ppm

EFFLUENT RECLAMATION PROCESSES

Effluents from various Vaal Reefs plants contain elevated levels of cyanide, copper, lead, zinc, mercury, manganese, arsenic, bismuth, ammonia, $SO_4^{=}$, calcium, suspended solids and others.

The effluents are currently treated by raising the pH to 9.5 by mixing pulp and effluents to yield an over-neutralized pulp with lots of iron added in the form of an acidic raffinate, all mixed in residue pachucas ahead of pumping the slurry mixture to tailings dams.

Effluent pulp treatment consumes 10-12 Kg lime per ton tailings slime treated.

At R80/ton CaO, the lime requirement would be 97,000 tpa lime costing R7,760,000 or $4.5 million per year.

The composition of tailings dam return water is:

CN	less than	1	ppm
Cu	less than	1	ppm
Pb	less than	1	ppm
Zn	less than	1	ppm
Mg		150	ppm
Mn	less than	1	ppm
NO_3		30	ppm
$SO_4^{=}$		2500	ppm
Ca		550	ppm
Suspended solids		20	ppm

EFFLUENT DISPOSAL

Water is lost from the system through evaporation from tailings dams and evaporation ponds. A significant amount of water is also lost by entrainment in tailings slimes.

Seepage from tailings dams, reclaim water ponds and evaporation ponds undoubtedly loses some potentially recoverable water. The magnitude of this solution loss has not been quantified.

According to the 1980 diagram of water flow effluents from Vaal Reefs East Gold and Uranium plants and from Vaal Reefs West slimes dam can be pumped to evaporation area A or to the water dam for irrigation of the wasterock dump adjacent to No. 3 shaft. It appears that irrigation of effluents to a wasterock pile would be an effective way to evaporate solutions, but also a potential source of seepage contamination of groundwater, or a source of runoff water contamination.

Disposal of all effluent streams including utility water processing concentrates, barren bleeds from the gold plant acid uranium tailings and raffinates via a central neutralization tank, etc. provides a simple but relatively expensive means of recycling water and precipitating undesirable contaminants. 10 to 12 Kg lime per ton solids is required for this purpose costing R0.80-R1.00 per ton which represents a fair percentage of the total metallurgical operating costs.

GOLD RECOVERY FROM RECYCLED WATER

Vaal Reefs employs carbon columns to recover gold from low grade streams of water at several points in the plant.

The gold plant filter tailings contain 0.4-0.5g Au/t undissolved and these then advance to the acid uranium leach operations. Final tailings contain only 0.25 gAu/t. The reason for this is that 40-50% of the gold is recovered in the flotation circuits in the complex. The gold is ultimately recovered in the calcine plants; i.e., after roasting of the pyrite. Tailings dam reclaim water at pH8-9 contains 0.01-0.03g Au/t as soluble gold.

1. Gold Recovery from Filter Wash Solution ahead of Washing

After filtration in the gold plants at the East and West divisions the filter cake is repulped with barren solution (ex the precipitation Stellars) and pumped to the Uranium Plants. This stream is refiltered to remove cyanide and improve the pulp density to the uranium leach. This filtrate is called "primary filtrate" and contains much of the gold plant soluble losses.

Vaal Reefs has for some time employed a set of fixed bed carbon columns to recover gold from primary filtrate. This column system and their performance was reported in Phase II of the Randol study "Innovations in Gold and Silver Recovery" Appendix II, page 398-402 and this information can be made available to Sponsors of this study on request.

2. Pinned Bed Columns

Anglo American Research Laboratories has developed a new concept of carbon adsorption columns known as the "Pinned Bed." This highly innovative gold recovery system has been proven in tests to be able to tolerate relatively high suspended solids levels - to the extent of treating dilute pulps, and to be particularly efficient at recovering gold from dilute solutions.

A pilot unit has been tested at the Vaal Reefs South Plant.

Results and description of this innovative design are confidential pending formalization of the patent applications but can be requested (once cleared for release) from:

Anglo American Research Laboratories Ltd.
P. O. Box 106
Crown Mines 2025
South Africa

Telephone: (011) 835-3251
Contact: Dr. Brian Loveday, Manager
Dr. Ray J. Davidson, Metallurgist

3. Au Recovery from Regen. Aqueous Solutions

Two sets of four small 14" Ø columns 6 ft. high in series are installed to recover gold from regen. aqueous solution used in the uranium SX plant at the East and West Divisions.

WATER TREATMENT PROCESSES

Apart from the effluent reclamation process, there are numerous other smaller needs for water treatment on Vaal Reefs plants. The sulfuric acid leaching of uranium requires steam heat and several boilers are employed.

Conventional boilers require very low levels of TDS to generate 600 psi steam. The Vaal Reefs boilers are simpler low pressure units and can tolerate 20 ppm TDS.

Vaal Reefs has installed a new type of R.O. module to treat reclaimed sewage water for use as boiler feed. This pilot unit is purely experimental and produces 1 m^3/hour.

The new tubular R.O. modules have taken an old R. O. concept and revitalized it by improving its design, cost and maintenance needs. More information on these R. O. modules and other innovative applications is provided in Chapter 15 on Reverse Osmosis.

The new R. O. modules installed at Vaal Reefs were supplied by:

Bakke Industries Ltd.
P. O. Box 344
Paarl
South Africa

Telephone: (02211) 23032
Contacts: D. B. Smit
Johan Barnard

Danie Bosman, Head of Environmental Services, Anglo American Research Laboratories has been involved in the applications development end of the Vaal Reefs R. O. installations (address given above.)

R. O. treatment of brackish water was estimated to cost R0.50/m^3 excluding capital cost items. The residues were being disposed of to the tailings dams.

ENVIRONMENTAL ASPECTS

Data provided by Vaal Reefs on the quality of effluents after lime treatment to pH9-9.5 indicates that heavy metals and manganese are very efficiently removed by this treatment. Cyanide is also effectively removed and, from the standpoint of toxic metals the approach appears to be very effective especially considering that as much solution as possible is recovered for re-use.

It is known that a South African impoundment lining company has installed activated clay linings for some ponds along the banks of the Vaal River. It is believed that these dams were lined to prevent seepage of raffinate into the river. No precise details were obtained except that they were installed by:

Aquasave (Pty) Ltd.
P. O. Box 68288
Bryanston 2017

Telephone: (011) 789-1206/7
Contact: Chris Lee

The hydroseal-processed bentonite applied at 10 Kg/m^2 results in a less expensive self-sealing lining. It has a higher gel density and gel rate than untreated bentonite and is applied as a layer without mixing into the soil. Aquasave claims that it costs a small fraction of a plastic liner.

South Africa is very concerned about the steady buildup of TDS in the water supply in the Vaal River and appears to be about to modify effluent regulation to prevent discharge of high TDS effluents. It is anticipated that 2-3 years from now there will also be restrictions of some kind on seepage losses of high TDS effluents which could impact groundwater quality. At that time it may prove necessary to examine seepage losses from wasterock piles, tailings dams, evaporation ponds and recycle water storage areas.

It is not known whether the metals precipitated in the effluent treatment plant are amphoteric. In other words, if the tailings dams are abandoned one day, and acid mine drainage results from the oxidation of the pyrite content in the tailings, will the precipitated metals redissolve and leach from the heaps?

CONCLUSIONS

1. Vaal Reefs uses about 1.0 m^3 new water per ton solids treated for uranium and gold recovery, which probably can be further improved.

2. Being located in a climate with a net evaporation it is possible to operate a zero discharge facility - any excess effluents can be evaporated.

3. Vaal Reefs makes an effort to recover as much recycled water as possible for reuse. There are possible losses to seepage from the tailings ponds, evaporation areas, reclaim water ponds etc. which are not lined. The fact that these facilities are underlain by clay-rich sediments does not mean that they don't leak.

4. The effluent treatment plant makes a low metal recycle solution by treating all effluents and tailings with lime to pH 9-9.5. This requires 10-12 Kg lime/t costing about R0.80/t or R7.3 million/year. The question could be asked whether it would not be more effective to separate the low pH raffinate for disposal through evaporation rather than having to neutralize it.

5. A detailed water (and salt?) balance now being prepared will lead to several ideas for further water savings and cost savings.

6. Vaal Reefs is able to recycle some sewage plant effluent to metallurgical processes without detrimental effect on gold and uranium recovery.

VAAL REEFS EXPLORATION AND MINING COMPANY LTD.

ANALYTICAL LABORATORY METALLURGICAL EFFLUENT DISPOSAL SAMPLES

Sample Date: 4-1-84

Sample	pH	SS	TDS	Ca	Mg	Na	Mn	Zn	SO_4	Cl	CN	NO_3	Au	U_3O_8
1.	No Sample Received													
2.	7.8	120	1370	180	100	120	<1	<1	670	100	<1	30	0.004	0.1
3.	8.2	1230	2550	310	150	190	<1	<1	1480	130	<1	25	0.002	0.1
4.	No Sample Received													
5.	No Sample Received													
6.	7.7	2	2750	320	140	290	<1	<1	1590	165	<1	50	0.003	0.1
7.	No Sample Received													
8.	8.6	850	1700	180	10	340	<1	<1	780	220	<1	170	0.067	0.1
9.	7.8	30	590	70	70	80	<1	<1	220	60	<1	0	0.002	0.1
10.	8.3	90	600	80	70	80	<1	<1	260	60	<1	0	0.002	0.1
11.	8.3	330	3840	610	80	450	20	<1	2320	210	<1	70	0.049	0.1
12.	No Sample Received													
13.	8.1	290	3760	660	40	450	<1	<1	2090	230	<1	50	0.031	0.1
13A.	7.4	85	4910	640	100	510	140	<1	2910	260	<1	50	0.088	0.1
15.	3.1	630	4750	350	180	500	100	5	2460	600	<1	220	0.349	0.4
16.	12.1	6680	4490	890	5	410	<1	<1	1560	280	<1	75	0.123	0.1
Reg.	8.2	0	610	90	40	80	<1	<1	250	60	<1	5		
P. S.	3.8	20											0.757	0.4

Sample numbers conform to circular dated 10 June 1984. All results in mg/l (ppm)

SS = Solids in Suspension

TDS = Total Dissolved Solids

OPERATION	BLACK MOUNTAIN MINERAL DEVELOPMENT CO. (PTY) LTD. PRIVATE BAG X01 AGGENEYS 8893 SOUTH AFRICA
TELEPHONE	(0254) 2205
CONTACTS	T. R. Twidle, Plant Superintendent P. C. Engelbrecht, Assistant Plant Superintendent H. van Aswegen, Resident Engineer J. W. S. Koel, Senior Plant Metallurgist
GROUP	Gold Fields of South Africa Ltd. Post Office Box 1167 Johannesburg 2000
TELEPHONE	(011) 639-9111
TELEX	80601 SA
CONTACTS	R. A. Snodgrass, Assistant Consulting Metallurgist R. Graham

INTRODUCTION

The Black Mountain operation near Aggeneys in the northwest Cape Province of South Africa treats a complex sulfide ore to recover copper, lead, and zinc concentrates with important silver values.

Unlike other massive sulfide mills in the Canadian shield, this one is located in an extremely arid climate with one of the highest evaporation rates in the world, where water costs R0.60/m^3 (U.S. \$0.30/m^3).

Several interesting observations have been made by Black Mountain staff in their quest to improve their copper recovery and concentrate grade. These include:

1. Comparison of bulk versus selective flotation results.

2. Impact of recycled water on flotation recovery.

3. Impact of cemented backfill on water quality and hence on flotation recovery.

4. Results of the treatment of recycle water by soda ash to remove calcium and the impact on flotation.

5. The need for aeration and the impact of corrosion of grinding media on water quality/flotation performance.

6. Effect of the use of corrosion resistant balls for grinding on water quality and flotation.

7. Effect of water conservation on operating costs at a location where water is expensive.

PRODUCTION DETAILS

A total of 3,300 metric tons of ore are treated daily for 340 days per year for a total of 1,125,000 tpa by flotation.

LOCATION

In the Kalahari Desert just south of the Orange River in the northwest Cape Province of South Africa near Aggeneys.

CLIMATE

1.9 m (65") evaporation per year. 100 mm (4") rainfall. Extremely hot summers. Cool winters but no snowfall.

ORE CHARACTERISTICS

Minerals to be recovered are chalcopyrite, galena, and sphalerite with associated silver.

Gangue minerals comprise pyrrhotite, pyrite, magnetite, quartz, amphibolite, and other silicates and occasional cement from backfill.

PROCESS

Crushing, grinding, and sequential flotation for recovery of chalcopyrite, galena, and sphalerite in that order. The high Pb:Cu ratio is the reason for choosing a selective float rather than a bulk float; the latter results in poor copper concentrate grade.

The distribution of metals and grades of concentrates were determined by tests done at MINTEK in the Transvaal and in a 2.5 t/h pilot plant at Black Mountain.

Nine reagents are added at up to forty three points for the three flotation circuits with comprehensive automated on-line monitoring by a Courier 300 X-ray analyzer which samples and analyzes fourteen streams for copper, lead, zinc, silver, iron, and solids on a continuous basis. Three process computers are employed with a control center to stabilize and optimize the flotation circuits.

The lead and zinc circuits were quickly brought to design performance, but the copper circuit failed to meet design performance both with respect to grade and recovery. The quality of recycle water appears to have a lot to do with this.

Design product recovery rate for the following tonnages of metal contained in concentrates:

32,000	Tons Copper per Year	68 tpd
134,000	Tons Lead per Year	394 tpd
35,000	Tons Zinc per Year	103 tpd
112	Tons Silver per Year	

The silver reports mainly with the lead concentrate (about 72%) and with the copper concentrate and accounts for more revenue than any other metal. When copper and lead concentrate recovery is optimized, it is found that silver recovery is also optimized.

RECOVERY

	Design	Actual	
Copper	76%	36.9%	At startup.
		57.8%	Change to dichromate adding Z-4, collector paddles installed on rougher cells.
		55.9%	After installing pre-aeration.
		62.9%	Bulk float result.
		67.0%	Aimed for after improving water quality and using corrosion resistant balls.

WATER COST

Water is supplied by a 60 kilometer pipeline from the Orange River. This clarified river water is supplied at a price of R0.60/m^3 by the Pella Water Board which is managed by Black Mountain Mineral Developement Co. Ltd. It is noted that most of the price of this water is to cover the fixed costs of operating the pipeline. Reducing the water consumption results only in a proportionate increase in the unit cost.

The Pella Water Board pays R0.23/m^3 to the Dept. of the Environment for raw river water. Black Mountain's annual water bill for the mill amounts to R900,000 (US$450,000).

WATER DEMAND

14,000-14,500 m^3/d in summer.
11,000 m^3/d average yearround.

WATER USE ALLOCATION

Metallurgical Plant	4,000 m^3/d
Township	4,000 m^3/d
Road Maintenance	500 m^3/d
To Backfill	1,200 m^3/d
To Shaft	800 m^3/d
Cooling, Compressors, etc.	500 m^3/d
Annual Average	11,000 m^3/d

NUMBER OF EMPLOYEES 250 + 500 + 700 = 1,450 total.

Water consumption for the township works out to 2.75 m^3 per person per day which is high by industry standards but includes desert vegetable gardening and the making of a habitable garden environment to attract good staff.

CAPITAL COST - WATER

The Pella Water Board capital cost for clarification, pumping station, and pipeline was R7.00 million ($4.2 million).

WATER RECYCLING

The Black Mountain plant uses 1,500 m^3/d or about 25% reclaimed tailings water. This percentage is dropped further if the 1,200 m^3/d fresh water used in the cement backfill plant is added in. In the water balance of January 19, 1984, a higher percentage of water was recycled. Water recycling has been identified as a cause of poor recoveries.

METALLURGICAL CONSIDERATIONS

GRAHAM AND HEATHCOTE (1982) described the effects of the oxidation state of the pulp on the selective flotation of chalcopyrite from Black Mountain ore. These details and additional later testwork is included in a paper by TWIDLE AND ENGELBRECHT (1984) which is inserted below because it is an excellent illustration of the complicated interrelationship between water quality, physical parameters (e.g., temperature), flowsheet layout, and reagent selection and their impact on metallurgical performance.

WATER BALANCE

A water balance dated January 19, 1984, is shown here which shows an arrangement in which 2,150 m^3/d of water is recycled at a total of 5,500 m^3/d to the grinding circuit or 40% recycle in the grinding circuit. In this water balance, 4,200 m^3/d of the total of 12,000 was fresh, i.e., 65% of the water used in the flotation plant (including reagent mixing) is recycled. However, only 1,400 m^3/d (12%) is reclaimed from the aging pond.

WATER QUALITY

Monthly water analyses for reclaim water and copper tails thickener overflow as received are shown here to provide an indication of the composition of this water.

It is noted that:

1) The calcium hardness of the copper tails thickener o/f water (1,000-1,500 ppm) and reclaim water (1,500-2,000 ppm) is high.

2) Calcium and sulfate levels indicate that the reclaim water is close to gypsum saturation. This is not surprising considering that pyrite/pyrrhotite is oxidized along with some other sulfides to generate sulfates; cement is used in backfill which contributes calcium in the shaftwater that is returned to the tailings dam.

3) Reclaim water contains 400-700 ppm total organics believed to be flotation reagent degradation products.

WATER QUALITY EFFECTS

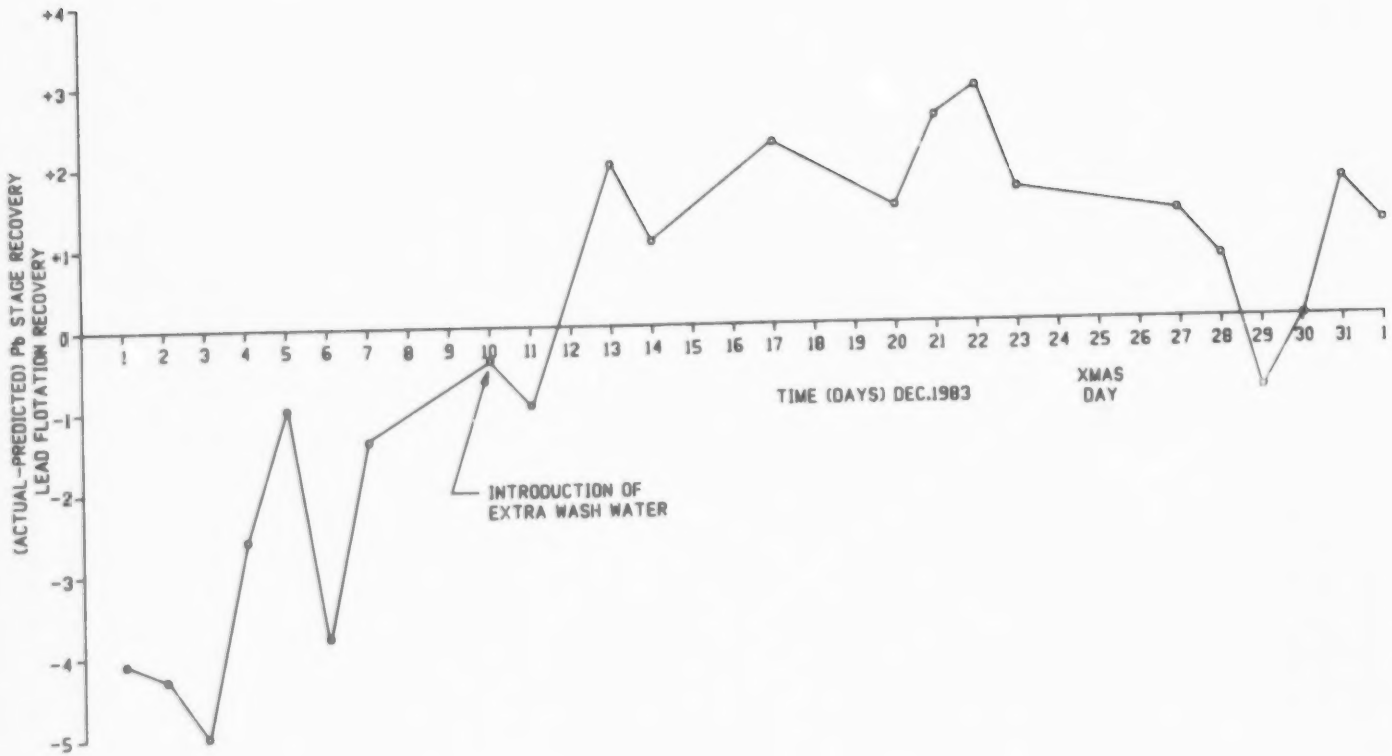
1. It is noted that 700-1,200 m^3/d of fresh water is consumed in the tailings backfill plant. 950 m^3/d of water recovered from the backfill mixing plant ends up in the tailings pond where it undoubtedly adds calcium to the decant solution in the pond. Black Mountain staff believe that the 500 ppm or so organics in recycled water would result in a weakened cement.

2. The aging pond and tailings dam are shallow ponds in a very hot climate with 1.9 m evaporation and 100 mm rainfall per year. This unquestionably has a concentrating influence on tailings reclaim water. It may also result in clogging of underdrains due to salt (gypsum) precipitation, although these effects are not readily apparent in the reclaim water quality data.

3. When pyrrhotite levels increase, this has sometimes been correlated with copper recovery reductions. This effect is counteracted by the operation of an aeration circuit.

4. A clearcut influence of using more fresh water in the flotation circuit on lead recovery is shown in the graph provided by the Black Mountain staff. What species in the recycled water causes the problem is not completely clear. See 6 below.

EFFECT OF FRESH WATER INCREASE AND IMPROVED WATER QUALITY



5. TWIDLE AND ENGELBRECHT (1984) point out the negative effects on copper recovery of using increased amounts of recycle tailings water irrespective of whether or not the pulp was aerated prior to flotation.

6. Bench flotation tests showed that a decrease of about 10% in the copper recovery was attributable to a cement contamination of 45 Kg of backfill per ton of plant feed producing a pH of 9.8.

7. When the feed pH was increased on account of backfill in the ore, increased amounts of sulfurous acid had to be added with a resulting extremely brittle shallow froth, although the selectivity of rougher flotation of copper versus lead improved when ore was contaminated by backfill.

8. The Redox potential of the pulp has a critical effect on copper recovery, and the EH, in turn, seems influenced by the type of grinding balls and the degree of aeration of the pulp.

9. Treating reclaim water with soda ash to modify pH in the lead circuit and to precipitate calcium from plant water, followed by filtration, improved lead recoveries considerably. Approximately 1.5 Kg Na_2CO_3/t is required at a cost of $0.33/Kg to reduce the calcium hardness of the water from 1,600 ppm $CaCO_3$ to less than 100 ppm in the lead circuit and to 500-750 ppm in the copper tailings thickener underflow.

10. Copper rougher froth quality and recovery was shown to be improved when reclaim water is treated in the same way with Na_2CO_3.

11. Work by MINTEK in Randburg, Transvaal indicated that removal of metal ions (Cu, Pb) and organic flotation reagent degradation products from plant water by activated charcoal would improve the selectivity of flotation when using this treated water. In tests at Black Mountain it was found that activated carbon was successful in removing Cu and Pb and Z-200 collector from recycled water. Tests using this treated water did little to enhance copper recovery or selectivity. Better metallurgy was obtained by diluting reclaim water with 25% fresh water.

12. Copper sulfate consumption in the zinc circuit could be halved when water was treated by Na_2CO_3, to below 100 g/t.

13. When soda ash treatment of water was in use, silver recoveries improved from 82.4% to 83.8%, and lead recoveries improved from 86.6% to 89.1% showing the effect of calcium on the recovery of these two metals which resulted in a net increase in revenue after deducting the cost of soda ash of R60,000/month.

14. When soda ash softening was used in a plant trial, it was found that the moisture content in concentrates increased which would lead to an increased cost of shipping.

WATER TREATMENT PROCESSES

1) Carbon Treatment

Pica carbon C210AS carbon was tested in a column by MINTEK who was able to remove most organics and metals from reclaim water as follows:

	Feed	Treated Solution
Cu	2.7 ppm	Less than 0.5 ppm.
Mn	2.3 ppm	0.5 ppm
Thionocarbamate	12.00 ppm	Less than 0.2 ppm.

2) CO_2 Blowing and NaOH Precipitation

The CO_2 process was able to achieve the following:

	Feed	Treated Solution
Mn	2.3 ppm	0.5 ppm
Ca^{2+}	790 ppm	18.0 ppm
Mg^{2+}	14 ppm	11.0 ppm

TAILINGS DISPOSAL

All tailings are pumped to the backfill plant where the coarser fraction is removed by cyclones for use as backfill. The cyclone overflow is pumped to the tailings dam and distributed to the dam wall at 60 m intervals.

The dam was designed and constructed by Steffen Robertson and Kirsten of Johannesburg and is fitted with piezometers.

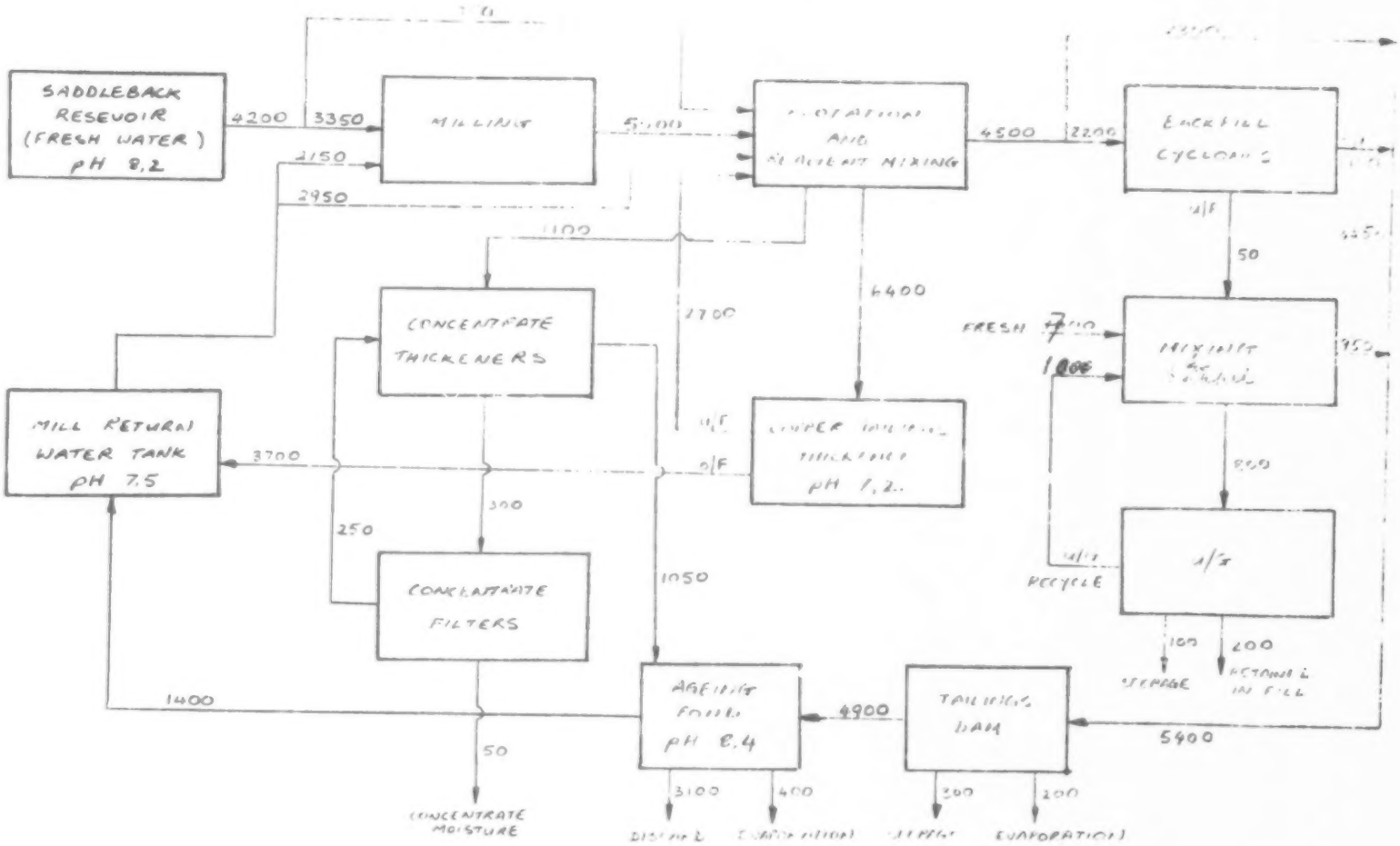
Although the operation is located in a very arid region which receives 2-4 inches of rain per year, the tailings dam is provided with a berm which serves as flood protection in the event of a flash flood.

BLACK MOUNTAIN MINERAL DEV. CO. (PTY) LTD.

WATER BALANCE FOR CONCENTRATOR AND BACKFILL PLANT

19/1/84

FLOWRATES IN m^3/DAY



BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

[illegible] ANALYSIS

SAMPLE Rooiwater

DATE	JAN											
SAMPLE LIMITS												
pH 5,5 - 9,5	8.0											
T.D.S. < 500 mg/L above intake	3970											
[illegible] < 75 mg/L	576											
[illegible] < [illegible] mg/L												
[illegible] ammonia												
[illegible] Sulphate < 25 mg/L	3											
[illegible] < [illegible] mg/L												
[illegible] < [illegible] mg/L	5.0											
[illegible] < [illegible] mg/L	7.2											
[illegible] < [illegible] mg/L	2.0											
[illegible]	0.1											
[illegible]	0.1											
[illegible]	6.5											
[illegible] Hardness	80											
[illegible] Hardness	1820											
Total Chlorides	580											
[illegible]	[illegible]											
[illegible] < 0,5 mg/L	[illegible]											
[illegible]	[illegible]											
Total Hardness	[illegible]											
[illegible]	[illegible]											
Electrolyte	[illegible]											
[illegible]	[illegible]											

BLACK MOUNTAIN

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

Temp due to change of analysis from Ion Exchange to Evaporation

SAMPLE RECLAIM H_2O

DATE 1983	JAN	FEB	MAR	MAR	APR	MAY	JUL	SEPT	OCT	NOV	DEC.
SAMPLE LIMITS											
pH 5,5 - 9,5	7.1	6.6	6.6	7.1	6.05	6.4	4.9	6.50	8.6	7.2	10,0
T.D.S. < 500 mg/L above intake	4218	4473	2850	4330	4870	2164	3105	3477	3467	3282	3578
C.O.D. < 75 mg/L	476	596	288	503	479	564	484	1070	624	840	551
O Abs. < 10 mg/L	–		–	–		–	–	–	–	–	
F & S Ammonia	–			–		–	–	–	–	–	
Susp. Solids < 25 mg/L	4	30	25	7	1	3	1	5	2	1	2
E. Coli < Nil/100 ml	–		–	–	–	–	–	–	–	–	
Cu < 1,0 mg/L	2.1	2.7	4.0	8.85	0.05	2.68	4.0	2.7	4.3	5.2	2.5
Pb < 1,0 mg/L	3.2	2.6	3.2	2.05	5.65	4.01	1.7	2.0	3.0	1.9	2,1
Zn < 5,0 mg/L	0.4	<0.1	1.2	0.4	1.05	0.45	1.5	0.0	0.4	2.6	2,0
Fe	0.4	<0.1	0.5	<0.1	0.50	0.23	0.5	3.8	2.5	0.6	<0,1
Cr	0.1	0.18	1.0	0.25	0.20	1.31	<0.1	<0.1	0.1	<0.1	<0,1
Mn	0.6	0.09	14.0	3.4	0.85	0.25	7.8	11.4	3.0	8.0	7,6
Mg HARDNESS	110	400	75	290	85	110	250	180	170	80	20
Ca "	1945	2090	1000	1875	2200	2170	1730	1400	1290	1480	1460
TOT. ORGANICS	576	636	529	578	743	–	4400	430	669	369	658
Cl^-	234	430	266	2.38	249	227	372	454	312.4	362.	340
$SO_4^=$ < 0,5 mg/L	1.12	–	2.1	2.48	0.39	<0.1	1.59	4.66	0.58	0,647	0,49
$SO_4^=$	1741	2858	1681	1778	1970	1925	1524	1546	1206.3	1284.1	1253
Total Hardness	2024	2490	1064	2165	2285	2280	1980	1580	1560	1560	1480
Na^+	181	131	70	173	164	178	125	96	86	239	430
HCO_3^-	52	50	40	51	104	50	21	39	52	54	42
Zeeo	5.61	8.4	13.70	11.16	26.4	10.55	8.87	9.58	8.93	7,65	10,76

BLACK [illegible] ESTATES MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

SAMPLE RECLAIM H_2O

ATE 1982	JAN	FEB	MAR	APR	MAY	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DE
AMPLE LIMITS													
H 5,5 - 9,5	7.4	7.4	7.4	9.2	8.9	7.1	7.3	9.2	7.4	7.8	7.5	7.6	7
T.D.S. <500 mg/L above intake	1852	1705	1445	1472	1470	1618	1222	2059	1871	1645	1945	1789	1
C.O.D. <75 mg/L		245	302	327	384	464	105	434	448	405	481	472	4
G Abs. <10 mg/L		223	–	234	54		61	104	191	316	227	211	1
F & S Ammonia			–	–	–	–	–	–	–	–	–		6
Susp. Solids <25 mg/L	12	7	8	11	6	3	4	6	1	8	1	13	2
E. Coli <Nil/100 ml			–	–	–	–	–	–	–	–	–		–
Cu <1,0 mg/L	2.2	0.2	1.4	2.8	2.0	5.9	1.9	2.5	2.3	6.0	2.0	2.2	3
Pb <1,0 mg/L	0.81	0.2	0.46	<0.1	0.4	0.1	3.0	1.8	1.0	0.4	1.4	1.1	1.
Zn <5,0 mg/L	0.24	0.1	0.04	0.1	0.4	0.1	0.4	0.3	<0.1	<0.1	0.9	0.9	0
Fe		0.2	0.2	1.2	0.9	0.1	0.1	0.4	0.1	0.1	0.1	0.1	0.
Cr	4.6	0.2	0.3	0.1	0.2	<0.1	0.6	–	<0.1	0.9	1.0	0.7	0.
Mn	22	2.7	3.7	0.4	0.3	1.9	0.1	<0.1	<0.1	<0.1	0.6	<0.1	0.
Mg HARDNESS	99	37	545	674	81	85	219	97	177	80	80	210	7
Ca •	118	1441	656	1162	1238	1311	1327	1508	1410	1500	1640	1640	19
Ag TOT ORGANICS			–	–	–	–	11	–	–	–	–	–	–
Cl^-	163	192	256	245	244	369	260	323	220	202	266	149	27
CN^- <0,5 mg/L		0.5	0.5	–	–	<0.05	<0.05		–	–	–	NIL	NI
$SO_4^=$	1165	1119	1124	1044	985	1435	1147	1254	1167	1232	1287	1251	17
Total Hardness			1201	1836	1319	1396	1540	1605	1596	1580	1720	1850	2
Na^+						–	120	125	110	133	130	128	18
HCO_3						–	62	59	84	80	90	81	7
Σ 200						–	11.7	15	12.2	11.6	11.7	9.58	5.

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

SAMPLE RECLAIM H_2O

DATE 1981	MAY	JUNE	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC			
SAMPLE LIMITS												
pH 5,5 - 9,5	7.7	7.0	9.0	8.7	8.6	8.1		7.6	7.3			
T.D.S. < 500 mg/L above intake	1518	1424	1866	1680	1757	1816		1917	1959			
C.O.D. < 75 mg/L	–	–	336	281	354	306		204	368			
[illegible] < [illegible] mg/L	–	–	460	250	141	10.8		247	250			
[illegible]	–	–	–	–	–	–		NR	NR			
[illegible] < 25 mg/L	22	26	6	44	7	48		26	18			
[illegible]	–	–	[illegible]	[illegible]	[illegible]	[illegible]		–	–			
[illegible] < [illegible] mg/L	2.2	1.0	1.05	18.2	16.1	4.30		1.18	1.38			
[illegible] < [illegible] mg/L	1.2	0.07	0.10	<0.1	0.11	0.2		0.94	1.07			
[illegible] < [illegible] mg/L	1.0	200	0.11	0.01	<0.1	0.5		0.21	0.01			
[illegible]	0.06	0.00	0.05	<0.1	<0.1	<0.1		<0.1	<0.1			
Cr	–	–	0.1	0.2	<0.1	0.1						
Mn	<0.1	–	6.16	6.69	6.0	8.8			15.2			
Ca^{++} HARDNESS	–	–	662	ND	ND	31		102	202			
Ca "	–	–	646	ND	ND	537		1224	1192			
Mg	–	–	–	0.03	–	–		NR	NR			
Cl^-	–	–	404	61	479	231		316	302			
$CO_3^=$ < 0,5 mg/L	25	–	0.2	0.1	0.05	0.1		0.2	0.1			
$SO_4^=$	959	–	867	1138	1181	1162		1162	1197			
Total Hardness	–	–	–	–	–	–		NR	NR			
% 200	12.2	–	–	–	–			NR	NR			

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

SAMPLE Cu Tails Th. Pit

DATE 1984	JAN											
SAMPLE LIMITS												
pH 5,5 - 9,5	6.4											
T.D.S. < 500 mg/L above intake	3000											
C.O.D. < 75 mg/L	792											
C Abs. < 10 mg/L												
F & S Ammonia												
Susp. Solids < 25 mg/L	7											
E. Coli <Nil/100 ml												
Cu < 1,0 mg/L	8.3											
Pb < 1,0 mg/L	5.8											
Zn < 5,0 mg/L	3.2											
Fe	<0.1											
Cl	91											
Na	13.2											
Mg Hardness	210											
Ca Hardness	1500											
K												
NO_3^-	438											
NO_2^- < 0,5 mg/L	<0.1											
$SO_4^=$	885.9											
Total Hardness	1710											
NH_3^+	90											
Bicarbonate	56											
Z 200	10.32											

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

SAMPLE GUTTAKS THICKNER 01

DATE 1983	FEB	MAR	APR	MAI	JUNI	AUG	SEPT * Soda Ash Test	OCT	NOV *	DEC
SAMPLE LIMITS										
pH 5,5 - 9,5	7,8	6,6	6,95	7,2	8,2	8,2	8,3	7,5	8,1	6,9
T.D.S. < 500 mg/L above intake	3136	3520	4156	1512	3541	3142	2671	2488	2720	2969
C.O.D. < 75 mg/L	655	435	592	530	511	575	812	848	428	712
O Acs. < 10 mg/L	—	—	—	—	—	—	—	—	—	
F & S Ammonia	—	—	—	—	—	—	—	—	—	
Susp. Solids < 25 mg/L	18	61	36	2	28	17	38	44	1	19
E. Coli < Nil/100 ml	—	—	—	—	—	—	—	—	—	
Cu < 1,0 mg/L	2,1	4,6	7,95	1,69	1,1	2,5	2,5	0,7	0,3	8,3
Pb < 1,0 mg/L	1,5	2,9	2,75	2,06	0,8	3,1	0,2	0,9	1,1	0,9
Zn < 5,0 mg/L	<0,1	1,2	0,70	0,09	0,9	0,4	0,2	0,9	0,5	2,1
Fe	0,25	1,2	1,65	0,5	<0,1	<0,1	0,1	0,1	0,2	<0,1
Cr	0,3	0,3	0,15	1,0	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Mn	0,4	11,6	11,55	0,39	5,2	1,9	1,3	3,4	4,3	2,5
Mg HARDNESS	44	150	75	160	100	50	20	330	100	80
Ca HARDNESS	1596	1935	1715	1490	1550	980	1000	1250	1050	1550
As	—	—	—	—	—	—	—	—	—	
Cl^-	330	270	273	245	340	430	547	369	494	309
CN^- < 0,5 mg/L	—	4,8	0,15	<0,1	1,29	5,85	5,06	<0,1	<0,1	<0,1
$SO_4^=$	1151	1537	1210	1051	1145	966	682	662	881,2	989
Total Hardness	1640	2035	1790	1650	1620	1030	1020	1580	1150	1630
HCO_3^-	32	42	51	30	66	111	108	75	89	71
Sodium	90	87	87	77	90	98	138	113	284	108
TOC	—	15,04	33,9	13,34	7,4	6,58	16,4	12,68	10,14	7,96

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

SAMPLE TAILS THICKNER O

DATE 1982.	JAN	FEB	MAR	APR	MAY	1/6	7/7	3/8	7/9	5/10	2/11
SAMPLE LIMITS											
pH 5,5 - 9,5	8,0	8,3	8,2	8,6	10,5	6,4	7,9	6,5	6,9	7,3	7,5
T.D.S. < 500 mg/L above intake	1308	1718	1379	1422	1110	1152	1994	1502	1400	1820	1610
C.O.D. < 75 mg/L	—	304	352	335	472	127	572	572	588	812	672
O Abs. < 10 mg/L	—	—	—	343	69	80	211	171	—	263	—
F & S Ammonia	—	—	—	—	—	—	—	—	—	—	—
Susp. Solids < 25 mg/L	44	41	4500	187	108	314	116	562	1372	671	626
E. Coli < Nil/100 ml	—	—	—	—	—	—	—	—	—	—	—
Cu < 1,0 mg/L	0,75	2,4	0,35	1,9	2,2	2,1	1,8	2,3	5,9	2,9	2,9
Pb < 1,0 mg/L	0,52	0,5	1,05	1,8	1,2	2,6	1,2	<0,1	1,7	1,5	1,4
Zn < 5,0 mg/L	0,01	0,10	0,27	0,6	0,9	1,7	0,8	<0,1	<0,1	0,8	0,8
Fe	—	0,2	3,00	1,3	3,2	0,2	0,5	0,13	0,9	0,2	0,2
Cr	—	0,8	0,4	0,1	0,3	0,8	—	<0,1	0,5	0,4	0,4
Mn	2,5	2,5	4,2	0,5	0,4	0,7	<0,1	<0,1	<0,1	0,7	<0,1
Mg HARDNESS	96	64	566	264	78	312	50	152	60	80	160
Ca HARDNESS	730	1336	814	1137	1226	1259	1411	1304	1350	1550	1520
Ag	—	—	—	—	—	—	2	—	—	—	—
Cl^-	78	112	263	249	278	230	321	—	167	217	202
CN^- < 0,5 mg/L	0,1	0,2	0,2	0,05	0,05	<0,05	—	—	—	—	—
$SO_4^=$	710	1032	1033	1018	1015	1092	1239	1328	1320	1345	1384
Total Hardness	916	1400	1380	1401	1304	1571	1461	1456	1410	1630	1680

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LTD

EFFLUENT ANALYSIS

SAMPLE CUTTAINS THICKNER 01

DATE 1981	13/6	14/7	4/8	1/9	DEC							
SAMPLE LIMITS												
pH 5,5 - 9,5	7.9	7.6	7.9	7.2	9.1							
T.D.S. < 500 mg/L above intake	2026	1712	1684	1649	1428							
C.O.D. < 75 mg/L	370	293	313	323	305							
U Abs. < 10 mg/L	—	—	—	—	—							
F & S Ammonia	—	—	—	—	—							
Susp. Solids < 25 mg/L	46	61	57	412	90							
E. Coli < Nil/100 ml	—	—	—	—	—							
Cu < 1,0 mg/L	2.09	9.0	9.4	1.59	1.64							
Pb < 1,0 mg/L	1.71	0.57	0.39	0.80	0.65							
Zn < 5,0 mg/L	0.56	3.25	1.13	1.2	1.02							
Fe	0.02	<0.1	<0.1	<0.1	<0.1							
Cr	0.4	<0.1	0.1	0.2	—							
Mn	5.36	14.7	10.0	10.4	1.33							
Mg	752	N.D	N.D	150	64							
Ca	160	100	N.D	446	551							
As	—	0.02	—	—	—							
Cl^-	401	61	430	227	213							
NO_3^- < 0,5 mg/l	0.02	0.1	0.05	0.1	0.5							
$SO_4^=$	939	1170	1133	1576	790							
Total Hardness	1352	N.D	N.D	550	950							

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PROPRIETARY) LIMITED

ANALYTICAL LABORATORY

WATER ANALYSIS

QUARTERLY

SAMPLE PLANT INFLUENT. SSS NO ..... DATE 12.12.83...

ANALYSIS	UNITS	RESULT	SPECS	REMARKS
pH		7.6		
Total Dissolved Solids	mg/l	3585		
Suspended Solids	mg/l	61		
Total Organics	mg/l	55		
Chemical Oxygen Demand	mg/l	826.9		
Absorbed Oxygen	mg/l	120.5		
Free Saline Ammonia	mg/l	2.5		
Total Hardness	mg/l $CaCO_3$	1680		
Calcium Hardness	mg/l $CaCO_3$	1400		
Magnesium Hardness	mg/l $CaCO_3$	180		
Sulphate	mg/l SO_4^{2-}	130		
Chloride	mg/l Cl^-	263		
Bicarbonate	mg/l $CaCO_3$			
Nitrate	mg/l N	0.0		
Fluoride	mg/l F^-	0.80		
Cyanide	mg/l CN^-	0.18		
COD	mg/l			
Copper	mg/l	1.7		
Lead	mg/l	1.2		
Zinc	mg/l	1.2		
Iron	mg/l	0.3		
Manganese	mg/l			
Chromium	mg/l			
Sodium	mg/l			
E. Coli Type 1	Counts/ 100 ml			
Colony Count	Counts/ml			

C.C. PLANT SUPT
ENG. OFFICER
SECT ENG TOWNSHIP.

CHIEF CHEMIST .....

BLACK MOUNTAIN MINERAL DEV. CO (PTY) LTD

EFFECT OF RECLAIM WATER/AERATION ON COPPER RECOVERY

Introduction

The poor performance of the copper circuit subsequent to aeration was believed to be due to the use of reclaim water and this hypothesis was tested on a laboratory scale.

Procedure

The procedure used was as follows :

Milling : 2 Kg -3mm ore ground with mild steel rods for 37 minutes in a lab. mill at 67% solids with 500g/t $ZnSO_4$.

Flotation Condition 5 minutes with
6 g/t MIBC, 9 g/t Z200 at pH 6,0
Float 3 minutes
Add SO_2 pH6
Float 3 minutes
Add SO_2 pH 6
Float 3 minutes

Some tests were done with reclaim water throughout and some with 30 minutes aeration prior to conditioning as follows :

Test No	1	2	3	4
Water Type	Reclaim	Fresh	Reclaim	Fresh
Aeration	Y	N	N	Y

Results

The results of the tests are appended.

Discussion

Graphs 1 to 3 show respectively the Cu, Pb and Zn recoveries against time for the various conditions.

Graph 1 shows clearly that aeration improves the rate of copper recovery with both fresh and reclaim water, but the curves for reclaim water have a slower rate than for fresh water, with and without aeration.

Graph 2 shows that aeration increases the rate of lead recovery with both fresh and reclaim water and that reclaim water give higher rates of recovery than fresh water.

Graph 3 reveals the expected feature that with no aeration reclaim water gives a higher rate of zinc recovery than fresh water. Aeration increased the rate with both water types but the fresh water gave a higher rate than reclaim water.

Conclusions

Reclaim water has a detrimental effect on rate of copper recovery both with and without aeration.

It would be worthwhile to repeat these tests to determine if the effect is consistent and to quantify the effect on plant results.

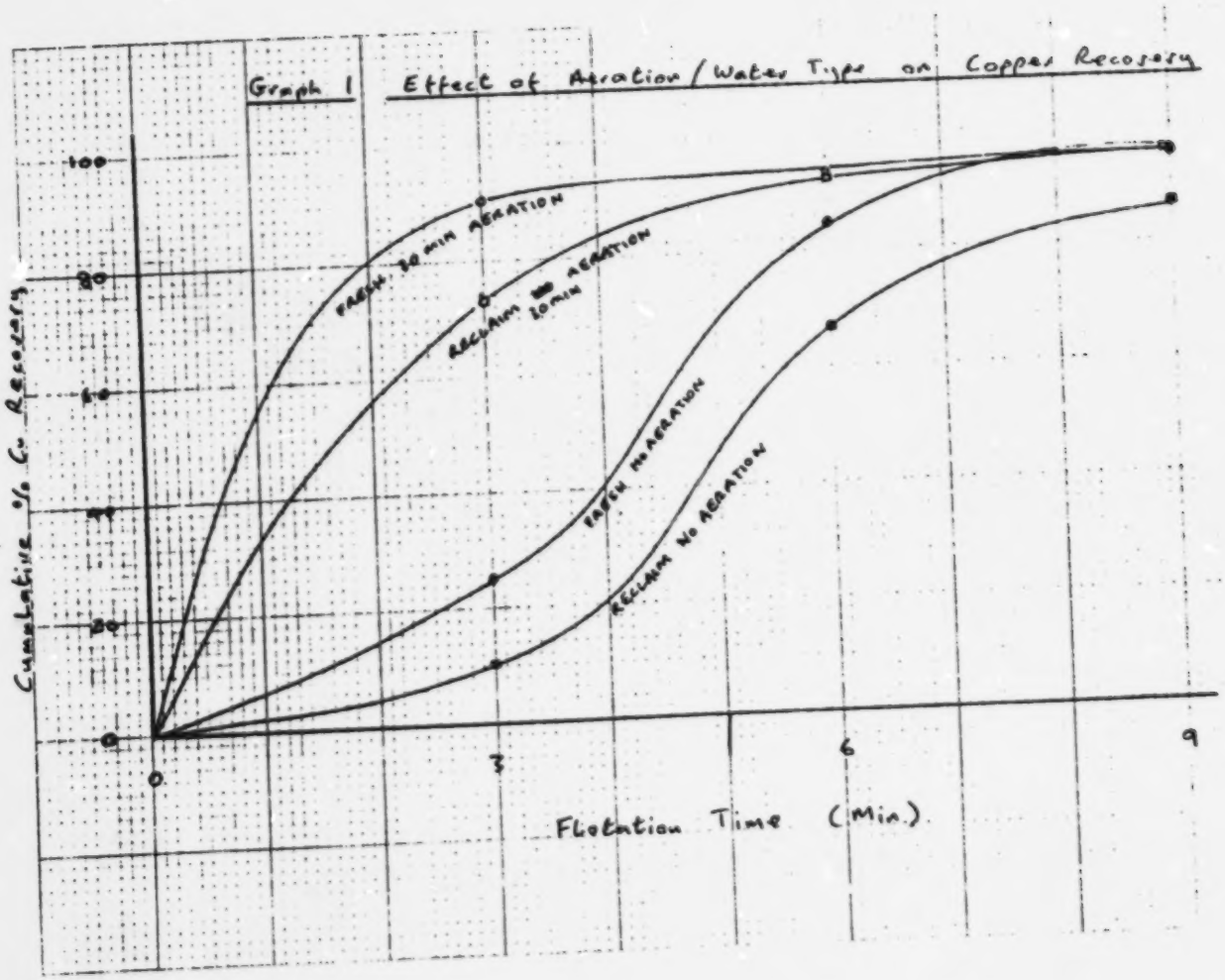
A. Norton

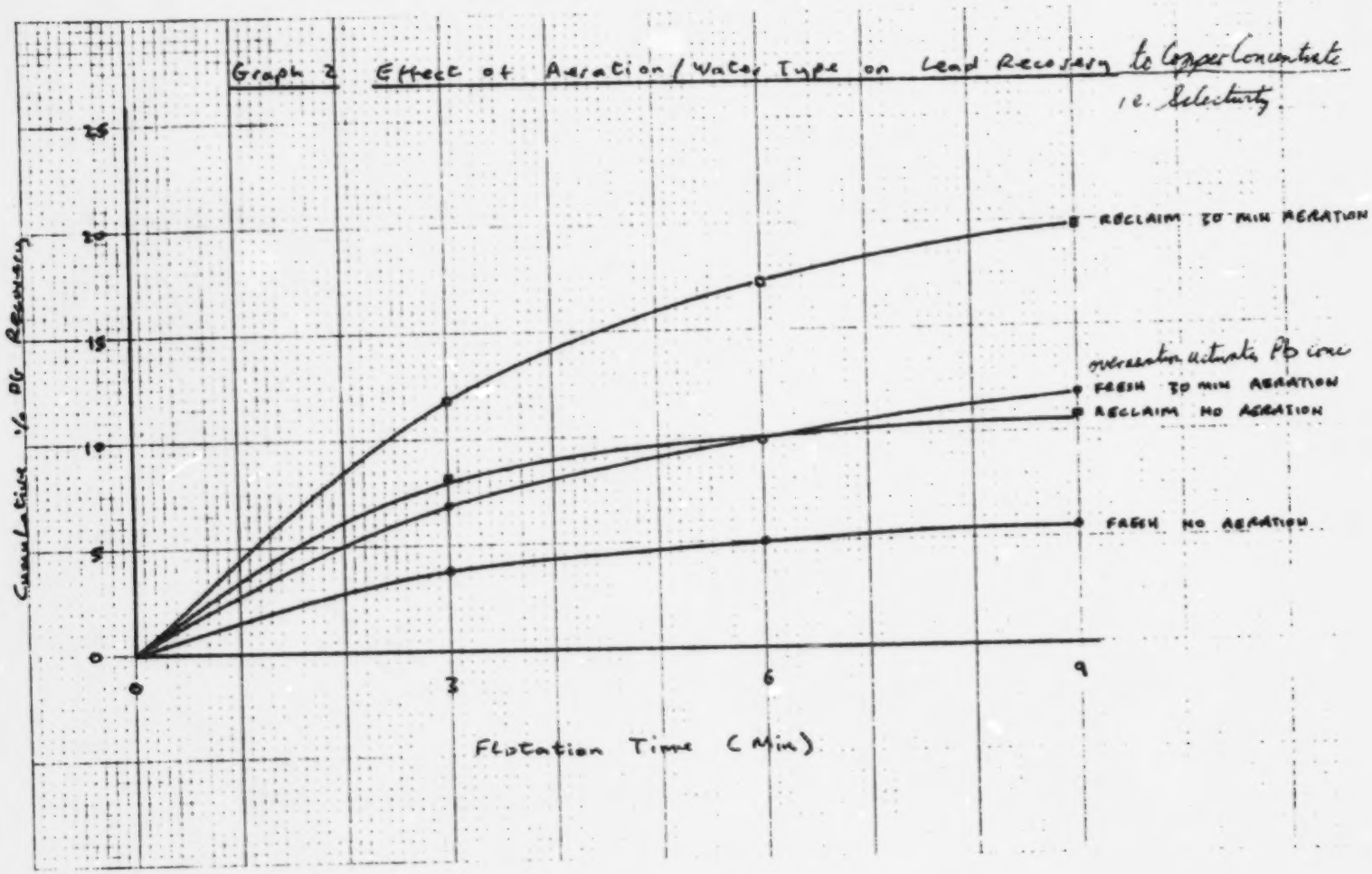
A.E. NORTON
PLANT METALLURGIST

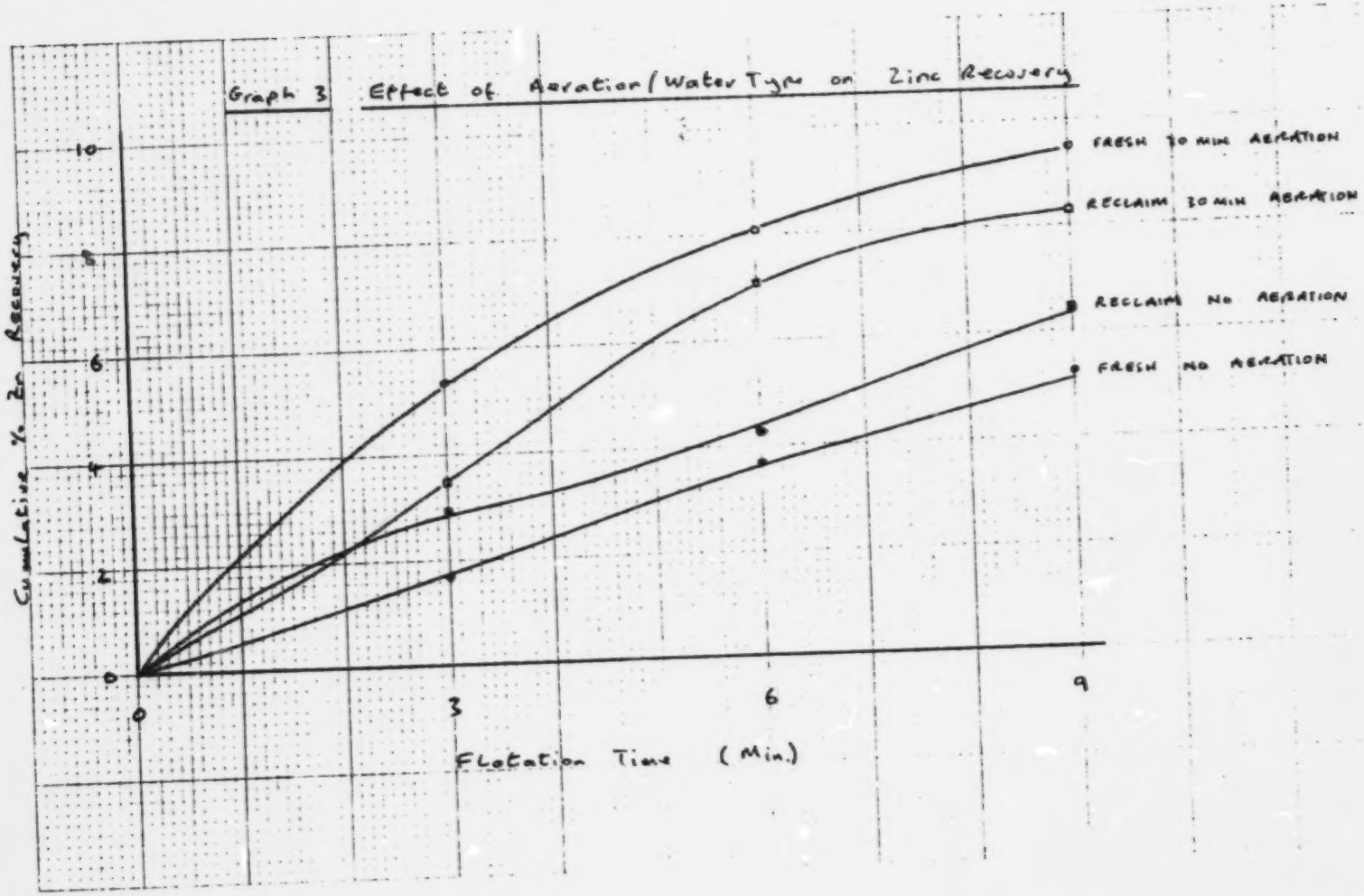
AEN/sh

TEST 1 RECLAIM WATER - 30 MIN. AERATION

Product	Wt%	ASSAYS % Cu	% Pb	% Zn	DISTRIBUTION % Cu	% Pb	% Zn
Conc 1	4,40	6,30	17,10	1,49	72,36	11,75	3,55
Conc 2	2,74	2,92	13,10	2,38	20,89	5,60	3,53
Conc 3	0,83	0,90	17,00	2,77	1,95	2,20	1,24
Tails	92,03	0,02	5,60	1,84	4,80	80,45	91,68
Calc Feed	100,00	0,38	6,41	1,85	100,00	100,00	100,00
TEST 2	FRESH WATER - NO AERATION						
Conc 1	1,39	6,90	17,70	2,27	25,88	3,80	1,71
Conc 2	1,10	20,00	6,80	3,40	59,37	1,16	2,03
Conc 3	0,43	8,20	8,80	6,40	9,51	0,58	1,49
Tails	97,08	0,02	6,30	1,80	5,24	94,46	94,77
Calc Feed	100,00	0,37	6,47	1,84	100,00	100,00	100,00
TEST 3	RECLAIM WATER - NO AERATION						
Conc 1	2,24	1,78	23,00	2,32	10,31	8,33	2,92
Conc 2	1,31	17,00	7,10	1,90	57,58	1,50	1,40
Conc 3	1,42	5,40	4,70	2,80	19,83	1,08	2,23
Tails	95,03	0,05	5,80	1,75	12,29	89,09	93,45
Calc Feed	100,00	0,39	6,19	1,78	100,00	100,00	100,00
TEST 4	FRESH WATER - 30 MIN. AERATION						
Conc 1	2,91	12,40	15,20	3,43	90,25	6,82	5,39
Conc 2	1,19	1,24	16,80	4,20	3,69	3,08	2,70
Conc 3	0,60	0,86	21,00	4,40	1,29	1,94	1,42
Tails	95,30	0,02	6,00	1,76	4,77	88,16	90,49
Calc Feed	100,00	0,40	6,49	1,85	100,00	100,00	100,00


Graph 1 Effect of Aeration / Water Type on Copper Recovery
Cumulative % Cu Recovery
100
80
60
40
20
0
0
3
6
9
Flotation Time (Min.)
FRESH 20 MIN AERATION
RECLAIM 20 MIN AERATION
FRESH NO AERATION
RECLAIM NO AERATION


Graph 2 Effect of Aeration / Water Type on Lead Recovery to Copper Concentrate
i.e. Selectivity
Cumulative % Pb Recovery
25
20
15
10
5
0
0
3
6
9
Flotation Time (Min)
RECLAIM 30 MIN AERATION
overaeration activates Pb conc
FRESH 30 MIN AERATION
RECLAIM NO AERATION
FRESH NO AERATION


Graph 3 Effect of Aeration/Water Type on Zinc Recovery
FRESH 30 MIN AERATION
RECLAIM 30 MIN AERATION
RECLAIM NO AERATION
FRESH NO AERATION
Cumulative % Zn Recovery
10
8
6
4
2
0
0
3
6
9
Flotation Time (Min.)

BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PTY) LIMITED.

SODA ASH PLANT TESTS.

1.0. INTRODUCTION.

Three plant trial tests were done during August/September 1983 to evaluate any benefits which may be obtained by using soda ash (Na_2CO_3) in the lead circuit as a replacement pH modifier for lime, in order to soften plant water to improve froth stability.

2.0. RESULTS.

2.1. A total of 150 tons soda ash was added to the lead conditioner as a ± 10% solution during the three test runs. Mixing and feeding procedures are described in a previous report.

2.2. Water softening was efficient at a dosage rate of 1.5kg/t, reducing calcium hardness from approximately 1600 ppm CaCo, to less than 100 ppm in the lead circuit, with calcium hardness in the copper tailings thickener underflow dropping from 1500 ppm to between 500 and 750 ppm.

2.3. Froth stability improved in all three circuits with a dosage of 1.5 kg/t: an increase to above 2,0 kg/t after steady state conditions had been reached, however, resulted in a shallow, slimey froth.

2.4. Soda ash addition rate could not be adequately controlled by means of the Pb conditioner pH, owing to pH fluctuations in the copper tailings thickener. During the first two runs Pb conditioner pH values of between 9,2 and 9,5 were attained with 1,1 kg/t Soda ash; in the final test, a pH of 8,5 could not be maintained without simultaneous lime addition.

2.5. Copper sulphate consumption in the zinc circuit during the soda ash runs was halved, with consumptions of below 100g/t being intermittently recorded.

2.6. During the third test run, 100 g/t soda ash was added to the rod mill for a period of 24 hours. No additional improvement in copper froth or recovery was apparent, however.

2.7. Daily lead and silver recoveries, together with soda ash consumption, are plotted in figure 1. The time scale extends from 26th to 27th September.

3.0. DISCUSSION OF RESULTS.

3.1. Average lead and silver recoveries during the period plotted were as follows:

Soda ash	off	on
Pb rec. to Pb conc (%)	86.6	89,1
Total Ag rec. (%)	82,4	83,8

Lead and silver recovery increases due to soda ash were thus 2,5% and 1,4% respectively. This includes the period during the third test when over-addition of soda ash led to froth deterioration and hence poor recoveries.

3.2. Based on a 2% Pb and 1,5% Ag recovery increase, a copper sulphate consumption reduction from 800 g/t (average January-August 1983) to 400 g/t, and a soda ash consumption of 1,5 kg/t, an operating costing would be as follows:

Metal prices:	Pb R427 / ton
	Ag R414 / ton.
Head grade:	9,5% Pb; 135 g/t Ag.
Milling rate:	94 000 tpm.

Soda ash (kg/t)	0	1,5
Pb recovery %	88,0	90,0
Ag recovery to Pb conc. %	70,0	71,5
Pb conc. % Pb.	70,0	70,0
Pb conc. g/t Ag	791	790
Tons Pb conc. pm.	11226	11481
R/ton conc.	360	360
Revenue from conc. (R pm)	4 041 360	4 133 160
Revenue difference (R pm)		+ 91 800
Cost of soda ash (R pm)		56 400
$CuSO_4$ cost reduction (R pm)		25 200
Nett revenue increase (R pm)		60 600

3.3. The potential increase in revenue derived from better copper and zinc metallurgy owing to better froth stability and circuit control cannot be assessed at this stage.

3.4. The only disadvantage in using soda ash established during the test periods was a deterioration in concentrate moistures (particularly copper and lead). Addition of lime to the concentrate thickeners and increased filter aid addition did not improve cake moisture: implementation of concentrate heating prior to filtration may prove necessary.

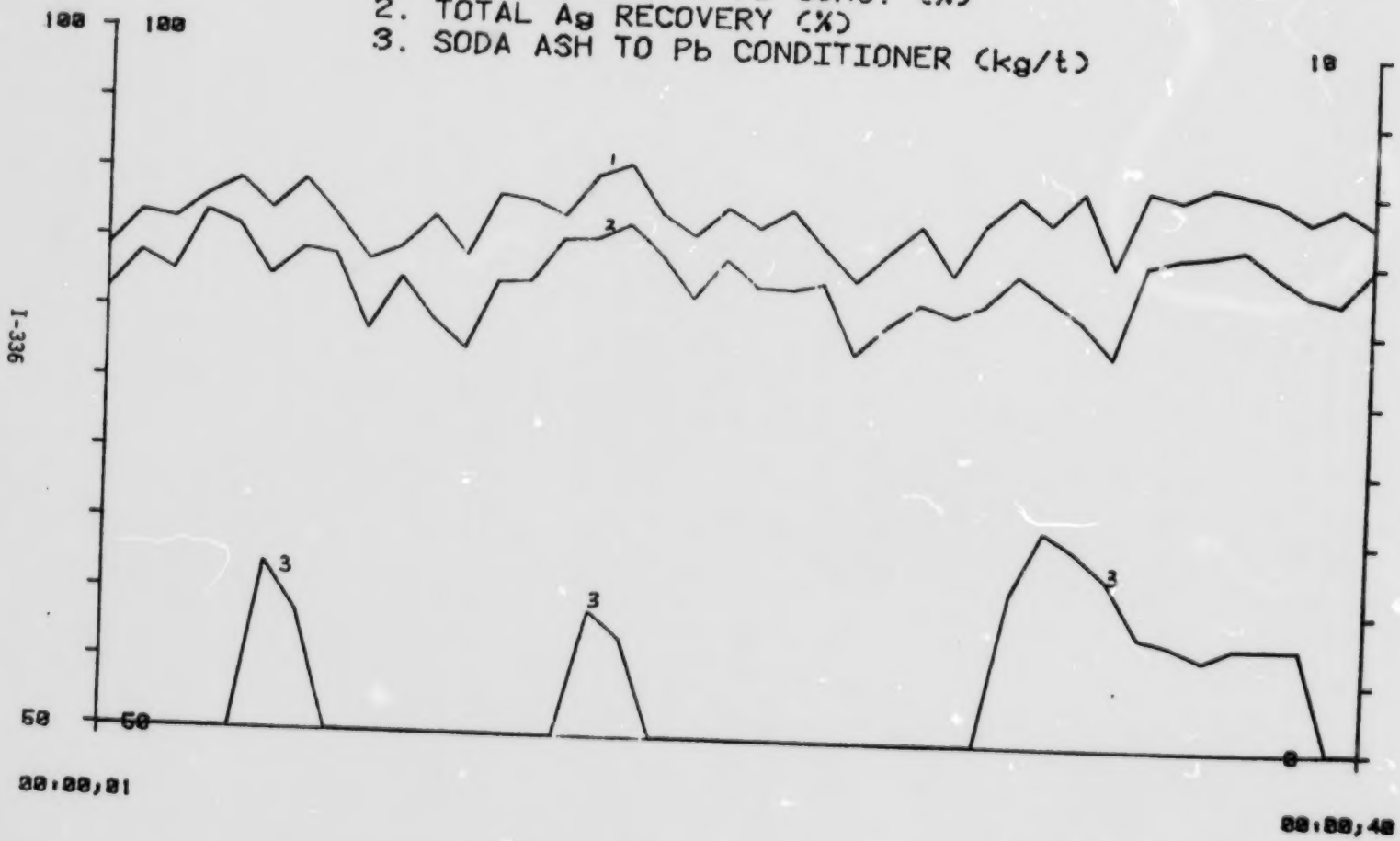
J. KOEL/mdp R + D MET.
12/9/83.

BLACK MOUNTAIN MINERAL CO

03-Aug-80 - 03-Aug-80

FIGURE 1.

1. Pb RECOVERY TO Pb CONC. (%)
2. TOTAL Ag RECOVERY (%)
3. SODA ASH TO Pb CONDITIONER (kg/t)



BLACK MOUNTAIN MINERAL DEVELOPMENT COMPANY (PROPRIETARY) LIMITED

BULK STORAGE, MAKE-UP AND FEEDING OF SODA ASH

EQUIPMENT

The following equipment would be required for a system to receive, handle and feed Soda Ash as a 10% strength solution to the lead conditioners, at a consumption rate of 1,5 kg/ton treated.

200m³ storage silo 230 tons @ 1,16 ton/m³

Gate valve

Rotary feeder (A) 40 kg/min

Screw feeder 40 kg/min

Measuring flask 0,6m³ @ 1,02 ton/m³

Rotary feeder (B) 120 kg/min

1 Automatically controlled valve (C)

0,3m³ conical bottom mixing tank

Agitator plus drive for mixing tank

2 x Transfer pumps 200 l/min each

40m³ Storage tank

Agitator plus drive for storage tank

2 x Delivery plus 50 l/min each

8 Valves (Saunders type)

5 Level Probes (HA, H, L, HH, LL)

Spillage retaining wall + Spillage pump

Vibrator unit

All steel work to be rubberlined.

MAKE-UP

A cycle would be as follows :

Add fresh water 400 l/min Weigh Soda Ash 40 kg/min	15 minutes
Charge Soda Ash 120 kg/min	5 minutes
Mix Soda Ash	10 minutes
Transfer batch 200 l/min	30 minutes

Daily consumption would be 5 to 6 tons of Soda Ash so that 8 to 10 batches per 24 hours would have to be mixed.

This could either be done entirely on the morning shift or continuously throughout the day, the latter arrangement probably being more suitabale.

By the use of level probes and a programmed sequence the mixing and transfer functions could be done automatically.

2/.....

REQUIREMENTS

It should be possible to resite one of the cement storage silos at the backfill plant for use as a bulk storage facility.

A 6,8m³ tank is available in the reagent mixing bay that is presently not being used, as well as an agitator shaft.

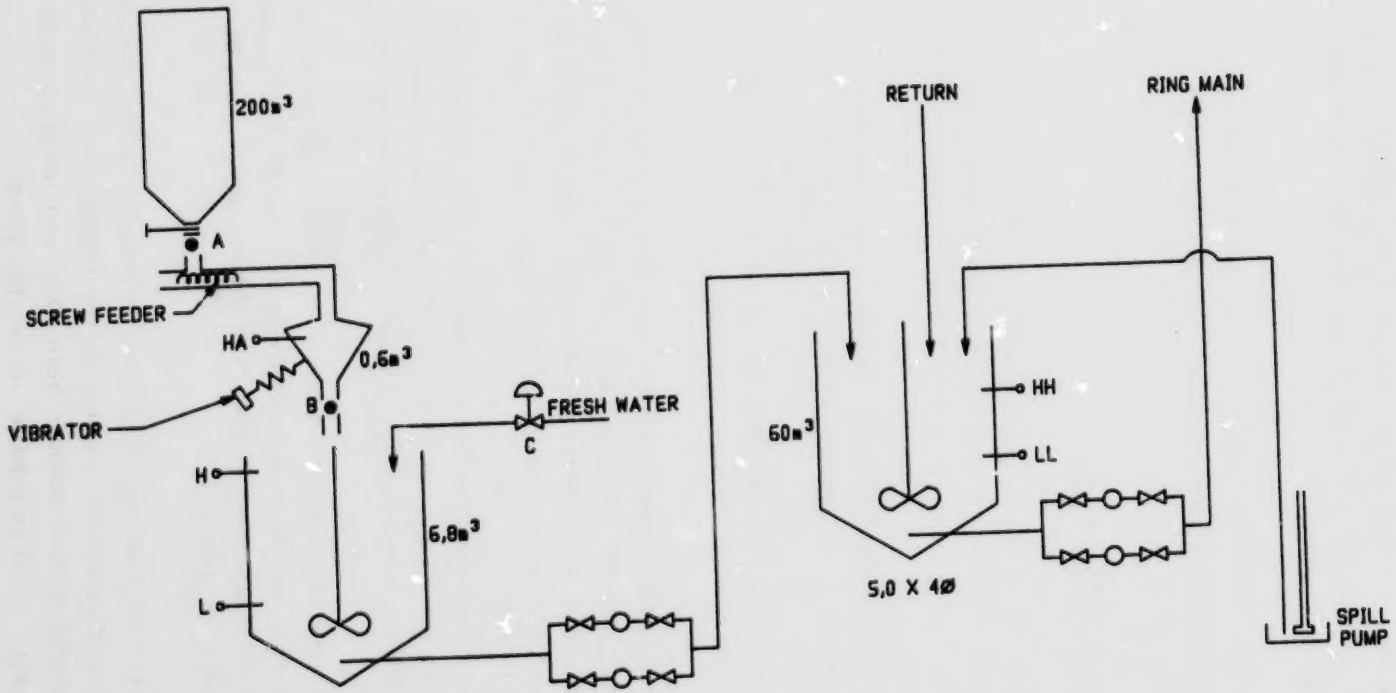
The screw feeder and measuring flask could be made at the concentrator and the second line ring main would serve as a feeding system.

All other equipment would have to be purchased.

T B [illegible]
Plant Superintendent

13th September 1983
/jr

BULK STORAGE, MAKE-UP AND FEEDING OF SODA ASH



The tailings dam is fitted with a blanket drain to drop the phreatic level in the tailings. It also is fitted with a decant tower. Flow from the decant tower and the blanket drains go through the tailings dam wall in pipes and then flow via an open ditch by gravity to a two compartment aging pond.

Drainage and decant from the tailings dam all flow into one ageing pond. Decant from the ageing pond is pumped back to the mill return water tank at the plant.

CONCLUSIONS AND DISCUSSIONS

1. Water quality of reclaimed solution may be improved if the surface area of the impoundments could be reduced or protected in other ways from evaporation which undoubtedly results in an increase in TDS of the reclaimed water.

2. At comparable bulk-float plants in Canada it has also been found that reclaim water upsets the selectivity of copper flotation in the presence of lead.

3. Aeration as a conditioning step has been found to be important in Canadian complex-sulfide plants, just as in this case.

4. Presence of calcium in water was found to cause a brittle froth with reduced copper recovery and reduced selectivity and also an important drop in silver recovery. This was overcome by treating reclaim water with soda ash to precipitate calcium carbonate which could be removed by filtration.

   Considering the high sulfate and virtually saturated gypsum content of the reclaim water and also the inverse solubility versus temperature relationship of gypsum, it is possible that froth embrittlement is caused by precipitation of gypsum in the froth.

   It would be very interesting to observe the effect on flotation results if, instead of adding soda ash, reclaim water was treated by seeded slurry R. O. to remove the whole spectrum of dissolved solids. Final pH adjustment might be achieved with soda ash or sodium hydroxide.

5. It is observed that fresh water is added to backfill tailings and cement mix. Water recovered from this step is returned to the tailings dam. If a way could be found of mixing backfill without needing fresh water and using reclaimed water, then the extra fresh water could be used in the flotation plant.

It was pointed out that reclaim water containing organics causes a weakened backfill. Were these backfill strength tests performed on reclaim water at the startup of the operation when ore contained large amounts of grease from the startup mining operation? Backfill practice and strength might be compared with other operations (e.g., Noranda Geco, Mattabi, and Kidd Creek Mines) which also employ backfill.

6. In Canadian complex sulfide mills SO_2 is also found necessary. In most cases, sulfurous acid is added directly in the mill itself. At one mill it is added after being mixed with NH_4OH. Possibly the same could be tried at Black Mountain. SO_2 is used in copper flotation.

7. Copper tailings thickener overflow water, which is added to the mill return water tank, appeared to be relatively high in suspended solids. The affect this has on flotation recovery or reagent consumption was not determined.

8. Considering the high rate of evaporation, it is to be expected that the solution in the exposed tailings dam would become increasingly concentrated due to the loss of water. For this reason it would be expected that gypsum or other salts may one day foul the blanket drain in the tailings plant. It is not known whether this will occur nor what can be done about it, if it does.

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SUDBURY OPERATIONS
FALCONBRIDGE, ONTARIO
CANADA POM 1S0

TELEPHONE (705) 693-2761

CONTACT John K. Weglo — Director Environmental Control

R. E. Michelutti — Senior Environmental Biologist

INTRODUCTION

Falconbridge mines, mills, roasts, smelts and refines nickel and copper on a large scale at their operations at Falconbridge, Ontario in the vicinity of Sudbury. In all 1800 tpd of sulfide concentrates are roasted and treated at the Falconbridge site. These concentrates are produced at the Falconbridge site and by the mines and a mill at Onaping about 25 miles north of Sudbury.

A complete description of the Falconbridge operations dealing with all aspects of environmental control that relate to water management, directly and indirectly, would make a very long and complex story but an interesting one.

Here, some of the more interesting highlights are reviewed:

1. Impact of changing the pyrometallurgical processing steps on water quality.

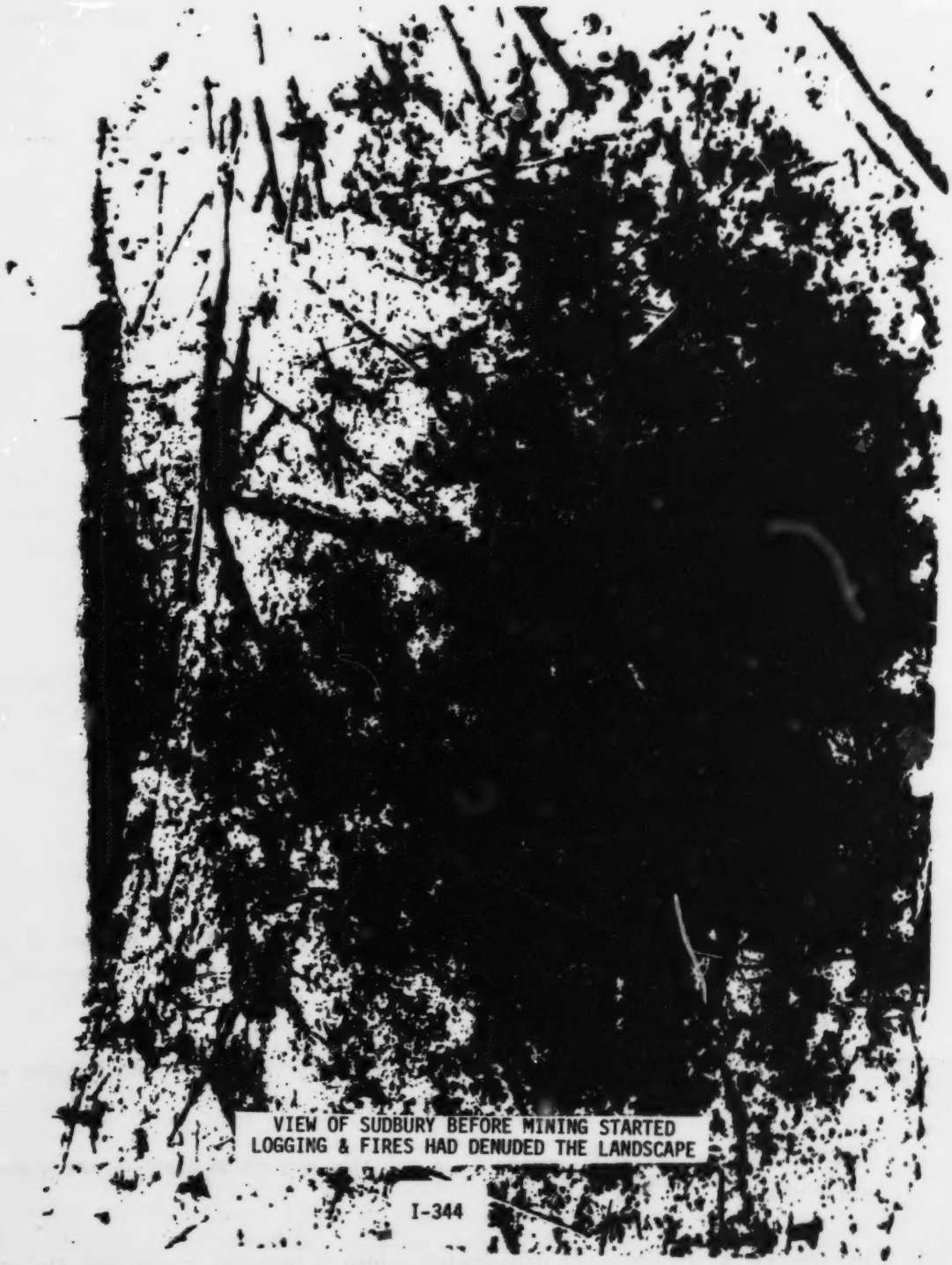
2. Designing and applying a systems approach which integrates management of water with the mines, mills and metallurgical recovery processes as well as wasterock, mill tailings, local municipal garbage, and sewage sludge disposal.

3. A most impressive use of a natural bog as a polishing step in treating recycled water and seepage from mill tailings.

4. Observations and recent improvements in housekeeping which avoid former impact on water quality.

5. Interception of contaminated groundwater which is pumped to the mill for use as process water.

6. Important observations as to where to apply lime neutralization in the water recycling loop.



VIEW OF SUDBURY BEFORE MINING STARTED
LOGGING & FIRES HAD DENUDED THE LANDSCAPE

PRODUCTION CAPACITY

Falconbridge mills 2000 tpd ore at Falconbridge and 7-8000 tpd at Onaping to produce 70,000,000 lbs nickel per year at current production.

LOCATION At Falconbridge, Ontario in the outskirts of Sudbury.

CLIMATE Mild summers with rainfall exceeding evaporation. Long frozen winters with heavy snowfall typical of the Canadian Shield.

ORE TYPE

The ore contains iron, nickel and copper primarily in the form of pyrrhotite, pentlandite, chalcopyrite. In addition to nickel and copper a number of other metals - cobalt, selenium, silver, platinum, palladium, rhodium, iridium and ruthenium are recovered from the ore. Common gangue minerals are feldspar, quartz, mica, talc and chlorite. The dominant sulfide mineral is pyrrohotite, Fe_7S_8 carrying 0.2-1.2% nickel. Falconbridge ore averages 25% pyrrhotite and 2-3% pyrite.

METALLURGICAL PROCESSES

Ore is crushed and ground to 60% minus 200 mesh and floated to recover a copper-nickel concentrate product by bulk flotation and a pyrrhotite concentrate that is discarded with the tailing slimes. The nickel-copper concentrate assays about 12% Ni + Cu and contains over 90% of the pentlandite and the chalcopyrite.

Flotation reagents used include sodium isopropyl and potassium amyl xanthates and a frother, either triethoxybutane or polypropylene glycol ether. Copper sulfate is used as an activator for the slow floating pyrrhotite; lime, soda ash and sulfuric acid are used for pH control. The Cu-Ni concentrates are roasted in a fluid bed roaster followed by smelting in electric furnaces. The melt is blown to remove iron and a copper-nickel matte produced for further electrolytic processing in Norway following a chloride leach.

TAILINGS TREATMENT

Tailings are deslimed using hydrocyclones and the coarse sand fraction pumped underground as backfill. Tfhe finer slimes are discarded to impoundment areas equipped with retaining dams and decant towers which overflow to the treatment plant. On average, 0.5 tons tailings is backfilled per ton of ore hoisted. The tailings sandfill plants incorporate both stirred and settled storage and also cement receiving and mixing facilities.

IMPACT OF CHANGING PYROMETALLURGICAL PROCESS

Earlier companies employed huge open roast yards (1888 to 1927) where the ore was roasted outdoors utilizing wood as fuel. Sulphur content in the ore was reduced from 25% to 7-10% with this method. Dense SO_2 clouds were given off at ground level for several months during each roast yard burn. Falconbridge Limited, incorporated in 1928, employed a tall stack at the outset. By the 1950s this process had been replaced by a sinter plant and a blast furnace. 80% of the sulfur was emitted to the atmosphere.

Since 1953 wet magnetic separation has been inserted into the flotation circuit to remove phrrhotite and further reduce sulphur emitted to the atmosphere. By 1960, only 50% of the sulphur was emitted to the atmosphere. In 1972, a $78 million nickel-iron refinery was built to further reduce SO_2 emissions by producing elemental sulphur. Technical problems and difficult financial times resulted in the closure of this plant. In 1978, a new smelter and acid plant were constructed for $85 million, again to improve the working environment and reduce emissions.

By 1982, improvements had been made to the acid plant and by installing fluid bed roasters and electric furnaces to replace the sinter plant and blast furnaces, only 16% of the contained sulfur was emitted. By 1984 further improvements had reduced the amount of sulfur emitted to 11% of that in the plant feed. From 1800 tpd of feed concentrate roasted, only 225 tpd of SO_2 is released.

The new smelter also reduced airborne nickel emissions by 94% and copper by 89%. Particulate emissions (7-8% Ni) were reduced from 17.0 tons/day to 1-2 tons/day.

Falconbridge Limited, coupled with Inco's environmental improvements over the years has resulted in improvements to the Sudbury area soil, lakes and vegetation.

50 Sudbury area lakes between 1974-6 and 1981-3 have had the following improvements:

89% of the lakes decreased in copper levels
75% of the lakes decreased in nickel levels
100% of the lakes decreased in sulfate levels.

Because of the historic lumbering, followed by processing of ores and concentrates, the soils in the Sudbury area had become acidic. Due to environmental improvements by both companies, the pH of soil in the area has started to increase. pH continues to be affected by snow and rain on the area with a low pH of around 4.3 and it is pointed out that SO_2 and NOx from the USA is a major contributor to the acid rain problem.

One way of reducing SO_2 stack emissions has been to separate the pyrrhotite and discard it to tailings where it potentially will generate acid. This appears as a trade-off with air pollution versus water pollution. Water pollution is, however, easier and less costly to control. Air pollution also leads to water pollution spread over a larger area.

Since cleaning the roaster gas there has been an improvement in water quality with respect to sulfate and nickel levels in the surrounding area lakes.

Improvements to the acid plant and resulting environmental improvements at Falconbridge are discussed in detail by NORMAN & MICHELUTTI which is inserted below.

Designing and Applying a Systems Approach

Removal of SO_2 and particulate materials from the gas emissions reduced the distribution of sulfates, Ni and copper to the general environment. This has had a significant impact on water quality and is just one part of an overall systems approach adopted at Falconbridge, some of which is described by NORMAN & MICHELUTTI. Some additional details are worth noting. The systems approach must cater to collecting and treating AMD from the tailings areas, inhibiting AMD and treating AMD to make it suitable for reuse and for discharge as an effluent.

EFFLUENT DISCHARGE

5480 Igpm or 37,000 m^3/d was discharged to Coniston Creek in 1979-80. Falconbridge's climate constraints make zero discharge an impossibility.

WATER TREATMENT

Average flow through the treatment plant in 1979-80 was 2511 Igpm (16,000 m^3/d). The aeration and lime addition plant is described by NORMAN & MICHELUTTI. Following precipitation the treated water is settled in a settling pond with 15 day retention, capacity of 286,000 m^3 and 0.63 km^2 area. A polyelectrolyte is added to accelerate the settling of precipitated solids. Capital cost of the water treatment plant was $257,000 in 1978.

Operating costs of the water treatment plant were C$104,600 in 1979 (1.8¢/$m^3$) and C$60,100 (1.0¢/m^3) in 1980 which works out to 4.6¢ per thousand gallons treated.

The reduction in costs in 1980 was due to reduction in lime consumption costs after lime addition was automated.

1970

How to establish vegetation on

By R. MICHELUTTI
Falconbridge Nickel Mines

The ore in the Sudbury Basin consists of a number of sulphide minerals composed predominantly of nickel, copper and iron with various other minor but valuable elements. To separate the valuable minerals from the gangue, the ore is crushed and ground to at least a fineness of 100% – 48 mesh. The copper-nickel sulphide minerals are separated from the gangue minerals by a combination of flotation and wet magnetic separation processes.

Three products result – a copper-nickel concentrate that is sent on for further processing, a pyrrhotite (iron-sulphide) concentrate that is either stockpiled or disposed of, and the tailings. Although consisting predominantly of silicate minerals, the tailings do contain minor amounts of sulphide minerals and a typical analysis will show about 0.85% sulphur. The pyrrhotite concentrate contains about 36.5% sulphur and 56.0% iron.

The relatively coarse tailings fraction, above 25 microns, amounting to about 70% of the total is separated by cycloning and returned to the mine for backfill. The fine tailings or tailings slimes, generally minus 25 microns in size, is discarded, either separately or mixed with the pyrrhotite, to tailings disposal sites.

A ton of average grade Sudbury ore produces 200 lbs of concentrate, 800 lbs of tailings backfill, 500 lbs of pyrrhotite and 500 lbs of tailings slimes. Thus, half of the ore mined consists of waste products that may be disposed of on surface. If possible, land-locked basins or lakes are selected as tailings disposal sites, but if such natural depressions are unavailable the tailings slimes must be contained behind artificial dams.

Falconbridge Nickel mines over 4 million tons of ore annually and therefore each year has to dispose of some 2 million tons of tailings slimes and pyrrhotite, which occupy a volume of over 35 million cubic feet.

Seepage

When a tailings disposal area reaches its designed capacity and is abandoned there are liable to be three major problem areas, acidic seepage or run off, dust and aesthetic appeal. A properly designed and maintained tailings disposal area will minimize the problem of acidic seepage and run off, however, it is unlikely that it can be completely eliminated.

The material constituting tailings is by its very nature a dust, and large areas denuded of vegetation may be picturesque in some locations on our planet but they cannot be considered as attractive features on the wooded landscapes of north-central Canada.

During the life of the tailings pond, water is continually seeping through it and becoming contaminated with iron and various metal sulphates. Because of the fine particulate nature of the tailings, the constituent minerals present a tremendous surface area, making them extremely susceptible to leaching and other chemical reactions.

Where sulphide minerals are present, sulphuric acid is generated, and depending on the amount of sulphides and the composition of the gangue minerals, the pH of the seepage effluent may be in the order of 3.0 or lower and if the volume is sufficient the downstream ecological environment may be seriously endangered.

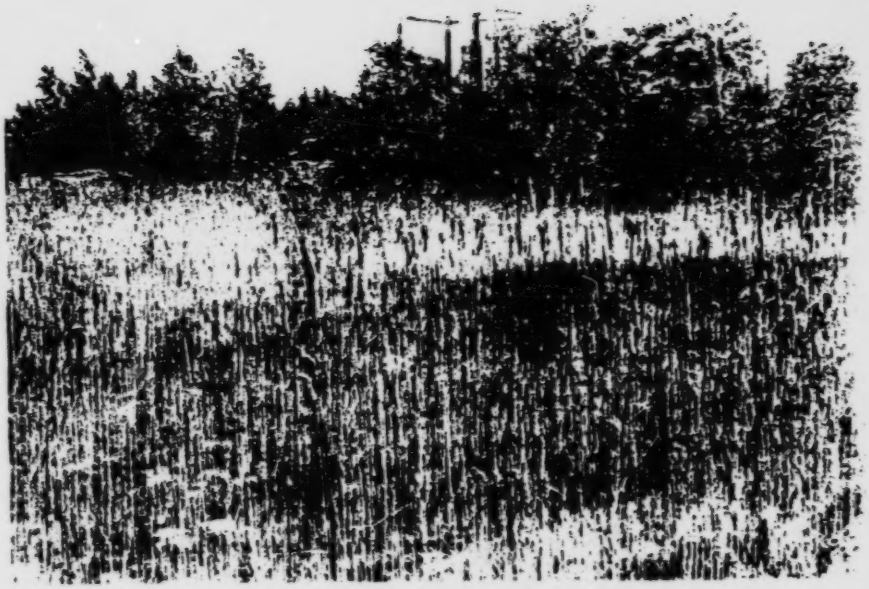
Dust storms

Once a tailings pond has dried up, the fine particles easily become windborne. This, coupled with the flat topography of tailings areas, results in severe dust storms, even at moderate wind velocities. Since the dust contains metallic salts and is easily dispersed throughout the adjoining area, widespread contamination of a watershed may result.

If residential areas or manufacturing industries are located nearby, the dust will present both a serious nuisance and increased problems and costs in the maintenance of machinery and equipment.

Although mining operations are usually located in remote areas, this is not

1971



1972

high iron-sulphur mine tailings

always the case, and even so, with our increasing awareness of the necessity to preserve wilderness areas for recreational purposes, the past practice of merely abandoning tailings areas without any attempt to restore them to their natural state is no longer acceptable.

Stabilization of tailings

Abandoned tailings areas must be stabilized to reduce or eliminate the problems previously mentioned. Various methods have been employed to reduce these problems, but most fail to eliminate all of the problems. Dust problems, for example, may be solved by placing an overburden of crushed slag, rocks or gravel on the tailings. This will not, however, reduce seepage or improve the appearance of the area.

Water cover

Another method is to completely cover the tailings area with water. Provided that dams are properly constructed to stop seepage this method will solve all three problems. The only disadvantage is that the area must always be maintained to ensure that dams won't fail and that the water cover remains. Once a mining complex becomes inoperative maintenance will normally cease and it is only under particular circumstances that this method could be acceptable.

Other methods, such as chemical stabilization with asphalt or polymers to produce a layer impervious to both air and water, also have the disadvantage of requiring maintenance. Furthermore, with this type of cover, the aesthetic quality of the area is hardly likely to be improved.

The obvious solution to the problem, if it can be achieved, is to restore the terrain to some reasonable semblance of its natural state by providing a cover of vegetation over the tailings. This method restores the aesthetic value and may even improve on the intrinsic value of the property.

Revegetation prevents the material from becoming windborne and will restrict, even though it may not entirely eliminate seepage. Also, with time, the endemic species will encroach to make the area self-sustaining.

The establishment of vegetation on tailings, unfortunately, is not a simple task, for the following reasons:

- Tailings are unsuitable as a soil for supporting plant life for a number of reasons. The material has a poor structure lacking in aggregates. Tailings are almost entirely deficient in nutrients and in an ion exchange capacity. Proper bacterial communities are absent, and toxic concentrations of heavy metals may be present.
- Because of the extremely fine particulate nature of the tailings, dewatering takes a long time and the area remains an inaccessible bog long after the surface has dried. Specialized machinery may therefore be needed to attempt the revegetation operation.
- Since the areas are large flat expanses composed of very fine particles, dust storms are common and for this reason it is essential that the entire tailings area be stabilized at one time. Otherwise established vegetation can easily be destroyed by sandblasting or burial by the unstabilized material. If it is not practical to vegetate an entire tailings area at one time it will be necessary to provide some form of temporary stabilization to the unvegetated portion.

Nickel Rim mine tailings

Nickel Rim Mines operated a mine and concentrator between 1952 and 1958 on a property located at the east end of the Sudbury Basin approximately 7 miles north of the town of Falconbridge. During these years, some 35 acres of land were covered with tailings.

In the Nickel Rim concentrator operation, no attempt was made to recover pyrrhotite which was discarded with the tailings. Neither was any tailings used for mine back fill at this operation so the material discarded consisted of approximately two-thirds silicate gangue minerals and one-third pyrrhotite.

Although the silicate gangue is inert the pyrrhotite is highly reactive (8)

times more so than pyrite), and under certain conditions spontaneous combustion will occur at room temperature.

$$3\ FeS + 5\ O_2 \rightarrow$$
$$Fe_3O_4 + 3\ SO_2 + 1.9 \times 10^3\ K.\ cal.\ lb^{-1}$$

Even when mixed with tailings the heat produced by the oxidation of the pyrrhotite, where any segregation has occurred, will be sufficient to prevent the growth of any vegetation.

The present surface of the Nickel Rim tailings, from 1 in. to 5 ft in thickness, is a reddish brown colored mass of hydrated iron oxides. Greater than average concentrations of iron and sulphur are present in this oxidized surface layer because of capillary action which brings dilute salt solutions from the interior of the tailings mass to the surface. Subsequent loss of moisture at the surface due to evaporation results in a build up of metallic salts. (Table 1)

The iron and sulphur accumulating at the surface produces a complex matrix known as a "ferruginous cap". This ferruginous cap may become as hard as concrete and virtually impossible to vegetate.

Another barrier to overcome in establishing vegetation on tailings which contain pyrrhotite is the production of sulphuric acid. Polythionates reacting with ferric sulphide result in the production of sulphuric acid which lowers the pH in the oxidized layer (Table 1) to values that are intolerable to any form of vegetation.

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \rightarrow 3\ FeSO_4 + 2\ S\ (7)$$

$$S + 3\ O + H_2O \rightarrow H_2SO_4$$

In 1964 Falconbridge purchased the Nickel Rim property to acquire the considerable amount of low grade ore that had not been mined. At the time pollution was not a serious concern but with changing conditions, Falconbridge subsequently became aware that it had not only purchased some low grade ore but also a pollution problem of considerable proportions.

Unique problem

Although the techniques for establishing vegetation on tailings piles of silicate minerals were well known, nothing had ever been done with the high sulphur content (pyrrhotite) tailings such as those at Nickel Rim. Falconbridge, therefore, found it necessary to embark on a research program with the objective of determining whether the establishment of a permanent cover of vegetation could be accomplished economically on this type of tailings.

This report is a summary of the research work performed by Falconbridge to date in its attempts to vegetate this troublesome area.

Research summary

Research on the vegetation of acid mine tailings commenced September 1970 by the Industrial Wastes Control Department at Falconbridge. Initial tests were conducted in a growth chamber to determine first of all whether plant life could be made to grow at all on oxidized high iron-sulphur and acidic mine tailings. The most economical neutralizing agent and fertilizer requirements had to be determined as well as the plant species that are best adapted to this environment.

Because of limited space in the growth chamber only one or two parameters could be investigated during each test.

TABLE 1 – ANALYSIS OF NICKEL RIM TAILINGS

	Upper Oxidized Layer	Lower Unoxidized Layer
Magnesium	4.25 %	6.4 %
Sodium	.16 %	1.64 %
Potassium	.41 %	.74 %
Calcium	4.44 %	5.53 %
Aluminum	2.3 %	3.2 %
Sulphur	6.23 %	2.31 %
Nickel	.05 %	.220 %
Copper	.031%	.063 %
Zinc	.003%	.0128%
Cobalt	.041%	.03 %
Iron	27.9 %	12.7 %
pH	3.0	4.5

Since any solution to the problem had to be economically viable, it was fundamental that in conducting the experiments the materials utilized would be locally available at a reasonable cost.

Neutralization

The initial series of experiments was set up by Fedko and Michelutti (1) to determine whether the acidity of the tailings could be neutralized by the application of agricultural limestone ($CaCO_3$) and/or lime (CaOH) and also whether a commercial grade fertilizer (10-10-10) would provide the nutrients required to sustain plant growth.

Slightly acidic alluvial sand from the Falconbridge area served as a control. Plant species for these tests were chosen from varieties suited to local climatic conditions and on proven ability to withstand acidity and drought, as well as their availability.

From these preliminary tests it was quite apparent that lime and/or limestone were essential for plant growth on acid tailings. The more agricultural limestone or lime applied to the tailings, the greater the plants' longevity, (Fig. 1).

In the initial experiment all plants died within 30 days but the length of survival was directly related to the amount of neutralizing agent provided. Since both lime and limestone produced similar results on plant vigor and longevity, the lime was discontinued because of its corrosive nature and its potential to produce a toxic alkaline soil by over liming.

No conclusions as to the suitability of the fertilizer utilized in the experiment could be drawn since all the plants died because of insufficient neutralizing agent. However, the control sand pots did indicate the best application rate for 10-10-10 fertilizer to be 1/2 ton per acre.

Optimizing limestone

Having determined that limestone was essential, a second set of experiments was designed and undertaken to determine just how much would be required to ensure plant survival. For these tests the fertilizer content was maintained constant at 1/2 ton per acre.

In January 1971, Hulley set out to determine the appropriate limestone requirements for Nickel Rim mine tailings. Besides limestone content, the advisability of using a straw-asphalt mulch cover was also tested. Although the duration of the test was restricted to a two month period, positive results were achieved as all plants survived during this period.

It was determined that for the Nickel Rim tailings an initial dosage of 10 tons of limestone per acre would be required. The test also showed that a straw mulch cover resulted in greater yields than no cover on both the sand control pots and the tailings pots, with all other conditions being equal. (Fig. 2)

Now that the appropriate limestone content had been determined and it had been shown that a mulch cover of straw-asphalt was beneficial, it was decided that the next step should be to perform experiments in the field to test the validity of the laboratory results.

In May 1971, Langford set up field tests using a randomized block design. Test plots were established on alluvial sand, inactive low iron-sulphide Falconbridge tailings (12% Fe, 1% S), and Nickel Rim mine tailings. The alluvial sand and Falconbridge tailings were to act as controls. Unfortunately the test plots on the Falconbridge tailings were mostly covered and destroyed by

blowing dust in a matter of only two weeks time.

So that there would be a basis of comparison with the lab tests the fertilizer (10-10-10) was still maintained at 1/2 ton/acre on all the plots. The agricultural limestone (not more than 40% + 100 mesh), was applied at 10 tons per acre on both tailings areas and at 4 tons per acre on the alluvial sand. These tests were, therefore, an attempt to duplicate in the field what was felt to be the proper fertilizer and limestone application, based on the laboratory tests.

Because of the success obtained in the growth chamber with a mulch cover, it was also decided to test various mulches in the field. The mulches tested were: straw-asphalt, curasol (a polymer dispersion material), and a 2 in. soil cover. At the same time, 16 different grass and legume species were tested, in a block design, under each mulch cover. Data accumulated between May and October was analysed by Langford (3) in March 1972, with the following conclusions.

- The plant species best suited to the acidic tailings were: fall rye, bromegrass, red top, colonial bentgrass, creeping red fescue, sheep fescue, sweet clover, alfalfa and white clover.
- The mulch covers all proved to be superior to no cover.
- The greatest differences in mulch covers appeared in the test plots on the Nickel Rim tailings where a 2 in. soil cover resulted in a healthy vegetation growth compared to the other plots on these tailings where the growth was stunted and had a high mortality rate. The exact reason why this plot was successful it still not known since the soil became very acidic with a pH of 3.5 in the space of a months time. Perhaps the soil contains a greater ion exchange capacity, beneficial microorganisms, or the micronutrients required by the plants which the fertilizer does not provide. Root studies the following year showed that the roots tended to fan out a great deal in the soil cover before eventually penetrating the tailings. Perhaps this soil cover helps to establish the young plants when they are most susceptible to adverse conditions and upon maturing their root systems are then able to invade the inhospitable high iron sulphur tailings.
- The physical grade of the limestone is very important in affecting a pH change since it must be solubilized to be effective. In one test plot that was treated with 50 tons/acre of a coarse limestone (80% + 10 mesh) compared to the finer grade (60% – 100 mesh) normally used, the seeds all failed to germinate. Even after a six month observation period, there was no growth on this particular test plot.

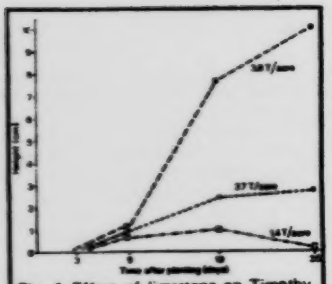


Fig. 1 Effect of limestone on Timothy in tailings

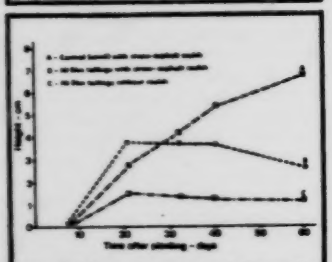


Fig. 2 Effect of straw asphalt mulch on legumes

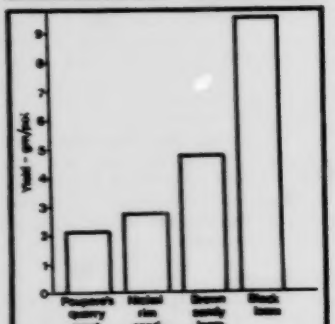


Fig. 3 Comparison of topsoils

The results of this initial field test work with the Nickel Rim tailings gave some hope that vegetation could not only be established but also maintained on this type of highly oxidized acidic tailings.

The next series of tests by Gaylor (4) set out to determine the best locally available soils for use as a cover and the optimum thickness of application. The soils were spread in 1 in., 2 in., 4 in. and 6 in. layers and not mixed at all with the underlying tailings. This was done in an attempt to reduce metallic salt concentration at the surface by applying soils having a lesser capillarity rate than the tailings.

Four locally available soils ranging from sand to loam were selected for testing in the growth chamber. 10 T/acre of limestone with 1/2 T/acre of fertilizer was applied on top of the soils. After two months, yields were determined and black loam at a 6 in. depth proved to be superior to the other soils. Even a 1 in. to 2 in. layer of black loam showed a definite improvement in plant growth over any of the other soils. (Fig. 3).

Tests conducted by Cyr (5) on soil properties had demonstrated that a loamy soil has a lower capillarity rate than sandy soils. This, coupled with the fact that black loam has a greater cation exchange capacity (8), could account for the increased yield.

A significant result was that the legumes did far better in these tests than any previous growth chamber tests, and appeared healthier than the grasses for the first time. A good legume catch is very significant in establishing vegetation over long periods of time because of their ability to fix atmospheric nitrogen in the soil.

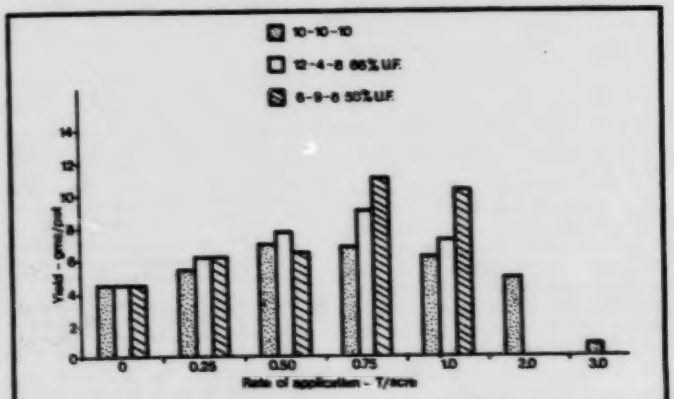


Fig. 4 Fertilizer application rates of three best fertilizers tested.

Fertilizer types

Up until this time, the fertilizer used

had been exclusively 10-10-10 N-P-K because it was readily available. Cyr (5), therefore, set out to determine whether there might be a better fertilizer to use for establishing vegetation.

Fig. 5

Five fertilizers were studied: CIL 10-10-10, CIL 6-9-6 50% U.F., CIL 12-4-8 66% U.F., CIL 15-5-10 40% U.F. and CIL 2-1-2 sheep manure.

The slow release fertilizer, 6-9-6 50% urea formaldehyde, performed the best at 3/4 T/acre (Fig. 4). The original 10-10-10 at 1/2 T/acre produced much lower yields during the 10-week duration of the experiment and over a longer period of time might have shown even greater differences. A significant observation, as shown in Fig. 4, is that an excess of fertilizer stunts plant growth and is more harmful than no fertilizer at all.

This situation has been termed physiological drought and exists when water is plentiful but a greater osmotic pressure results in the soil because of the high salt content compared to the plants roots. Water will then leave the plants to reduce the pressure gradient created and in this way the plants dehydrate. As previously mentioned, legumes are important as soil enrichment agents, and once properly established the fertilizer requirements may then be substantially reduced.

The field plots set up by Langford during May 1971, were examined by Johnston (6), Oct. 1972, for legume root nodules (Fig. 5). Preliminary observations showed that alfalfa has more nitrogen nodules than sweet clover and that legumes growing in the 2 in. soil cover have much better nodulation than legumes growing directly in the tailings.

The plants on the soil cover had most of their root structure fanning out in the soil with portions penetrating down into the tailings. Most of the nodulation in these plants occurred in the upper root zone growing in the soil cover. This is probably attributable to a proper bacterial ecology in the soil cover, especially the nitrogen producing bacteria, nitrosomonas and nitrobacter which oxidize ammonia to nitrate.

Even though good nodulation was observed in some plants, none had the characteristic healthy pink coloration. The pink coloration is hemoglobin produced symbiotically by the bacteria and legume. More tests are therefore necessary to determine if these nodules are adequate for soil enrichment or if healthier nodulation can be induced by innoculation with the appropriate bacteria. Tests are now under way to determine the effects of innoculation on legumes.

From all the data accumulated over the past two years, some basic conclusions can be made at this time on the vegetative stabilization of the acidic high iron-sulphur tailings at Nickel Rim.

Conclusions

- The tailings area should be first covered with a 4–6 in. layer of the best locally available soil. If this soil is low in organic content, it should be supplemented with sewage sludge, manure or loam. This should reduce the rate of salt build-up at the surface as well as increase the cation exchange capacity.
- High grade fine pulverized agricultural limestone (60%-100 mesh) at 10 T/acre should then be applied to the soil cover.
- 6-9-6 50% U.F. fertilizer should then be applied at a rate of 3/4 T/acre. The slow release factor of the fertilizer will help sustain the plants for the maximum possible period of time without maintenance. Instant release fertilizers can dissolve and wash away during periods of heavy rain fall and may therefore be largely wasted.
- The seed mixture to be used on these tailings is: fall rye, bromegrass, red top, colonial, bentgrass, creeping red fescue, sheep fescue, sweet clover, purple alfalfa, and white clover. For all the test plots rye was maintained at 60 lbs/acre and the other seeds were applied at a combined total of 90 lbs/acre.
- Finally, a mulch cover of straw is extremely beneficial in protecting the young seedlings. This will however, greatly increase the cost, and further work is necessary to determine whether the extra expense is justified.

The research performed to date has resulted in a far better understanding of the problem of establishing vegetation on highly acidic iron-sulphur tailings. The effectiveness of this method in establishing a permanent cover of vegetation that will require little or no continuing maintenance has still to be determined. Also to be determined is whether a cover of vegetation will reduce the seepage from the tailings areas sufficiently to prevent or reduce to acceptable proportions the contaminants that get into the adjacent surface drainage systems. Only by continuing lab and field test programs may it become possible to find answers to the particular questions and problems which arise when attempting to vegetate troublesome areas.

Acknowledgements

The author wishes to gratefully acknowledge the criticism and advice by W.L.W. Taylor, manager technical services, and J.H. Christiansen, industrial wastes engineer, both Falconbridge Nickel, Nickel Division-Sudbury operations, Falconbridge, Ontario.

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Nitrosomonas: $NH_4 + 1.5\ O_2 \rightarrow NO_2 + 2\ H^+ + H_2O + 75{,}000$ cal.

Nitrobacter: $NO_2 + 0.5\ O_2 \rightarrow NO_3 + 20{,}000$ cal.

WASTEWATER TREATMENT SYSTEM AT

FALCONBRIDGE ONTARIO

R.E. Michelutti
Environmental Department
Falconbridge Nickel Mines Limited
Canadian Nickel Division
Sudbury Operations
January 1981

Introduction

The new tailings area and wastewater treatment system at Falconbridge was put into operation during the latter part of 1978 at an approximate cost of 3 million dollars. This report summarizes the data and chemical results for this treatment system during the first two years of operation.

Summary

1. The tailings and polishing ponds required 13 weeks to fill to their respective operating levels, for a total of 368 x 10^6 Imperial gallons.

2. The settling pond downstream of the neutralization plant has a retention time of approximately 15 days at 2,900 I.G.P.H. inflow, with a volume of 63 x 10^6 Imperial gallons.

3. The average flow leaving the treatment plant during 1979-1980 was 2,511 I.G.P.H. The total average flow being discharged to Coniston Creek was 5,480 I.G.P.M. during this period.

4. Sulphate concentrations decrease with distance from the source.

5. pH values are 3.5 during summer months and 6.5 during winter in the tailings ponds. This is due to varying oxidation rates of sulpho-salts by chemical and or bacterial action.

6. Nickel concentration in the wastewater inflow dropped considerably from 1979 to 1980. (0.7 ppm to 0.1 ppm respectively).

7. Dissolved nickel concentrations increase downstream from the inflow as well as downstream from the treatment plant.

A possible explanation is the solution pickup of nickel from the bog area.

8. The suspended solids 2 year average leaving the settling pond was 5.8 ppm, indicating that a clarifier is not warranted. It will require approximately 65 years to accumulate 1" of sludge in the settling pond at the present rate of deposition. In fact, this rate will decrease with the mining out of Falconbridge Mine in approximately 8 years.

9. pH depression caused by organic acids in the bog area downstream of the treatment plant was corrected by discharging excess lime.

10. The treatment plant treated 3.6 x 10^6 I.G.P.D. at a cost of 4.6 cents per 1,000 gallons during 1980. On average, 0.84 tons of hydrated lime/day were consumed during 1980.

11. Treated alkaline wastewater has resulted in a rapid colonization of the denuded bog by aquatic plants and wildlife. As a result, the area has been designated a "Conservation Area".

1. Physical Data

1.1 Pond Elevations and Volumes

1.1 (a) Tailings Pond

Wastewater commenced flowing into the new tailings area on August 21, 1978 at approximately 1,500 I.G.P.M. (Figure 2) The water level behind dam #6 rose from 941.7' to 959.4' in nine weeks time. (Figure 1) Based on an inflow rate of 2,808 I.G.P.M. the tailings pond volume is 255 x 10^6 Imperial gallons.

Wastewater Treatment System at
Falconbridge Ontario
Page 2A

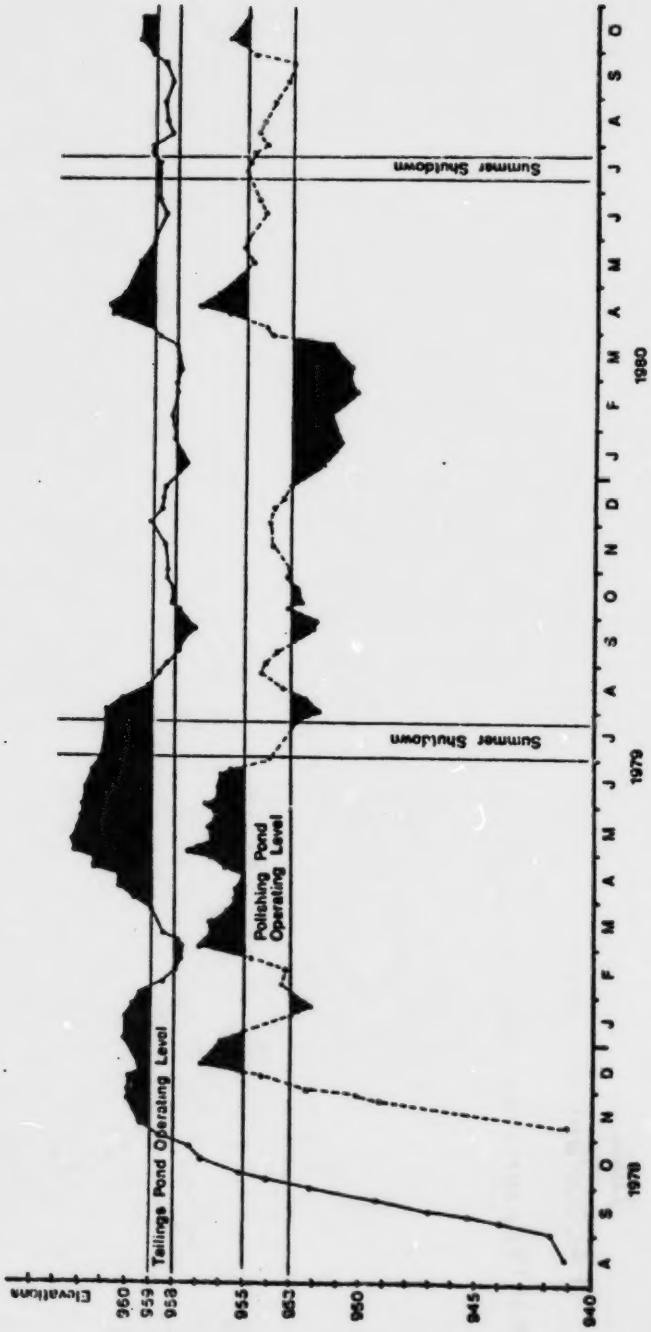


FIGURE 1 - POND ELEVATIONS

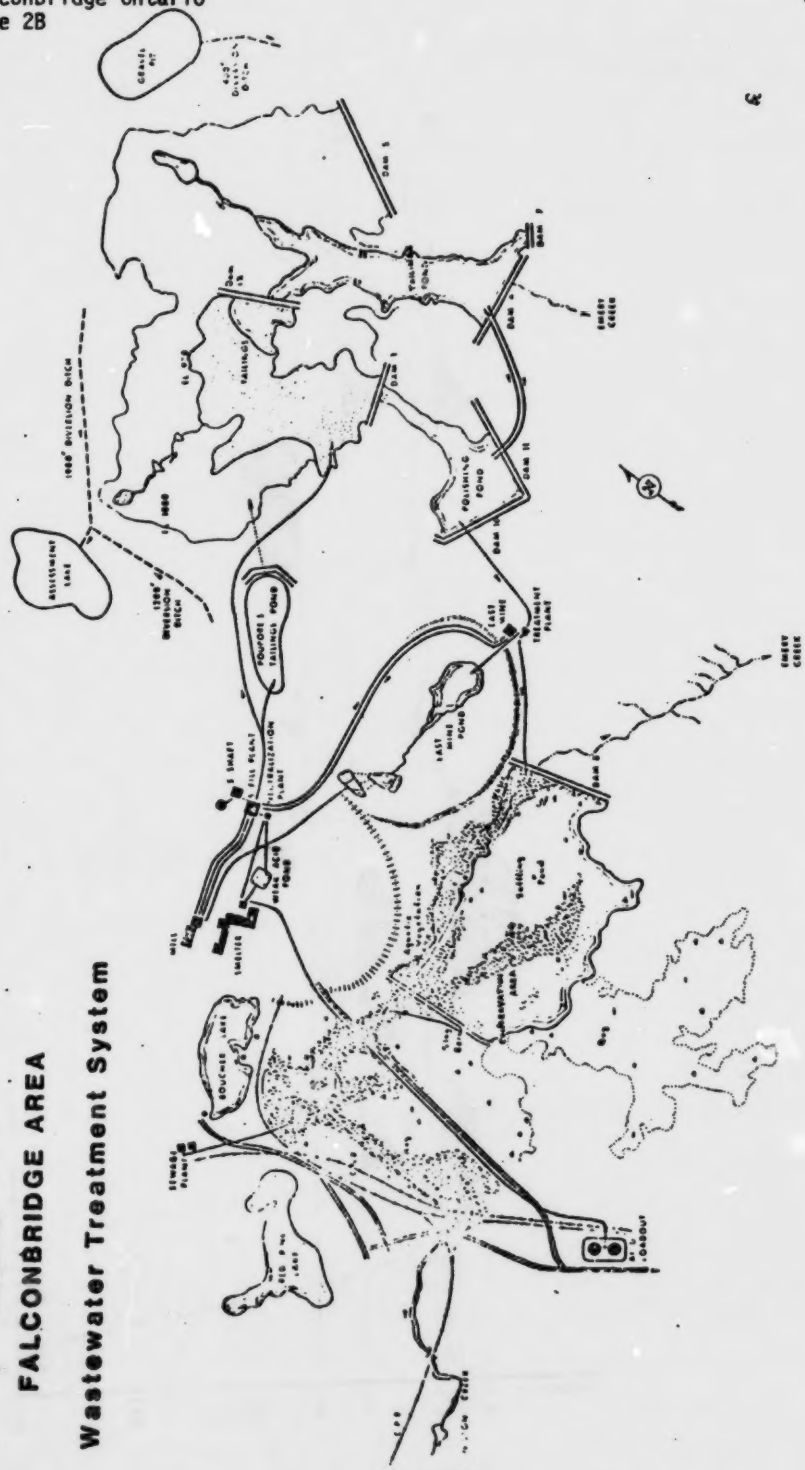


FIGURE 2
FALCONBRIDGE AREA
Wastewater Treatment System

Contributing to this inflow are the following estimated flows: (Reference 1)

(a) 1,566 I.G.P.M. - Tailings and Process Water

(b) 500 I.G.P.M. - Ground Water

(c) 742 I.G.P.M. - Precipitation

1.1 (b) Polishing Pond

The polishing pond water levels rose from 941.1' to 954.2' in four weeks time. At the above inflow rate of 2,808 I.G.P.M. this represents 113 x 10^6 Imperial gallons.

Water levels fluctuated considerably during 1979 and 1980 coinciding with rainfall and spring freshet. (Reference 1) During January, February and March of 1980 the water level in both ponds was intentionally lowered, in order to accommodate the spring flows. (Figure 1) Even though both ponds are designed to accommodate a Timmin's storm (7.61 inches in 12 hours) this procedure allows the containment of a Timmin's storm coupled with a spring snow melt. A snow melt is 1.1 inches in 5 hours. (Reference #6)

1.1 (c) Settling Pond

The settling pond area was increased during 1980 by extending the slag berm several hundred feet. This resulted in a pond area of 155 acres versus 115 during

1979, or a 35% increase in size. At an approximate depth of 1.5 feet this represents 63 x 10^6 Imperial Gallons. The retention time of the settling pond at 2,808 I.G.P.M. is therefore 16 days.

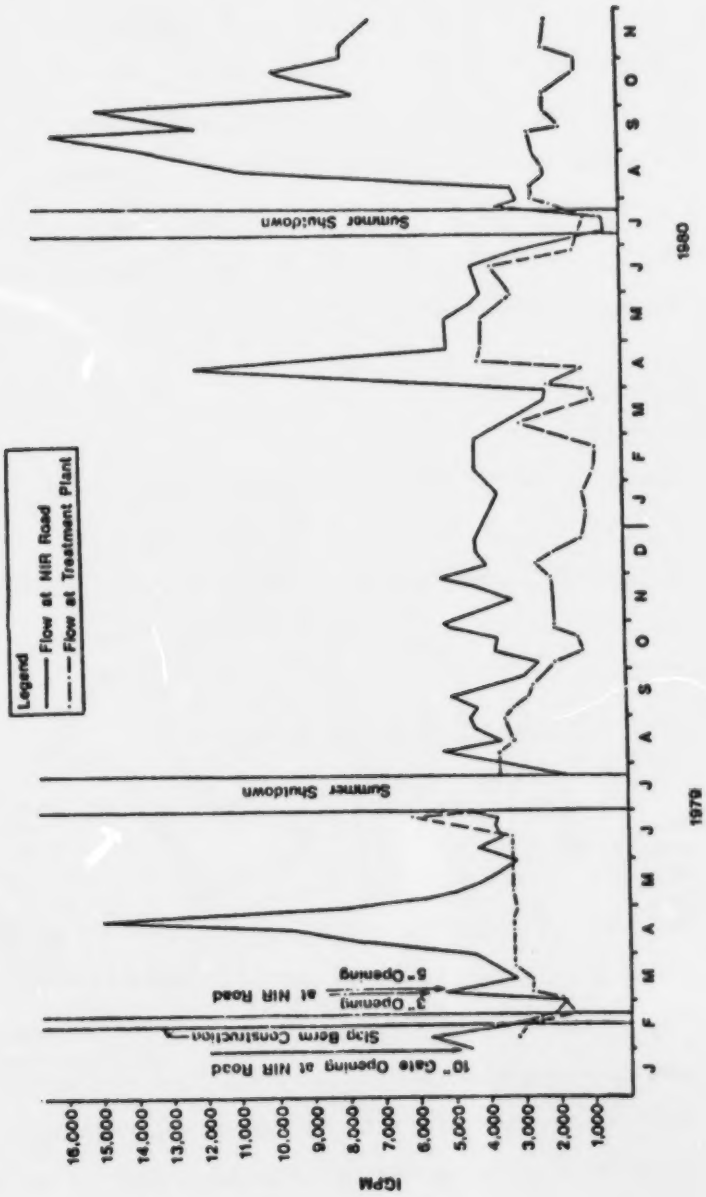
1.2 Flows

Flows leaving the treatment plant averaged 2,900 I.G.P.M. during 1979 which coincided quite well with the estimated flow of 2,808 I.G.P.M. During 1980, however, the flows averaged only 2,122 I.G.P.M. Flows are automatically recorded with an ultrasonic level measuring instrument and a rectangular weir plate. The 1980 recorded flows were on occasion lower than the actual flows due to some problems with the temperature compensator of the ultrasonic meter during winter months.

Total effluents leaving the Falconbridge property at the N.I.R. road average 4,403 I.G.P.M. during 1979 and 6,557 I.G.P.M. during 1980. (Figure 3) The higher flow rates during 1980 may be attributed to a 35% higher than normal rainfall which occurred mostly during the latter part of the year. The unusually high flows during August to October of 1980 was a result of the release of more water from the settling pond coupled with fall rains.

Flows are regulated at the NIR road area to minimize any flooding that may occur downstream. This is accomplished by

FIGURE 3 - FLOWS



use of two circular gate valves similar to the decant structures at the tailings ponds. Even with maximum flows of 15,000 I.G.P.M. during 1979 and 16,300 I.G.P.M. during 1980 there was no flooding downstream at Goodwill Drive. An independent report by S. A. Kirchhefer, consulting engineer and planner, indicated that Falconbridge's effluents at peak flows would contribute 2% of any flooding occurring at Goodwill Drive. (Reference #6)

2. Water Chemistry

2.1 Sulphates

Concentrations of sulpho-salts and sulphates entering the tailings area are erratic due to operational procedures and feed variability. (Figure 4) The tailings pond and polishing pond exhibit a considerable reduction in total sulphates, from the inflow. (Table 1)

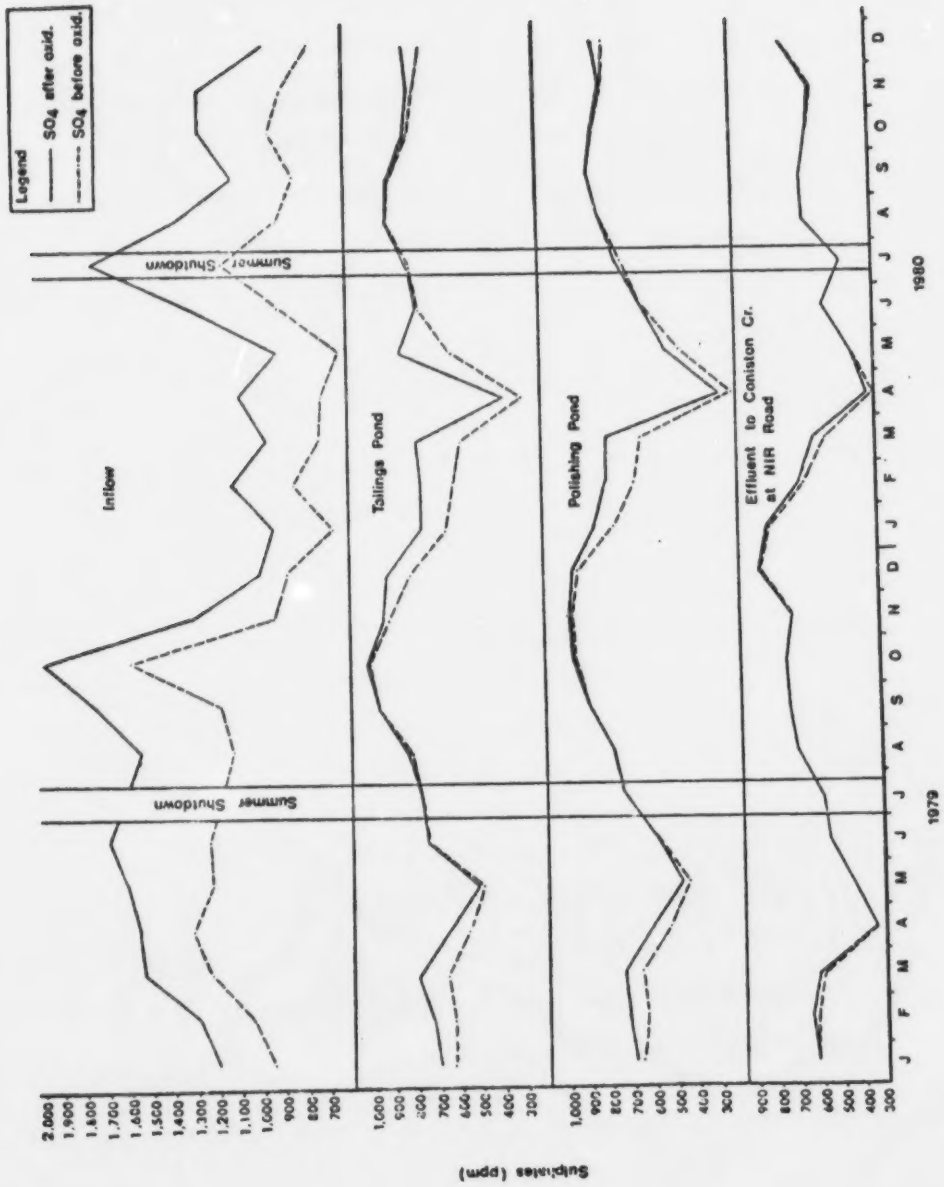
Table 1

Total Sulphates - 1979 - 1980 Average

	Tailings Inflow	Tailings Pond	Polishing Pond	Effluent to Coniston Creek
Total Sulphate	1,328	790	748	601

Sulphates also continue to decrease downstream of the treatment plant. (Table 1) This may be attributed to increased dilution coupled with some precipitation of the sulphates. The effect of dilution is particularly evident during the spring thaw, April to May. Sulpho-salts are measured indirectly by subtracting sulphates before oxidation from sulphates after oxidation. When all the sulpho-salts are oxidized to sulphate, then acidification ceases.

FIGURE 4 - SULPHATE BEFORE AND AFTER OXIDATION



From Figure 4 it may be observed that the sulpho-salts decrease with distance from the inflow. This decrease is a result of the sulpho-salts becoming oxidized to sulphates during the treatment retention time of 15 weeks. The final effluent has very few sulpho-salts remaining, and are evident mainly from January to April. Overliming at the treatment plant was practiced during this period, to prevent acidification downstream.

2.2 Nickel

Nickel concentrations in the tailings pond and polishing pond have dropped by approximately half during 1980 compared with 1979. (Table 2)

Table 2 - Dissolved Nickel (ppm)

	Inflow	Tailings Pond	Polishing Pond
1979	0.7	0.7	0.9
1980	0.1	0.3	0.5

This drop in nickel concentrations during 1980 is attributed to the very low dissolved nickel concentrations entering the tailings area. (Figure 5) Several factors are believed to have contributed to this drop. One factor is the increased nickel recoveries in the Falconbridge Mill (88.07% in 1980 versus 84.37% in 1979)

Another contributing factor to the drop in nickel concentrations during 1980 is the increased lime consumption in the mill and weak acid plant.

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FIGURE 5 - DISSOLVED NICKEL

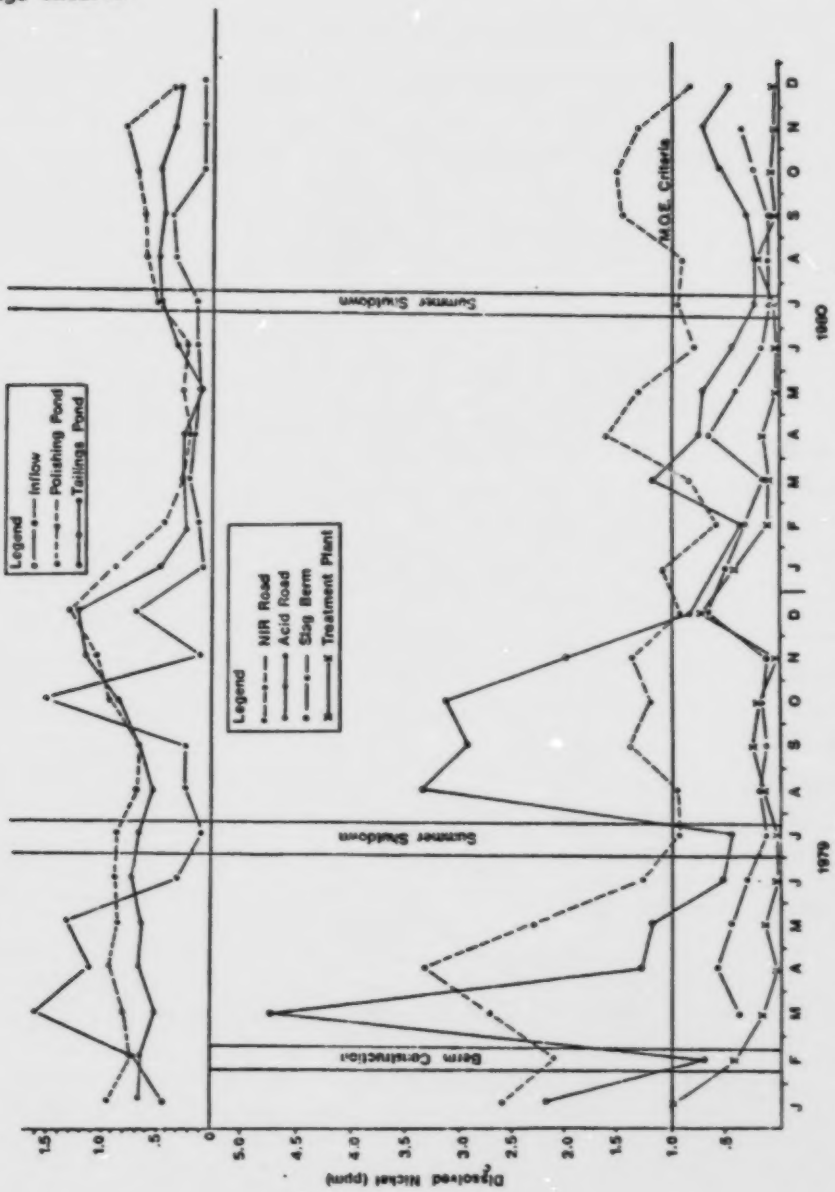


Table 3 shows that lime to the tailings area (A + B) increased by 12% in 1980 compared with 1979.

Table 3 - Lime Consumption (Tons) - charged out (not an absolute figure for the month)

	(A) Mill (Hydrated Lime) $Ca(OH)_2$		(B) Weak Acid Plant (Quick Lime) CaO		Wastewater Plant Hydrated Lime)		Total	
	1979	1980	1979	1980	*1979	1980	1979	1980
January	47	65	102	36	50	25	199	126
February	72	62	13	49	75	25	160	136
March	98	70	43	71	75	25	216	166
April	103	83	46	270	75	25	224	378
May	107	112	96	91	75	25	278	228
June	100	157	251	46	75	0	426	203
July	33	114	14	46	12	50	59	210
August	87	128	110	82	50	50	247	260
September	47	83	125	61	75	25	247	169
October	107	50	44	102	75	25	226	177
November	103	129	42	69	75	25	220	223
December	81	53	30	104	75	8	186	165
TOTAL	985	1106	916	1027	787	308	2688	2441

* Quantities used per month during 1979 are estimated.

Finally the drop in nickel concentrations may be attributed to operational changes coupled with dilution.

(a) Increased pyrrhotite was sent to the smelter in 1980 compared with 1979 (51.4% versus 47.7% pyrrhotite in copper-nickel concentrate). Less pyrrhotite is therefore available for leaching in the tailings pond.

(b) Pyrrhotite roasting was initiated in September 1978 and ceased November 4, 1979. The pyrrhotite calcine would be expected to be leached more readily than a sulphide.

All this occurred at a time when the tailings ponds were being lowered to accommodate the spring freshet. (Figure 1) The impact due to dilution would therefore be significantly increased.

The polishing pond continues to have higher nickel concentrations than the tailings pond. (Table 2) The reason for this is unknown, however, it is believed that particulates containing nickel are entering and depositing in the polishing pond. Since the polishing pond is slightly more acidic than the tailings pond (Figure 7) then dissolution of these particles would increase the dissolved nickel content.

The treatment plant has consistently produced an effluent <1.0 ppm nickel (0.2 average). However, as mentioned in the previous report (Reference #1) and depicted in Figure 5 it may be seen that dissolved nickel increases downstream in the bog area. During high flow periods such as spring and fall, nickel is being flushed out contributing to the higher concentrations. (Figure 5) Peaks of 1.6 ppm (Spring) and

1.5 ppm (Fall) were recorded during 1980 compared with a peak of 3.3 ppm nickel during the spring of 1979. As predicted, nickel concentrations are decreasing as more of the bog area becomes neutralized and covered with vegetation.

2.3 Suspended Solids

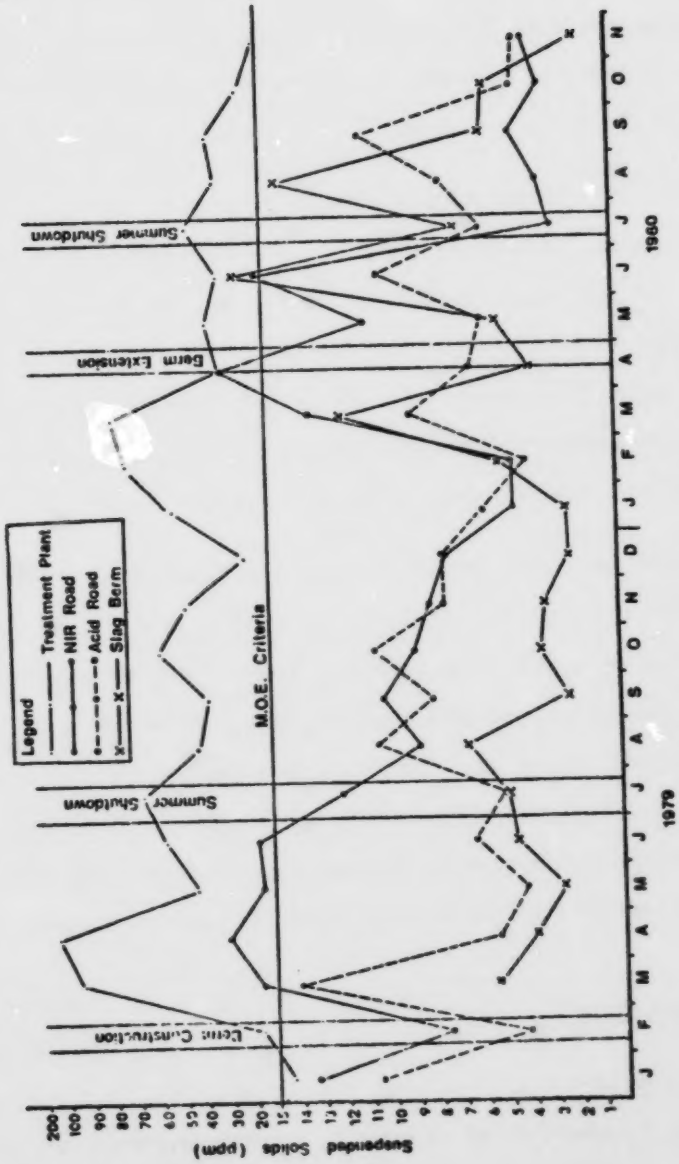
Suspended solids leaving the treatment plant ranged from 74 ppm to 17 ppm during 1980. (Figure 6) These solids settle out in the 155 acre settling pond area such that the effluent leaving this pond meets the Ministry of the Environment guideline of 15 ppm. (5.8 ppm - 2 year average)

With an average of 44.5 ppm suspended solids entering and 5.8 ppm leaving the pond, then 38.7 ppm remain in the pond. Based on an estimated specific gravity of 64 lbs./cu. ft. for the solids and an inflow rate of 2,900 I.G.P.M., then 0.2 acre ft. of sludge per year settles in the pond. At this rate it would require 64.5 years to accummulate one inch of sludge.

Except for high flow periods (Spring freshet in 1979 and 1980) the suspended solids have met Ministry of the Environment guidelines at the N.I.R. road. The average for 1980 was 8.9 ppm.

Some suspended solids were picked up between the slag berm and the N.I.R. road. This is due to construction upstream (slag berm) and/or organics being washed out of the bog area.

FIGURE 6 - SUSPENDED SOLIDS



2.4 pH

The pH's entering the tailings area fluctuated considerably with a range of 6.8 to 12.5. A good correlation is observed with lime used in the mill and weak acid neutralization plant versus pH. (Figure 8)

In the tailings and polishing ponds the pH's exhibit a seasonal fluctuation. During May the pH's begin to drop due to increased chemical and assumed microbial activity until a stable pH of 3.5 is attained in June. (Figure 7) The pH stabilizes at 3.5 during the warm months since most of the sulpho-salts are oxidized to sulphates. As temperatures decrease fewer sulpho-salts become oxidized and higher pH's are recorded. (Figures 7 and 4)

The treatment plant effluent continued to have higher pH's than required to precipitate heavy metals. While pH's of 7 to 8 were required, pH's of 9 to 10 were discharged. This was done intentionally to neutralized organic acids in the boy area downstream. At the acid road, pH's were near neutral, except during January - February of 1980. This drop was most likely due to problems with incorrect flow measurements at the treatment plant since lower pH's were observed leaving the plant. (Figure 7)

3. Treatment Plant

3.1 Operation

The treatment plant operates on a continuous basis and is fully automated. On average the plant treats 3.6 x 10^6 I.G.P.D.

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FIGURE 7 - pH

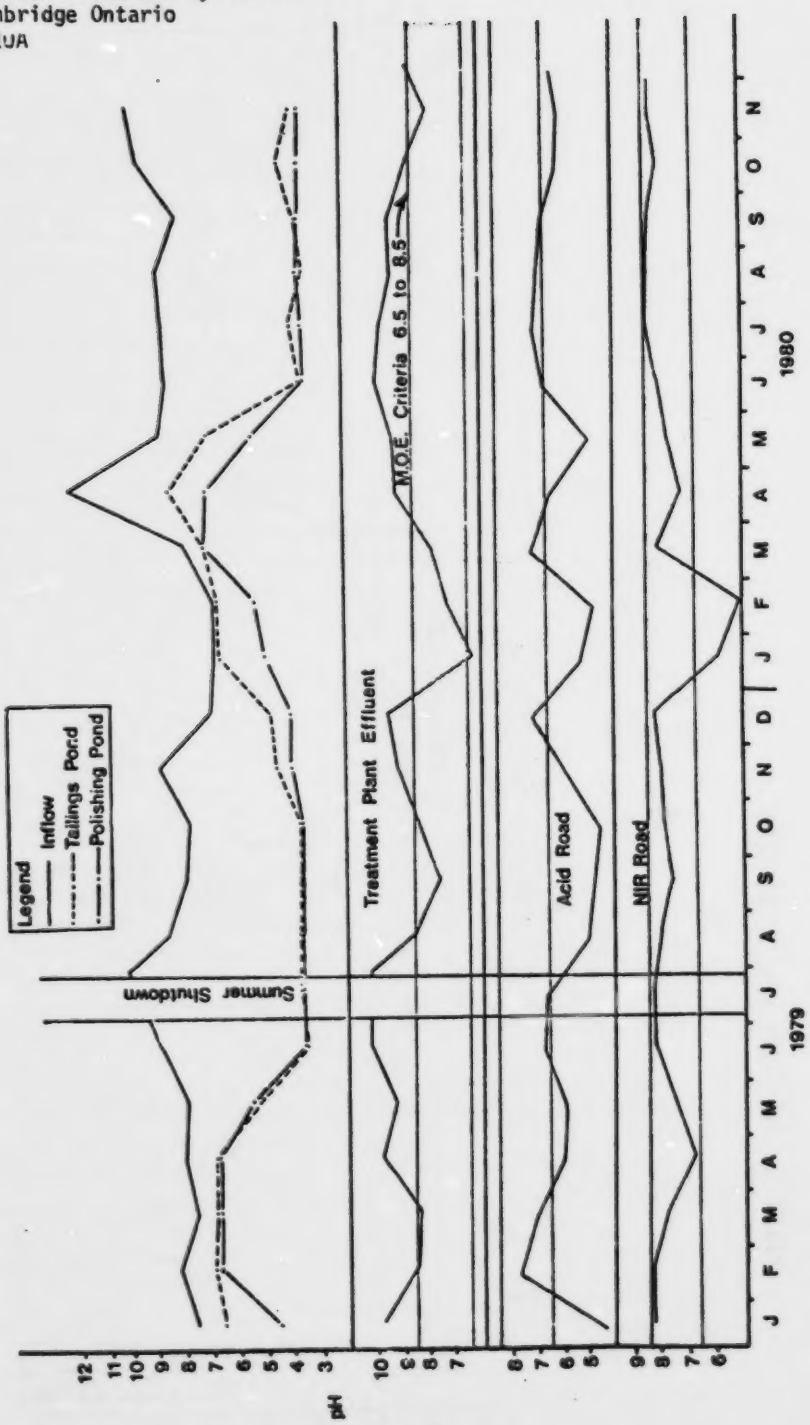
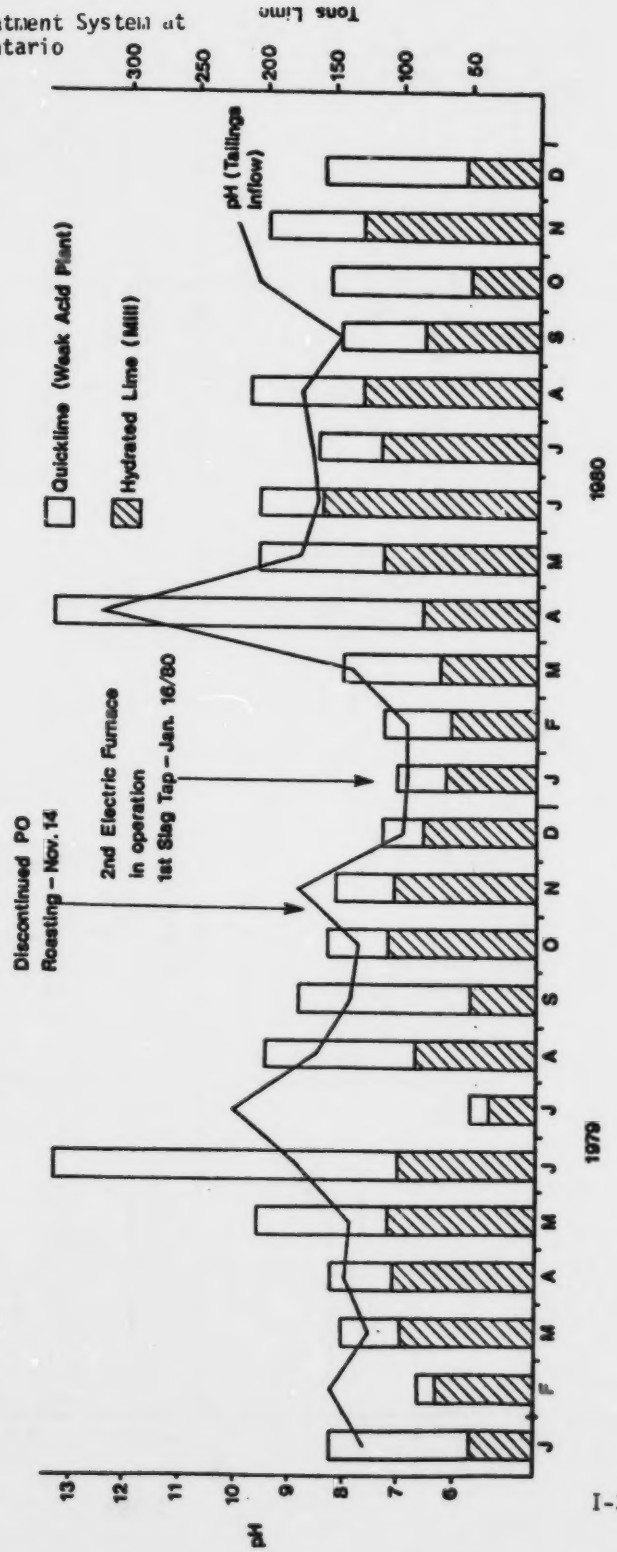


FIGURE 8 - pH VERSUS LIME CONSUMPTION



of wastewater. Effluents have been acceptable from day one with relatively few start-up problems. Wastewater enters the plant via a 28" diameter polyethylene pipe which then reduces to a 17" diameter stainless steel line equipped with a Dezurik flow control butterfly valve. A 10% to 15% lime slurry is injected into this line which then discharges into a concrete mixing basin outside. (Flow Diagram - Figure #9) Mixing is performed by an air bubble system receiving 6 P.S.I. air from a 10 H.P. Gardner-Denver compressor in the plant. Lime is injected by a solenoid valve regulated by an automatic pH controller. The pH controller receives a signal from an ultrasonic flow recorder and pH probe to determine quantities of lime required. The temperature compensator for the ultrasonic flow meter has on occasion not worked properly during very cold weather, resulting in lower flow readings. The 1980 flow data is therefore suspected of being lower than normal during January - February.

An air dryer is located in the plant to ensure that the air activited instruments receive dry air to prevent corrosion. Since the plant has been fully automated an alarm system monitoring several critical areas has been installed. The alarm signals are located at #5 Fill Plant which is a 24 hour/day manned operation.

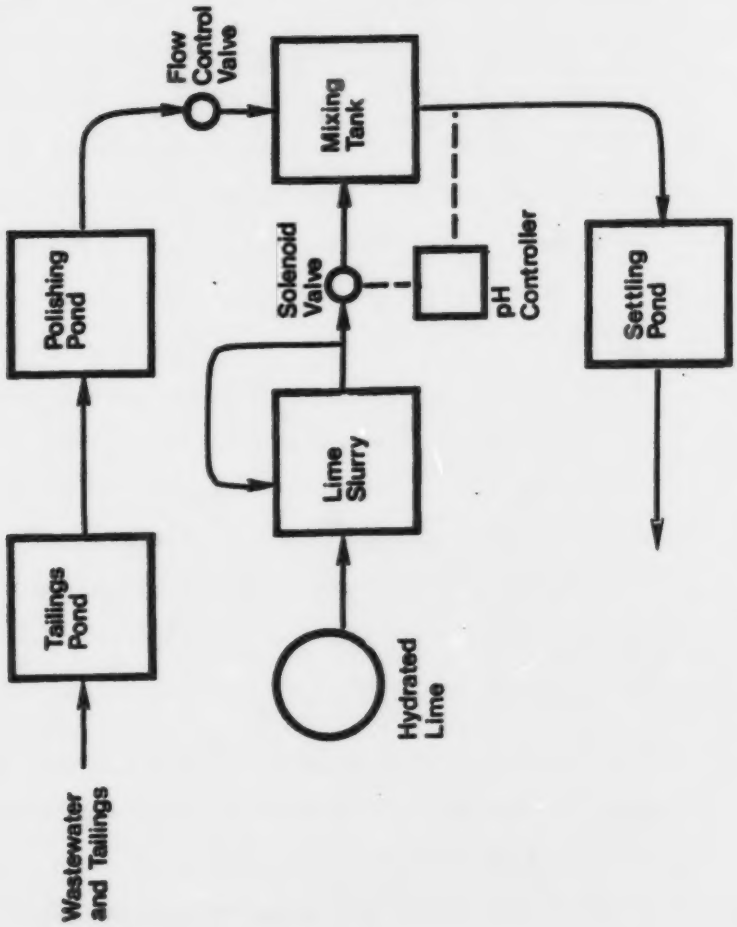


FIGURE 9 - TREATMENT SCHEMATIC

Table 4 - East Mine Treatment Plant - Cost Analysis

(to nearest $100.00 Canadian)

	1979	1980
Labour	$ 3,900	$ 200
Supervision	$ 11,700	$ 11,500
Lime	$ 48,100	$ 23,700
Polyelectrolyte	$ 2,200	0
Building Repairs	$ 1,000	$ 800
Equipment Repairs	$ 12,000	$ 6,800
Instrumentation Repairs	$ 23,900	$ 17,100
Supplies	$ 1,800	0
TOTAL	$104,600	$ 60,100

At a flow rate of 3.6 M.G.P.D. the 1980 costs were 4.6¢ per 1,000 gallons treated.

4. Conservation Area

The settling pond and downstream bog area became colonized with numerous aquatic plants due to the inundation of this area by alkaline water. (Reference #1) This resulted in a rapid colonization of the area by hundreds of water fowl (mostly mallards and blacks) as well as shore birds (plovers and killdeer) and songbirds (red winged blackbirds). Presence of small mammals such as muskrats, field mice, chipmunks and beaver was also

evident. Small suckers and minnows were also sighted and future surveys will indicate quantities present. In order to support the fish and bird life in this area insects must be fairly abundant. A planned benthic survey will indicate type and quantities present.

Wahnapitae River water was pumped into Red Pine Lake at a rate of 500-1000 G.P.M. in order to recharge the Falconbridge deep wells. This resulted in a dramatic improvement in Red Pine water quality such that the lake has been stocked by the Ministry of Natural Resources with speckled trout. A picnic and beach area has been added to the landscape, such that local residents now use the lake for fishing, boating and swimming.

Acknowledgement

Advice and constructive criticism by J.K. Weglo - Director Environmental Control is gratefully acknowledged.

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East Mine Treatment Plant Costs

	1979	1980
Labor	$ 3,900	$ 200
Supervision	11,700	11,500
Lime	48,100	23,700
Polyelectrolyte	2,200	0
Building Repairs	1,000	800
Equipment Repairs	12,000	6,800
Industrial Repairs	23,900	17,100
Supplies	1,800	0
Total	$104,600	$ 60,100

Swamp Polishing Pond

Several hundred acres (over one square kilometer) of barren land downstream from the lime treatment plant have been restored as a result of the reduced stack emissions and through deliberate efforts of the environmental control staff.

Prior to receiving treated effluent, the pH of the denuded bog area soils were around 3.5 and the area was barren of plants, toxic and very dry.

The area was dammed off and by raising and lowering the water level for a period of 4 months, the toxic metals were rendered insoluble and therefore non-toxic as the pH was raised. Alternate raising and lowering of the water allowed more area to become inundated, treated and recolonized. The area now constitutes a very large bog covered with cattails with a wide variety of aquatic plants and algae interspersed. The bog acts as an excellent polishing area because of the high surface area of the plants which physically filter suspended solids from the water. In this way, the metal hydroxides are efficiently removed from the water treatment plant effluent.

The Biology Dept. of Laurentian University is supporting a M.Sc. thesis on the Falconbridge swamp to study the species distribution and their effect on water quality.

In some bog areas it has been observed that as the biomass dies and sinks to the bottom of the bog an anaerobic reaction takes place whereby sulfate is converted to hydrogen sulfide in minute amounts which can exert an additional polishing effect by removing metals from solution as sulfides. It would be interesting to learn whether this mechanism plays a role in Ontario bogs as expected.

The pH at the head of the bog is 9 and drops to pH 7 at the road downstream due to watershed inflow and other streams.

Dissolved nickel concentration has been found to increase downstream from the treatment plant. This has been construed as possibly due to flushing of dissolved nickel from the original contamination in the bog area soils.

Inspection of the area downstream from the settling pond in the bog revealed a considerable seepage flow from the base of the tailings and slag area into the bog. This is likely to add dissolved metals to the bog although as the seepage was coming into contact with the settling pond overflow at a high pH, a considerable degree of precipitation could be observed.

pH depression has also been construed to be possibly due to organic acids from the swamp. This is corrected for by adding excess lime to the effluent. The effluent meets M. O. E. criteria and ultimately discharges in the Wanapitei River via Coniston Creek.

Nickel is metabolized to some extent by cattails (Typha Lahfolia) in the swamp and reputedly can reach 3-4% Ni in the biomass, depending on the pH and dissolved nickel content of the surrounding water.

TAILINGS AND WASTEROCK DISPOSAL

The systems approach also has taken into account the disposal of tailings and wasterock. Sulfide rich tailings and pyrrhotite bearing tailings and wasterock will also generate acid and dissolved metals properly disposed of.

HIGH IRON-SULFIDE TAILINGS DISPOSAL

Falconbridge segregates high sulfide and low sulfide tailings and wasterock. MICHELUTTI (1978) described experiments to establish vegetation on high iron-sulfur mine tailings by appropriate use of overburden.

He concluded that the ideal overburden for high iron-sulfur tailings is a 3" layer of coarse (¼") crushed material overlain by a 3" layer of loam. The coarse material acts as a capillary barrier and prevents upward leaching of solubilized metal salts. The loam provides the growth media.

Several additional observations were made:

1. Low sulfide tailings should be pumped over the pyrrhotite stockpiles during final stages of the tailings pond to eliminate the need for overburden emplacement.

2. The use of domestic garbage, low sulfide mine wastes etc. should be investigated as overburden for the high sulfide tailings pond.

3. It was pointed out that planning between operating departments would save dollars; e.g., disposal of the open pit mine overburden materials onto tailings areas saves considerable future reclamation costs.

4. There is a need to periodically monitor vegetation to determine the effectiveness of the overburden material in achieving a maintenance free vegetation cover.

These observations were made in 1978. Since then Falconbridge has implemented all of these items and concludes that:

1) High iron-sulfide tailings and heavy metals containing materials can be segregated into a separate area of the tailings impoundment. By using coarse wasterock and domestic garbage as an overburden, such tailings can be successfully revegetated.

2) Revegetation requires a capillary barrier of some sort to prevent upward migration of acid and metals. This results in excellent vegetative growth and virtually no maintenance needs. Native species eventually encroach and restore the area to a natural environment.

Although it is now well established that covering high sulfide tailings with coarse wasterock and domestic garbage provides a way to revegetate the surface of such tailings ponds, it is still not demonstrated that acid mine drainage from such tailings will be prevented or inhibited.

M. Collins in 1975 investigated methods for inhibiting the dissolution of pyrrhotite in tailings and storage piles at Falconbridge. He concluded that pyrrhotite concentrates oxidize less readily than pyrite concentrates when stored under water. However, oxidation rates of moist pyrrhotite concentrates are increased by a factor of 10 over dry concentrates.

The Canadian Mining Association has proposed to commission a major study on all aspects of inhibiting acid mine drainage generation from high sulfide tailings such as the pyrrhotite concentrates that must be disposed of at Falconbridge and elsewhere.

Aspects of High Sulfide Tailings Disposal Regarding:

Site Hydrology

Continuity and direction of flow
Seasonal variations - flooding downstream
Flushing effects
Soil composition - effect on leachates-porosity
Groundwater slope and direction
Maximum storage capacity
Diversion of clean water

Deposition of Tailings - Method

Expected slope deposition of the material
pH of material
Acid generation - Mechanism and chemistry
Ponding
Under water deposition
Mixtures and layering
Bacterial activity
Wind Action : on water and solids
Freeze drying effects
Effect of compost and revegetation

Miscellaneous

Need for impermeable barriers
Lake or pond bottom binders
Natural regeneration of ecosystems
Surface binders
Effect of metal uptake on vegetation
Bio magnification effects

It has been found that a mixture of pyrrhotite and tailings oxidizes less rapidly than when the pyrrhotite is separated. One concept is to place the bulk of the tailings with pyrrhotite mixed and to segregate a sulfide-free slimes at the final stage to cover the tailings site, then disposing of the separated pyrrhotite under water.

SEWAGE DISPOSAL

Raw sewage from holding tanks and septic tanks are mixed directly with tailings.

SMELTER DUST DISPOSAL

Valuable matte dusts, concentrates and particles lost from the process collect in floor and yard drains which discharge into a settling pond adjacent to the smelter building. It has recently been established that the 2-3000 ton accumulation of material with 4-5% Ni has been contributing nickel via seepage to the marsh polishing pond and groundwater, but also represents metal values worth around $1.5 million. The material will be reclaimed and smelted with ore. In this way improved housekeeping will improve overall recovery of metals and avoid a former source of water contamination.

THIOSULFATE GENERATION

Ore is milled at pH 9 which is controlled by lime addition. At this high pH thiosulfates are generated. pH is adjusted during the various flotation steps and tailings leave the mill at pH 7.2. At the decant end of the tailings pond, thiosulfate oxidation has dropped the solution pH. How far the pH has dropped depends on the time of the year and the amount of thiosulfate present and the degree of oxidation. In summer, a decant solution pH of 3.0 to 4.0 is typical. In winter it is closer to pH 6.5. Thiosalts are oxidized in a large aging pond prior to lime treatment.

Weak acid from the acid plant was neutralized with lime prior to discharging to the tailings area. It has been found that lime addition was not necessary since the weak acid became neutralized once mixed with the alkaline tailings - Po, at the fill plant, prior to disposal. Operating costs were, therefore, significantly reduced.

A general layout of the mine-mill-tailings dams showing the water treatment plant, the settling pond and the marsh polishing pond is included in NORMAN & MICHELUTTI's paper.

RED PINE LAKE

Falconbridge's potable water deep wells located near Boucher Lake and Red Pine Lake had become contaminated due to years of fallout and proximity to Po disposal areas. Although acceptable in water quality, a deteriorating trend over the years was evident. This situation was resolved by taking the following actions:

(a) The deep well closest to the plants area was taken off the potable supply system and pumped to the mill for process water. This intercepted and contained most of the contaminated groundwater.

(b) 500 gpm of clean Wanapitei River water was pumped into Red Pine Lake to act as a recharge area for the other wells. Also, this clean recharge water forced the contaminated ground water away from the main potable well.

Red Pine Lake, a previously dead, contaminated lake, became exceptionally clean after recharging. This allowed speckled trout to be stocked in the lake, such that the area has become a recreational fishing, swimming area for the local residents.

DRAINAGE DIVERSION SYSTEM

A major diversion ditch system has been constructed and berms constructed where necessary to prevent precipitation from draining into the mine-mill-smelter-tailings concept.

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NORMAN, G.E. and MICHELUTTI R.E. ( ) Environmental Improvements at Falconbridge Limited. CIM Bultetin. Date not identified Vol. 7, No. 866, pp. 93-98.

PROJECT DEVELOPMENT AND OPERATION

Environmental improvements at Falconbridge Limited

G.E. NORMAN and R.E. MICHELUTTI
Falconbridge Limited
Sudbury, Ontario

Introduction

One of the major objectives of Falconbridge has been and continues to be, to minimize the impact of its operations on the environment around its Sudbury operations.

The approach to achieving this objective and the results, are discussed under the following topics.

1. Sulphur Dioxide Emission Improvements.
2. Effluent Treatment Improvements.
3. Effect of the Envrionmental Improvements.

Sulphur Dioxide Emission Improvements

History

The rejection of pyrrhotite in the concentrators is one method of reducing the amount of sulphur to the smelter and therefore the sulphur dioxide emissions. In the 1950s and 1960s, Falconbridge developed the capability to remove 54% of this pyrrhotite. Numerous attempts were made to increase this amount by treating the pyrrhotite for recovery of nickel and in some cases elemental sulphur. Processes tested and operated were: hydrometallurgical pilot plant, roast-leach commercial operation and nickel-iron refinery. None of these processes proved to be commerically successful for both technical and economic reasons.

Falconbridge therefore redirected its efforts to reducing sulphur emissions by improving its smelting process under The Smelter Environmental Improvement Project. A major component of this project was the installation of a sulphuric acid plant to recover the SO_2 in the roaster off-gases.

G.E. Norman

G.E. Norman graduated in 1950 from the University of Toronto in metallurgical engineering. He has worked for Algoma Ore Properties and Noranda Mines Ltd. becoming superintendent of the latter's acid plant at Cutler. After 4 years in the die-casting industry he joined Falconbridge Limited in 1968.

He was closely involved in the design, start-up and initial operation of their present smelting process and associated acid plant. Currently he is chief metallurgical engineer - projects at Falconbridge.

R.E. Michelutti

Bob Michelutti is an environmental biologist with Falconbridge Limited, Falconbridge, Ontario. He has been in the environmental control department for the past 14 years and is primarily responsible for water quality, land reclamation and disposal of hazardous wastes. Prior to joining Falconbridge, he has worked briefly with the Ontario Water Resources Commission - Great Lakes Branch. He holds a Bachelor of Arts degree in general sciences from Queen's University, majoring in biology.

Keywords: Environmental Control, Sulphur dioxide emissions, Effluent treatment, Smelting process, Sulphuric acid plant.

Acid Plant

Process and Equipment Description

The specifications for the sulphuric acid plant called for a higher order of reliability than in a standard acid plant in order to minimize its effect on smelter operations. The process and equipment for this acid plant are described in the following sections (Fig. 1).

Gas Cleaning and Cooling
Conversion of SO_2 and SO_3
Acid Production
Acid Storage and Loadout

Gas Cleaning and Cooling

A special effort was made to provide a clean gas to the converter to maximize time between cleaning and replacement of the catalyst.

The gas scrubber-cooler was designed for 98% efficiency and an outlet dust loading of 0.95 gr/Nm³. The bottom tray of this scrubber consists of Venturi tubes while the top three trays contain perforated plates. The gases from this vessel are at 40°C.

Weak acid circulating through the scrubber-cooler is cooled in both impervious graphite shell and tube exchangers and a plate type heat exchanger. These are compared in a later section. A continuous bleed-off of weak acid is neutralized in pachuca tanks using lime, slaked on site. The gypsum slurry produced is pumped to the mill tailings pond.

Six electrostatic mist precipitators are provided, 4 primary units in parallel, followed by 2 secondary units. These precipitators are built from chemical lead and designed for 11 kPa. To prevent the tubes from collapsing, polyurethane foam was blown between the tubes on the primary units while the secondary precipitators were provided with a pressure equalizing chamber around the tube section. This chamber is vented to the outlet duct from the precipitator.

OPERATION	FALCONBRIDGE ONAPING OPERATIONS FALCONBRIDGE LTD. ONAPING, ONTARIO CANADA P0M 2R0	
TELEPHONE	(705) 966-3411	
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INTRODUCTION

Falconbridge Limited operates several mines and a mill at Onaping, Ontario, 30 miles (48) km) N. W. of Sudbury. Copper, nickel concentrates are shipped by rail from the Onaping mining and milling complex to Falconbridge Limited's smelter at Falconbridge, Ontario, 12 miles N. E. of Sudbury.

The Onaping Complex consists of:

Mines:	Strathcona	
	Fraser	
	Onaping	
	Craig	(under development)
	Fecunis	(shut down)
	Longvack	(shut down)
	Hardy	(shut down
Mills:	Strathcona	
	Fecunis	(shut down)
	Hardy	(shut down

The Onaping operations recover a nickel-copper concentrate from ore that is also very high in pyrrhotite and low in pyrite and marcasite. Because the ore is milled at a high pH, sulphur salts (thiosulphates, polythionates) are generated. Pyrrhotite is active and oxidizes readily. The iron sulfide minerals are routed mainly to tailings impoundment areas where they generate acid and introduce some soluble nickel and other metal salts into the downstream watershed. Falconbridge Onaping operations are a good example of a systems approach to water management and environmental control.

Water management is integrated with mill tailings discharge and decantation, water recycle needs, minewater discharge and a lake system. Contaminated seepages outside of the treatment area are intercepted and pumped back for treatment. Refer to Figure 1.

The overall objective of Falconbridge's environmental control program has been to control the release of contaminants (mainly nickel) to the greater lake system outside of those lakes and ponds already affected. The second objective is to develop a tailings impoundment area that is compatible with long term restoration.

Full details of the complete system and stategy are an interesting story, but are specific to the Onaping area and circumstances, both historical, present and future. Accordingly, it is proposed to outline some of the main features and to highlight some of the more innovative aspects that may find more general application. One of the most important aspects is, of course, the overall systems approach to effluent discharge and environmental control. Sponsors are referred to Falconbridge should they be interested in more detail.

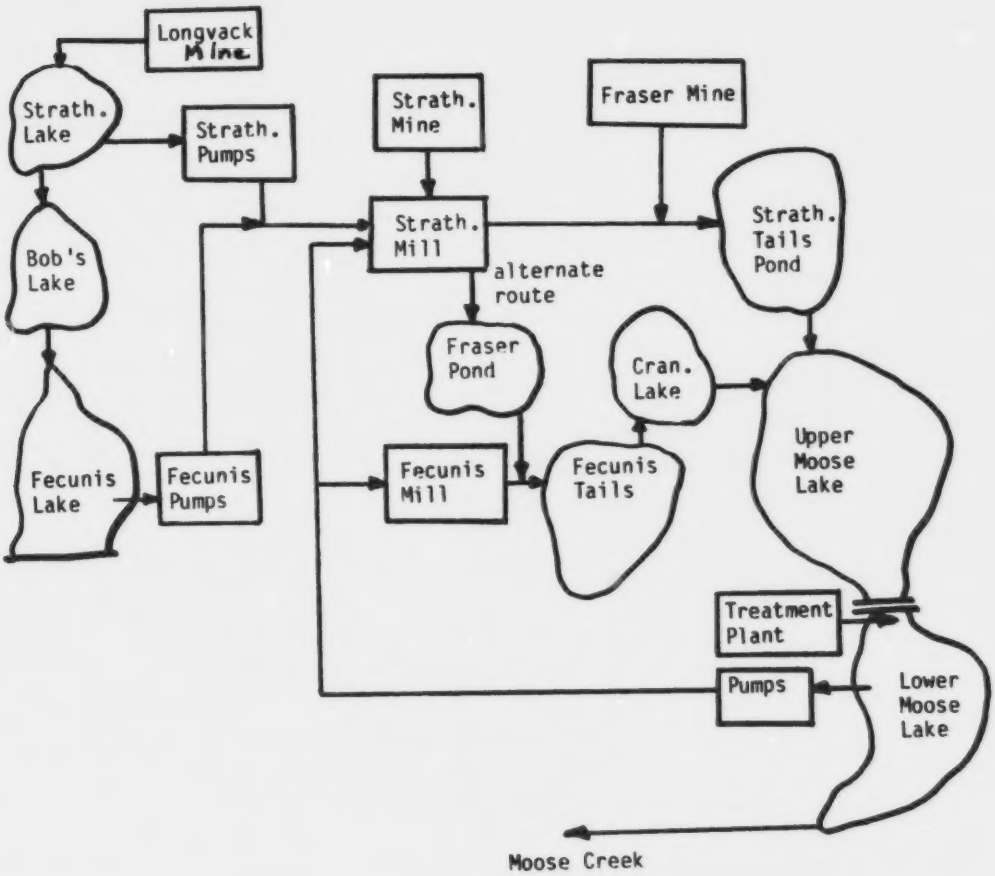
Strathcona Mill

Typical water usage rates for the present 300 dry short ton per hour production rate at Strathcona Mill are outlined below.

The source and destiny of each water stream in and out of the mill was not investigated in detail, consequently, the internal recycling of water will not be discussed in this paper. The new water intake to the mill is a blend of water from lower Moose Lake with that from Fecunis Lake.

Figure 1

Schematic Integrated Water Management System



Water Requirement at Strathcona Mill at 300 DSTPH

To Rodmill A	125 US gpm
	50 US gpm with ore
To Rodmill B	125 US gpm
	50 US gpm with ore
To Cyclone Pumpbox A	400 US gpm
Cyclone Pumpbox B	400 US gpm
Ballmill A	300 US gpm
Ballmill B	300 US gpm
Rougher Circuits	100 US gpm
No. 1 and 2 Concentrate Thickener	320 US gpm
Primary Scavenger Flotation	250 US gpm
Primary Scavenger Con Thickener	125 US gpm
Scavenger Con Regrind Mill	80 US gpm
Primary Scalp Flotation	150 US gpm
Secondary Scavenger Flotation	100 US gpm
Secondary Scavenger Con Thickener	125 US gpm
Secondary Scavenger Con Regrind Mill	50 UA gpm
Secondary Scalp Flotation	100 US gpm
Tailings Repulp Station	100 US gpm
Excess Reclaim Water to Tails	470 US gpm
Launder Sprays - floor washing	200 US gpm
Total	3,920 US gpm

Water Leaving the Strathcona Mill

H_2O contained in CuNi Concentrate shipped	70 US gpm
No. 1 and 2 Thickener Overflfow	800 US gpm
Primary Scavenger Conc. Thickener o/f	875 US gpm
Secondary Scavenger Conc. Thickener o/f	425 US gpm
Underground backfill	O to 1,000 US gpm
To Tailings pond (70 tph @ 14%)	1,750 US gpm
Total	Max. 3,920 US gpm

Net water consumption was given a 4,000 US gpm; i.e., equivalent to 3.23 tons water per ton of ore (2.9 cu.m. of water/ton ore).

The use of 2.9 cu.m. per ton ore fed to a flotation mill is relatively high and reflects the abundant availability of water at this central Ontario location.

Moose Lake Treatment System

Falconbridge has operated a concentrator at Fecunis Lake in the Onaping area of its Sudbury District operations from 1957 to 1975. Later on, Strathcona Mill began production in 1968 at a rate of approximately 2.1 million tons per year. Both mills pumped their tailings to areas which decanted into Moose Lake (see Figure 2 for geographic locations).

During the first ten year period that the Fecunis concentrator had been in operation, the water decanting from its tailings disposal area had resulted in the water of Moose Lake becoming appreciably acid (3.7). This is due to the fact that during grinding and flotation operations in the concentrator, a small amount of sulphur from the mineral pyrrhotite dissolves in the water. As a result, the chemical oxygen demand is approximately 50 parts per million. The products of oxidation called polythionates, with time, generate sulphuric acid which causes the pH of the water to decrease to levels toxic to aquatic life.

The only available solution to the acidification problem is to neutralize the acid after it has been formed. This meant the neutralization of all the decant solutions from the Fecunis tailings and Strathcona tailings areas at a location where the sulphur compounds in the solutions had become completely oxidized to sulphuric acid. Of the neutralizing agents available, limestone was the most advantageous with respect to cost and ease of handling.

Neutralization Plant

The scheme finally adopted was to wet-grind limestone chips (-1/2" +1/4") extremely fine (minus 325 mesh) dilute the wet thick slurry and introduce it into the acidic water overflowing the weir. The neutralization plant layout and equipment is shown in Figure 2 (a) and (b).

Limestone is loaded once weekly through the bucket elevator into the 50-ton bin. It is fed through the screw feeder at rates varying between 3.5 to 9 tons per day, depending on the rate of water flow in the weir, directly into the ball mill. Water, added at a rate of 1 gallon/minute serves to effect wet grinding at about 60% solids in the mill. The grinding medium consists of 275 lbs. of 2.5" diameter and 700 lbs. of 1" diameter steel balls. For the average grinding rate of 4.5 tons per day, about 15 lbs. of steel are consumed.

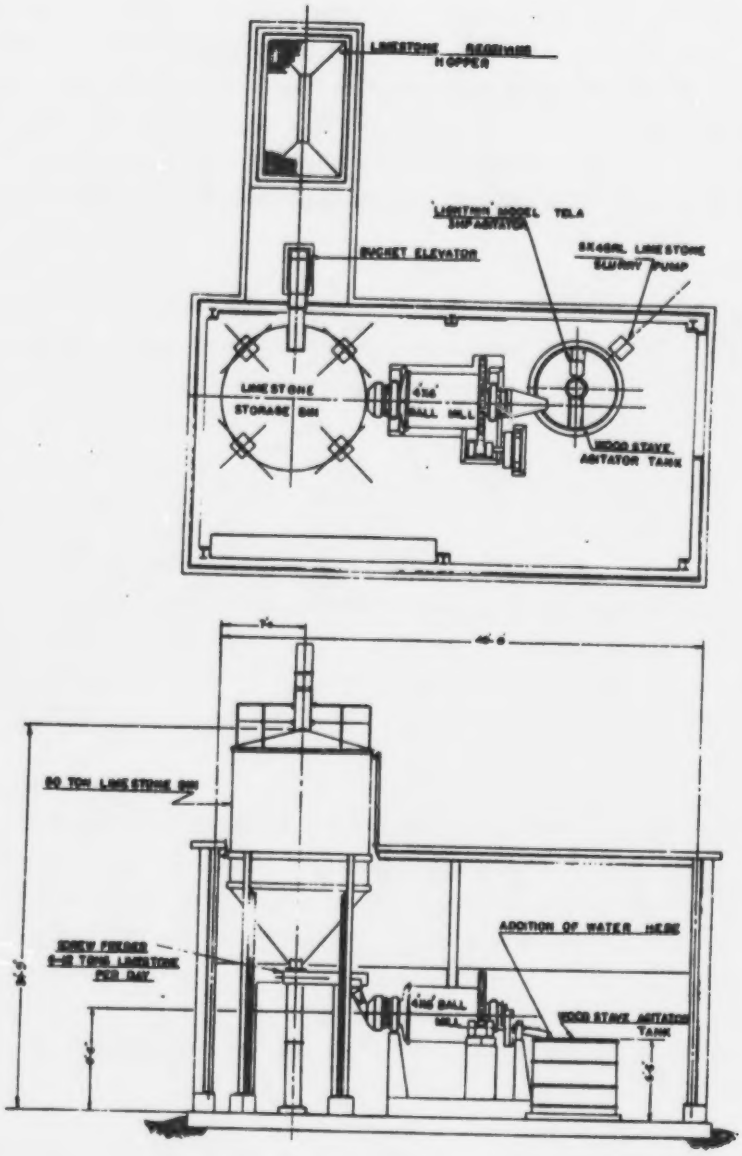


FIGURE 2 4: NEUTRALIZATION PLANT LAYOUT

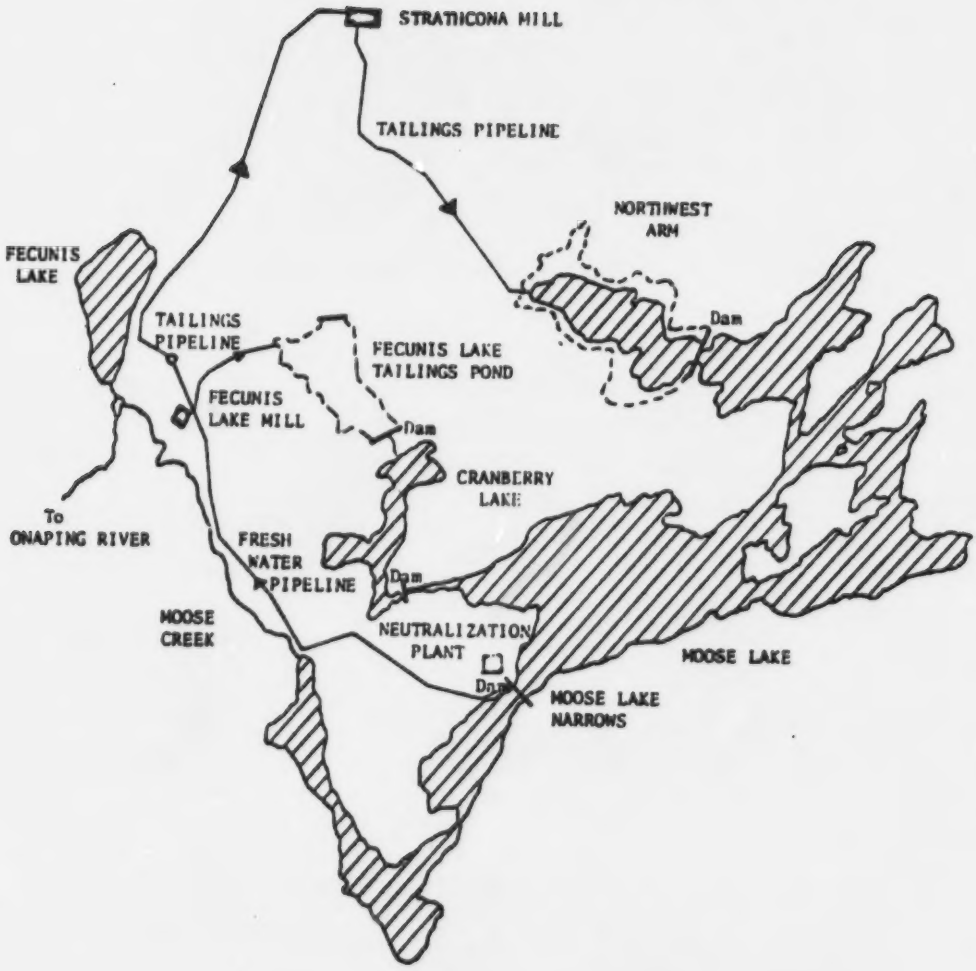
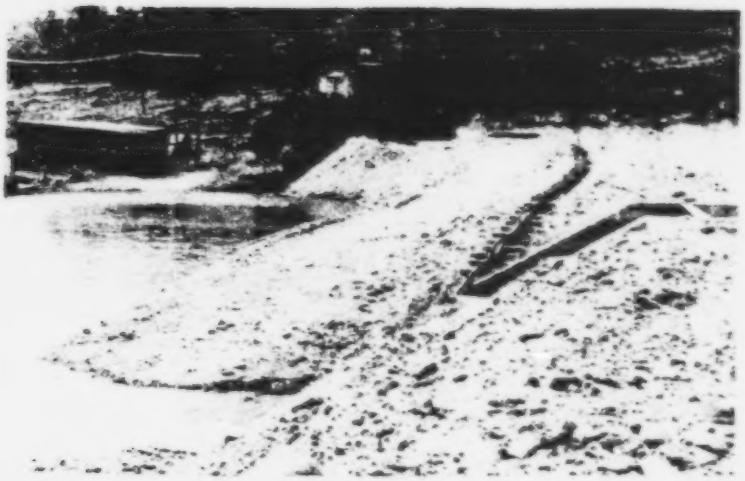


FIGURE 2.4 MOOSE LAKE SYSTEM (1)



LIMESTONE MILL IN BACKGROUND, LIME ADDITION WEIR FOREGROUND

FLOW RATE CONTROL AT WEIR

DILUTE LIMESTONE SLURRY ADDITION TO TURBULENT FLOW

The annual operating expense of the plant is shown below in Table 1. The ball mill is alarm-coupled to a service station located at Strathcona Mill to ensure continuous surveillance by maintenance personnel.

TABLE 1

1981 Lime Plant Costs were:

Labor	C$25,500	
Fringes	11,000	
Supplies	35,200	including limestone
Electricity	7,500	
Maintenance	17,000	
Total	C$95,000	

Results and Discussion

The lengthy retention time of the tailings water in Moose Lake allows for complete oxidation of the dissolved polythionates to sulphuric acid and the year round discharge, despite seasonal temperature fluctuations and water rates runoff, has no C. O. D. A comparison between the water quality at the tailings pond outlets during the winter and Moose Lake system outlet, before and after neutralization, is shown in Table 2.

TABLE 2

Effect of Retention Time and Neutralization
(Typical Assays)

Analysis Results ppm	Tailings Water at Tailings Dam	Moose Lake Before Neutralization	Moose Lake After Neutralization
Suspended Solids	1.5	1.0	1.0
Sulphate before oxidation	700	600	550
Sulphate after oxidation	1,000	600	550
Total Fe	6	2	0.6
Total Ni	3.0	1.2	0.8
Total Cu	0.5	0.1	0.1
pH	6.4	3.5	7.2
C. O. D.	46	less than 1	less than 1

The concentration of polythionates is determined by noting the difference in the sulphate concentration in the water before and after oxidation.

It appears that in order to ensure that neutralization will be effective, a retention period of approximately six weeks under open water and an active biological environment must be available from the time the effluents discharge from the tailings dam to the time the neutralizing limestone is added. In the spring, eight weeks are required from the time the ice has vanished to the time the biological system of the lake becomes sufficiently active to oxidize the polythionates.

Several water management and water treatment features of particular interest were observed at the Onaping operations.

1. A macro water recycling system which includes several tailings impoundments, lakes and streams has been established, thereby requiring a mimimum of water treatment facilities while gaining effective control of contaminant releases to the greater environment.

2. If a similar mine-mill complex were to be established from scratch today environmental considerations would enable advance planning so that a much smaller overall volume of water and tailings would be impacted. The Strathcona systems approach is an innovative retroactive program for a large area which had been impacted for many years before.

3. A deep natural lake was used for tailings disposal, water storage, aging and settling ponds. The lake's seasonal turnover phenomenon is taken into account as well as spring runoff effects in meeting permit effluent requirements. Some understanding and manipulation of the lake chemocline is underway.

4. Recent testwork in progress has high pyrrhotite-pyrite tailings impounded separately from low sulfide tailings, to enable sealing of the Po at a later date. Techniques are under development to use a wasterock layer as a capillary barrier in the restoration of high sulfide tailings.

5. Nickel is the most serious contaminant threat to receiving waters. It has been found that if nickel in the effluent meets the regulatory limit of 1 ppm, then everyone of the other limits is likely to be taken care of.

6. Tests are presently underway at the Fecunis tailings area to cover pyrrhotite tailings with tailings slimes to reduce nickel leaching.

7. Falconbridge employs limestone neutralization to meet the pH limits of water effluents from Moose Lake. Although limestone does not achieve pH levels required to effectively precipitate nickel, concentrations in Moose Lake do not warrant further treatment at this time. The limestone is, however, adequate to meet pH requirements and to precipitate iron.

8. By increasing the height of the neutralization dam, effluent release is now controlled at an average of 12 million US gallons per day, or 43,600 cu. m/day. Formerly, the discharge used to vary between 60 million US gpm during spring runoff and zero in summer. The uniform discharge allows better control and uniform operation of the treatment plant.

9. Falconbridge has evaluated various neutralization chemicals including limestone, quicklime, lime, cement kiln dusts, etc. Kiln dust, a cement plant waste product, was very effective in treating the water, but was uneconomical because of transportation costs.

10. Falconbridge employs coarse tailings for mine-backfill strengthened by cement. This results in alkaline minewater.

11. "Biological" removal of nickel from effluents after limestone treatment is believed to be occurring in lower Moose Lake during the summer. Nickel loading before and after treatment decreases substantially during this period, which proves that the mechanism is not dilution.

12. Metals including nickel are precipitated from water in Fraser Pond by adding tailings decant water at ph 9.

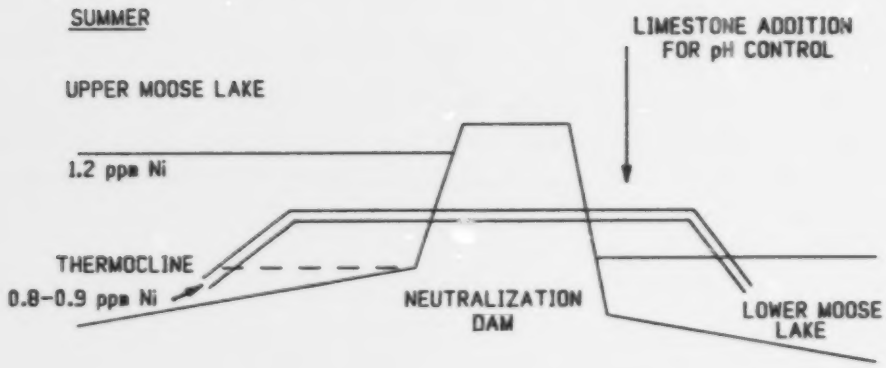
13. Control of high pyrrhotite tailings by covering with less mineralized lower sulphur content tailings over the now abandoned Fecunis tailings area will decrease the amount of nickel that leaches into Upper Moose Lake. Covering the pyrrhotite tailings will result in less oxygen reaching the pyrrhotite and therefore reduce nickel leaching and acid generation.

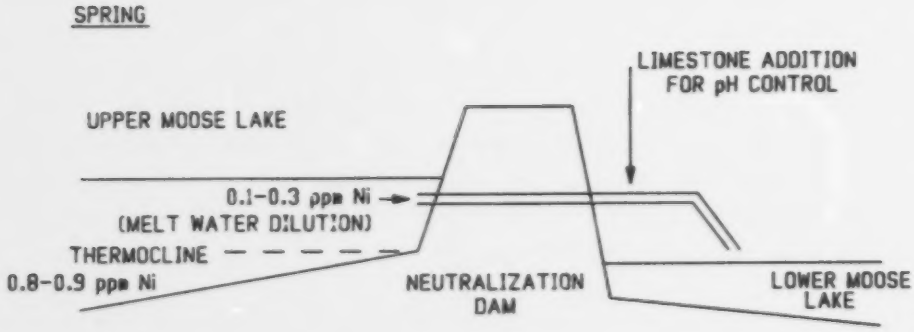
14. Testwork on compartmentalization of the pyrrhotite (Po) at the Strathcona tailings area is underway. The objective is to systematically dispose of the Po in the compartments and cap the Po with less mineralized tailings once the compartment is full. Local community garbage is being used to build the compartments. This will reduce the amount of nickel in water draining from the Strathcona tailings to Moose Lake.

15. The Strathcona tailings disposal integrates disposal of local garbage and sewage sludges.

Figure 3

FALCONBRIDGE ONAPING





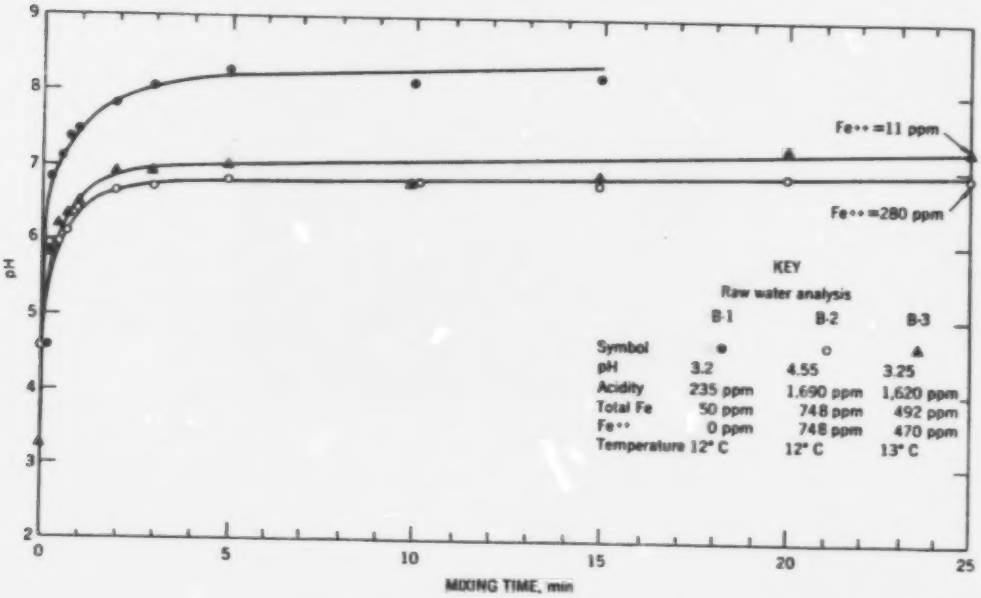
LAKE TURNOVER MANIPULATION

Water in deep lakes located in cold winter regions "turns over" twice a year. During summer the epilimnion water (surface) increases in nickel concentration to say 1.2 ppm while the hypolimnion (deeper water) may run 0.8-0.9 ppm.

During the spring runoff, there is a considerable dilution due to the extra water flowing into the lake. Proper utilization of this cleaner water for dilution is achieved by drawing from the epilimnion or hypolimnion during different time of the year.

The deeper water can have a higher TDS level with $SO_4^{=}$ at around 600 ppm in summer while the surface may only run 3-400 ppm $SO_4^{=}$. Consequently, the denser water at th lower level beneath the chemocline may even prevent the turnover of water in late fall. Unless the lake turns over in the fall, there will remain a high nickel level in the surface water. To bring it down it may be necessary to induce the lake to turn over artificially. If this became necessary, the lake may be induced to turnover by sparging the lower depths with air.

By alternately drawing from the top of bottom (Figure 3), then the nickel concentrations may be more effectively regulated to achieve M. O. E. guidelines.



Limestone Neutralization of B-1, B-2, and B-3 Mine Waters.

BARREN WASTEROCK COVER OVER
HIGH SULFIDE TAILINGS

MUNICIPAL GARBAGE SEGREGATES POND
INTO COMPARTMENTS

TAILINGS AREAS

375 dry short tons per hour dstph of ore are milled to yield 215 dstph of tailings at 13% solids; i.e., 1600 US gpm. 55 dstph of solids end up in the tailings slimes to the pond with a composition average as follows: (for a typical day; e.g., 12-14-84)

% Ni 0.16
% Cu 0.04
% S 1.55
pH 9.0

SEGREGATION OF TAILINGS

(a) Slimes rejected from fill contain 0.1% nickel. These do not have adequate percolation rate to dewater and, therefore, won't form a proper cemented backfill.

(b) Pyrrhotite with 0.6% Ni and 23% S or more cannot be used as backfill, due to the high reactivity which will cause underground fires.

(c) Sand is also used as underground backfill after mixing with cement. There is usually not enough coarse tailings so it has to be mixed with quarried sand. About 73% of the mill tailings coarse fraction are pumped back underground as fill.

Tailings types (a) and (b) for surface disposal are kept separate. The slimes support plant growth and are a good oxygen barrier. In one case, Falcongridge Onaping has covered pyrrhotite tailings with slimes to reduce the sulphur oxidation.

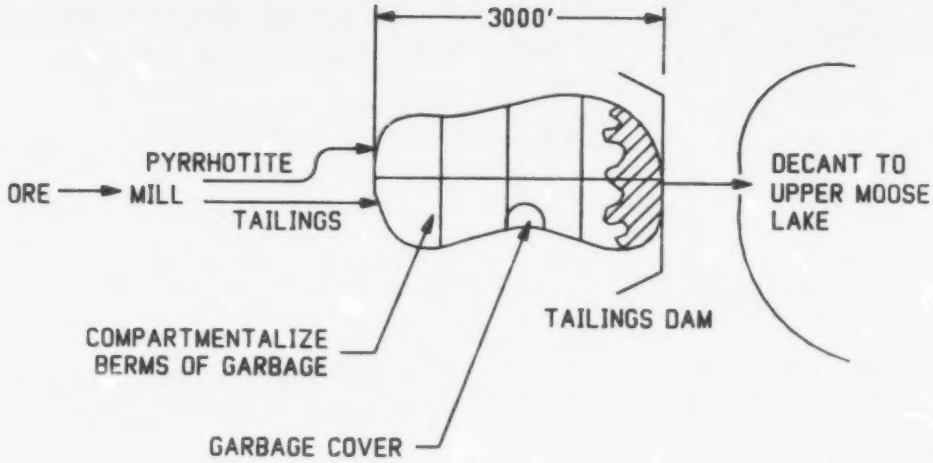
STRATCONA TAILINGS

The plan is to compartmentalize the Strathcona active tailings pond using wasterock and domestic garbage. Pyrrhotite will be placed into one section while covering the rest with final tails. This will reduce the nickel amount exposed to natural leaching processes. (Figure 4)

It is planned to reduce the nickel load emanating from the active tailings pile to Moose Lake in this way.

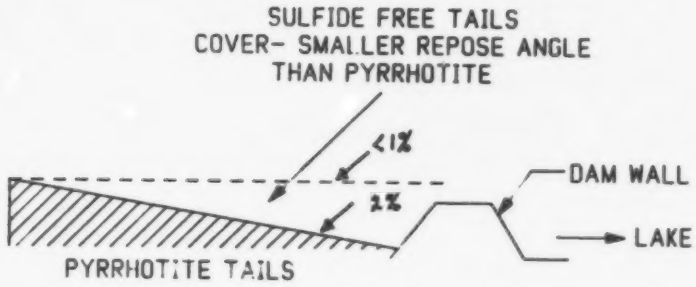
The Strathcona tailings pond yields less soluble nickel than the smaller inactive Fecunis tailings area. This is a result of the increased oxidation taking place at Fecunis, due to the area not being utilized.

Figure 4


3000'
PYRRHOTITE
ORE
MILL
TAILINGS
DECANT TO
UPPER MOOSE
LAKE
TAILINGS DAM
COMPARTMENTALIZE
BERMS OF GARBAGE
GARBAGE COVER

Currently (1984) the ratio of pyrrhotite tailings to final tails is variable but around 2:1. The pyrrhotite settling slope is steeper (2%) than for the tailings slime (<1%). (Figure 5) Consequently, if the pyrrhotite is eventually to be covered, it may be necessary to raise the height of the dam wall which is expensive. Availablity of wasterock for all the proposed applications to make berm dams and to cover pyrrhotite may be inadequate or expensive.

Figure 5



FECUNIS TAILINGS

The inactive Fecunis tailings area was generating over 50% of the nickel loading to Moose Lake due to accelerated oxidation upon closure. The material originally deposited at this location comprised of a Po-tailings slimes mix at a 2:1 ratio respectively. To reduce acid formation and Ni leaching, it was decided to cover this area with lower sulphur nickel tailings slimes. This is being accomplished by rerouting the tailings slimes via Fraser Pond (Figure 2) to the Fecunis tailings area.

A further benefit is that the alkaline tailings slimes water (pH - 9.0) is precipitating out heavy metals. Contaminated water being displaced from Fraser Pond during this restoration measure was spilling into upper Moose Lake which was tending to raise overall Ni levels in Moose Lake. This was temporary condition, with the water quality now back to original concentrations, and steadily improving.

ANALYSIS AND MONITORING

Nickel is analyzed in a sample of Moose Lake effluent at least once a week. The discharge flow rate is gauged by measuring the flow depth in a calibrated square cross section culvert five days a week to compute a daily nickel load.

Because of the huge volume of water in the system, nickel concentration varies very little from day to day. Trends are observed seasonally and over several years.

The M. O. E. has issued a contol order to Falconbridge Limited requiring the Moose Lake Water treatment system to achieve improved effluent quality over a five year program from 1984 to 1988. Falconbridge is required to progressively reduce the total nickel loading of effluents to Moose Creek.

Regulatory Authority

Ministry of the Environment
Ontario Provincial Government
135 St. Clair Ave., W.
Toronto, Ontario
Canada M4V 1P5

Telephone (416) 965-6954
Contact: John Hawley

Effluent Limits

	M. O. E. Limit (maxima)	Currently Achieved	
M. O. E. limit Ni	1.0 ppm	0.9 - 1.0	ppm
M. O. E. 1988 Objective Ni	0.2 ppm		
Cu	1.0 ppm	around 0.1	ppm
Pb	1.0 ppm	less than 0.02	ppm
Cumulative Cu, Pb, Zn plus Ni	1.0 ppm max.		
pH	6.5 - 8.5	6.7 - 7.2	
Sulphates	as low as possible using Best Practicable Technology	400-800	ppm
Fe	1 ppm	0.6	ppm
TDS	to be kept as los as possible using Best Practicable Technology		

REVEGETATING HIGH SULFIDE TAILINGS

In abandoned impoundments containing high iron sulfide concentrations, an extremely hard cap about 1" to 3' thick forms, depending on the moisture regime. Beneath this crust, tailings, even after many years, will remain wet and unoxidized as indicated by their grey color and chemical analysis.

It has been found at Onaping that every summer, the surface of the pyrrhotite rich tailings turn from red-brown to white as soluble salts migrate to the surface by capillary action and concentrate by evaporation. The vertically migrating salts are extremely soluble, mainly iron sulphates.

If such tails are simply covered with a thin layer of clay or loam (6" to 1') and revegetated, the salts will eventually migrate to the surface of the soil by capillary action, and the plants will die. Coarse sand or gravel must, therefore, be used to stop the upward movement of water. (Ref. How to Establish Vegetation on High Iron-Sulphur Mine Tails, R. E. Michelutti, Canadian Mining Journal.)

At the north half of the Fecunis tailings site, an experiment was tried utilizing a gravel and wasterock layer over the high sulfide tailings in a layer about 4' thick. Then the town sewage sludge was pumped over the rock layer to act as an oxygen barrier to prevent oxidation of the tailings below, and also as a nutrient source.

Several plants were growing on the sewage sludge coated wasterock including many tomatoes. Some of these areas have been grassed. Ohers seem to be supporting stands of very juvenile poplar trees. This work is still experimental and not conclusive.

Very successful reclamation work has already been accomplished on the Hardy Po tailings area, and the Longvack Po tailings area. Overburden from the Hardy open pit mine was used to cover these areas at little or no cost towards reclamation. Because of the coarse overburden layer, capillary water movement has been interrupted such that the vegetation has remained very healthy with no maintenance for the past ten years.

STRATHCONA CREEK POLLUTION ABATEMENT

The Strathcona Creek watershed (Strathcona Lake, Bob's Lake and Fecunis Lake) became more acidic and contaminated with time. In 1971, Ni concentrations in Strathcona Creek averaged about 1.0 ppm while in 1984, the average concentration was 15 ppm. This was due mainly to leaching of mineralized wasterock and minor concentrate spills along the concentrate loadout track. Vast quantities of wasterock had been utilized for roads, railbeds, yards, etc. To remove the source of contamination was, therefore, not practical.

The treatment approach adopted by Falconbridge Limited was, therefore, to construct dams at Strathcona Lake, Bob's Lake and Fecunis Lake for impoundment of the contaminated water. Pumphouses at Strathcona Lake and Fecunis Lake are then used to pump the water back to Strathcona Mill. By utilizing the impoundment areas, flows may be seasonally moderated so that all of the water is contained and pumped to Strathcona Mill, negating the cost of a large pumping facility for the spring freshet.

The contaminated Strathcona Creek water is used at Strathcona Mill for process water. Since the flotation circuits require pH 9 to 11, then the water is subsequently treated. Strathcona Mill tailings water contains only 0.1 ppm dissolved nickel where it enters the tailings pond.

ADVANTAGES

1. Use of contaminated water from Fecunis Lake which contains 15 ppm Ni at pH 4 in the Strathcona Mill results in nickel removal at the high operating pH. Subsequent solution decanted from the Strathcona Mill tailings contains approximately 0.1 ppm Ni. In this sense, the mill itself is used as a water treatment plant.

2. It avoids the need for another water treatment plant.

3. It provides a backup water supply for the Strathcona Mill.

4. Lower flotation reagent consumption may result in the mill by utilizing softer Fecunis Lake water (unproven).

5. Inco Limited operates the Coleman Mine close to the Strathcona Mine and Mill. This mine also contributes to the contamination of water in Fecunis Lake. Since recycle of this water to the Strathcona Mill effectively treats this water, then Inco and Falconbridge Ltd. jointly share in the operational costs at a savings to both companies.

6. Since all of the water is contained and pumped back to Moose Lake, then only one discharge point need be closely monitored for regulatory purposes.

7. Any potential spills at the mill or minesites are now totally contained due to this system.

Waste Rock

Between 300 to 500,000 tons of waste rock are produced annually in the Onaping Area mines. The amount of waste produced at each mine varies greatly depending on the stage of mine development, the size of the mine and the ore body. Mine waste must be managed to ensure:

1. that waste production meets demand for roads, railroads, building foundations, yards, dams, etc. If demand exceeds production, projects must then be prioritized.

2. that the waste will have minimal environmental impact through its utilization or disposal.

3. that waste is utilized or disposed of in the most economical manner.

Waste is broken into two categories at Falconbridge. The first category is barren waste, or waste containing no sulfides. This material, generally found only in new mines or mines at early stages of development may be utilized anywhere. The second category is waste bearing sulfides, but at grades which are not economic to be treated. As such, it is a source of acid and heavy metals and its indiscriminate use can lead to contaminated seepage water. Therefore, the management plan requires that all sulfide bearing waste must be utilized or disposed of within the drainage basin of the Moose Lake treatment system.

After construction and reclamation requirements are met, the remaining waste must be disposed of. Disposal sites are selected for:

1. high relief to minimize its exposure to water. Alternate wet and drying of the waste in low relief areas is believed to enhance the leaching of contaminants.

2. the location must be within the drainage basin of the Moose Lake treatment system to ensure that all leachates are treated.

3. maximized depth of the disposal site to minimize the area of future reclamation.

4. minimized cost of disposal by minimizing bulldozer and haulage costs.

Reclamation with waste has several advantages on pyrrhotite tailings ponds. Direct seeding in pyrrhotite tailings is not economically feasible due to high maintenance costs. Therefore, the surface of the pond must be covered with a material suitable for grassing. The waste has several advantages, including:

1. It is readily available and close at hand.

2. Its coarseness prevents the vertical migration of toxic contaminants by capillary action.

3. It stabilizes the tailings to prevent erosion.

4. Its lower contaminant concentration vs. pyrrhotite exposes less contaminant to leaching, therefore, decreasing the contaminant load downstream.

5. It reduces the volume of water and oxygen in contact with the tailings, therefore, decreasing leaching of tailings.

6. It is the most inexpensive method of covering the tailings, and at the same time provides an inexpensive waste disposal site. Falconbridge is now experimenting with municipal sewage sludge on the waste surface. Preliminary experimentation has shown that the cost-free sewage with the waste will support plant growth and further large scale experimentation is underway on the Fecunis tailings pond.

Another approach to a leachate problem occurred in conjunction with the Onaping area potable water supply. Leachates from a waste rock railroad bed and mill concentrates leaked from rail cars and resulted in increasing nickel concentrations in nearby well water. This problem was solved with improved rail cars to prevent leaks, removing material from the surface of the track bed to the mill for processing, then adding hydrated lime to the tracks. The lime increased soil pH, and this reduced leaching by neutralizing rain, precipitating nickel and eliminated the biological leaching of the sulfide oxidizing Thiobacillus bacteria which are active only at low pH's.

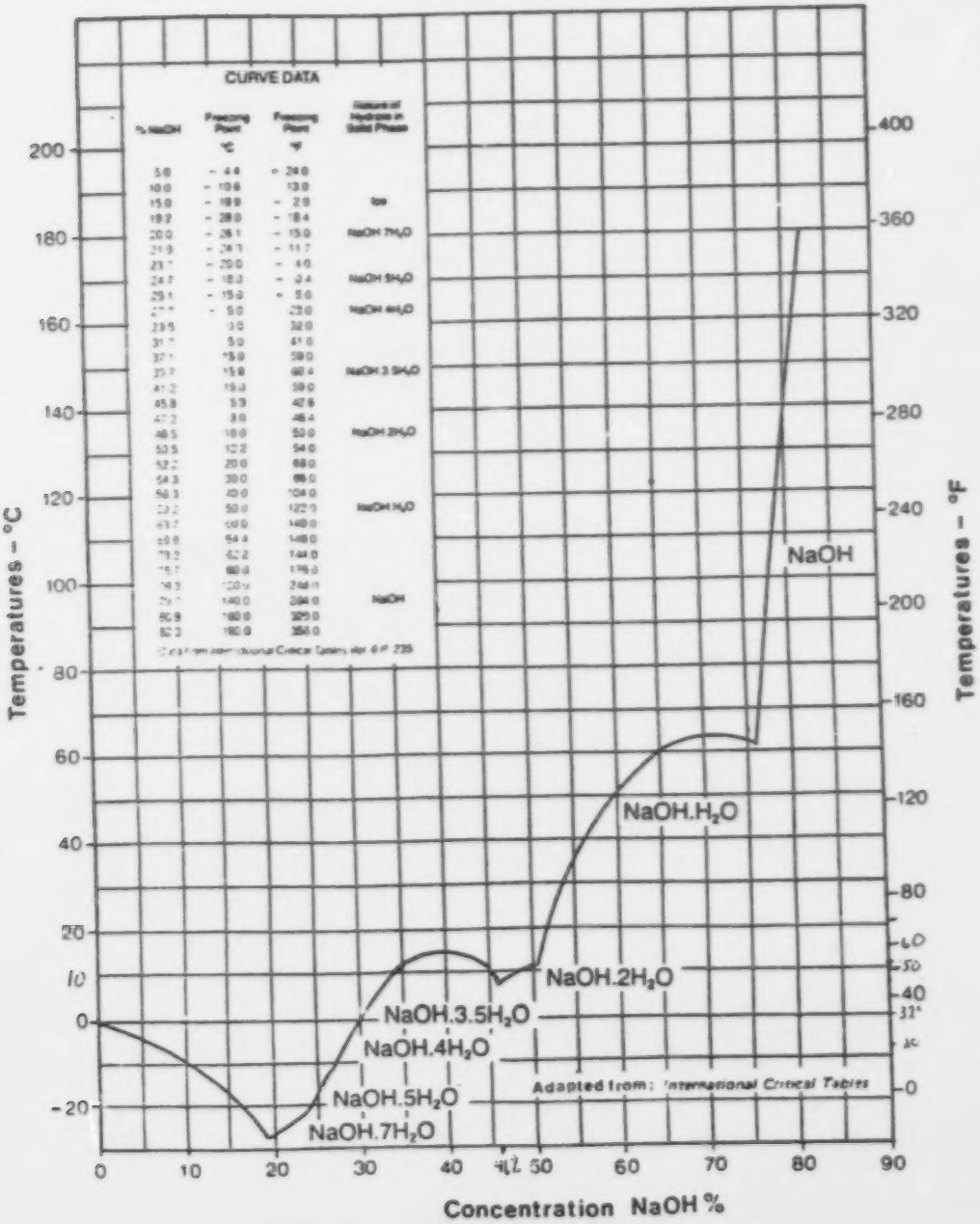
Mine Water Management

Mine water quality and quantity vary with each mine, and vary with time at each mine. volumes range from 30 to 300 US gpm. Mine water pH can be as low as 6.3 in Onaping Mine which had been shut down, but cemented backfill at the other mines generally maintains pH's between 9 and 12.5. Nickel concentrations in the lower pH ranges tend to be high, occasionally reaching 16 ppm, but generally, due to this high pH, range below 1 ppm.

Onaping Mine

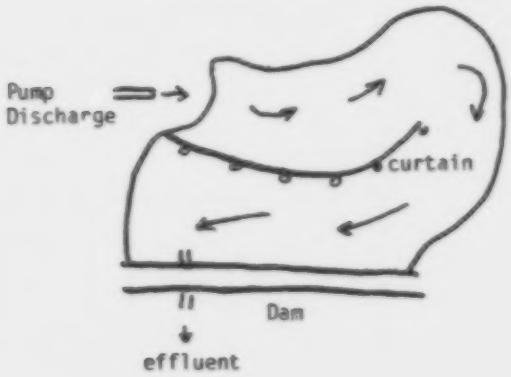
Due to the small volume of mine water and yard drainage generated at Onaping Mine, it is most economical to precipitate nickel from solutions utilizing NaOH. A 50% NaOH solution is fed from 45 gal. drums with a small metering pump, with NaOH consumption ranging between 15 and 45 gallons of NaOH/day. The small NaOH system is significantly cheaper than the more elaborate requirements of a lime system, and does not have the problem of limestone buildup in lines. (Note: When large water volumes must be treated, lime systems are more economical due to lower reagent cost.) The only significant problem with the 50% NaOH solution is its relatively high freezing point (53° F) making it essential to maintain the reagent warm at all times. Diluting the NaOH solution can significantly reduce freezing problems (see Figuyre 6) if heating is a problem, but will require space for tanks and larger pumps and resultant cost increases.

Freezing Points of Caustic Soda Solution



The mine water, yard drainage and NaOH discharge to a small settling pond. To increase the small pond's efficiency, an inexpensive makeshift boom and curtain was installed in the pond. (Figure 7)

Figure 7 - Onaping Mine Pond



Precipitates from this pond can periodically be dredged and processed in the mill as the sludge averages 6% nickel.

Organics such as raw sewage should be kept out of small treatment ponds. Bacterial generated gases in the organics can cause precipitates to float and result in elevated nickel concentrations in the effluent.

Long range plans could result in the elimination of the Onaping Mine water treatment system. The future Craig Mine is in planning stages. Since Craig and Onaping are to be connected underground, the Craig minewater pumping system will be designed to handle all the water from both mines. Craig and Onaping minewater will then be discharged to the existing Moose Lake water treatment system, rendering the Onaping Mine water treatment pond and pumping systems unnecessary. One pumping and treatment system will be cheaper and more effectively maintained. In addition, at Craig Mine, small clay-lined dams have been constructed to ensure that all yard drainage will drain to the Moose Lake treatment system.

Strathcona and Fraser Mines

Strathcona minewater is pumped to surface at Strathcona and pumped over a hill to the Strathcona tailings pond. Fraser minewater is pumped to surface at Fraser Mine and also drains to the Strathcona tailings pond. The Strathcona system is older and has expensive maintenance problems. Since the Strathcona Mine production is decreasing

and minewater volumes are also decreasing, it was determined that the Fraser system could handle the water volume of both mines. Since by 1986, Strathcona and Fraser Mines will be connected underground, it is proposed that all water be pumped to surface at Fraser Mine eliminating the need for the costly Strathcona pumping system, and decreasing water disposal costs.

Conclusions

1. Environmental control around a multi-mine and mill complex requires long range planning. A holistic approach rather than individualistic approaches can save money and improve operating efficiency.

2. Waste rock as well as tailings must be managed to prevent long term water contamination problems.

3. Selection of neutralization reagents depends on water volumes requiring treatment as well as the degree of treatment desired. For example, limestone was most cost effective at Moose Lake whereas NaOH was preferred at Onaping Mine.

4. Waste products such as mine waste, garbage, sewage and low grade tailings may be utilized to improve environmental problems. Control of natural processes such as bacteria and lake turnover, as well as flow rates, are useful tools in environmental control.

OPERATION GILMAN MINE
GILMAN, CO 81631

COMPANY Miller Enterprises
Gilman, CO 81631

TELEPHONE (303) 827-5761

CONTACT Mr. Glen Miller, Owner
Mr. Jack Merchant (303) 328-6349

INTRODUCTION

The Gilman Mine is located on the mountainside above the Eagle River near Vail, Colorado. This zinc mine was operated since the turn of the century by The New Jersey Zinc Company and when, in the latter company's opinion, the ore deposits were exhausted, the property was sold to Mr. Glen Miller, a local entrepreneur who continued to mine a silver vein to produce direct shipping ore.

1. The Gilman Mine is interesting for several reasons. The mine is perched on the side of a very steep mountain where there was no room for a mill and concentrator. It is one of the few locations in the world where a complete mill was installed underground.

2. The underground mill was dismantled some years ago and the underground cavity was used to install a water treatment plant to adjust pH and to remove metals from acid mine drainage generated underground. Not all minewater requires treatment so a major part of the water has been segregated and discharged separately.

3. The acid mine drainage from the Gilman Mine contains relatively high levels of manganese and several interesting methods were tested to remove manganese from the effluent.

4. During 1984 the operators reputedly ran out of operating funds which presents an interesting example of the fate of worked out mines once an operation dies.

5. Gilman tailings historically were deposited on the flood plain of the Eagle River below the mine portal. This site has been declared a superfund site on account of the acid mine drainage it generates. It is reported that surface drainage from the tailings improve in quality when they flow through a cattail marsh which may be a useful location at which to study natural biological polishing phenomena.

ORE DEPOSIT & MINE

Sulfide ore deposits occurred in the dolomitic Leadville limestone formations. Mine workings dipped into the mountain at 12° and the ore was mined to formations of 30 million years of age. Sulfide chimneys extended well below the limestone formations into the underlying quartzite. The formations are underlain by Precambrian granites.

The mine portal for the Newhouse Tunnel was at the 16 level at an elevation of 8514 ft at the head of an inclined shaft. 350' below the 16 level portal at 8168 ft elevation is the 20 level sump from which there is also a portal, where both clean and contaminated acid water are collected in separate sumps and pumped to the mill level above for discharge and treatment plus discharge respectively.

The Newhouse Tunnel has been plugged and water from that level drains via three 5½" Ø holes to the mill portal level just below it where it has been treated.

Toward the portal end of the 20 level, acid metal contaminated water accumulates in a sump from where it is pumped to the underground treatment plant above before being discharged.

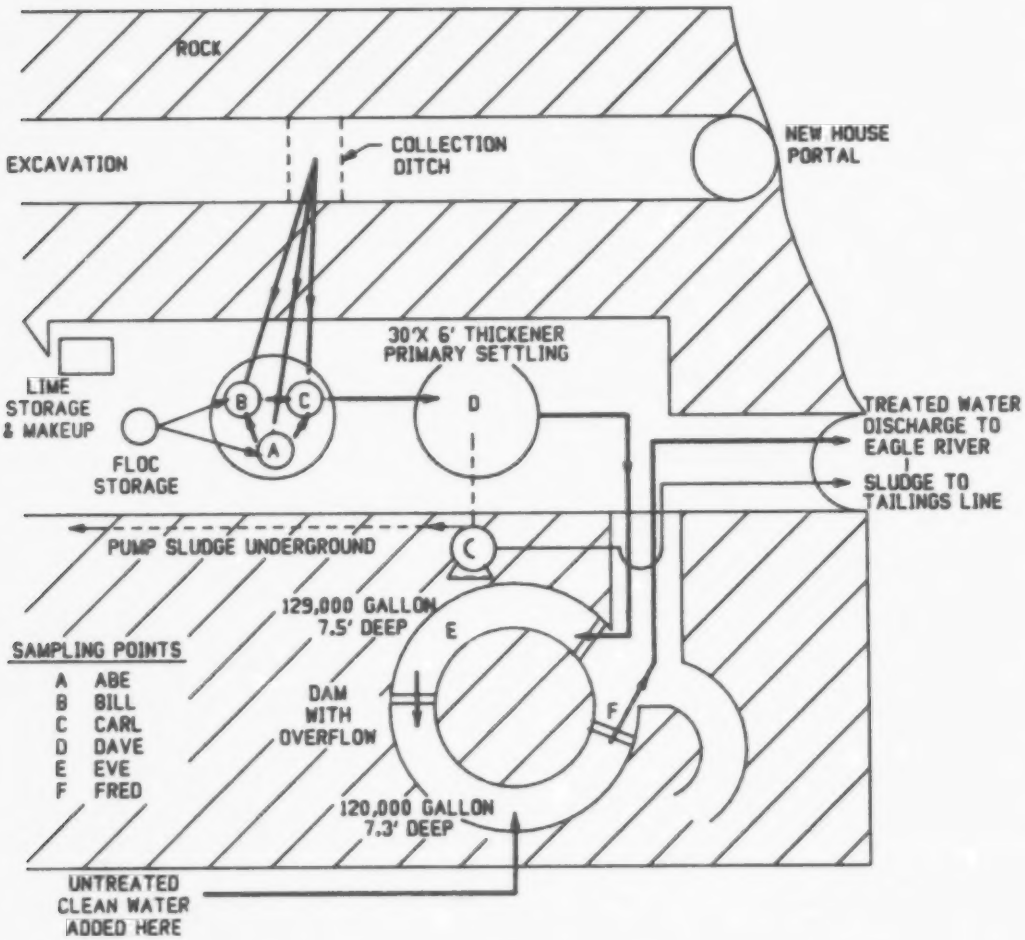
Further into the 20 level incline shaft is a second sump where clean water is collected and pumped separately from the mine.

Water from the Newhouse Tunnel A is collected at 16 level and piped via three 5½" Ø holes to the treatment plant in the mill cavity about 50 ft below.

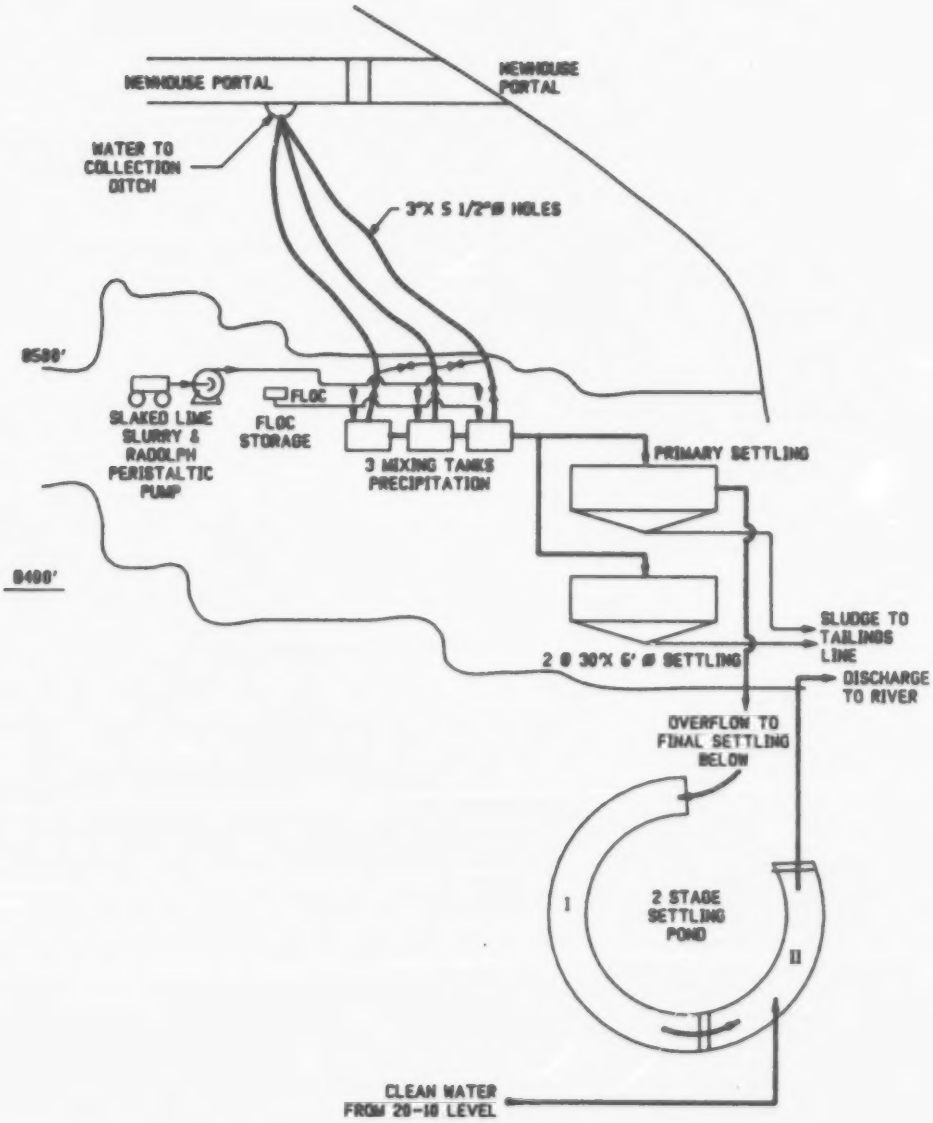
Water from the 24 level has a temperature of 80° F and it was once used to preheat boiler feedwater in the plant.

Since operations have curtailed the deeper workings have been allowed to flood. There are now two pumps on the 20 level one to lift the clean water and the second to lift acid mine drainage.

UNDERGROUND WATER TREATMENT- PLAN VIEW



UNDERGROUND WATER DISPOSAL & TREATMENT



FLOWRATES

	Winter	Summer	Spring
Water requiring treatment 20 level	90-100 gpm	200 gpm	300 gpm
Water not requiring treatment	200 gpm	200 gpm	200 gpm

QUALITY OF AMD REQUIRING TREATMENT

	Before Treatment (Point A)	After Treatment (point F)
pH	2.8	9.6
Cd (ppm)	0.15	0.003 (usually 0.001)
Cu	1.5-4.0	0.000-0.018
Zn	130-300	0.5 ppm
Fe (Total)	50-180	0.1-1.20
Fe (Soluble)		0.1 ppm
Mn (Total)	80-453	1-12 ppm
Mn (Soluble)		1-12 ppm

QUALITY OF MINEWATER NOT REQUIRING TREATMENT

Water from 20-10 Incline

Zn	0.35 ppm
Fe	0.18 ppm
Pb	0.005 ppm
Cu	0.077 ppm
Mn	0.32 ppm

Flowrate about 200 US gpm

MINEWATER SAMPLES AT POINT A

	Cu	Zn	Fe	Mn
Jan 1984	1.96	167	81.3	101
Nov 1983	1.91	172	104	110
Oct	2.33	218	93.2	135
Sept	2.56	287	386	143
Aug	2.52	273	96.5	155
July	3.87	288	110	157
June	3.68	218	118	133
May	2.08	188	65	97
Apr	2.00	159	58.7	85.1
Mar	1.83	140	55	88.1
Feb	1.54	130.5	67.8	-
Jan	1.78	135.6	71	-
Ave.	2.34	198	108.8	120.4
lb/d 12 mo	6.0	498	264 or 255	319

TREATMENT PLANT

The AMD treatment plant is installed in the old u/g excavation for the mill. Water collected from 16 level above and AMD from 20 level AMD sump is pumped to one of three agitators, A, B and C, where lime and flocculant are added. The neutralized solution flows to a primary thickener D. Sludge from the thickener seldom exceeding 3% solids is pumped via the existing tailings line to tailings or to underground disposal.

Thickener overflow is directed to three underground chambers in series through which the primary clarifier overflow flow in series. These are old storage rooms that have been dammed up as indoor settling ponds. The untreated clean water joins the treated water stream in the second compartment of secondary settling, the commingled water is then discharged to the Eagle River.

The treatment plant was said to get good results as long as the flowrate through it does not exceed 150 gpm. Typical analyses of the treated water at F are shown in the following table. It is clear that manganese seldom meets the permit limit of 1 ppm Mn.

MINEWATER TREATED EFFLUENT (F) (mg/l)

Date	Zn	Fe		Mn		Cd	Cu	Pb
	Total	Total	Sol.	Total	Sol.			
5/31/81	0.38	0.20	-	1.03	0.690	0.00	0.008	0.001
7/27/81	0.49	0.06	0.28	2.78	0.003	-	0.000	-
9/01/81	0.60	0.13	0.04	2.62	0.463	-	0.000	-
12/28/81	0.410	0.67	0.53	2.59	1.80	-	0.004	-
4/26/82	0.690	0.50	0.00	4.10	4.10	-	0.000	-
5/24/82	7.02	0.23	0.09	12.0	12.0	-	0.006	-
Average 12 mo	0.507	0.48	0.094	2.62	1.57	0.0008	0.009	-
Jan 1983 (Ave)	2.25	0.47	0.13	5.29	4.96	-	0.011	-
Mar 1983 (Ave)	0.33	0.10	0.035	0.29	0.09	-	0.010	-
Jun 1983 (Ave)	3.6	0.42	0.11	19.2	18.0	-	0.011	-
Sep 1983 (Ave)	0.46	0.12	0.007	5.69	4.07	0.0012	0.009	0.000
Dec 1983 (Ave)	0.90	0.29	0.003	0.65	0.32	0.0013	0.014	0.001
Feb 1984 (Ave)	0.53	0.25	0.11	0.67	0.56	0.001	-	0.003

TAILINGS POND DECANT DISCHARGE TO EAGLE RIVER

Feb 1983 (Ave)	0.22	0.10	0.20	3.68	4.88	0.001	0.016	0.004
May 1983 (Ave)	1.50	0.76	0.25	31.46	25.0	0.006	0.001	0.003
Jul 1983 (Ave)	0.85	0.57	0.04	5.38	6.02	0.004	0.012	0.009
Sep 1983 (Ave)	0.17	0.18	0.03	2.13	1.68	0.001	0.012	0.000
Dec 1983 (Ave)	0.44	0.29	0.04	4.57	0.55	0.002	0.004	0.001
Feb 1983 (Ave)	0.12	0.15	0.06	1.91	0.28	0.000	-	0.009

TAILINGS PONDS

The final tailings pond was fitted with an underdrain which has plugged up. Now the water level has risen in the ponds and discharges over the top. After heavy rains it is found that the pH of the effluent drops and the metal levels increase.

MINE CLOSURE EFFECT ON WATER QUALITY

On closing the mine water will rise in the workings thereby flooding the 20 level. Already as a result of the rising water, acid mine drainage was spilling over from the

acid mine drainage sump into the 20-10 level clean water sump. One problem expected is failure of the clean water pump because of particulates and acid in the acid mine drainage now pumped through the clean water pump which is not designed for that duty.

The first effect of rising water levels is that the underground water from the 20 level will no longer be segregated into clean and contaminated streams. This means that the full flow of water (both streams combined) will become contaminated and even if the water treatment plant were to be restarted, it does not have the capacity to treat the combined flow.

FLOCCULANT

Nalco 7871 liquid flocculant is used to aid in settling the precipitate. It is non-ionic and is added at the discharge to the lime addition reactor. Flocculant is stored underground.

LIME SYSTEM

Two lime storage tanks each hold 60 t lime pebbles. Lime solution is made up with a variable speed lime pebble feeded and a slaker. The overflow from the lime system flows by gravity to the tailings line where it raises the pH of the sludge.

DISCHARGE TO RIVER

There are two tailings ponds in the floodplain of the Eagle River below the mine. The precipitate sludge from the treatment plant is discharged to one of the ponds. Water from the mine after treatment has a pH of about 10.5. The treated water discharge flows via the wet tailings pond and decants to the river, at pH below 9 after being in contact with the tailings pond.

In May 1984 at the time RANDOL visited the property the power bill was being paid by a state agency long enough to remove transformers (containing PCBs) from the stopes before they flooded. The lime supply had reputedly been cut off because the bills had not been paid. Operators were also laid off for lack of funds to pay them.

CONCLUSIONS

1. No matter how strong a mining company may be, ownership or fortunes can change in time. Eventually a mine, even after an exceptionally long life such as at Gilman will be exhausted.

2. Gilman tailings and now the mine itself appear about to become a burden on the taxpayers.

3. For some years Gilman has experienced difficulty in removing manganese from mine drainage solutions. Manganese levels up to 31 ppm average for a month have been measured. Interesting testwork by The New Jersey Zinc Company on manganese removal using pyrolusite are described below.

COLORADO SCHOOL OF MINES RESEARCH INSTITUTE

PREDESIGN CAPITAL AND OPERATING COST ESTIMATES FOR PROCESS FOR REMOVAL OF MANGANESE FROM TAILINGS WATER

Prepared for

The New Jersey Zinc Company
Gilman CO 81634
Colorado School of Mines Research Institute
Golden CO 80401

March 26, 1974

DISCUSSION

In its water discharge Permit No. CO-0000035 the United States Environmental Protection Agency stated as a condition that the manganese in the tailings water discharge should be reduced to 1 mg/liter within 12 months following issuance of the permit.

The Research Institute (CSMRI) has conducted a series of investigations of potentially applicable water treatment systems to achieve the desired reduction in manganese levels in the tailings pond effluent. Systems or approaches studied included the following:

1. Addition of freshly precipitated $Mn(OH)_2$ to tailings effluent during lime treatment in an effort to catalyze precipitation of Mn (II).

2. Precipitation of manganese carbonate rather than hydrous manganese oxide.

3. Adsorption or absorption of manganese on limestone or pyrolusite.

Experimental details and complete results of these tests are presented in the project report by D. E. Hyatt and Truman E. Louderback of October 18, 1973. With respect to the present report, it is sufficient to note that, of the procedures summarized, only the removal of Mn (II) by pyrolusite sorption was deemed practical. The other approaches failed to provide adequate Mn (II) removal or required clearly excessive reagent consumption and cost.

Based on the preliminary indications of success in using pyrolusite to remove Mn (II) from the tailings effluent, additional studies were conducted in early 1974 to ascertain likely scale-up factors in adapting laboratory findings to field conditions. Investigations, using actual tailings effluent and

FIGURE 1

Process Study 1

Pyrolusite Adsorbtion System for Treatment of Tailings Effluent at the Gilman, Colorado Operation of The New Jersey Zinc Co.

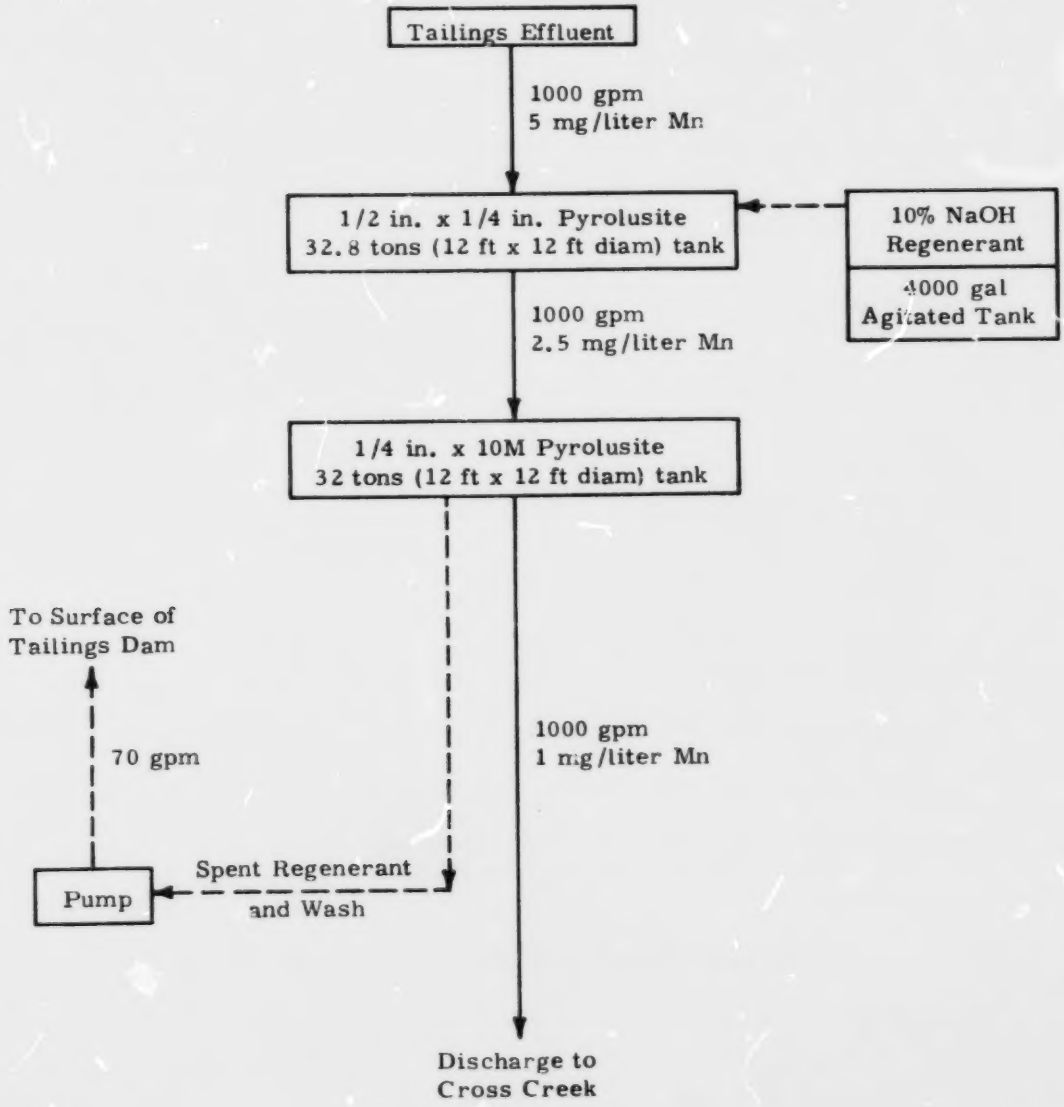


TABLE 1

Equipment Costs

Item	No.	HP	Cost
12 ft 4 in. x 12 ft 4 in. tank, steel, false bottom, open	2		$ 3,800
9 ft x 9 ft agitated tank, steel	1	5	2,300
Pump, 70 gpm, soft rubber-lined, 2-1/2 in. x 2 in.	1	3	800
Pipe, 3 in. Schedule 40, steel at $2.11/ft	1000 ft	-	2,110
Fittings for 3 in. pipe at 25% of pipe cost			528
Freight, Tax, Handling at 8%			762
		Total	$10,300

TABLE 3

Estimated Annual Operating Costs

Chemicals	
2231 gal 50% NaOH at $3.80/100 lb (d = 12.68 lb/gal)	$1075
Maintenance at 4% of Fixed Capital/yr	1068
Labor -- assume no add on cost.	$ 8000 year
Power -- as power would be used only during regeneration, this cost is assumed as negligible.	
Total Estimated Yearly Cost	$2,143

10,143

Colorado School of Mines Research Institute

PO BOX 112 • GOLDEN, COLORADO 80401
PHONE (303) 279 2581
CSMRI

New Jersey Zinc Company
Gilman, Colo.

Date Received MAR 16

March 15, 1974

CSMRI Pr

Mr. A. S. Winters
Manager
The New Jersey Zinc Company
Gilman, Colorado 81634

Dear Mr. Winters:

The purpose of this letter is to report on the test work to determine the adsorption rate of Manganese II from your tailings effluent water on Gilman pyrolusite. Also a preliminary sizing is given of an adsorption system for lowering the manganese in 1000 gpm of water from 5 mg/liter to 1 mg/liter.

SUMMARY

1. Gilman pyrolusite again demonstrated an adsorptive capacity for MnII from plant tailings water.

2. Based on the test work conducted, a preliminary design indicates the need for two 12 ft diameter tanks in series, the first containing a 5 ft depth of $\frac{1}{2}$ in. x $\frac{1}{4}$ in. Gilman pyrolusite and a second containing a 5 ft depth of $\frac{1}{4}$ in. x 10 mesh Gilman pyrolusite. A supplementary tank for mixing regenerating solution should also be provided as well as a pump to elevate spent regenerative solution to the surface of the tailings dam.

DISCUSSION

Water Sample

A 55-gallon sample of clear effluent was collected from the Gilman, Colorado operation of the New Jersey Zinc Co. on February 22, 1973. The sample container was plastic lined. The water at the time of sampling had a pH of 10.4 and a temperature of 2°C. The manganese content of the water which was determined upon return to Golden was 0.05 mg/liter.

Pyrolusite

A 100-lb sample of pyrolusite was obtained from the New Jersey Zinc Co. from a bin on the mining property.

This mineral, which is native to the mining area, was reportedly extracted and stored in this bin in the 1940s. The particles in the sample ranged in size from about 3 in. down to fines. The sample was split in half and one-half retained for possible future use. The other half was crushed to minus ½ in. size and separated into ½ in. x ¼ in. size and minus ¼ in. size. The specific gravity of this sample of pyrolusite was determined to be 3.3.

Adsorption Tests

Unfortunately the pH of the sample was adnormally high and the sample contained little or no manganese in solution. Adjustment would have been necessary in any case to develop the relationships necessary for the preliminary design.

Two solutions were prepared from the tailings effluent for adsorption tests. Reagent grade $MnSO_4$ was added to one solution to obtain approximately a 5 mg/liter concentration of manganese and the other solution to obtain a concentration of 2.5 mg/liter. The pH of each solution was then adjusted to a pH of 7.8 by addition of sulfuric acid. The analysis of the solutions for Mn content after preparation was as follows:

Solution 1 -- 5.0 mg/l of Mn
Solution 2 -- 2.55 mg/l of Mn

Two adsorption columns were prepared using ½ in. x ¼ in. pyrolusite in 250 ml burets and 359 grams of the pyrolusite were required to fill the burets. The void volume in these burets after pyrolusite addition was determined at approximately 46%. In the various tests, the prepared solutions were percolated upwards through these columns, and in each test after the percolation of several void volumes, a sample was taken and analyzed for manganese content. The results of these tests are summarized in the following table.

Feed Solution 5 mg/liter Mn			Feed Solution 2.55/liter Mn		
Percolation Rate, ml min	Solution Retention Time, min	Effluent mg/liter Mn	Percolation Rate, ml min	Solution Retention Time, min	Effluent mg/liter Mn
7.2	20.0	0.6	7.8	17.8	0.62
10(1)	14.4	0.8	20.0	7.0	0.80
15.0	9.6	1.4	25.3	5.5	1.53
20.0	7.2	1.5	46.0	3.0	1.72
38.7(1)	3.7	2.2			
70.0	2.0	2.8			

1/ pH adjusted to 8.8 before percolation

These results permit the following observations:

1. The efficacy of Gilman pyrolusite for adsorption of Mn II from the tailings water was again demonstrated.

2. The adsorption rate was shown to be a function of the manganese content of the feed solution and the retention time in the column.

3. pH apparently did not influence the adsorption rate between the ranges tested (7.8 to 8.8).

These results are expressed graphically in Figure 1 with adsorption rate as mg of manganese per minute per square meter of the surface of the pyrolusite plotted against percent removal from the feed solution. As can be seen, as the percentage of removal increases, the amount removed per unit of surface area in a given time decreases.

The adsorption system using pyrolusite for removal of soluble MnII is, according to the literature, self-regenerative to a degree. MnII is adsorbed and in time oxidized to $MnO_{1.3}$ to $MnO_{1.9}$ which is an adsorbent for incoming MnII in solution. In time, however, the size of the particles in the column increase due to adsorbed manganese and other metals and the flow of the solution becomes restricted. In this event, the column must be treated to restore permeability. One method that

has been used i the soaking of the column in a 10% solution of caustic for several hours followed by a water wash. The washings in this situation could be returned to the surface of the tailings dam.

The pyrolusite must be crushed to prepare adsorption columns or tanks in order to prepare a size that has a considerable surface area compatible with a reasonable downward percolation rate. For purposes of preliminary design, we have considered crushing to minus $\frac{1}{2}$-in. size and preparing three sizes as follows:

1. $\frac{1}{2}$ in. x $\frac{1}{4}$ in. for the first column
2. $\frac{1}{4}$ in. x 10 mesh for a second column
3. Minus 10 mesh for addition to the surface of the plain upstream from the existing measuring weir.

A preliminary study has been conducted considering the design of the first column for removal of 50% of a 5 mg/liter concentration from a flow of 1000 gallons per minute and a second column to remove 60% of the manganese remaining.

The first column would thus remove 2.5 mg/liter and the second column 1.5 mg/liter. The first column where the maximum amount of manganese would be removed would be packed with $\frac{1}{2}$ in. x $\frac{1}{4}$ in. pyrolusite and the second column with $\frac{1}{4}$ in. x 10 mesh pyrolusite. Using this approach, the column with the smallest voids would be removing the lesser amount of manganese and this would extend the time before regeneration was necessary. Moreover, the second column would treat a weaker solution which has a lower adsorption rate per unit of surface area. This column, however, with finer particles would have a higher surface area per unit weight of pyrolusite.

A ton of pyrolusite at $\frac{1}{2}$ in. x $\frac{1}{4}$ in. size at a specific gravity of 3.3 was computed to have approximately 165 square meters of surface area and a ton of $\frac{1}{4}$ in. x 10 mesh pyrolusite, 393 square meters of surface area.

A flow rate of 1000 gallons per minute at 5 mg/liter of manganese would be equivalent to 18, 925 mg/min and at a 50% removal according to Figure 1 at this concentration, an adsorption rate of 1.75 mg/minute/square meter of pyrolusite surface.

$$\frac{18,925 \times 0.5}{1.75} = 5407 \text{ square meters of surface area required}$$

$$\frac{5407}{165} = 32.8 \text{ tons of } \tfrac{1}{4} \text{ in. x } \tfrac{1}{4} \text{ in. pyrolusite}$$

The second column at 60% removal from a 2.5 mg/liter solution and an adsorption rate of 0.45 mg/minute/square foot of surface area would be:

$$\frac{9463 \times 0.6}{0.45} = 12,616 \text{ square meters of surface area required}$$

$$\frac{22,616}{393} = 32 \text{ tons of } \tfrac{1}{4} \text{ in. x 10 mesh pyrolusite}$$

Assuming the weight of the struck volume of the pyrolusite at 120 lbs per cubic foot, and a bed volume of 5 ft depth, the contact columns or tanks should consist of two - 12 ft diameter tanks. These tanks could be constructed of either steel or wood staves. They should be fitted with a false bottom to retain the pyrolusite and a system to distribute the feed solution fairly equally over the surface of the pyroluste.

A sand filter system which is generally 4 ft deep and composed of both gravel and sand has a percolation rate of between 2 to 3 gallons per minute per square foot. This system would be required to have a percolation rate of 8.85 gallons per minute per square foot which would seem conservative for a gravel system without sand. It is recommended that about 12 ft by 12 ft tanks be used allowing 1 ft for the false bottom, 5 ft for pyrolusite and 6 ft of freeboard. More and more freeboard will be required as the size of the particles increase during adsorption. The need for regeneration would be determined when the tank is near overflowing with water.

A supplementary tank should be provided for mixing solution for regeneration or cleaning the pyrolusite. Moreover, a pump should be provided for elevating the solution from regeneration to the surface of the tailings dam.

This proposed design for the manganese adsorption system is preliminary. I am sure we will wish to discuss the amount of pyrolusite available, how it may be crushed and sized, tanks for the columns that might be available of a different size, etc. We will look forward to your comments.

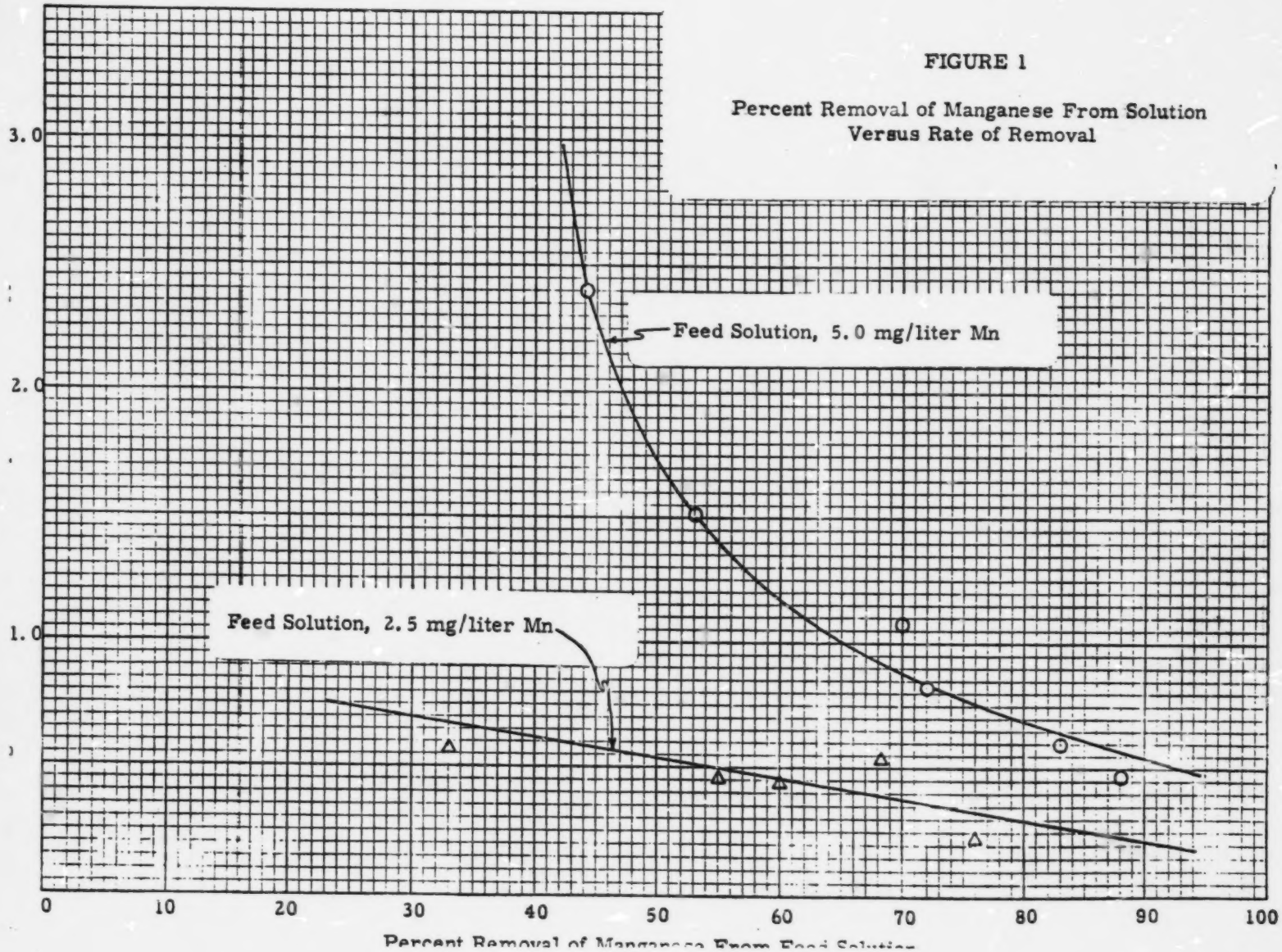
Yours sincerely,

F. T. Davis, Director
Environmental Technology Division

/laj
cc: Russell Wood

FIGURE 1

Percent Removal of Manganese From Solution
Versus Rate of Removal



OPERATION	INCO LTD. COPPER CLIFF, ONTARIO CANADA POM 1NO
TELEPHONE	(705) 682-8341
CONTACT	H. R. Butler Supervisor - Environmental Control
COMPANY	INCO LTD. First Canadian Place Toronto, Ontario M5X 1C4
TELEPHONE	(416) 361-7511
CONTACTS	Warner Stewart Vice President Environmental Affairs Charles Ferguson

INTRODUCTION

INCO, the company around which Sudbury has grown into a small city, operates 11 mines and three concentrators within Ontario. The Copper Cliff facility covers an extensive area - perhaps 25 square miles. In addition to the mines and mills, it includes the Copper Cliff flotation plant which separates bulk concentrates into copper, nickel and pyrrhotite concentrate and tailings, fluid bed roasters, a large acid plant, a copper and a nickel smelter and copper and nickel refineries.

This brief summary does not go into much detail on the metallurgical operations, but it is possible to highlight some of the principles on which INCO's water management and treatment program is based. Managing water and controlling the environment around such a huge and complicated mining and metallurgical complex is no mean feat.

Aspects of particular interest are:

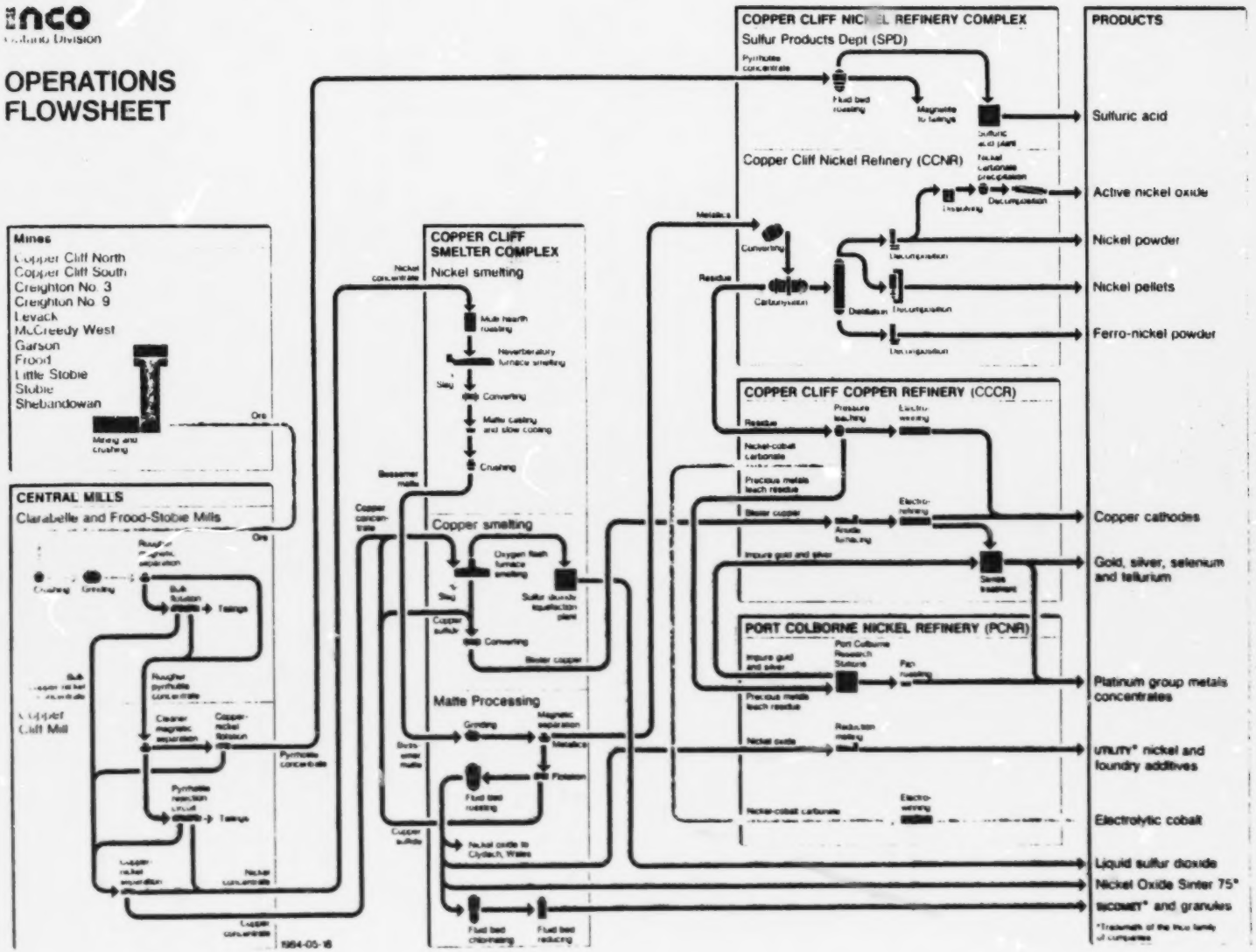
1. The macro management of Water & Recycling.

2. The Copper Cliff Water treatment plant.

3. Tailings Disposal and Site revegetation program.

4. Reference to an improved arsenic removal process.

5. Recycling of water containing thiosalts.


inco
Canada Division
OPERATIONS FLOWSHEET
Mines
Copper Cliff North
Copper Cliff South
Creighton No. 3
Creighton No. 9
Levack
McCreedy West
Garson
Frood
Little Stobie
Stobie
Shebandowan
Mining and crushing
Ore
CENTRAL MILLS
Clarabelle and Frood-Stobie Mills
Crushing
Grinding
Bulk flotation
Tailings
Rougher pyrrhotite concentrate
Cleaner magnetic separation
Copper-nickel flotation
Pyrrhotite concentrate
Pyrrhotite reaction circuit
Copper-nickel separation
Nickel concentrate
Copper concentrate
Copper Cliff Mill
1984-05-18
COPPER CLIFF SMELTER COMPLEX
Nickel smelting
Nickel concentrate
Multi hearth roasting
Reverberatory furnace smelting
Slag
Converting
Matte casting and slow cooling
Crushing
Bessemer matte
Copper smelting
Oxygen flash furnace smelting
Sulfur dioxide liquefaction plant
Copper sulfide
Converting
Blister copper
Matte Processing
Grinding
Magnetic separation
Metallics
Flotation
Fluid bed roasting
Copper sulfide
Nickel oxide to Clydach, Wales
Fluid bed chlorinating
Fluid bed reducing
COPPER CLIFF NICKEL REFINERY COMPLEX
Sulfur Products Dept (SPD)
Pyrrhotite concentrate
Fluid bed roasting
Magnetite to tailings
Sulfuric acid plant
Copper Cliff Nickel Refinery (CCNR)
Nickel carbonate precipitation
Insolubility
Decomposition
Metallics
Converting
Residue
Carbonylation
Distillation
Decomposition
COPPER CLIFF COPPER REFINERY (CCCR)
Residue
Pressure leaching
Electrowinning
Nickel-cobalt carbonate
Precious metals leach residue
Blister copper
Anode furnace
Electro-refining
Impure gold and silver
Slimes treatment
PORT COLBORNE NICKEL REFINERY (PCNR)
Impure gold and silver
Port Colborne Research Station
Pan roasting
Precious metals leach residue
Nickel oxide
Reduction melting
Nickel-cobalt carbonate
Electro-winning
PRODUCTS
Sulfuric acid
Active nickel oxide
Nickel powder
Nickel pellets
Ferro-nickel powder
Copper cathodes
Gold, silver, selenium and tellurium
Platinum group metals concentrates
utility* nickel and foundry additives
Electrolytic cobalt
Liquid sulfur dioxide
Nickel Oxide Sinter 75*
INCONEL* and granules
*Trademark of the Inco family of companies

6. Handling of sewage.

7. Avoiding hydraulic fluid in reclaim water.

LOCATION

In the outskirts of the City of Sudbury, Ontario.

CLIMATE

Continental with 8" net rainfall over precipitation and a long frozen winter.

TOPOGRAPHY

Rolling hills with rock outcrops and with numerous lakes and creeks flowing through the area.

PRODUCTION

The Copper Cliff plant has a nickel production capacity of 220,000,000 lbs per year (100,000 mtpy). Production capacity has been pared back considerably due to present environmental protection constraints particularly with respect to SO_2 emissions. But for these restrictions, capacity would be around 375 million lbs nickel/year.

THE INCO PROCESS

Ore from 11 copper-nickel mines is milled at three plants and a bulk concentrate delivered mainly by pipeline to the Copper Cliff plant for separation. The operations flowsheet is depicted above and gives some idea of the complexity of the total operation.

The Copper Cliff mill receives around 12,000 tpd of bulk copper-nickel-pyrrhotite concentrate from the satellite mills. Copper Cliff tailings (two types) are pumped together with Clarabelle and Frood-Stobie mill tailings to two sand plants and a disposal area.

The general arrangement of mills and smelter is depicted schematically below as shown in "Milling Practice in Canada (1978)" and the general arrangement of the Copper-Cliff-Clarabelle circuit is shown also.

Water requirements, management and effluent disposal around such a multi-faceted mine-mill-smelter-refinery-tailings-wasterock-townsite is complex, especially at first sight. For the casual visitor, just grasping the general arrangement of the various components of the operation even with the help of an excellent model of the area, is difficult at first.

Flotation of the bulk Cu-Ni-Pyrrhotite concentrate is carried out at pH 6.5-7.5 using K-amyl xanthate as collector.

The separation flotation is carried out at pH 11.0 and above in heated pulp with cyanide and $CuSO_4$ addition using a reagent K-amyl xanthate which under these conditions is very selective for copper sulfides.

Roaster gases from the Nichols-Herrschoff multi-hearth furnaces yield a roaster gas with only 2% SO_2 which is too low to make sulfuric acid. Pyrrhotite is roasted in fluid bed roasters and yields 12% SO_2 in the offgas which is diluted to 8% at the converter for optimum results.

INCO at one time released 6-7000 stpd SO_2 to the atmosphere. This has been reduced to 2200 stpd SO_2 under present conditions with further pending measures to reduce the SO_2 levels still further.

In order to control the metal contact of aqueous effluents it is important to look at gaseous emissions and aqueous emission control as one integrated problem.

MACRO MANAGEMENT OF WATER & RECYCLING

The Ontario Division of INCO Ltd. uses 89.1% recycled water, although no detailed water balance has been developed.

Net new water consumption by INCO's Ontario Division is as follows:

Plants	53,418 m^3/d
Townsites	59,072 m^3/d
Mines	18,479 m^3/d

Reclaimed water use amounted to the following:

Mill Water Recycling	98,795 m^3/d
Smelters	26,473 m^3/d
Mines	48,000 m^3/d

Total volume of water recirculated in the operations amounts to 636,678 m3/d, which includes all internal water recycle loops. At Copper Cliff all yard drainage water is collected and treated in the Copper Cliff Treatment Plant.

WATER SOURCES

Water is drawn from two rivers and one lake in the region.

Water supply in most of Ontario which has a net positive precipitation and numerous lakes and rivers is seldom a problem. Consequently, considering the large number of potential water supply sources in the vicinity of the complex, this aspect did not deserve attention. A considerable amount of water is collected from surface drainage and used with recycled process water. The INCO tailings dam system also includes a very large water impoundment to smooth fluctuations in supply. The cost of fresh water to INCO is C$0.70/1000 Igal or US$0.21/m^3.

Fresh water is drawn from the Vermilion river 7 miles from the site and pumped to a central potable water supply reservoir with 16,000,000 I gallon (73,000 m^3) capacity. Potable water is treated by prechlorination, sediment settling, filtration, postchlorination, fluoridation and distribution.

The main principle employed in water management at INCO's operations is to bring all tailings, slimes and decant water to the central tailings pond for aging before discharge via a treatment plant or recirculation. The central tailings pond had a 2 billion gallon (9 million m^3) inventory of recycled water. At one point residence time of water in the central tailings pond was measured to be only two hours which indicated an amazing degree of short circuiting. This is one more example of a case where shear size of an impoundment does not mean an equivalent residence time. The most significant recycle loop is from Copper Cliff Creek upstream of the effluent treatment plant where water is collected from a weir and pumped to the upper pond reservoir. 20 million Igpd (90,000 m^3/d) of water is recycled in this main loop.

COPPER CLIFF WATER TREATMENT PLANT

Water decanted from tailings and surface runoff collects in the Copper Cliff Creek flowing Southeast. As much water as is required is pumped from the creek to the upper pond reservoir. Immediately after the pumphouse, treatment of the balance begins with addition of slaked lime slurry directly to the creek upstream of the treatment plant.

An average of 60 million I gallons/day is treated, i.e., 272,000 m^3/d. Total treatment costs are C$0.30/1000 I gallons (US$0.06/m^3) or C$18,000 per day.

The Copper Cliff water treatment plant was installed in 1975 at a cost of C$4.1 million.

The water treatment plant consists of a two compartment raw water well into which the Copper Cliff Creek flows at around pH 10-10.5 which is at or close to the theoretical minimum solubility of nickel according to JENKINS, et al. (1964). The two compartments are separated by a trash screen which prevents trash, including vegetation matter such as cattail leaves, etc., from getting into the pumps. Three vertical shaft pumps each with 15,000 gpm (100,000 m^3/d) capacity are installed in the second raw water well to pump the water to two EIMCO 135'Ø reactor clarifiers, with 22' sidewalls and 2.5 mm US gallon capacity, installed in parallel.

Alchem 8C26 polyelectrolyte liquid polymer delivered at 0.5-1.0% concentration is diluted 10:1 and dosed at 0.6-1.5 ppm via metering pumps to the feedline to the two reactor clarifiers. The polymer works best around pH 10.0.

AVR blowers are installed to aerate the surface of the clarifier water in winter as a de-icing measure.

Clarifier overflow is collected in submerged (3') radial launders which allow the outdoor clarifiers to function even when covered by a layer of ice in winter. The reactor clarifier is operated with a sludge blanket.

Underflow sludge density is around 2% and is discarded with tailings to the tailings area, being mixed at the tailings pump sump. Each sludge pump has a capacity of 450 gpm (120 m^3/h). The sludge runs 3.4% Ni and 0.2% Cu with iron hydroxide as the main constituent.

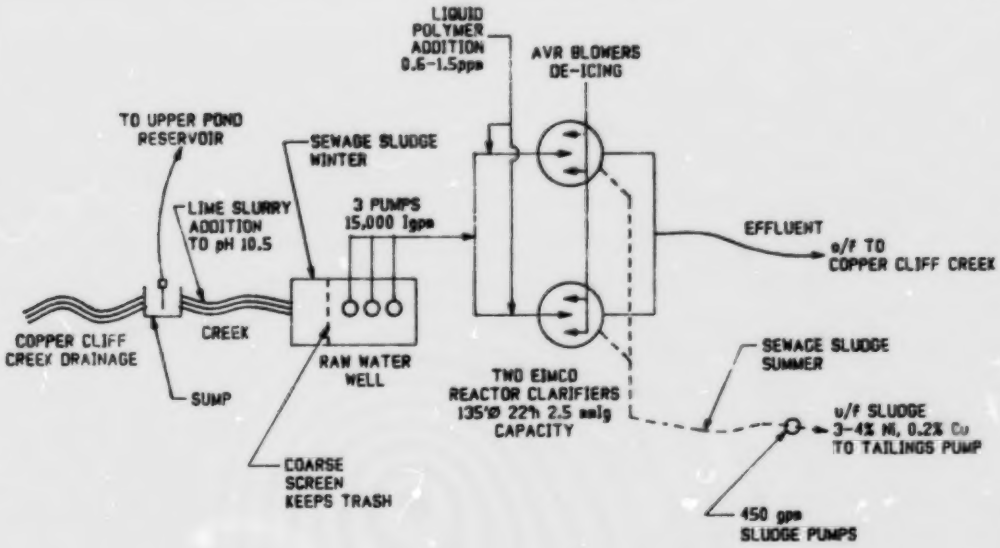
Normally sewage is added to the underflow sludge ahead of being pumped to the tailings pond, except during winter when it is added to the effluent stream in the first stage of the raw water well.

The Copper Cliff water treatment plant uses quicklime for pH adjustment. The lime is supplied from a source in Michigan. Total quicklime purchases for environmental uses at INCO Ltd. is 4000-5000 tpa.

Operating at pH 9.5-10.5 for metal precipitation means that nickel close to its minimum solubility, and at this pH, copper and iron are also effectively removed.

INCO has found that moving the addition of lime to the stream a distance ahead of the clarifier system has resulted in a significant improvement in the reactor-clarifier performance and in the quality of the final effluent.

INCO LTD., COPPER CLIFF WATER TREATMENT



INCO WATER TREATMENT PLANT COST COMPARISONS

Plant Location	Plant Capacity	Year Installed	Capital Cost C$
Nolin Creek	6.3 mm Igpd (28,000 m^3/d)	1975	C$1.9 million
Copper Cliff	60 mm Igpd (272,000 m^3/d)	1975	C$4.1 million
Port Colborne	9 mm Igpd (41,000 m^3/d)	1981	C$5.1 million

WATER TREATMENT PLANT PERFORMANCE

	Influent	Effluent
pH	4.4-5.5	10.2
Cu	0.8 ppm	0.1 ppm
Ni	9.5	0.1
Fe_T	13.4	0.35
S/S	14.0	2.7

EFFLUENT COMPOSITION

	Range		
pH	7.5	-	12.3
Cu_T	0.005	-	0.10
Ni	0.09	-	0.58
Fe	0.02	-	5.9*
Co	LT 0.002	-	0.003
Zn	0.003	-	0.03
Mn	0.003	-	0.30
Cd	LT 0.002		
Cn	0.002	-	0.005
Pb	LT0.002		
Mg	0.8	-	21.0
Al	LT0.5	-	1.7
SO_4	400	-	1300
Cl	40	-	150
P	LT0.02	-	0.04
Hg	LT0.001		
As	LT0.005		
Alkalinity (Total)	28	-	700
Kjeldahl N	1.1	-	4.5
NH_3 as N	0.1	-	4.0
S/Solids	2.0	-	14.0
Total Solids	650	-	2300

*Atypical
LT = Less Than

PIPES

INCO Ltd. has used Woodstave lines with success but recently all new pipe being installed is high density polyethylene.

TAILINGS DISPOSAL & SITE REVEGETATION PROGRAM

The INCO complex includes very large tailings disposal areas in various stages of development, activity or restoration. In 1984 a 2500-acre new tailings area was being developed which will store 48 million tons of pyrrhotite of the overall 400 million tailings to be disposed of. The new area will cover Meatbird Lake and surrounding land. A map of the area reveals several above-ground tailings ponds:

'M' Tailings Area - Active
'M' Tailings Area - Abandoned
'C' & 'D' Tailings Area - Abandoned
'Q' Tailings Area
'P' Tailings Area

The overall tailings area measures 15,000 ft by 18,000 ft and it takes advantage as much as possible of a natural depression in the topography to the west of Copper Cliff.

Tailings are pumped to a sand plant at Creighton Mine where the sand is used as backfill. Slimes and the cyclone overflow are pumped back to the tailings area. Minewater removed from the underground mines is pumped back to the tailings pond with the slimes fraction.

At South Mine and the Clarabelle Mill, all tailings are cycloned, to separate sand for backfill, and slimes are pumped to the tailings pond. The underground minewater sump from South Mine is pumped direct to the tailings pond.

All effluent and sewage from the Nickel Refinery Complex and Iron plants are pumped to the tailings area where they are decanted.

No linings or geotextiles are used in the tailings pond construction. The tailings dams are constructed one at a time in sections which when full can be reclaimed and vegetated. In 1971 the decision was made to construct a very large tailings dam with the objective of establishing a substantial body of water which would be useful in smoothing out the water balance.

INCO has developed a technique for revegetation of their tailings areas. Lime and fertilizer is disced into the surface of the tailings which are then seeded. Tom Peters at INCO, Sudbury, is in charge of the agricultural division which has been experimenting in several innovative ways of using mine tailings and underground stopes for agricultural purposes.

When tailings are placed on the pond the surface is stabilized to minimize dusting problems. The cost of chemical stabilization of tailings solids runs around C$750,000 per year, of which C$250,000 is for the chemical itself.

A product known as HERCOBOND from Hercules Chemical Co. is used at INCO for tailings stabilization. It is one product of several used by the INCO Agricultural group and costs C$0.65-0.70/Kg. The Hercobond is applied using a track vehicle which exerts 3-5 psi to pull a hydroseeder. Several other products have been tested including Curasol (an oil derative), Coherex (used by Climax Molydenum Division, Utah International Copper Division, and Kennecott at Bingham Canyon).

TAILINGS DECANT SOLUTION SIPHON SYSTEM

The largest INCO tailings dam at Copper Cliff was equipped with a 120 ft decant tower which fed an underground tunnel to recover excess water from the pond to Copper Cliff. Around 1982 windblown iceflows caused the decant tower to break off at the base at the point where it was joined to the mouth of the tunnel. This resulted in the draining of the tailings pond to Copper Cliff Creek with considerable silting problems in the creekbed and water treatment plant as well as minor flood damage.

The tunnel opening was sealed by dropping a concrete plug into it. The decant tower has been replaced by a 3,200 ft long siphon with a 80 ft vertical drop from the tailings pond level to the Copper Cliff Creek.

A total of 66,000 USgpm peak flow must be accommodated in the design. This is provided via two parallel steel pipes each with 33,000 USgpm maximum capacity. Normal operation will be at 22,000 USgpm.

Vacuum is provided by two NASH CL202 vacuum pumps capable of evacuating both lines to 22" mercury in two hours. The system can be operated so that one pipe is connected to the vacuum pump in a compressor mode allowing it to blow out the water from the static line to prevent freezing in winter.

Because the lines are buried well above the phreatic surface of the tailings dam wall, this wall would not be in any danger of failure even if there was to be a pipeline failure.

The lines were laid across the tailings surface over a bed of geotextile and crushed rock which serve as foundation for the pipeline.

The steel pipelines consist of 42"Ø 0.404" steel wall lines with 24"Ø 0.375" wall pipes for the last 400 ft. The purpose of the smaller diameter tail section is to put less pressure on the discharge valve.

Problems with frazzle ice formation at the outlet which caused problems at the water treatment plant downstream on Copper Cliff Creek were solved by installing tailpipe extensions right down to the Copper Cliff Creek water level. Severe vibration of the tailpipes occurred until the problem was solved by drilling holes to allow air to enter at the junction of the tailpipe sections to the end of the siphon.

Behrent Engineers of Toronto acted as consultants in the evaluation of the siphon system. Major advantage of the siphon system are:

- It is safe
- It can be readily automated
- Flow can be inercepted by breaking the vacuum.
- It is less espensive than the system it replaced.

Other siphon water transfer systems have been installed in North America at Kennecott Minerals Company's Bingham Canyon operation (2 @ 24"Ø) by Ontario Hydro at Orillia, Ontario for a hydro electric scheme (72"Ø) and ERCO in Newfoundland (34"Ø).

COPPER REFINERY 'BOSCHWATER' TREATMENT: ARSENIC REMOVAL

In the copper refinery, anode cooling water is recycled to a separate pond using surface aerators to cool the water. Overflow from the pond is discharged to Copper Cliff Creek.

Effluent from the Copper refinery which contains arsenic is discharged to the tailings pond. Addition of excess calcium to this stream precipitates the arsenic as Ca Fe Arsenate which is found by INCO to be insoluble at relatively low pH - even lower than rainwater, i.e., pH 5-6.

No details were provided on the performance or nature of the arsenic removal process and further engineers were referred to:

INCO Ltd.
First Canadian Place
Toronto, Ontario M5X 1C4
(416) 361-7511

Dr. Stewart Warner, Vice President Environmental
Charles Ferguson

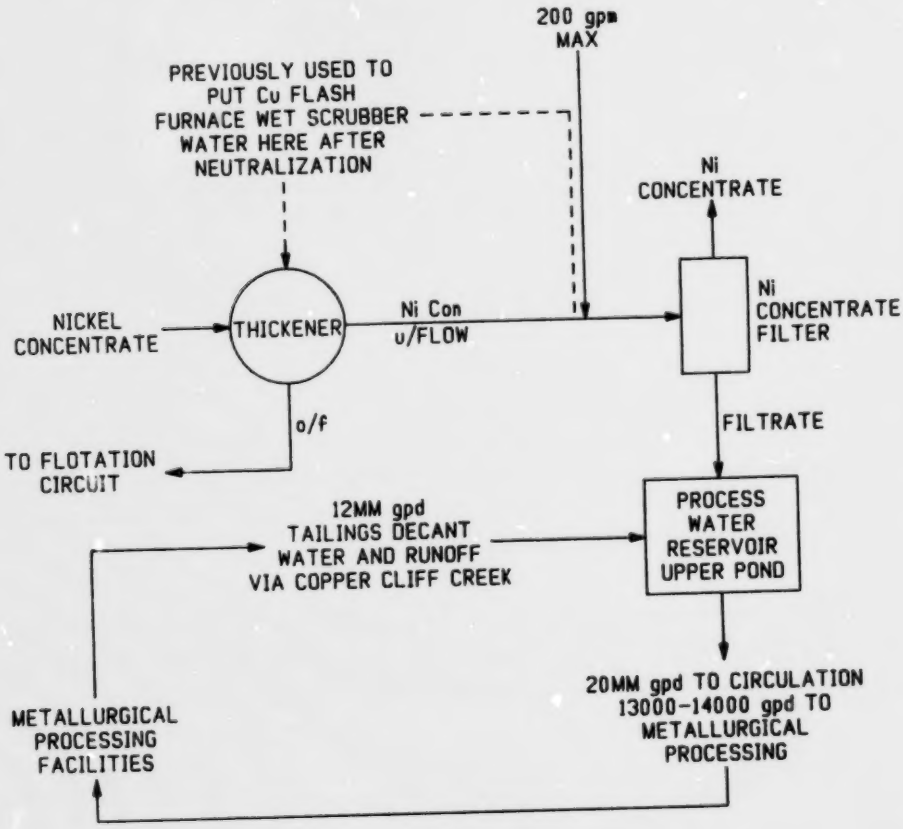
RECYCLING OF WATER CONTAINING THIOSALTS

Copper-Nickel-Pyrrhotite bulk concentrates are delivered to the Copper Cliff flotation plant where the various concentrates are separated at a high pH. Some evidence is found of thiosalt generation, and there is some sign of pH depression in Lake Kelley into which the Copper Cliff Creek flows with Copper Cliff effluents.

Thiosalts and thiosulfate are generated from sulfide ores particularly those that contain pyrrhotite when they are milled at a high pH.

At INCO's Longvack mill there was a pH drop due to thiosulfate oxidation. The Longvack Mill was shut down due to poor economics.

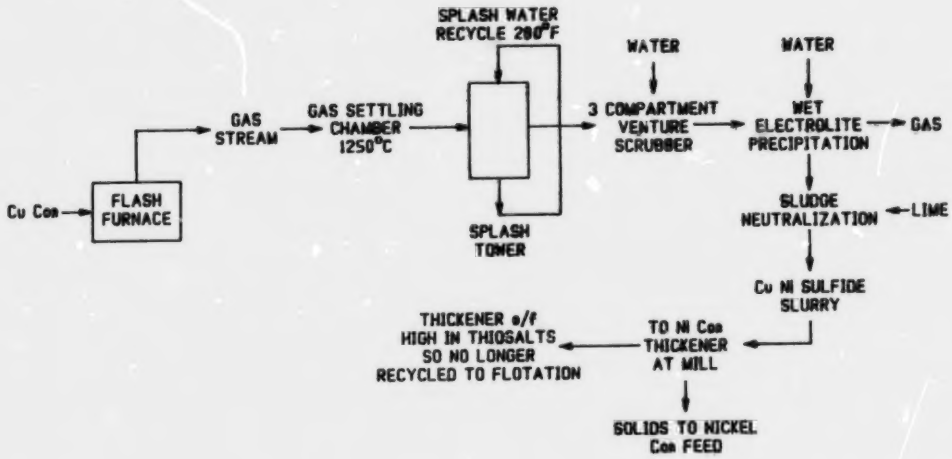
According to INCO, the worst impact of thiosulfate on an aqueous environment is the lowering of pH as below pH 5.5 fish egg hatching is adversely affected.



The direction of all tailings to a large central tailings pond with around 2 billion gallon capacity. One purpose of this is to allow the water to age whereby thiosulfate can be oxidized. However, tests have shown that actual residence time in the pond is surprisingly short due to short circuiting.

Thiosalt levels have been found to be very high in some internal circuits which contain effluents generated by wet scrubbing of exhaust gases from the furnace. The thickener overflow after dewatering the Cu Ni dust slurry from the wet electrostatic precipitators is high in thiosalts and as a result this solution had to be redirected to a different part of the circuit. It used to be used in the flotation plant.

INCO



The Nickel concentrate filtrate now ends up with the thickener overflow and is directed to the upper pond where it is mixed into a very large volume of water and then returned to the mill process in diluted form. Flash furnace water contributes a mere 200 gpm to the 13,000-14,000 gpm Upper Pond water recycle flowrate.

Due to thiosalt and thiosulfate levels there is virtually no oxygen in the recirculating millwaters used at INCO's Copper Cliff operation. It is important to aerate all pulps in flotation circuits to replenish oxygen levels for the flotation process to work well.

SEWAGE

The Copper Cliff complex employs a large sewage treatment facility. Sewage reclaim water is segregated. 250,000 - 1,000,000 lgpd sewage reclaim water is generated (ave. 23 mm lgpm) which is equivalent to an average of 480 m^3/d. Reclaimed sewage water is used as process water in the smelter as well as for mill glandwater and firehydrants. Sewage sludges are disposed of with the water treatment plant thickener underflow which are pumped to the tailings pond. The Copper Cliff sewage plant includes an activated sludge digestor to remove BOD. Sewage reclaim water is used in the venturi scrubbers for dust collection and cooling of SO_2 containing gases as a means of scrubbing SO_2.

EFFLUENT DISCHARGE

The Copper Cliff plant discharges 86,000 - 160,000 m^3/d treated water. The Copper Cliff Creek eventually drains via Lake Kelley to Lake McCharles which supports sportfishing. The effluent treatment plant may contribute up to 50% to the flow of Copper Cliff Creek.

HYDRAULIC FLUIDS IN PROCESS WATER

Mine-Mill-Smelters-Refineries-Tailings complexes using an integrated water system require that a systems approach be adopted. Factors at one end of the process, say in one of the mines, could end up causing a beneficial or a deleterious effect at another end - say in the flotation recovery efficiency.

A routine survey of various consumables turned up the fact that 900,000 gallons per year of oil were being consumed underground. This was tracked down to frequent breakage of hydraulic hoses on scoop trams underground which were using oil as hydraulic fluid. It was found that the temperature rating of the hydraulic hoses was inadequate but has been rectified.

The advantage of using engine oil as a hydraulic fluid in underground mines is that only one oil container need to be transported underground.

The oil lost underground reported with the ore and minewater and was suspected of interfering with the flotation process. Now each mine has waste oil tanks and oil is recycled.

CONCLUSIONS

1. Even on such a large complicated mining and mineral processing complex as INCO Ltd's operations at Copper Cliff, it is possible to simplify the overall water management plan. Recycling of water on a macro scale results in no noticeable deterioration in flotation recoveries.

2. Even a simple water treatment process - addition of lime to an effluent ditch and settling in reactor clarifiers, results in an effluent that has been found acceptable to regulatory authorities.

3. Numerous innovations have taken care of ad hoc problems such as disposal of sewage, oil disposal in mines, thiosulfate generation in gas scrubber circuits, etc.

   An interesting sideline of the same survey that identified the hydraulic oil problem was a survey of pH of the 28 varieties of soap used on the INCO complex. The pH's ranged from pH 7.5 to 12.0. The high pH soaps caused a high incidence of dermotitis which was a factor in absenteeism until corrected.

4. INCO is not interested in the incorporation of biological polishing marshes to treat their final effluent - Cattails break loose and have been found to become a significant nuisance in water courses especially where the water is to be recycled.

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JENKINS, S.H., KNIGHT, D.G. and HUMPHREYS, R.E. (1964) The Solubility of Heavy Metal Hydroxides in Water Sewage and Sewage Sludge I. The Solubility of Some Metal Hydroxides. Internat. J. Air Water Poll., 8, p537-556.

OPERATION KIDD CREEK MINES LTD.
BAG 2002
TIMMINS, ONTARIO P4N 7K1

TELEPHONE (705) 267-2161

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CONTACTS George Podolsky Vice President Research & Development

INTRODUCTION

The Kidd Creek copper-lead-zinc-silver-tin complex is one of the richest ever discovered. The Kidd Creek orebody is separated in two distinct zones, a North orebody and a South orebody. Two main ore types occur within the North Orebody - a siliceous copper ore containing stringers of chalcopyrite in a cherty breccia with occurrences of massive chalcopyrite, and a massive sphalerite-pyrite ore containing native silver and galena. The South orebody is characterized by a mixed ore containing massive chalcopyrite and sphalerite with lower silver, pyrite and galena concentrations.

From 1965 to 1977 when the 800 ft. deep open pit mine phased out 50,000,000 tons of wasterock, some containing sulfides, accumulated on the surface around the minesite. Since 1977 production has been from underground mine operations which today yield 19,000 tons per day of ore 5 days per week which is transported by company rail line to the metallurgical facility about 17 kilometers to the southeast. There are two mineshafts, No. 1 to 3000 ft and No. 2 to 5000 ft.

CLIMATE

The mine is located close to 49° north latitude in a continental climate region. Up to 120 inches of snow can fall annually. Net precipitation is typically 17" but varies significantly year to year. For example 1982 was such a dry year that the potable water supply was threatened. 1984 was a year of record rainfall.

During 1984 with its exceptionally high rainfall and runoff volumes, it has been difficult to achieve the 1 ppm THM target at the treated effluent discharge point.

GRADE CONTROL

The Kidd Creek orebody is zoned and is variable. Parts of the orebody can range up to 60% chalcopyrite. The concentrator can handle feed with up to 3% chalcopyrite, 4% lead, and 5% zinc. Consequently ore must be blended before it is shipped to the mill. 1984 budgeted ore quality is:

Pb	0.9%
Zn	7.0%
Ag	202g Ag/t
Chalcopyrite	3%

Ore is crushed to minus 6" underground and stockpiled in various piles for blending to meet the above grade.

WATER TREATMENT PROGRAM

Drainage from the wasterock as well as the ore stockpile areas, yards, open pit and underground workings covering 2,200 acres is collected to a treatment pond system.

Lime is added and thoroughly mixed with this water as it passes through two corrugated culverts.

pH of the water is raised to above pH 10.5 to precipitate heavy metals. Water pumped from the mine varies from 500 gpm to 1600 gpm depending on the time of year. (2700-8700 m^3/d).

Total average flow through the treatment ponds, including surface drainage to the treatment ponds, is approximately 3,000 gpm (16,000 m^3/d).

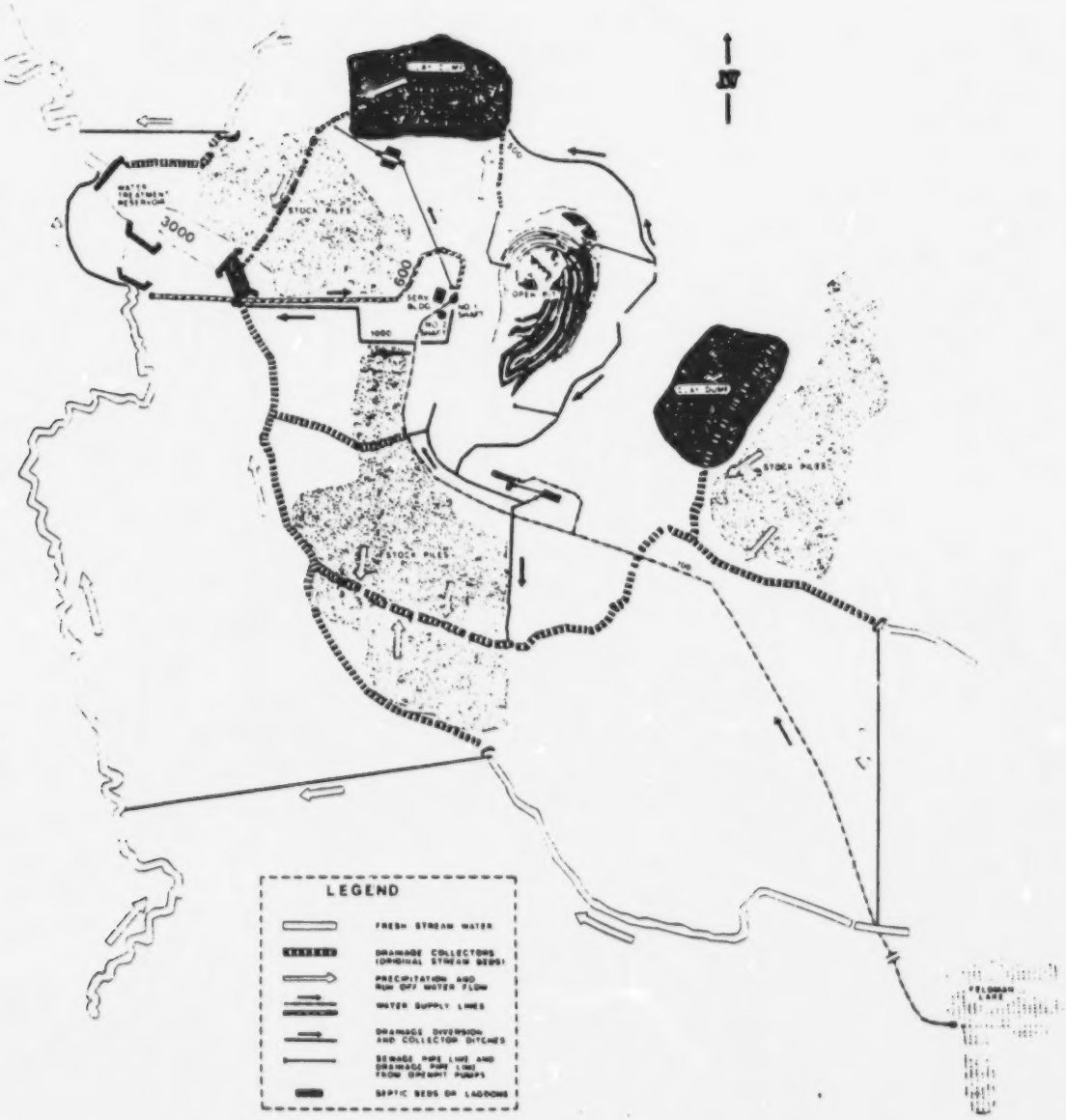
Lime consumption is approximately 1100-1400 short tons per year to keep heavy metals below compliance levels (0.3 ppm Zn max). The rate of automated lime addition is adjusted manually based on metal content and flow of the incoming water. Past investigations have shown that heavy metals in the effluent are at a minimum when the pH is controlled at pH 10. The lime plant shuts down for the winter from October of each year when the tailings pond decant freezes.

The following diagram shows the layout of the mine complex in relationship to the creek and the water treatment reservoir. Typical analyses of the water supply, treated effluents, recycle water and receiving waters at the minesite are provided below.

TEXASGULF CANADA LTD.

KIDD CREEK MINE AREA

DRAINAGE AND WATER TREATMENT SYSTEM



Laboratory Report

Kidd Creek Mines Ltd.
B-2002, Timmins, Ontario P4N 7K1

DATE 1984/06/21

SAMPLE DATE 1984/06/18

MINESITE WATER SAMPLES

T Fontana

	1	4	5	6	6A	C	
pH	7.8	10.6	9.0	7.6	9.3	10.3	
Zn ug/mL	0.3	1.0	0.4	15	4.6	1.3	
Fe ug/mL	0.3	<0.1	0.4	0.4	0.1	<0.1	
Cu ug/mL		<0.1					
Pb ug/mL		<0.1					
Mg ug/mL							
NH3 ug/mL		2.3	2.4	2.7			
SS ug/mL		<10		<10			
T/S ug/mL		402					
SO4 ug/mL		165					
Cl ug/mL							
As ug/L ppb		<10	<10				
Hg ug/L ppb		<1	<1				
Flow		6100					

Laboratory Report

Kidd Creek Mines Ltd.
B-2002, Timmins, Ontario P4N 7K1

DATE July 7, 1984

SAMPLE DATE July 7, 1984

MINESITE WATER SAMPLES

	1	4	5	6	6A	C	A
pH	7.1	9.1	7.8	7.3	9.3	9.1	8.6
Zn ug/mL	<0.1	10.0	2.9	11.0	11.5	12.3	8.3
Fe ug/mL	0.2	0.6	0.6	0.7	0.7	0.6	0.5
Cu ug/mL		0.4					0.4
Pb ug/mL		<0.1					<0.1
Mg ug/mL							
NH3 ug/mL		1.3	2.0	1.7			1.2
SS ug/mL		<10	15				25
T/S ug/mL		334					278
SO4 ug/mL		200					200
Cl⁻ ug/mL							
As ug/L ppb		<10	<10				<10
Hg ug/L ppb		<1	<1				<1
Flow		n.a.					n.a.

Laboratory Report

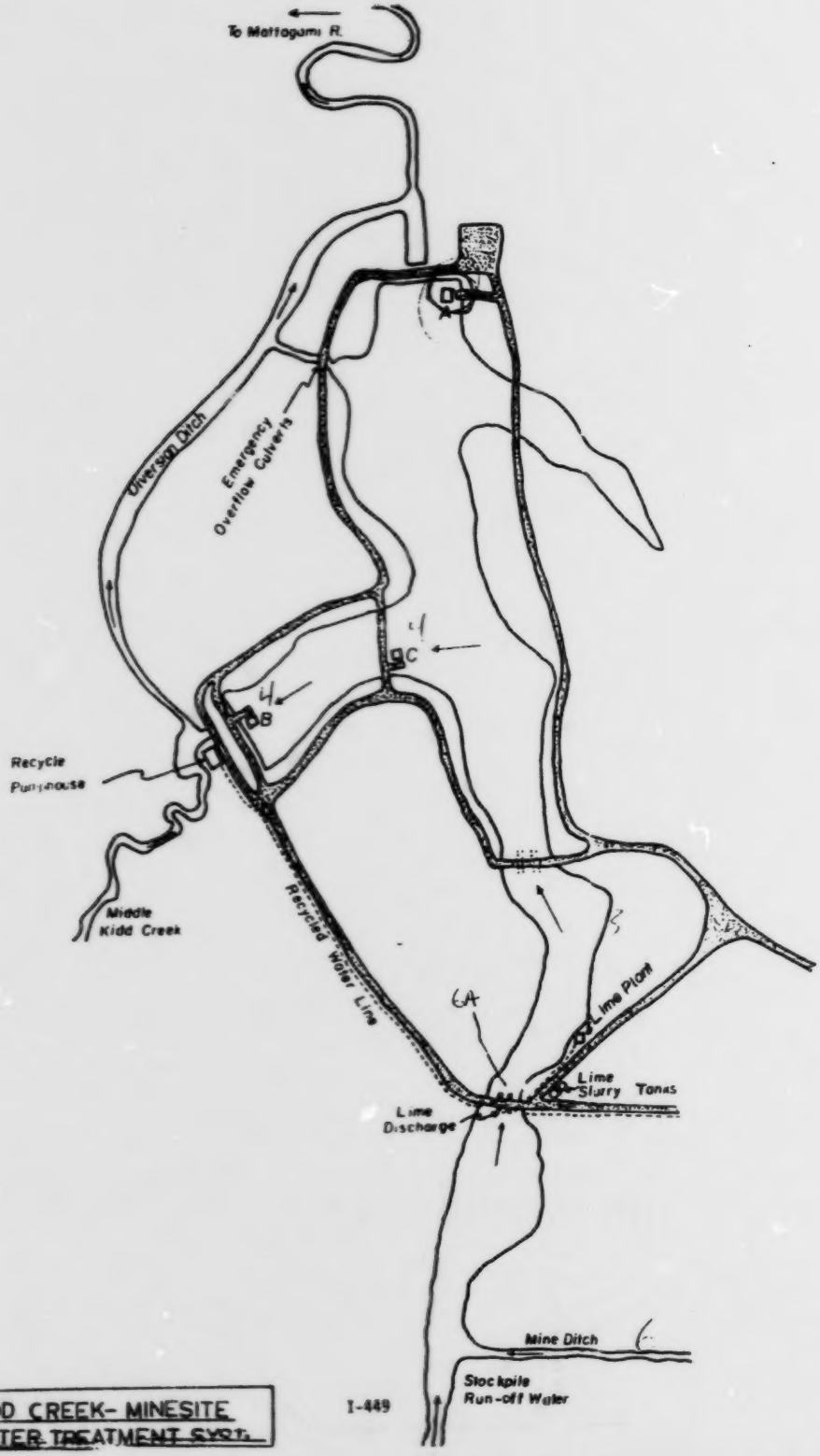
Kidd Creek Mines Ltd.
B-2002, Timmins, Ontario P4N 7K1

DATE 1984/06/22

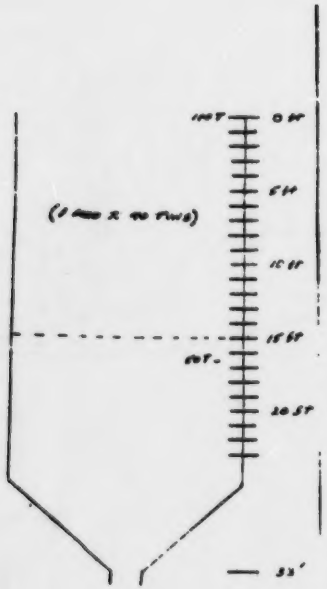
SAMPLE DATE 1984/06/21

MINESITE WATER SAMPLES

	4	5	6	6A	C	9	
pH	9.8	7.3	7.4	11.1	9.7	7.7	
Zn ug/mL	1.8	0.3	15	1.0	1.8	0.3	
Fe ug/mL	0.1	0.3	0.5	<0.1	0.1	0.5	
Cu ug/mL	<0.1						
Pb ug/mL	<0.1						
Mg ug/mL							
NH3 ug/mL	2.0	3.1	3.4				
SS ug/mL	<10		<10				
T/S ug/mL	473						
SO4 ug/mL	165						
Cl⁻ ug/mL							
As ug/L	<10	<10					
Hg ug/L	<1	<1					
Flow	6000						

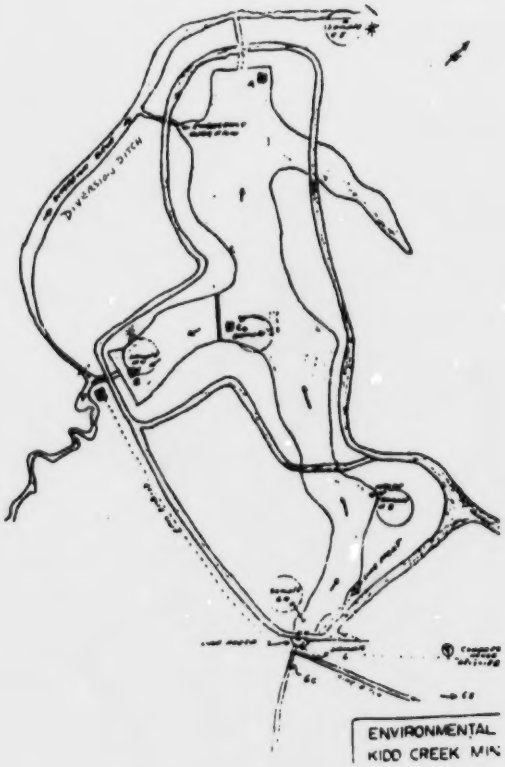


KIDD CREEK- MINESITE
WATER TREATMENT SYST.



RESERVOIR DISCHARGE OF EFFLUENT & EFFLUENT WATER SAMPLES

STATION	LOCATION	EFFLUENT PH RANGE	EFFLUENT CONC. Zn
W.1	FISHING LAKE	6.0 → 6.5	< 0.1 ppm
6	HAUL DISCHARGE	—	—
6A	1st POND IMMEDIATELY AFTER LINER	9.0 → 10.5	< 0.1 → 1.00 ppm
C	2nd POND EFFLUENT TRENCH "C"	9.0 → 10.5	< 0.1 → 0.5 "
4	DISCHARGE @ EFFLUENT TRENCH "B"	9.0 → 10.5	< 0.1 → 0.5 "
A	DISCHARGE @ EFFLUENT TRENCH "A"	9.0 → 10.5	< 0.1 → 0.5 "
5	KIDD CREEK POND STREAM OF PONDS	6.0 → 9.0	< 0.1 → 0.3 "
9	RECEIVING CHNL. U/S	< → 110	—



All water from the site ultimately drains via the Kidd Creek to the Mattagami River.

Underground minewater has a temperature of around 45°F right through the year.

Water pumped from the mine including water used for mining operations averages approximately 1000 gallons per minute. Minewater is slightly alkaline and is very low in heavy metals - (normally well below levels in natural creek waters), but the water from surface stockpiles contains elevated levels of metals. Even the runoff water metal levels are normally below the concentrations accepted as TLV's for a public drinking water supply in Canada (5 ppm Zn), but of course way in excess of levels considered to be harmful to aquatic ecologies.

Oxidation of sulfide minerals is enhanced at temperatures above 10°C, and accelerates as the temperature rises. Dissolved metals then are flushed out during periods of precipitation and when a heavy runoff of surface water occurs.

POTABLE WATER

100 gpm of water is pumped 4 miles from Feldman Lake (which is spring fed as well as receiving surface drainage) and rendered potable in a chlorination plant for use in service shops, offices, surface change and washrooms, underground lunchrooms, drinking fountains, and toilets.

Treated potable water is delivered to the mine by a separate small line in the shafts to lunch and washrooms on all main levels. Potable water and service water are kept separate.

The mine workforce numbers 900. Potable water use is allocated as follows:

Workshops	30%
Fireline	14%
Backfill Batch Plant	4%
Compressor Cooling	4%
#1 shaft underground drinking water	12%
#2 shaft underground drinking water	2%
Administration Building (incl. showers)	34%
	100%

About 600 gpm (3300 m^3/d) of treated water is recycled from the creek for use in mining and drilling equipment, water sprays for dust abatement, washing down roadways and other miscellaneous underground requirements.

SEWAGE TREATMENT

Waste water from surface washrooms located near the two mine shafts is treated in a sewage lagoon. The treated effluent drains into the treatment ponds.

Wastewater from washrooms in the maintenance shops and warehouse areas is treated in a large septic tank and disposed of through a large tile bed.

Wastewater from underground washrooms on each main level is treated in small septic tanks. The septic tanks are emptied periodically and the material disposed of in the surface sewage lagoons.

TREATMENT PONDS

The treatment ponds were constructed in the bottom of a natural creek bed. A bypass ditch was excavated to carry the creek water and the treated effluent around the treatment ponds and back to the original creek bed. There are three distinct ponds interconnected with decant towers so that the water level can be controlled in each section. Provision for emergency overflow is provided in case there is a flash flood - e.g. spring runoff or from rainfall in excess of 2 inches in 24 hours.

LIME PRECIPITATE MANAGEMENT

Metal hydroxide precipitates that settle in the pond are removed as a consolidated sludge by dragline from the first pond once a year. The material is stable and high in lime and is piled at the sides of the pond.

TREATED WATER RECYCLE

A pump station capable of returning up to 1000 gpm (5500 m^3/d) through a 6" insulated surface pipeline is installed adjacent to the outlet culvert of the last decant tower. This pumping station was located to draw water from a basin that would receive most of the creek water plus treated effluent. The water level in this pond is maintained within a narrow range by constructing stone dams or weirs in the creek bed and bypass ditch. Recycled water is delivered to the main water lines in the shafts, for distribution to the different levels and all the working areas of the mine.

PEATMOSS EXPERIMENT

Kidd Creek Mines Ltd. propose to experiment with the use of peatmoss as a passive water treatment step to remove metals ahead of lime precipitation. The motivation is to use less lime, generate less sludge and to yield lower metal levels in the effluent.

MINE DRAINAGE AND GROUNDWATER

Mine drainage water, groundwater etc. is treated to remove most of the suspended solids before pumping to surface. The sludge collected is also pumped to surface, and the decanted water drains into the treatment ponds. Studies are still in progress to determine the optimum method to recover the metal values. It also contains 12 ppm NH_3 due to the use of explosives.

SURFACE DRAINAGE REDUCTION

Overburden slopes from rock edges of the pit have been sloped back at 10%. These areas have been revegetated with self propagating grasses. Natural shrubbery and small trees are establishing themselves.

As stockpiles of ore are shipped to the mill and as wasterock is used up for mine backfill, these areas will also be revegetated. The more wasterock is used in underground backfill, the less there will be to generate acid mine drainage.

As ore is removed, the mined out areas are filled with cemented backfill so that when the ore is mined out, most voids will be filled up to the bottom of the pit. When mining operations are completed the mining site will be restored with natural vegetation except for a lake in the open pit. Due to the deep water in the pit it is aimed to make this a habitat for lake trout.

A landscape firm has been retained to revegetate the site:

EROCON LTD.
Timmins, Ontario
Herman Keller - Horticulturist

LIME CONSUMPTION

Lime is delivered in tanker trucks from Reiss Lime Co. in the Toronto area.

Price of lime is C$96/st delivered.

1984 consumption of lime is budgeted at 1100 st.

1984 lime cost is budgeted at C $106,000.

UNDERGROUND SLUDGE

Composition of the sludge settled from water underground is as follows:

Pb	0.31%
Cu	1.36%
Zn	6.27%
Ag	0.3 oz Ag/t

Size distribution

-54 u	98%
-12 u	53%

Flotation tests as a way of recovering the metal values were discouraging. Poor selectivity suggests contamination with oil and grease.

One alternative is to filter the sludge underground in the stopes. Another is to mix it into the cemented backfill. There is limited storage capacity in the creekbed for disposal of the sludge.

TYPICAL ANALYSIS OF MINESITE WATERS

	pH	Zn ppm	Fe ppm	NH_3 ppm	As ppb	Hg ppb
Fresh Water from Feldman Lake	7.0	0.1	0.3	-	-	-
Mine Drainage Water from u/g	8.5	* 0.1	* 0.1	12.4	* 10	* 1
Surface Drainage Water before Lime Treatment	7.3	4.8	0.3	-	-	-
Treated Water in Holding Pond	10.3	* 0.1	* 0.1	1.2	* 10	* 1
Recycled Water	8.8	0.1	0.4	1.0	* 10	* 1
Kidd Creek Water after mixing with Treated Water	8.9	0.1	0.5	1.3	* 10	* 1

* Less than

EFFECT OF CEMENTED BACKFILL

The strength of concrete roadways underground is noted to have some effect on minewater quality. Because underground minewater is basic it does not attack concrete. $SO_4^=$ ions can be detrimental to concrete however.

Kidd Creek Mines keeps the water content of backfill low. Normal construction concrete needs 600 lb water per m^3 concrete to get 4" - 5" slump. For backfill purposes concrete with 1.9 t/m^3 density is used which equates to only 95 lb water per m^3 backfill.

The conventional setting retardant used in backfill curing cost about 10¢/ton ore. This was replaced with cheaper ligno-sulfonate from the paper industry which frothed badly - a problem that was overcome by adding an anti-frothing agent.

Ground copper smelter slag retards the cement setting rate because the slag lacks tricalcium silicate $(CaO)_3SiO_2$ which is formed in slag only at temperatures above 1250°C and is consequently not used in the Kidd Creek Mine.

The hydration of cement is discussed in the STANDARD HANDBOOK for Civil Engineers pp 3-5. Kidd Creek's backfill practice and technology is discussed by YU and COUNTER (1983).

A source of information and technology for granulation of slag for use in mine backfill is:

National Slag Company
Burlington, Ontario

Telephone (416) 547-2131
Contact Bob Cotsworth, Vice President

CONCLUSIONS

1. Use of cement in backfill has little or no effect on the metallurgical process because the minewater system is not integrated with water supply for the concentrators which are located 15 miles away. No mention was made of metallurgical interference due to chunks of cemented backfill getting into the ore, or even whether this occurs.

2. The site lends itself to establishing an engineered aquatic bog to polish the effluents and help settle any residual suspended solids in summer, but not during the Spring runoff.

3. Straightforward addition of lime to a ditch is not a very efficient way to treat water. Lime consumption could certainly by reduced through use of a somewhat more efficient dosing and mixing system. The total lime cost at C$106,000/year does not leave much of an incentive to install a more sophisticated plant, however.

The Kidd Creek Mine is planning the restoration of the minesite in advance to have minimum impact on aesthetics and water quality. This is in stark contrast with the nearby Kam Skotia Mine which is an example of what happens when such measures are not adopted on a timely basis.

REFERENCES

, T.R. & COUNTER, D.B. (1983) Backfill Practice and Technology at Kidd Creek Mines, CIM Bulletin, Vol. 76, No. 856, pp. 56-65.

ANDARD HANDBOOK FOR CIVIL ENGINEERS (1968) Frederick S. Merritt, Ed., McGraw Hill.

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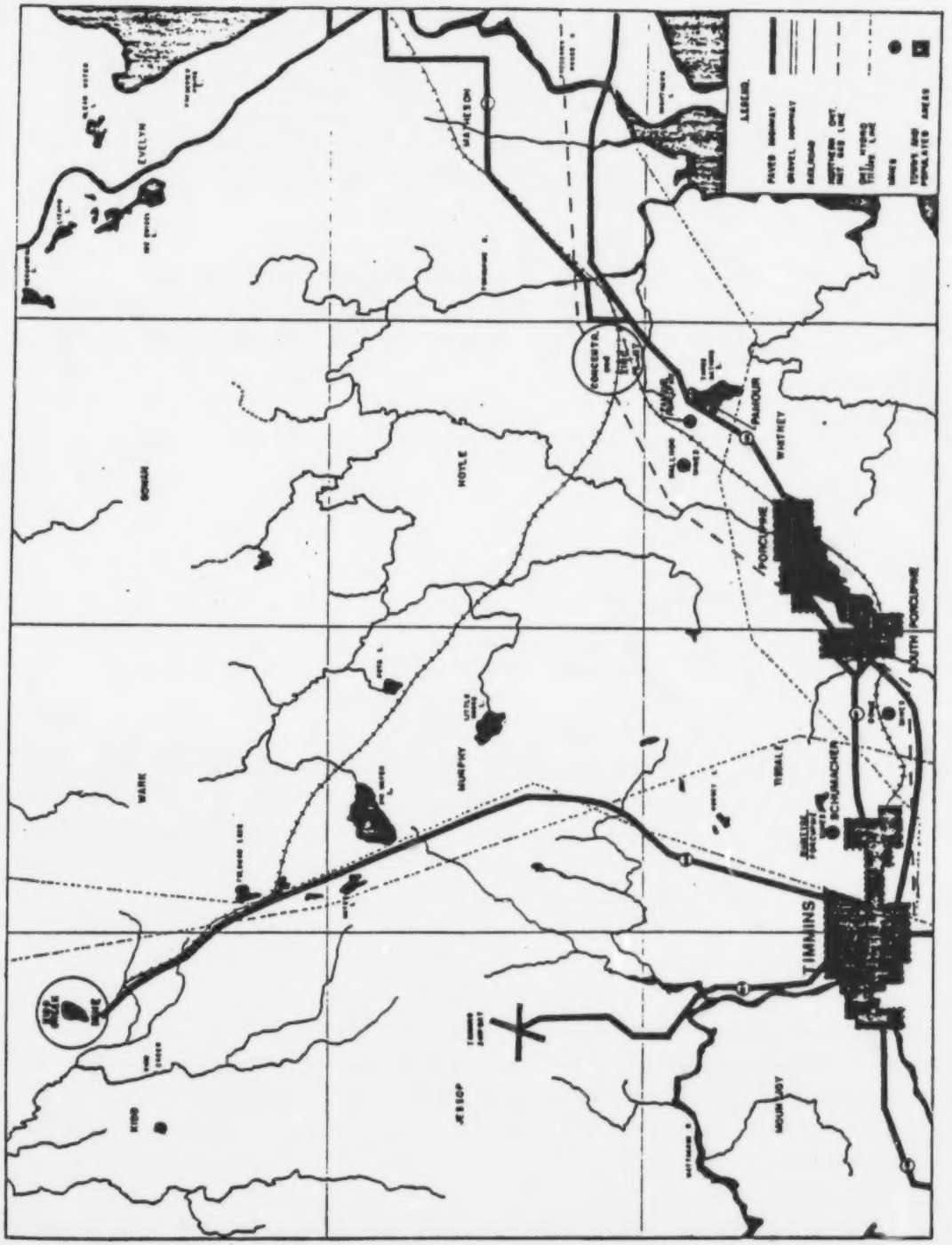
Colin Chapman Chief Metallurgist

MAIN CONCLUSIONS Copper, lead, zinc concentrating and refining from sulfide ores can be conducted on a massive scale without serious environmental impact. Water treatment using lime only can achieve an effluent where combined heavy metals do not exceed 1.0 ppm.

INTRODUCTION

The Kidd Creek copper-zinc-lead-silver-tin mine in northern Ontario is one of the richest base metal resources ever to have been discovered. Because of unsuitable ground conditions at the minesite, ore is transported by rail to the fine crushing, milling and concentrating plant located 17 miles to the southeast of the minesite in the greater Timmins area.

The mill and concentrator treat 13,000 tons per day of ore to yield zinc, copper and lead-silver concentrates. Zinc is refined on the site using an electrolytic jarosite process and half the copper is shipped to Noranda while the remainder is smelted at Timmins at the Kidd Creek plantsite.


LEGEND
PAVED HIGHWAY
GRAVEL HIGHWAY
RAILROAD
TIMMINS
SOUTH PORCUPINE
PORCUPINE
WHITNEY
PEMBROKE
SCHUMACHER
TISDALE
MOUNTJOY
HOYLE
MURPHY
WARE
JESSOP
EVELYN
MASSEY

There are several items of interest:

1. The 3000 acre tailings disposal site which uses the Robinsky thickened tailings concept.
2. Disposal/storage of a large volume of pyrite-silver concentrates.
3. Water management at a large integrated mill-concentrator-smelter-refinery complex.
4. Effluent treatment before discharge.
5. Effect of water recycling from tailings to the mill on metallurgical recovery.
6. Effect of thiosalts.
7. Use of cyanide for pyrite depression.
8. Process improvement due to a water temperature increase brought about by slag granulation in the copper smelter.
9. Recent increase in selenium in the tailings effluent.
10. Potential for an effluent polishing marsh.

LOCATION

The Mine is located just north of Timmins, Ontario. The mill is located 17 miles southeast of the mine and 15 miles east of the center of Timmins.

CLIMATE

Continental with heavy snowfalls in cold winters. There is an average net 17" precipitation annually. Temperatures vary from -40°F in January to 75-85°F in July. Snow accumulations in winter range up to 120".

STARTUP

The first mine-mill operation started up in 1966 just three years after the first drill hole indicated copper-zinc mineralization. The second and third grinding-flotation divisions started up in 1967. Further development milestones are:

1970 : Computer control of reagent addition

1974 : Recovery of pyrite-tin concentrates and startup of a tin plant

1974 : The concentrator is fed entirely by underground ore as the open pit is exhausted.

1975 : Recycling of mill water is implemented.

1979 : Startup of a fourth grinding-flotation circuit to treat an additional 3300 tpd bringing total production to 13,300 stpd.

1982 : Startup of a new copper smelter

Flotation

COPPER-ZINC ORE

After primary grinding to 50 per cent minus 325 mesh, the copper-zinc ore is conditioned with lime, sodium dithiophosphate, MIBC and sulphur dioxide. The lime and sulphur dioxide assist in pyrite and sphalerite depression.

Coarse copper recovery is performed in primary roughers operated at a pulp density of 52 per cent solids and a pH of 6.7 (Fig. 2). The primary rougher tailing undergoes secondary grinding to 80 per cent minus 325 mesh, and subsequent conditioning with sodium dithiophosphate before the secondary roughing stage. Following the secondary roughers, sodium dithiophosphate and sodium isobutyl xanthate are added for copper scavenging.

Three stages of cleaning are performed on the combined primary and secondary rougher concentrates and the first scavenger concentrate. Sodium cyanide is added to the first cleaner for additional pyrite depression. Flotation middlings are reground to 98 per cent minus 325 mesh and recycled to the secondary roughers.

The copper scavenger tailing is conditioned before zinc flotation with sodium isobutyl xanthate, copper sulphate, Dowfroth 250 and lime to a pH of 10.0. Zinc roughing is followed by the addition of more sodium isobutyl xanthate before two-stage scavenging. The rougher and first scavenger concentrates undergo three stages of cleaning after conditioning with lime to pH 10.5. The cleaner tailing and second scavenger concentrates are reground to 98 per cent minus 325 mesh, conditioned with sodium isobutyl-xanthate, copper sulphate and Dowfroth 250, and then recycled to the middle of the rougher flotation bank.

The products are a copper concentrate and a low-silver zinc concentrate. Tables 2 and 3 summarize flotation metallurgy and reagent consumption.

The copper cleaner cells are No. 30 Denver DR machines. All other flotation cells are No. 66 Wemco Fagergren machines.

SILVER-LEAD-ZINC ORE

After rod milling, the silver-lead-zinc ore undergoes closed-circuit primary and secondary ball milling to 75 per cent minus 325 mesh (Fig. 3). Copper flotation is conducted at 40 per cent solids and a pH of 7.6. Flotation is preceded by aeration with sulphur dioxide to depress galena, sphalerite and pyrite, and conditioning with sodium isobutyl xanthate and Dowfroth 250. Copper rougher tailing is treated with sodium isobutyl xanthate and Dowfroth 250 before scavenging. The rougher and scavenger concentrates undergo a three-stage cleaning after the addition of lime to pH 11.5. The first cleaner tailing is pumped to the lead-circuit conditioner. Each subsequent cleaner tailing is recycled to the head of the previous cleaning stage.

Copper scavenger and first cleaner tailings are conditioned with sodium dithiophosphate, sodium isobutyl xanthate, MIBC and soda ash in preparation for lead flotation. The soda ash raises the pH to 8.5. The rougher and first scavenger concentrates are cleaned in three stages. The third cleaner tailing

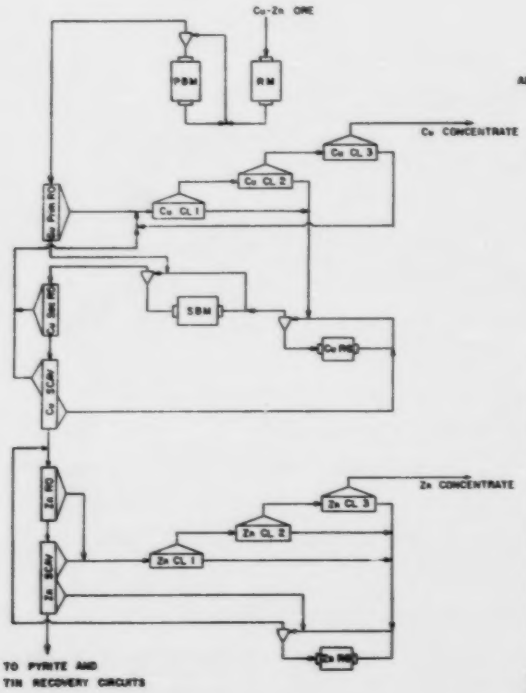


FIGURE 2 — Flowsheet for the treatment of Cu-Zn ore.

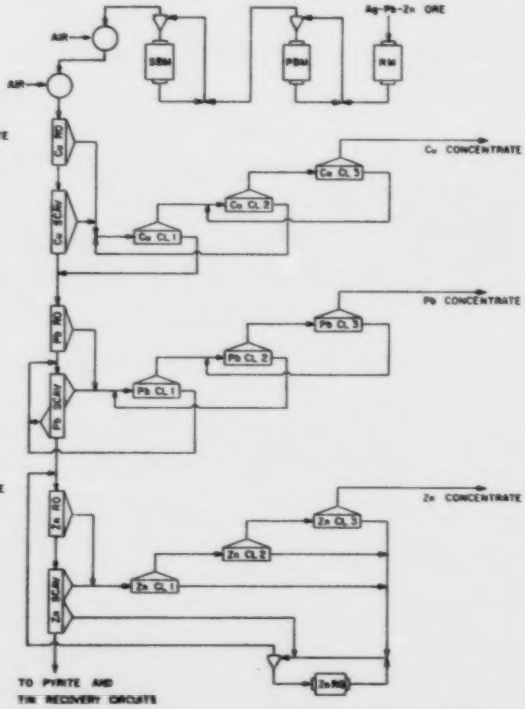


FIGURE 3 — Flowsheet for the treatment of Ag-Pb-Zn ore.

TABLE 2 — Metallurgy (1975)

(a) Cu-Zn Ore	Feed Rate	Assays				Distribution — %			
	tons/day	Cu(%)	Pb(%)	Zn(%)	Ag(oz/ton)	Cu	Pb	Zn	Ag
Head	6693	2.25	—	6.84	1.49	100.0	—	100.0	100.0
Cu Concentrate	592	24.16	—	5.43	13.20	94.9	—	7.0	78.1
Zn Concentrate	733	0.47	—	54.54	1.24	2.3	—	87.3	9.1
Zn Tailing	5368	0.08	—	0.48	0.24	2.8	—	5.7	12.8
(b) Ag-Pb-Zn Ore		**Cu(%)**	**Pb(%)**	**Zn(%)**	**Ag(oz/ton)**	**Cu**	**Pb**	**Zn**	**Ag**
Head	3253	0.43	0.81	9.75	6.44	100.0	100.0	100.0	100.0
Cu Concentrate	28	16.66	6.23	3.97	272.40	33.7	6.7	0.4	36.9
Pb Concentrate	87	5.34	13.83	6.35	53.42	33.1	45.9	1.7	22.2
Zn Concentrate	545	0.43	0.89	50.90	6.80	16.8	18.5	87.5	17.7
Zn Tailing	2593	0.90	0.29	1.27	1.87	16.4	28.9	10.4	23.2
(c) Tin Plant			**Sn(%)**	**S(%)**	**Ag(oz/ton)**		**Sn**	**S**	**Ag**
Head	7738		0.13	11.86	0.89		100.0	100.0	100.0
Pyrite Concentrate	1394		0.12	41.66	2.46		17.0	63.3	49.8
Tin Concentrate	3		35.79	0.06	—		10.4	—	—
Tailing	6341		0.11	5.31	0.54		72.6	36.7	50.2

feeds the second cleaner, while the first and second cleaner tailings and the second scavenger concentrate are recycled to the scavenger cells, to which sodium isobutyl xanthate is added.

Zinc flotation of the silver-lead-zinc ore is similar to that of the copper-zinc ore except that pH is maintained at 10.5 in roughing and 11.0 in cleaning to assist in pyrite rejection.

The products are a high-silver copper concentrate, a lead concentrate and a high-silver zinc concentrate. Tables 2 and 3 summarize flotation metallurgy and reagent consumption.

The copper cleaner cells are No. 24 Denver Sub A machines. All other flotation cells are No. 60 Wemco Fagergren machines.

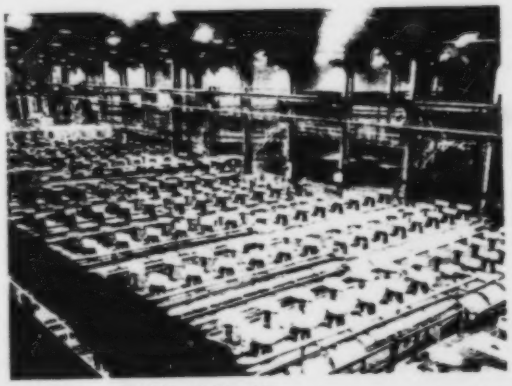


FIGURE 4 — Kidd Creek flotation.

Flotation Control

Flotation grade and recovery are controlled by computer addition of flotation reagents. The reagent control strategy utilizes a computer program to adjust collector addition based on maximum economic efficiency. Copper sulphate addition is based on the zinc content in the zinc circuit feed.

The pH at critical control points is monitored by electrodes immersed in conditioners.

Seventeen continuous samples are required to provide assay information for computer-controlled reagent addition. The sample streams are pumped to head tanks above the X-ray room at a rate of 50 gpm, of which approximately 4 gpm is sampled for X-ray analysis. The overflow from the head tanks is cut once every 20 minutes with a Denver gang sampler for daily wet chemical analysis. Densities of concentrate streams are measured and controlled to improve accuracy of X-ray analysis.

Two ARL PCXQ Model 44000 X-ray units, each capable of handling 15 process streams, assay for lead, zinc, iron and copper concentrations. The X-ray voltages are read by an interface console which provides digital and analog signals to a Modcomp MC II/25 computer. The Modcomp computer converts voltages to assays, and does the necessary calculations to allow pulp densities, assays, recoveries and economic efficiencies to be logged every 12 minutes for copper-zinc ore and every 6 minutes for silver-lead-zinc ore. Alarms resulting from X-ray malfunctions, or out-of-range densities, grades or recoveries are also printed out.

Computer-generated signals for reagent additions are transmitted to a Reagent Interface Panel, where conversion to pneumatic signals for valve control occurs. Four Brooks rotameter control panels with needle valves provide manual flow control when required.

Manually set Moore level controllers control the pulp levels in the flotation banks. The implementation of computer level and frother control is under development to complement the current reagent control strategy.

Mill Control

A central control complex, located between the grinding and flotation sections, monitors and controls all mill functions except concentrate drying. It houses the central control room, the computer room, the rotameter room, the X-ray analyzer room, the instrument repair shop and the shift foreman's office. Plant communications are relayed to and from central control via a public-address system, direct-line and dial telephones, and a VHF linkage is used to communicate between the minesite, railroad, river pump-house and mobile units.

There are eight control panels in the central control room, one each for fine crushing, tin plant, tailings thickener, reagent control and mill services, and three for grinding and flotation. The major equipment items, depicted graphically on flowsheets, are equipped with lights displaying stop, start or fault conditions. Pumps, which must be started locally, are equipped with high-level alarms on their respective pump boxes.

Annunciator alarms indicate high lube oil pressures, bearing and motor winding temperatures, thickener and drive torques, and pressures in gland water systems. Ammeters indicate motor drives and pump loadings. Also present are tonnage totalizers for feed and dried concentrate production as well as pH and density recording at key process points.

Programs responsible for the calculation of X-ray assays, process monitoring and control, and alarm reporting are performed on a Modular Computer Systems II/25 computer. The computer has a memory capacity of 64K words of core storage along with 2.5M words of bulk storage on two Diablo moving-head disks.

All data and alarm messages are logged on KSR-38 and RO-38 teletypes. The system also includes peripherals and a Tectronix CRT to provide access to stored data.

A Centronics line printer, a magnetic tape drive and a second CRT with hard-copy capability are used for on-line programming.

TABLE 3 — Reagent Consumption (1975) — lb/ton of ore

(a) Copper or Lead Flotation

	Cu-Zn	Pb-Zn	
	Cu	Cu	Pb
Soda Ash	—	—	0.75
Lime	0.61	0.12	—
Sodium Isobutyl Xanthate	0.04	0.24	0.009
Sodium Dithiophosphate	0.19	0.009	0.020
MIBC	0.016	0.002	0.003
Dowfroth 250	—	0.027	—
Sulphur Dioxide	1.18	0.74	—
Sodium Cyanide	0.032	—	—

(b) Zn Flotation

	Cu-Zn	Pb-Zn
Lime	1.73	3.61
Sodium Isobutyl Xanthate	0.15	0.24
Copper Sulphate	0.94	1.97
Dowfroth 250	0.013	0.017

(c) Tin Plant (Pyrite Flotation)

Sodium Isobutyl Xanthate	0.25
Dowfroth 250	0.0035
Sulphuric Acid (to leach circuit)	1.18

(d) Tailing Effluent (Neutralization)

Lime	0.63

(e) Concentrate Handling

	Cu	Pb	Zn
Lime	0.70	2.52	0.44
Lignosol	0.24	0.36	0.31
Superfloc	—	0.013	0.008

Tin Plant

Pyrite and tin concentrates are recovered by flotation and gravity techniques from the zinc circuit tailing (Fig. 5). The zinc tailing is deslimed to reduce the reagent consumption in the pyrite flotation circuit and then conditioned with sodium isobutyl xanthate and Dowfroth 250. This is followed by a pyrite flotation circuit comprised of roughing, scavenging and three stages of cleaning at pH 10.2. Roughing, scavenging and the first cleaning are performed on No. 600 Denver DR machines; No. 300 Denver DR machines are used for the second and third cleanings. The pyrite concentrate is thickened in Lamella thickeners and impounded for possible future recovery. Coarse silica particles are eliminated from the pyrite tailings by cycloning and elutriation.

A series of 45 Bartles-Mozley gravity concentrators are the first stage in the gravity process. The Bartles-Mozley tailings are discarded, while the concentrate is sent to Holman slime tables for

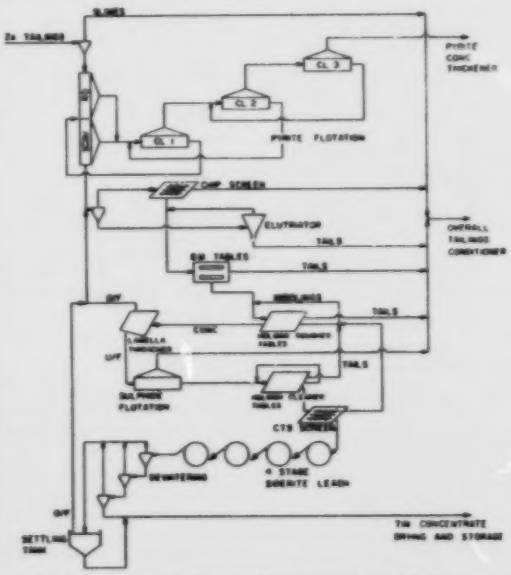


FIGURE 5 — Flowsheet for the recovery of pyrite and tin concentrates.

PRODUCTION

	Lead concentrate
	Silver
130,000 st/year	Zinc
65,000 st/year	Copper metal
65,000 st/year	Copper in concentrates
500 st/year	Cadmium
250,000 st/year	Sulfuric acid

PROCESS

The Kidd Creek concentrator was described by THOMPSON et al. (1978). There are four milling and flotation circuits which treat two main ore types - a copper zinc ore and a silver-lead-zinc ore. The two flotation circuit arrangements are shown below as reported in the CIM book on Canadian Milling Practice. The 1975 reagent consumption is also shown below.

Key flotation reagents used are SO_2 in the front end of the circuit to depress galena, sphalerite and pyrite. Xanthate at pH 7-7.5 floats copper. Dithiophosphate floats galena at pH 7-7.5, finally after addition of lime and copper sulfate to activate the sphalerite, it is floated too.

1. TAILINGS DISPOSAL

Originally a perimeter dike discharge system was employed for tailings disposal, but was revised to incorporate the central discharge of thickened tailings onto a cone as developed by ROBINSKY (1981). Two separate mill tailings products are treated and stored in the tailings area - overall mill tailings and a pyrite concentrate containing silver. The tailings area which comprises three ponds covers 3000 acres and has a rectangular shape.

Kidd Creek Mines employ the Robinsky thickened tailings disposal method. Final mill tailing is pumped 15,000 ft. through two 18 inch pipelines to two 371 ft diameter Dorr-Oliver-Long caisson-type thickeners. The pulp - thickened to 55% solids - is pumped to the spigotting area and discharged so as to build a conical mound in the central tailing area. Thus, the height of the perimeter dike is kept to a minimum.

Outflow from the tailing area is treated with lime before being discharged to a large settling pond where heavy metal hydroxide precipitates are allowed to settle before the decanted effluent is discharged.

By thickening the tailings from 20% solids to around 55% at the disposal site, a considerable amount of water can be reclaimed for reuse, thereby reducing water consumption compared with other tailings systems. About 60% of the water used in the mill is reclaimed from the tailings system.

Figure 1 Comparison of the conventional and thickened tailing disposal systems

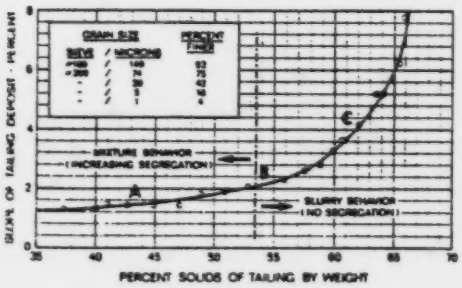


Figure 2 Typical laboratory tailing deposition test results

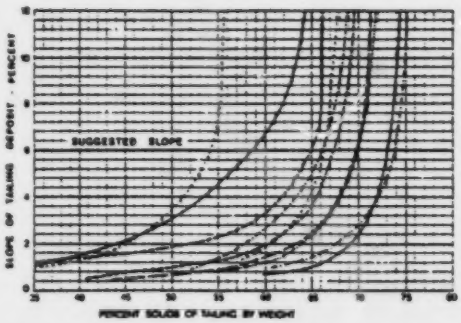
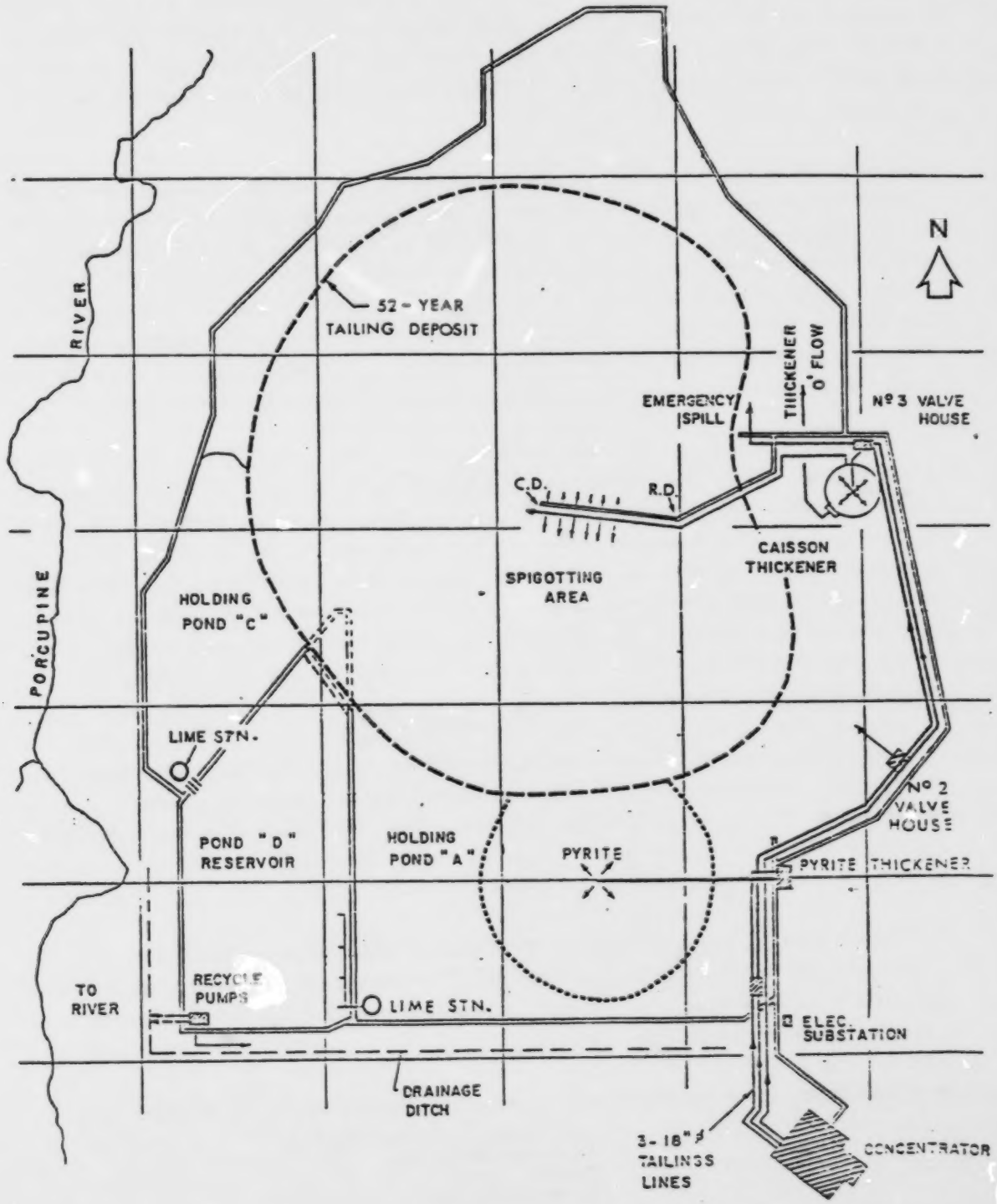


Figure 3 Laboratory test results showing tailing deposition curves. Tailing samples were obtained from different mines

Source: ROBINSKY (1981)



SCHEMATIC PLAN OF TAILING DISPOSAL AREA.

The ROBINSKY technique reduces the initial capital and operating costs of tailings disposal. Reduced seepage to the surrounding environment and maximum evaporation is claimed. Runoff is also optimized and, according to ROBINSKY (1981) dusting is eliminated. The ROBINSKY system also eliminates the need for high and costly dam walls and dikes.

The principle of his design is to discharge thickened tailings from a central point in the tailings impoundment. The tailings flow outward thereby forming a cone with about 6% slope from the center. Thus, more material can be disposed of in the same surface area than when peripheral discharge is employed. Critics of this technique point out the dangers of thixothropic tailings in an earthquake. ROBINSKY counters this by pointing out that in earthquake zones a shallower slope of 4½° can be used. Earthquake effects tests have been simulated by Geotechnical Engineers Inc., Winchester, MA, but, in any case, the Timmins area is a stable continental shield area and not earthquake prone.

This system of tailings is described by ROBINSKY (1981). During a visit to the Kidd Creek tailings site in 1984, there was no apparent dust problem. A recent rainfall had dampened the tailings surface. Plant personnel indicated, however, that during spells of dry weather a considerable amount of dust is generated to the extent of presenting unpleasant conditions when the wind blows toward the plant. Certainly a very large surface area of tailings is presented and a freeze drying surface effect would be expected in winter. The designer claims that since the tailings do not segregate by particle size to the same extent after thickening, capillary rise will be maintained due to the clay particles which should allow the surface to remain wetted.

Although this area may be more compact as claimed, a fair degree of channelling was observed on the surface flow. Also, since the whole surface of the impoundment is active for the full life of the project, it does not present an opportunity for progressive restoration of the area. Restoration must wait until the end of the life of the project when the whole area must be restored in one shot.

Cyanide is used to depress pyrite in the flotation sequence and when the tailings are spread over the thickened tailings cone there is a lot of exposure to sunlight and wind to degrade any residual cyanides. However, cyanide in these tailings is most unlikely to be a problem whatever the tailings system.

More information about the ROBINSKY thickened tailings system can be obtained from:

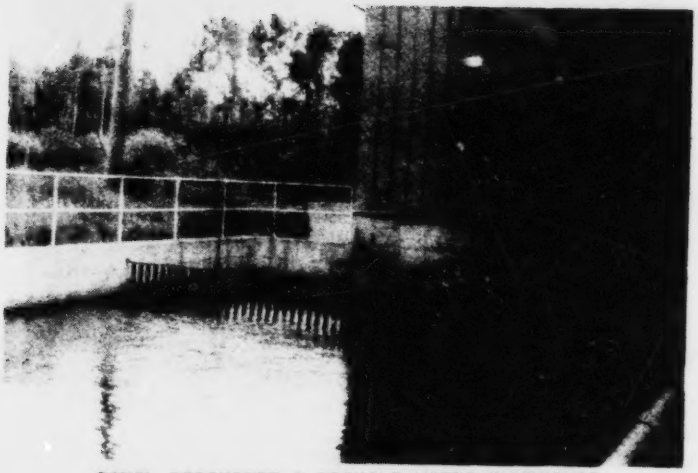
E. I. Robinsky Associates Ltd.
66 Lytton Boulevard
Toronto, Ontario
Canada M4R 1L3

Telephone 481-8384
Contact Dr. E. I Robinsky

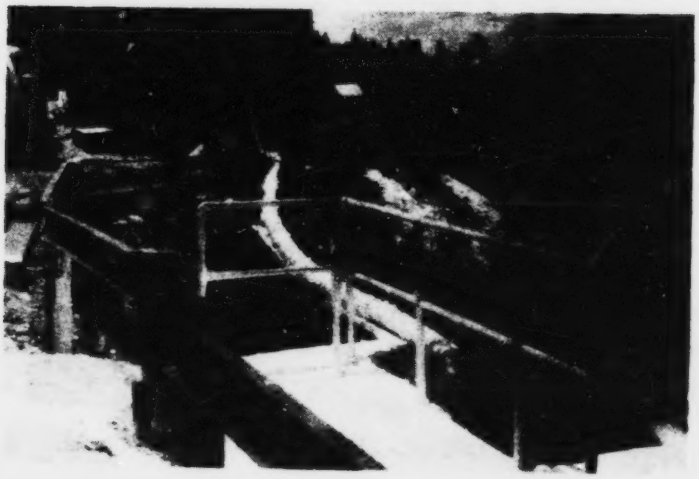
TAILINGS THICKENER AT KIDD CREEK CONCENTRATOR

THICKENED TAILINGS CENTRAL DISCHARGE POINT

CENTRAL DISCHARGE FOR PYRITE TAILINGS



FINAL DISCHARGE & RECYCLE WATER PUMPHOUSE



LIME TREATMENT AND SETTLING STATION

During the 1984 visit to the site, it was noted that problems have been experienced with a leak in one of the caisson tailings thickeners. Concrete tailings lines have been replaced by schlairpipe (polyethylene) lines and the operators were struggling with line blockages and pipe bursts for reasons that were not established.

Because pyrite has been separated (90% recovery) from the bulk of the tailings, the potential for acid mine drainage from this impoundment will be much reduced (but not eliminated). This will make the final restoration and revegetation of the tailins impoundment a lot easier,

2. DISPOSAL/STORAGE OF LARGE VOLUMES OF PYRITE CONCENTRATE

A 33% pyrite concentrate is separated in the flotation circuit and pumped to a second thickened tailings impoundment with a central discharge point. Although THOMPSON et al. (1978) refer to lamella thickeners for the pyrite, none were observed during the plant visit in 1984. It is believed that pyrite being so dense, settles readily and dewaters in a cone shaped tailings pile allowing decant water to be collected on the periphery of the impoundment.

The pyrite concentrate contains about 2.3 oz Ag/st and is the subject of a project to determine the best metallurgical approach. Apparently about 1 ounce of silver per ton can be leached by conventional cyanidation.

The final disposition of the pyrite concentrate is still not clear. It is possible that these will one day be treated to recover silver in the future if a profitable process can be developed, at which point the pyrite will be disposed of in a permanent fashion.

A cursory inspection of the pyrite concentrate, stockpiled using the Robinsky central discharge method, revealed that the surface of the pyrite was stable enough to walk on. Surface oxidation was occurring as was evidenced by the fact that the odor of SO_2 could be detected in the air and even the cattails in the peripheral decant water ponds appeared to have a struggle staying alive.

While on the one hand the pyrite tailings have been segregated into a smaller (but still extensive) impoundment than the main tailings, reducing the potential for acid mine drainage from the main impoundment, there remains the question of potential for acid mine drainage generation from the smaller pyrite concentrate impoundment.

At this point in time while the plant is still in operation and the tailings are still active, AMD is not a problem at this site. The question only arises with respect to ultimate disposal of the pyrite. In this respect, possibly the Robinsky central discharge concept has some advantages if the peripheral ponds can be limed or covered in ground limestone

and converted to a large aquatic ecosystem designed to clean up the AMD that would collect in them. Being located in the perimeter of the impoundment, the potential exists to create a very large engineered bog to filter out metal hydroxides with hopefully minimal maintenance needs.

According to MARSHALL (1979) the water that decants from the pyrite concentrate impoundment contains up to 14 ppm Zn, but this solution drains to a lime station after which it mixes with decant from the main tailings area.

SULFIDE TAILINGS DISPOSAL STUDY

CANMET is undertaking an industry cooperative study to develop improved ways of disposing of sulfide mine tailings. Sponsors of the study include:

COMINCO	Walter J. Kuit
NORANDA	Bruce Wallace
KIDD CREEK MINES	Colin Chapman
INCO LTD,	Norm Paterson, Bob Butler

More information can be obtained from:

CANMET
555 Booth Street
Ottawa, Ontario
Canada K1A 0G1

Telephone (613) 995-4194
Contact Eddie Joe

3. WATER MANAGEMENT AT A LARGE MILL-REFINERY-SMELTER-TAILINGS COMPLEX

At the Kidd Creek mill site there are four milling and flotation sections, a zinc roaster and electrolytic refinery, a copper smelter and two acid plants.

The Kidd Creek metallurgical facility is located in a net precipitation climate which means that zero discharge is not a reasonable goal. To treat 13,000 tpd ore, a total of 11.50 mm US gallons of water is discharged to the Porcupine River. (43,560 m^3/d = 3.60 m^3/ton ore)

About 9,500 US gpm (51,800 m^3/d) fresh water is drawn from the Frederickhouse River and 9000 US gpm (49,000 m^3/d) is reclaimed from the tailings area decant system for use in the concentrator and the copper plant. Four pumps installed at the Frederickhouse River can deliver up to 10,000 igpm water through a 5 mile 28 inch Ø corrosion protected all welded steel pipeline to a 750,000 gallon raw water storage tank.

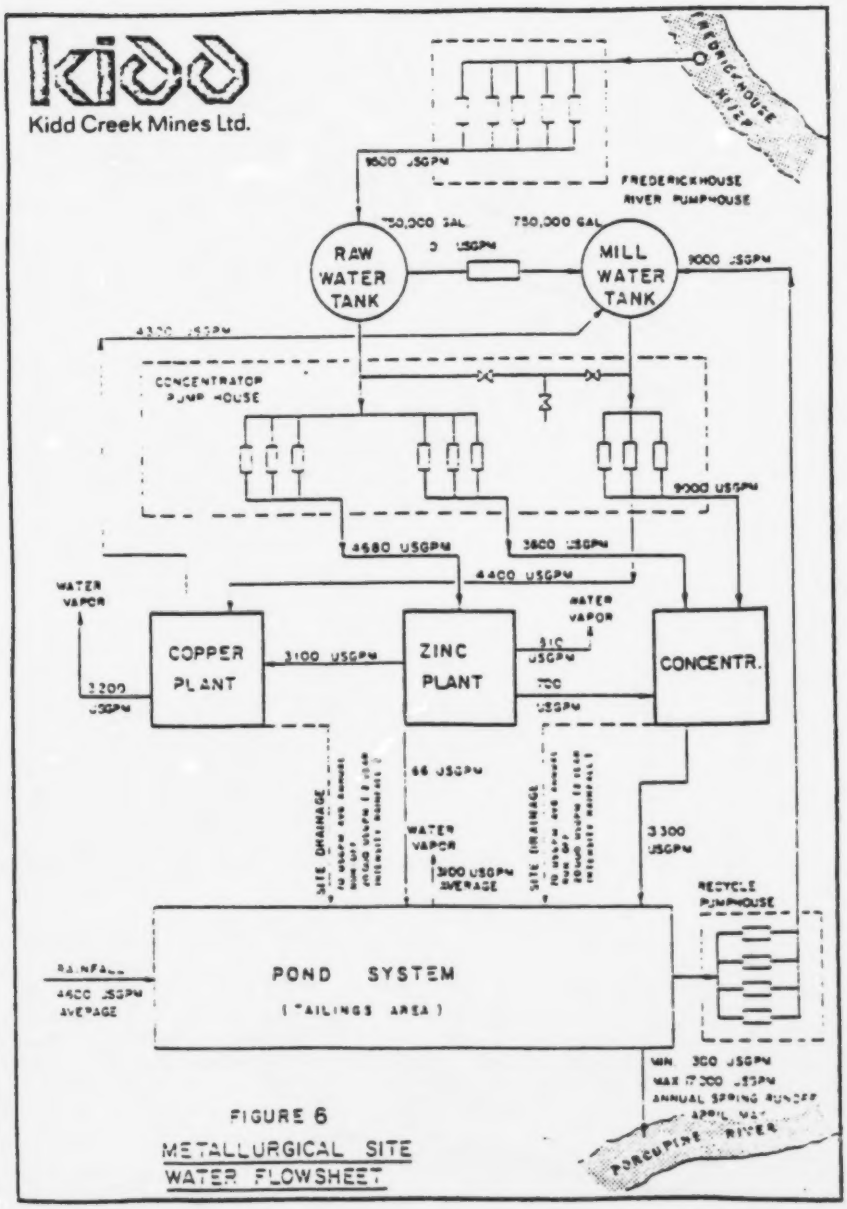
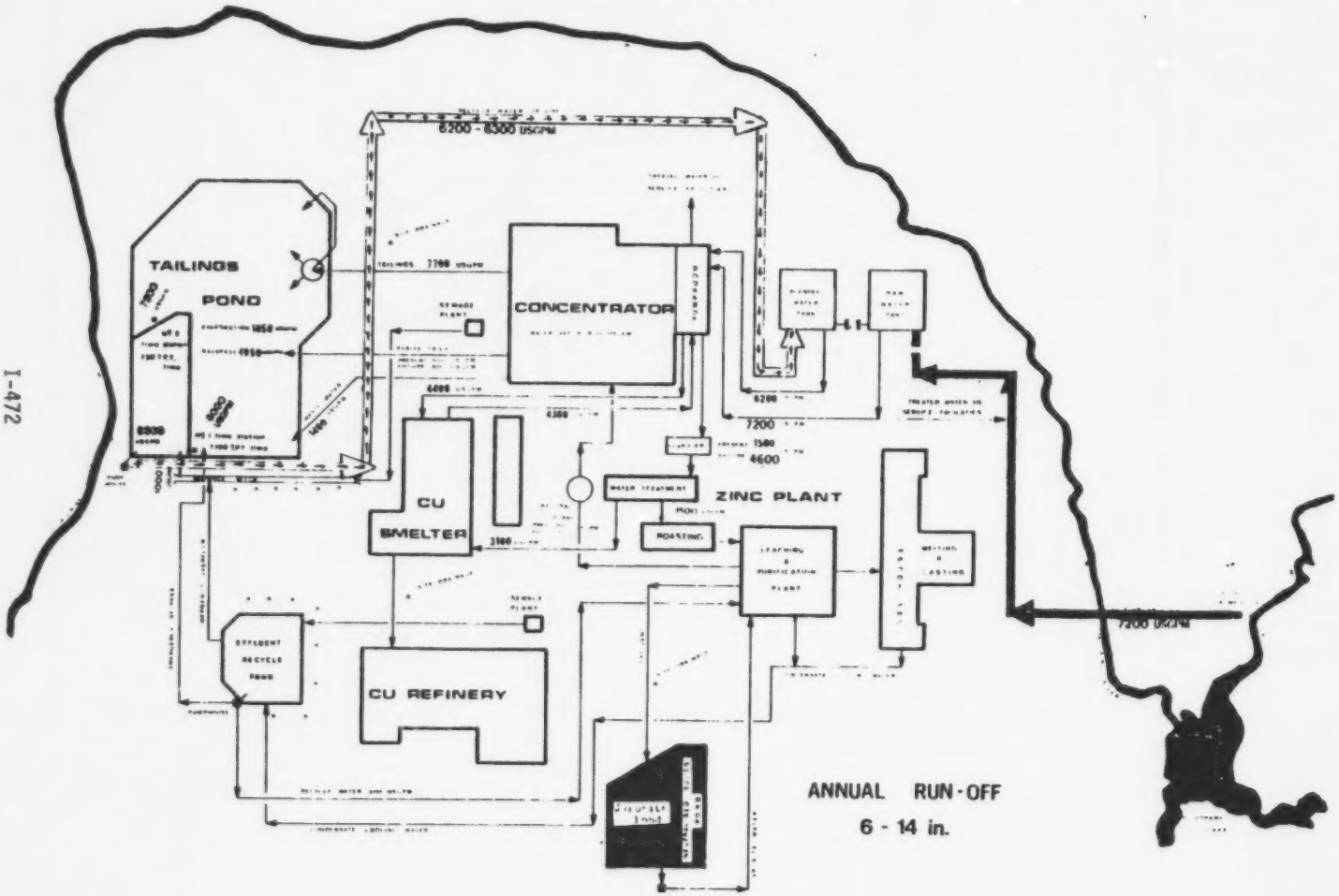


FIGURE 6

METALLURGICAL SITE WATER FLOWSHEET

TEXASGULF CANADA LTD.

METALLURGICAL SITE
SCHEMATIC OF WATER USAGE
AND LIQUID EFFLUENTS



LAFOREST et al. (1983) make the statement,

> "Since 1975 water conservation at the metallurgical site has been given high priority. With the expansion of existing facilities and the construction of the new copper smelter, a complete study was made of anticipated water usage to determine the most effective method of minimizing our water consumption. From this study a new water flowsheet for the site was developed. This led to the construction of a pumphouse to recycle water from our tailings ponds and the use of cooling towers to recycle water from the Hazlett casting machine, acid plant coolers, compressors, furnaces and the converting slag granulation. Slag granulation water is returned to the concentrator where the higher temperature further improves metal recovery."
>
> "The implementation of this new water distribution system has significantly decreased the fresh water requirements, reduced the amount of effluent discharged into the Porcupine River and minimized capital expenditures for the water management system expansion."

The 1982 water balance for the metallurgical site was:

Fresh water	6.9×10^6 US gpd	26,136 m^3/d	2.16 m^3/t ore
Recycle water	7.5×10^6 US gpd	28,410 m^3/d	2.34 m^3/t ore
Discharge *	11.5×10^6 US gpd	43,560 m^3/d	3.60 m^3/t ore

* Discharge includes surface runoff from the 3600 acre drainage area.

Use of 2.16 m^3 fresh water per t ore treated (which includes both milling flotation, tailings discharge and the smelting and refining operations including the acid plants), is relatively water efficient. In the Kidd Creek climate, water is not exactly a scarce commodity and the general principle of "The amount of water needed for a metallurgical facility is proportional to the amount available." is indicated.

Nonetheless, the discharge of a further 3.60 m^3/t ore treated to the Porcupine River indicates that there is a significant potential to recycle considerably more water - possibly avoiding the need for any fresh water from the Frederickhouse River. However, in considering the overall achievements with respect to environmental control at the site and reported analysis of the effluent, there would not seem to be an economic incentive to recycle more water which would increase pumping costs and might require some additional water treatment steps to make reclaimed water more suitable for all uses in the plant.

A degree of macro-recycling occurs in that water discharged to the Porcupine River eventually returns via Nighthawk Lake to the Frederickhouse River from which the plant draws its fresh water. Ultimately the Frederickhouse River flows north into James Bay.

ZINC & COPPER PLANT PROCESS WATER AND POTABLE WATER

A plant treats 3200-3600 US gpm of raw water for zinc plant consumption and potable water for the whole facility.

Raw water is first clarified in a 60' Ø x 15' straight Ecodyne reactivator followed by six sand filters. Sand filter discharge is stored in a 1.25 million gallon storage tank, and is used for plant service water.

Service water also provides feed to the demineralizing train which produces process water and boiler feed water.

Demineralized water is generated by ion exchange for leaching the zinc calcine as the electrolytic process is sensitive to metal impurities other than zinc.

ZINC PLANT WATER MANAGEMENT

All waste water and drainage water from the zinc plant area is collected in an effluent recycle pond and recycled for process water in the zinc plant. This pond also collects any contaminated drainage water from the new copper smelter. A neutralization plant and clarifier have been installed to treat any excess water and to return it to the concentrator for use or disposal through the tailings system. The liquid effluent from the containment pond for "jarosite" (mainly iron hydroxide but rich in zinc and other metals) is returned to the zinc leaching plant for recycling as process water.

COPPER SMELTER WATER MANAGEMENT

Water requirements for the copper smelter are primarily for cooling, temperature control of the furnaces, slag granulation and treated feedwater for the waste heat recovery boilers. All water used by the copper smelter and refinery operations is contained, recycled internally or recycled through the concentrator.

JAROSITE POND

The jarosite and neutralized solids ponds were modelled after the central discharge tailings area. Jarosite is discharged from selected points along the center dike separating the two ponds.

Originally the rate of neutralized solids production was expected to be about half of the jarosite production. Hence, the total pond area is divided 1/3 for neutralized solids and 2/3 for jarosite. By discharging evenly from both sides of the central discharge dike, this dike would be supported by solids building up equally on each side. However, neutralized solids production was dramatically reduced early on by recycling the

neutralization thickener underflow to the neutralizing circuit. Consequently a gravel counterbalancing berm had to be constructed along the central dike.

The jarosite pond is lined with natural clayey material that occurred at the site and according to SWEET (1980) the buildup of jarosite increases the impermeability.

Jarosite pond water typically analyses :		
	pH	2.7
	zinc	9300 ppm
	iron	100 ppm
	copper	100 mg/l
	lead	1.1 mg/l
	cadmium	46 mg/l

The perimeter dikes are designed to minimize any seepage of this water to the surrounding swamp. SWEET (1981) discusses the design of the jarosite pond and the neutralization solids pond, and provides several interesting comments on the design of such installations.

FIRE WATER SYSTEM

The plant's fire water pumps are also located at the main pumphouse located at one of the two 750,000 gallon (3000 m^3) water tanks. If necesary the fire fighting pumps can draw water from both storage tanks to supply five water mains, hydrants and sprinkler systems.

4. EFFLUENT TREATMENT BEFORE DISCHARGE

Clear decant solution from the peripheral collection system of the tailings site is treated with lime and then collected in a large holding pond. About 1800 tons per year lime is used to treat an average flow (including runoff) of 14,000-15,000 US gpm (75,000-80,000 m^3/d) of water.

Lime addition is controlled to keep the zinc level below 0.3 ppm which it is found equates with total heavy metals generally under 0.5 ppm to meet the 1 ppm guideline requirement.

At the discharge point from the holding pond, a pumphouse with 3 pumps capable of recycling 9000 gpm (5000 m^3/d) through 24" schlairpipe has been installed, to feed the 750,000 gallon storage tank at the concentrator. Water that is not recycled overflows the intake chamber for the recycle pumps and is discharged through a weir to the Porcupine River. Discharge varies from almost nothing to 20,000 gpm (109,000 m^3/d). The use of a plastic reclaim water line and plastic coated storage tank and FRP internal piping avoided many of the corrosion problems that can occur when reclaim water is used.

Although the tailings thickener overflow is discharged to the perimeter pond around the tailings pile at pH 9-10, oxidation of thiosulfate in summer results in a pH drop to 3.5-4.0. In winter, however, the pH drops to around 7 by the time the water reaches holding pond "C" ahead of the lime station.

PROVISION FOR SPRING RUNOFF - HEAVY RAINFALL

During spring runoff, or if there is an unusually heavy rainfall, the catchment pond around the plant might overflow. Overflow water is then collected in a drainage ditch, collecting uncontaminated surface drainage water from the concentrator and service building areas. This water is then directed through a culvert to pond "D" where it is mixed with lime and treated water from #1 lime station.

Some years ago the area experienced a phenomenal deluge known as "the Timmins Storm" which is now used as the standard for tailings impoundment design in northern Ontario.

ENVIRONMENTAL CONTROL AND MANAGEMENT

An important part of the management of water in a large integrated mill-tailings-concentrator-refinery-smelter system is the control of the environment. An important aspect of environment control is the quality of water that is discharged as an effluent.

LAFOREST et al. (1983) have successfully shown how air pollution control and water pollution control are interrelated. Through very good air emission control, the distribution of heavy metal particulates over the site and drainage area is kept to a minimum. This undoubtedly has as much of a positive influence on the quality of aqueous effluents from the site as the management of water quality per se, especially one with a 3600 acre drainage.

In order to manage the quality and quantity of the final discharge from the site holding ponds, measuring and sampling stations and treatment facilities have been incorporated into the design of the tailings impoundment area. The final discharge is monitored on a daily basis for pH, suspended solids and dissolved heavy metals concentration. In addition, individual effluents from the plant are spot sampled at source to detect abnormal conditions.

The following Table shows a six year analysis summary of the final effluent and indicates that no significant differences have occurred in the water quality since startup of the copper smelter. The cumulative concentration of heavy metals is well within the guideline of 1 mg/l.

WATER QUALITY MONITORING
ANALYSIS OF FINAL EFFLUENT

	Flow m^3/min	pH	S/S mg/l	Copper mg/l	Lead mg/l	Zinc mg/l
1982	30.2	8.4	10	LT 0.1	LT 0.1	0.3
1981	30.9	8.4	10	LT 0.1	LT 0.1	0.1
1980	31.4	7.6	20*	LT 0.1	LT 0.1	0.3
1979	30.6	7.2	10	LT 0.1	LT 0.1	0.3
1978	22.8	6.6	10	LT 0.1	LT 0.1	0.3
1977	19.2	6.7	10	LT 0.1	LT 0.1	0.5

LT = less than

* Suspended Solids in the fresh water intake frequently exceed the 15 mg/l guideline that Kidd Creek effluent must meet.

Clear peripheral decant solution is treated with lime to reduce the zinc content to 0.3 ppm before the solutions flow to a large holding dam.

BIOLOGICAL SAMPLING

LAFOREST et al. (1983) describe a diverse biological program at Kidd Creek's metallurgical plant. The program consists of benthic fauna sampling, bioassay testing, mossbag surveys, rain, snow, soil and vegetation sampling. A buffalo herd is maintained immediately adjacent to the south boundary of the metallurgical plants as a token of the company's continued desire to be a good citizen.

Benthic fauna surveys are conducted on the Porcupine River system to examine the impact of Kidd Creek's tailings discharge on bottom dwelling organisms. Such surveys have been conducted since 1971 at various locations upstream and downstream of the tailings discharge. Water quality can be assessed by the presence and relative abundance of certain indicator species which are known to be sensitive, moderately tolerant or tolerant organisms. Results over the last twelve years indicate that the effect of so large a metallurgical plant on the aquatic environment has been minimal.

Although slight increases in sulfates, total solids, total hardness, calcium and zinc concentrations are noted immediately downstream from the discharge, these concentrations return to normal levels within four kilometers of the discharge. The fact that similar populations of macroinvertebrates are found upstream and downstream of the discharge indicates that the tailings discharge has no lasting significant effect on the Porcupine River system.

TYPICAL ANALYSIS OF METALLURGICAL SITE WATER

LOCATION OF WATER SAMPLES	pH	Total Solids ppm	Susp. Solids ppm	Sulphates ppm	Ca ppm	Fe ppm	Cu ppm	Pb ppm	Zn ppm	NH_3	HG ppb
Raw Water From Frederickhouse River	8.5	224	52	-10	27	4.9	-0.1	-0.1	-0.1	-	-
Upstream Porcupine River	7.6	458	0	210	-	-0.1	-0.1	-0.1	-0.1	-	-
Drainage Water From Rock Tailing Storage Area Before Liming	2.7	950	2	575	-	3.0	-0.1	-0.1	0.3	-	-
Drainage Water From Pyrite Tailings Storage Area Before Liming	4.0	-	-	-	-	-	-	-	14.0	-	-
Surface Drainage Water	7.5	-	-	-	-	-	-	-	2.0	-	-
Treated Waste Water Discharged to Porcupine River	6.0	995	8	771	-	0.3	-0.1	-0.1	0.1	0.5	-1
Downstream Porcupine River	7.6	652	3	450	-	0.1	-0.1	-0.1	-0.1	-	-

SOURCE: MARSHALL (1979)

Bioassay Testing

The 50% survival requirement for rainbow trout in the static 96 hour bioassay test has consistently been met since 1977 when the tests were started according to LAFOREST (1983). Apparently, since their paper, there was a short period during which the LC50 96 hour test was marginal, but this was suspected as being the result of faulty trout from the hatchery. Nonetheless, since then, the LC50 test results have returned to normal.

Mossbag Surveys

Mossbag surveys were started in 1980 and are a relatively new means of monitoring airbourne heavy metals deposition. Heavy metals are efficiently adsorbed and retained on moss by an ion exchange process in amounts directly proportional to exposure regardless of meteorological conditions, and are used as semi-quantitative indications of heavy metals in the atmosphere.

Mossbags have distinct advantages over vegetation sampling because moss is similar to epiphytic organisms in that the possibility of contamination via root uptake is eliminated. The method is described by LAFOREST et al. (1983).

The Mossbag results indicate a pattern of copper, zinc, lead, iron, cadmium and arsenic fallout around the metallurgical site which return to background levels within 2 km. Levels of 4000 micrograms copper per gram of moss per month are, however, measured in the immediate proximity of the copper smelter.

Kidd Creek Mines Ltd. designed their operations with environmental protection in mind even before effluent treatment was a regulatory requirement. Perhaps because the operation has had such a good track record in the past, people at the Kidd Creek operation are more aware of their company's interest, than they are of the details.

5. EFFECT OF WATER RECYCLING FROM TAILING TO THE MILL ON METALLURGICAL RECOVERY

Based on data provided by MARSHALL 1979) the water draining from the main tailings area before and after liming has the following composition:

	Before Liming	After Liming
pH	2.7	6.0
TDS ppm	950	995
S/S	2	8
$SO_4^=$	875	771
Ca	-	-
Fe	LT 3.0	0.3
Cu	LT 0.1	LT 0.1
Pb	LT 0.1	LT 0.1
Zn	LT 0.3	0.1
NH_3		0.5
Hg ppm		LT 1.0

Water is recycled to the mill after liming. The TDS of this water is relatively low at 995 ppm, and although the $SO_4^=$ is 771 ppm and calcium and magnesium levels not shown, it appears that these are low enough not to be a major concern in the flotation separation and recovery of sulfides. Although 60% of the water used in the concentrator comes from the tailings water reclaim station, it must be remembered that it is significantly diluted by precipitation and that it has been neutralized and aged prior to return to the plant.

$SO_4^=$ apparently in the levels encountered does not seriously affect flotation performance at Kidd Creek. $SO_4^=$ balance is however critical in the electrowinning tankhouse. $SO_4^=$ is bled from the system with jarosites. CHAPMAN (1985) confirmed that recycle water quality has no noticeable effect on metallurgical recovery.

$S_2O_3^=$ (thiosulfate) generated through SO_2 addition is needed to achieve a selective copper float after the grinding step. The $S_2O_3^=$ depresses pyrite and sphalerite.

The presence of sulfate and carbonate (the latter due to carbonate addition as soda ash) will precipitate lead from solution effectively.

PERMITTING

In 1984, effluent and operating permits at both the mine and metallurgical plant sites were reviewed and approved without changes. This is an indication that the regulatory authorities are satisfied with the measures adopted at the site.

ULTIMATE DESTINY OF HEAVY METALS

Kidd Creek Mines Ltd. sell their anode slimes after these have been deleaded. These contain up to 45% Ag, under 5% Pb, 30-45% Se and 1% Cu. The slimes are sold to processors in Europe and to Noranda.

Heavy metals and indium are also tied up in the jarosites. Flue dusts containing indium, cadmium, copper, lead, zinc and silver are generated.

Precipitated heavy metals as hydroxides are left in the tailings material and in the settling pond after the lime station.

Cadmium leaches from the calcine with zinc and is precipitated from solution using zinc dust ahead of the electrolytic tankhouse. This drops cadmium from about 0.02% in the electrolyte. The precipitated cadmium sponge is treated to yield a cadmium product.

6. THIOSALTS

Tailings are discharged to the Robinsky impoundment system at pH 9-10. By the time the solution decants to the lime addition plant, it has dropped to pH 7 in winter and pH 3.5 in summer, presumably due to oxidation of thiosulfate. After lime addition to pH 10.5, the decant solution is aged in a holding pond where the pH drops again and in which metal hydroxides settle out.

7. USE OF CYANIDE FOR PYRITE DEPRESSION

Sodium cyanide is believed to be used for pyrite depression in the zinc flotation tailings. However, to be effective for this purpose only a small dose would be needed. Using computerized control of the flotation circuits, cyanide addition is very carfully controlled based on the amount of pyrite left in the zinc concentrate. Cyanide is added to achieve a surface effect so the cyanide is tied up on the solid particles. If there is any residual cyanide in solution it would likely be removed from solution on the Robinsky tailings over which the solution decants in a thin layer. More likely cyanide will be "fixed" on the particle surfaces.

8. PROCESS IMPROVEMENT DUE TO WATER RECYCLING

When water temperatures drop, it is believed by the operators that copper recovery drops. Although there is no firm data to prove this, it is believed that when the copper smelter slag granulation water is recycled to the flotation plant that the slight increase in temperature results in an improvement in recovery.

600 tpd of granulated slag is generated. Originally this was to be ground and used to substitute for cement in the backfill. However, because of the way it is made and the composition (low Ca and Ferrous^{++}) it does not have the anticipated pozzolonic effect. The slag is now used to construct berms for the tailings dams.

9. SELENIUM

Recently, selenium levels in the ore have increased. Selenium occurs with pyrite, mainly in the copper minerals, and with the sphalerite in solid solution.

Apparently selenium levels in the final effluent have been reaching levels around 0.3 ppm which have made it necessary to start seeking ways to remove it.

One method under review is to intercept the smaller effluent stream in the plant that is the main contributor of selenium so that this source of selenium can be removed.

One or two methods for selenium removal from solution are discussed in the volume on Contaminant Removal.

SEWAGE

There are two sewage treatment plants on the metallurgical treatment facility. The sludges from the septic system are occasionally pumped with the tailings to the pond but the volume of this material is not enough to make an impact.

10. POTENTIAL FOR EFFLUENT POLISHING MARSH

Although base metal level averages in Kidd Creek effluent discharge meet the regulated limits, no data on day-to-day analyses were reviewed. Physical examination of the site and treatment system indicated that the simplest of lime addition systems is employed. The site is located in an area of flat swampy land which would lend itself ideally to the development of a large meander system with an engineered bog in which aquatic plants and algae could be grown to polish the effluent. Such a bog would, of course, be functional in summer only. It would serve to remove suspended metal hydroxides and potentially also remove dissolved metals through metabolic uptake. In addition, as the ecological system recycles over several seasons the rotting vegetation in the lower levels will generate small amounts of "marsh gas" H_2S which can be expected to precipitate metals to lower levels still as sulfides. Examples of such working bogs are to be found at AMAX's Buick Mine, a St. Joe Minerals mine in New York, and at Falconbridge, Ontario.

BRIERLY et al. (1984) discusses partial biological removal of Selenium from acidic uranium mill effluents in New Mexico. It is expected that there would be a good chance that selenium would also be polished - possibly more effectively - by a mature aquatic bog system. This is a RANDOL speculation, however, based on the fact that selenium is efficiently polished by sulfide addition even though it does not itself form a sulfide.

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TELEPHONE	(303) 349 6681	
CONTACTS	Chris Harnish	Site Manager
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COMPANY	CLIMAX MOLYBDENUM COMPANY Division of Amax Inc. 1707 Cole Boulevard Golden, CO 80401	
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CONTACTS	W. W. Bilhorn	President
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	Gary G. Van Riper	Deputy Director, Environmental Control

INTRODUCTION

When AMAX discovered the Mount Emmons molybdenum orebody in the 1970's, it was expected to bring it into production. In order to gain access to the ore to draw a bulk sample for metallurgical testing, AMAX acquired the adjoining zinc mining property known as the Keystone Mine. This mine had ceased operation some years before, but the site was in need of reclamation.

When AMAX purchased the Keystone Mine, they inherited all the environmental problems of the property including four tailings ponds and acid mine drainage from the workings above. The tailings ponds were unstable, and in fact one had failed.

After stabilizing the Keystone site, a water treatment plant was installed to treat water from the Keystone operations.

The $12-14 million spent on site stabilization and water treatment is relatively small compared with the $700-800 million expected investment for mine development. For its current job, the plant may be excessive, but at the time it was installed, it was a demonstration of exceptional commitment to improve water quality from the site in support of the planned development of a new molybdenum mine.

AMAX's work at Mount Emmons has involved the reclamation and revegetation of the Old Keystone Mine and tailing pond complex. A water collection and treatment system utilizes the heavy metals removal plant seen at bottom right.

The molybdenum ore body, which AMAX proposed to mine, lies 1200 feet below the square-topped summit of Mount Emmons.

After installing the water treatment plant, the decision to proceed with development of the molybdenum mine and mill was put on hold. The water treatment plant continues to treat water from the Keystone mine site as described below.

The Mt. Emmons water treatment facility is of interest for several reasons:

1. It is the most recent AMAX water treatment installation incorporating the SWIFT LECTROCLEAR flotation process to remove precipitated metal sludges by special coagulation around gas bubbles and microfiltration. It provides insight into the performance of a third generation plant design of this type.

2. It is an example of the kind of capital investment required for water treatment if the decision is made to "go whole hog" to satisfy environmental pressures.

3. Before the AMAX site reclamation and water treatment plant was installed, the receiving water, Coal Creek Canyon, was a dead stream. Today it supports trout.

4. The application of LECTROCLEAR flotation is a demonstration of a successful adaptation of a process developed for one industry (meat packing waste removal from effluents) to another.

5. Zinc is reduced from 125 ppm to 0.05 ppm Zn in this plant i.e. 99.96% removal which is an excellent performance.

Items of special interest at the facility are:

- Performance of the Swift Lectroclear process.
- Belt press dewatering of heavy metal sludges.
- Cement stabilization and disposal of sludges.
- General management philosophy and safeguards against performance failure.

This plant received the National Environment Industry Award for the Application of Advanced Environmental Technology in 1981 and 1983.

PLANT LOCATION

The Keystone Minesite is now known as the Mount Emmons operation of Climax Molybdenum Company and is located 3½ miles up Coal Creek from the town of Crested Butte, Colorado, at an altitude of 11,000 feet.

CLIMATE

High altitude Rocky Mountain climate with heavy snowfalls and snow cover from late October to May. Some years experience in excess of 400" snow.

CAPITAL INVESTMENT

Site reclamation, stabilization of existing tailings pond, appropriate drainage diversions, etc., cost $1.9 million.

The water treatment plant required an investment of a further $10.9 million.

OPERATING COST

$750,000 - $1 million per year

DESCRIPTION

1. Four existing Keystone Mine tailings ponds were reclaimed. The dam walls were strengthened; the tailings were covered, contoured, and seeded. Seepage from the four ponds is collected via a series of underground pipelines to a central pond.

   All four of the original tailings ponds were covered with minewaste from exploratory drifting during the evaluation of the molybdenum deposit. The wasterock was rich in clays, particularly bentonite. A geotexile covering was placed over all four tailings sites. Three of the sites were then covered with soil, lime, fertilizer, and sewage sludge and reseeded. Tailings dam No. 4 was compacted for use as a yard and storage area after the surface was sealed. Seeding was carried out using a hydromulcher.

   Surface drainage from undisturbed and/or reclaimed areas is collected by appropriate contouring and is discharged to the creek bypassing the water treatment plant.

   The reclaimed tailings dam toedrain seepage is collected at a rate of 0-150 gpm. It has a pH of 2.5-4.0 depending on seasonal dilution effects. This water has a high heavy metals content including, typically, 125 ppm Zn.

2. The Old Keystone Mineworkings

   All mine buildings were removed and the site cleared except for the few that were needed for maintenance and for the exploration operation.

Mine drainage leaves the excavations at a single point where flowrate is measured across a Parshall Plume. Flowrate of minewater varies between 180 and 540 gpm (540 gpm is the maximum measured since 1981).

This water has a total heavy metal loading ranging between 380-800 ppm.

The original Keystone water collection dam used to hold water with 9,000-12,000 ppm TDS and is very high in heavy metals.

This pond was enlarged and sealed. It has a capacity of 8 acre feet.

This pond presently serves as an emergency surge pond for seepage collection from the tailings ponds, and its contents are gradually blended into the water treatment plant feed.

An interceptor canal was constructed along the entire northern edge of the affected area to intercept and divert hillside runoff water, which is now discharged via a drop station at a point downgrade from the heavy metals pond into Coal Creek.

3. Water Management System

The water treatment consists of the following:

- Parshall Plume flow measurement station.
- Concrete lined settling ponds to drop grit from mine drainage.
- Concrete lined equalization ponds fitted with an air sparging system.
- Heavy metals removal plant described in detail below.
- Sewage plant.
- Retention pond with bypass possibility to Coal Creek.
- Pumps and pipelines to divert treated water to the surge pond if it does not meet effluent discharge limits.
- A potable water supply.

DISCHARGE PERMIT

Since the Mount Emmons plant discharges to a river, an NPDES (National Pollution Discharge Elimination Service) permit is required. The State of Colorado administers the NPDES discharge permit on behalf of the EPA. This is done by the Colorado Department of Health.

These limits are shown in the following table. It is clear that for some elements, e.g., As (0.05ppm), Cadmium (0.015 ppm), and Mercury (0.05 ppb), these limits are very low indeed.

The residual chlorine limit at 0.002 ppm is also very low.

The levels set for the limits are based on ambient levels in the Rocky Mountain streamwater which for some elements are below detection limits achievable by routine analytical techniques.

FLOW CONTROL

Initially there was only a very small retention dam at the Keystone Mine site. Included in the implementation of the wastewater management system was the provision of additional surge capacity to even out flows subject to treatment as a result of precipitation and/or snowmelt. However, due to limited areas available for this surge capacity, the treatment plant itself can accommodate a range of flows from 220 to 2200 U.S. gpm of which the mine drainage is the greatest and most variable contributing flow. Interestingly enough, the minewater flowrate peaks in July, about one month after the spring runoff.

FLOW MEASUREMENT

A 9" Parshall Plume is located at the degritting pond at the head of the process. It is fitted with a Robertshaw Level Probe.

PLANT CAPACITY

The Mount Emmons plant was designed to treat 2200 U.S. gpm and to handle a flowrate varying from 220 to 2200 U.S. gpm. The highest flow rate that it has handled to date has been 1750 gpm although the operators believe it could handle 2000 gpm.

When the flow rates reach their maximum, the metal loadings drop--this helps.

The primary constraint in plant capacity is sand filtration which can become clogged if the flotation cells are not operating at peak performance.

The flotation units were designed for 97% metal removal at design feedrate with 1000 ppm TDS. After installation, the best achievable was 97% solids removal from 480 ppm TDS. Subsequent innovations allowed 98% solids removal at 700 ppm solids.

At low flow season the plant can be shut down for one shift. During high flow season, all units may be operated as necessary for 24 hours a day, seven days a week.

EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

During the period beginning immediately and lasting through June 30, 1984 the permittee is authorized to discharge from outfall serial number 001, the final outfall from the wastewater treatment facility as referenced in Figure 2, page 20 of this permit.

1. Effluent Limitations

Effluent Parameter	Discharge Limitations			
	Maximum Weight kg/day (lbs/day)		Maximum Concentration mg/l	mg/l
	30-day avg. a/	Daily max. b/	30-day avg. a/	Daily max. c/
Flow - m^3/Day(MGD)	N/A	N/A	N/A	N/A
Total Suspended Solids	N/A	N/A	20	30
Total Dissolved Solids g/	N/A	N/A	N/A	N/A
Total Arsenic	N/A	N/A	N/A	0.05
Total Cadmium	N/A	N/A	N/A	0.015
Total Residual Chlorine h/i/	N/A	N/A	N/A	0.002
Total Copper	N/A	N/A	N/A	0.04
Total Iron	N/A	N/A	0.5	1.0
Total Lead	N/A	N/A	N/A	0.15
Total Manganese	N/A	N/A	0.5	1.0
Total Mercury j/	N/A	N/A	N/A	0.00005
Total Molybdenum	N/A	N/A	1.0	2.0
Total Zinc	N/A	N/A	N/A	0.6

Oil & Grease shall not exceed 10 mg/l in any grab sample nor shall there be a visible sheen.
The pH shall not be less than 6.5 standard units nor greater than 9.0 standard units c/

There shall be no discharge of floating solids or visible foam in other than trace amounts. Any untreated overflow which is discharged from facilities designed, constructed, and operated to contain or treat as applicable all process generated wastewater and the surface runoff to the treatment facility from a 10-year, 24-hour precipitation event shall not be subject to the limitations set forth in this section. The 10-year, 24-hour precipitation event for this facility is 2.4 inches. The official precipitation gage station identified with the facility shall be Crested Butte Index No. 1959. The permittee has the option of operating and maintaining a precipitation gage at the facility.

EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS (Continued)

2. Monitoring Requirements

In order to obtain an indication of the probable compliance or non-compliance with the effluent limitations specified in Part I, the permittee shall monitor and report all effluent parameters at the following required frequencies.

Effluent Parameter	Measurement Frequency d/e/	Sample Type f/
Flow - m^3/Day (MGD)	Daily	Continuous
Total Suspended Solids	Weekly	Grab
Total Dissolved Solids g/	Monthly	Grab
Total Arsenic	Monthly	Grab
Total Cadmium	Monthly	Grab
Total Residual Chlorine h/ i/	Weekly	Grab
Total Copper	Monthly	Grab
Total Iron	Weekly	Grab
Total Lead	Monthly	Grab
Total Manganese	Monthly	Grab
Total Mercury j/	Monthly	Grab
Total Molybdenum	Monthly	Grab
Total Zinc	Weekly	Grab
Oil & Grease	Daily	Visual Observation
pH	Daily	Grab or In-situ

Self-monitoring samples taken in compliance with the monitoring requirements specified above shall be taken at the following location: at the final outfall from the treatment plant as referenced in Figure 2, page 20 of this permit.

FEED TO THE TREATMENT PLANT

During the week immediately prior to the Randol visit, feedwater to the treatment plant contained 705 ppm suspended solids.

Blended feed to the plant is not routinely analyzed but rather the individual streams. Data for 1982 ranges on the influent streams were provided as follows:

		Mine Discharge	Tailings Seepage
Flow Rate (USgpm)		180 - 540	0 - 140
pH			
Fe	ppm	27 - 43	700 - 800
Zn	ppm	10 - 115	150 - 300
Mn	ppm	6.5 - 79.0	400 - 500
Cu	ppm	3.0 - 8.2	
As	ppm	Trace	1 ppm
Cd	ppm	0.42 - 0.70	1 ppm
Mo	ppm	LTDL	LTDL
Pb	ppm	0.8 - 1.0	
Hg	ppm	not measured	not measured
TDS	800	- 1000	6 - 7,000

LTDL = Less than detection limit.

The main precipitate forming metals in the feed streams are manganese, zinc, and iron.

WATER TREATMENT PLANT AND PROCESS

- Incoming mine water at pH 2.5-3.5 arrives at an outdoor retention pond.

- The water next passes via a Parshall Plume to one of two degritting ponds connected in parallel to drop as much suspended solids from the water as possible.

- Decanted overflow from the degritting ponds next enters an equalization pond where various waters are mixed. An air sparging system provides air induced oxidation and prevents freezing in winter. Originally hydrogen peroxide was added to oxidize iron, but it has been found that air induced oxidation works more reliably. There was a problem with the feeding system for H_2O_2 addition. The water is thoroughly mixed at this point, still outdoors. All iron is oxidized to the ferric state before lime addition.

- pH of the feed stream is raised to around 10.6 by lime addition in a 12,000 gallon mechanically agitated tank located inside the plant building. Typical flowrate is 400 gpm. All iron at this point is precipitated as ferric hydroxide.

- The lime precipitated dilute slurry is next coagulated in cells operated at up to 5000 amps after addition of Nalco 8815 surfactant. The surfactant modifies the surface tension and results in smaller air bubbles in the next step - Electroclear flotation. Dosage of NALCO 8815 is 1.5-3.5 ppm depending on the solids loading. At the coagulant cell overflow weir 1-3 ppm Percol 278 Allied Colliods Cationic Polymer flocculant are added. Nalco 8815 costs $1.61 per pound, and annual costs for this surfactant amount to $5000.

  The coagulated feed passes over a Parshall Plume and is next fed to one or more of the three Swift dissolved air microflotation basins. Two of the Swift Lectroclear cells have 750 U.S. gpm capacities, and the third has a capacity of 550 U.S. gpm for a total of 2000 U.S. gpm.

- Precipitated solids are removed in floated skimmings at 2-3% solids.

- The solution now containing less than 2 ppm solids is dosed with a further 8 ppm polymer via an automated system, then filtered through downflow gravity flow sand filters. These are open top gravity flow tanks which contain 42.5 tons of media in each filter.

- The filter clarified water goes to a clearwell. Some is drawn off for use as glandwater for the pumps. The rest passes across a rectangular weir so flowrate can be measured and recorded.

- Flowrate and pH measurement signals automatic acid dosing to adjust pH to within the discharge limits of 6.5-9.0. Normal operation achieves a discharge at pH 7.8. Acid addition is set to provide a constant dose which is automatically adjusted to match fluctuations in feed flowrates.

- pH is measured automatically at the discharge, and, if it falls outside the limits of pH 6.5-9.0, then the water is automatically diverted to the emergency surge pond. The pH can be changed by dialing in a new acid dose rate on the acid ratio feed station.

- The sand filters are backflushed every 45 minutes. The filters tend to become sealed by the flocculated metal hydroxides unless the flotation cells are operated at peak efficiency. The sand filter capacity is the main constraint. Backflush is pumped to the equalization pond to be mixed back into the feed flow.

- Lectroclear flotation skimmings are stored in a holding tank. Flocculant Percol 728 (an Allied Colloids Cationic polymer) is added at a rate of 90 ppm ahead of the belt presses. Skimmings are dewatered to about 12% solids on two Parkson-Magnum belt presses. The dewatered cake is conveyed to the feed end of an automatic cement dosing and mixing station.

- 90 lbs. cement are added to each 100 lbs. of skimmings and mixed in a Pettibone Speed Mixer. The apparently dry cake discharge from the belt presses is thixotropic. The cement stabilized sludge drips to a holding point below which it is stored prior to shipment by truck for disposal.

  In 1983 a total of 3,275 tons of fixed sludge was hauled away. During the same period, cement usage amounted to 694,163 lbs. The dry solids content of the skims was 696,000 lbs., the balance was water.

347 tons cement	(11%)
348 tons skims solids	(11%)
2580 tons water	(78%)
3275 tons fixed waste	

WATER TREATMENT PLANT LIMITATIONS

1) The precipitation of manganese plus zinc and Lectroclear microflotation process is accomplished at pH 10.6. To precipitate metals adequately, the pH must be kept between pH 10.2-10.8. It is critical to achieve around 98% or more flotation efficiency in the cells.

2) The Lectroclear flotation step must remove precipitates as efficiently as possible or else the four sand filters clog up.

3) If the acid dosage is incorrectly set, or if a fault arises in the acid dosing system or the pH meters and the discharge pH measures outside the set limits of pH 6.5-9.0, then the water product automatically is diverted to the emergency surge pond to await retreatment.

4) In an emergency, for example, if the sand filters clog and overflow, etc., the building sump gathers spills which are then pumped to the emergency surge pond.

5) Mining operations introduce hydraulic oil into the minewater. Unless it is removed, the reference bulb of the pH probe is likely to become coated and give an erroneous reading leading to faulty operation of the pH adjustment step. An oil boom consisting of floating plastic foam is installed at the overflow from the degrit pond to remove any floating oil film. Hydraulic oil in the water is no problem except when work is in progress underground.

THE ELECTRO COAGULATION CELL

The coagulation cell applies an electric current to the high pH feed solution with lime precipitated suspended precipitates. The process causes flocs to form around small air bubbles.

Up to six amps per gpm of throughput flow are applied in the coagulation cell. This requires currents up to 5000a at the Mount Emmons operation. Depending on conductivity, the higher the amps applied. The more loaded the water, the more amps are generally used.

The coagulant cell consists of a rectangular plan tank with overflow weir at the discharge end. The tank has a V-shaped bottom. The cell is fitted with wire electrodes to which high amperage DC current is applied to the cell which is electrically connected to the flotation basin tank to provide cathodic protection for the steel tank.

Solution flows across a series of horizontal electrodes in the coagulation cell tanks. Exactly how this cell works was not explained by the operating staff. Sketches of the cell showing where it fits in the plant layout, and also of some of the galvanic protection detail, as well as the busbar and electrode arrangement, are provided here.

The power is applied to the electrolytic coagulation cells via a Clinton DC rectifier operated at 28 V and 3000-5000a, the amperage varying with conductivity of the water. Roughly 6a are applied for each gpm of flowrate. The rectifier was supplied by:

CLINTON SUPPLY CO.
Rectifier Manufacturing Division
Chicago, Ill.

The electrodes in the cells are reversed every so often, or the amperage would drop due to a coating that builds up. Approximately every hour, the polarity of the cell is reversed. The electrodes are made of sintered steel by the DURIRON COMPANY. Precise details of the operation and design of the Lectroclear, as well as prices, can be obtained from the supplier:

DRAVO RECOVERY SYSTEMS, INC.
222 Third Street
Neville Island, PA 15225
Telephone: (412) 777-5241
Contact: Ogden Clemens
Robert Merdes

Additional reference to electrocoagulation for metal hydroxide removal has been made by: RAMIREZ & GIANINI (1977), GOTT & LAFFERTY (1977), and RAMADORAI (1978).

LECTROCLEAR FLOTATION

Three Lectroclear flotation basins are installed at Mount Emmons with flow capacities of 500 U.S. gpm, 750 U.S. gpm, and 750 gpm respectively at 750 ppm total suspended solids. The 750 gpm units have a flotation basin capacity of 22,500 U.S. gallons in the bath.

The flowrate and metal concentrations into the water treatment plant at Mount Emmons varies considerably during the year, and the installation of three units was selected so that the smaller unit could be operated for 12 months of the year and the remaining two started up as needed during the 8 months of higher flow.

At the time the plant was installed, Lectroclear flotation in conjunction with electric coagulation cells was the only proven process for removal of the precipitated metals to desired levels. The problem lies in getting the precipitates to coagulate in the very cold water during winter when feed enters the plant very close to 0°C.

More detailed information of the Lectroclear flotation process can be obtained from the vendors, DRAVO RECOVERY SYSTEMS, INC.

The Electrocoagulation and Lectroclear flotation process works well at Mount Emmons. However, it is clear that the units are expensive to install and operate. Electrode life was mentioned as being short enough to add expense. Power requirements amount to somewhere around $150,000/year based on a total power consumption estimate of $180,000 for 1984.

At Mount Emmons, feed to the flotation units runs up to 750 ppm suspended precipitate solids during the low flow season and at these loadings, the flotation units barely remove enough solids to avoid "bombing out" the sand filters. One answer is to dilute the flow with recycle solution to drop the TSS to 400-450 ppm TSS.

To avoid problems with the sand filters at Mount Emmons, the flotation step must work at peak efficiency all the time. The Mount Emmons Lectroclear treated effluent contains 20-30 ppm solids with the discharge from the sand filters at less than 5 ppm.

One of the operating tricks of the Lectroclear cells is to adjust the variable speed skimmer so as to keep the flotation sludge at a density between 2-3%. Outside this range the system performs less well. DRAVO claims that intermittent skimming results in a higher skimmings density up to 3½% solids.

The flotation system works better when flocculant is added as a very dilute solution.

The flotation basins are operated at 25 volts DC maximum, and energy consumption of 3a per gpm is typical.

DRAVO CORPORATION points out that acid mine drainage yields a very gelatinous floc which is more difficult to dewater and dispose of than are precipitated metal hydroxides from plating wastes.

DRAVO claims that the combination of Lectroflotation after Lectro coagulation helps to dewater the floated metal precipitates.

POLYMER SYSTEM

Percol 728 Allied Colloids polymer is delivered to the plant in 50 lb bags. A packaged polymer system is used to make up and age polymer solution.

Percol 728 is supplied by: ALLIED COLLOIDS, INC.
P. O. Box 820
Suffolk, VA 23435

Percol 728 costs $2.25/lb., and annual consumption cost is $10,761.

The polymer makeup plant works well and can take 2 bags of polymer feed per batch. It consists of:

1 Polypak Polymer Feeding System for Adding Dry Polymer to the Mixing Tank
1 Polymer Mixing Tank with Agitator
1 Polymer Aging Tank
1 Milroyal Solution Dosing Pump

Suppliers are:

Milroy solution dosing pump: MILTON ROY COMPANY
1300 E. Mermaid Lane
Philadelphia, PA

Polypak dry Polymer dosing feeder:

BIF - Unit of General Signal Co.
West Warwick, R. I. USA

LIME SYSTEM

Polymer solution is dosed in proportion to flow rate using an automatic addition system which works well at Mount Emmons.

Two lime silos, each with 150,000 lb. capacity, are installed at the site.

These feed two 1000 lbs,/hour lime slakers to make a 6-8% slaked lime slurry.

The lime system was supplied by Wallace & Tierman, Division of Pennwalt Corp.

pH PROBES

Lime addition is automatically controlled by a pH meter and a level probe. A backup system is always maintained on standby:

Great Lakes Instruments Inc.
8855 N. 55th Street
Milwaukee, WI 53223
Telephone: (414) 355-3601

BELT PRESS

The flotation skimmings at 2-3% solids are accumulated in a tank. Percol 728 cationic polymer is added at a dose rate of 90 ppm ahead of the belt press.

Two Parkson Magnum Belt presses are installed. No vacuum is applied to achieve 12% solids in the cake that is discharged.

The Parkson Belt Filter Press is available from:

Parkson Corporation
5601 NE 14th Avenue
P. O. Box 24407
Fort Lauderdale, FL 33307
Telephone: (305) 772-6860
Contact: Michael G. Schill
Sales Manager

Filter cloth lasts over a year, then it starts to tear or fold resulting in a drop in solids level in the cake, or it clogs and doesn't clean up.

The lower media fabric is EE 470.

The upper media fabric is PE 470.

Each media cloth costs $1200.

The Parkson-Magnum presses seem to be doing a reliable job. DRAVO claims now to offer a belt press for this application, too. One problem encountered with acid mine drainage treatment at Mount Emmons is the possibility of sporadic occurrence of hydraulic fluids in the water which saponify at the high pH and could end up blinding the filter press media unless removed.

CEMENT SYSTEM

Cement powder is stored in a 300,000 silo. On demand, the dry powdered cement is fluidized and pneumatically advanced to the cement mixing chamber for mixing with the wet dewatered skimmings.

The purpose of cement stabilization is to make the precipitate easier to handle and to fix the metals. The sludges stabilized in this way were tested and found to meet prevailing leach criteria for landfill disposal.

The pneumatic cement storage and dosing system was designed by Dravo and supplied by:

LUCAS ENGINEERING
Seminole, Florida
Telephone: (800) 237-8989

OPERATORS AND MANPOWER

The Mount Emmons site employs a total crew of six men including the site manager, the water plant supervisor, a night watchman who doubles as relief operator, three plant operators (one of whom takes care of sampling and environmental records) and two additional mechanics, who include electrician and filter skills on a part time or contractual basis.

PLANT CAPACITY

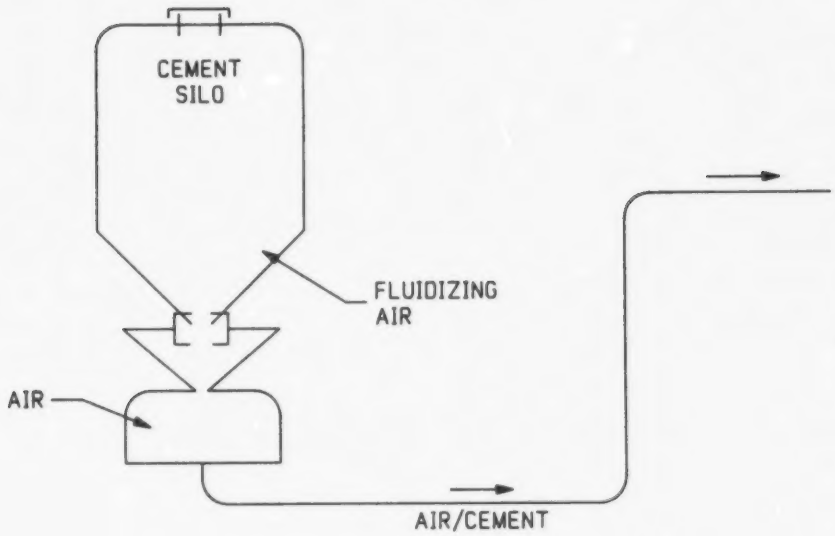
The plant was designed to treat 2200 gpm water. The highest rate at which it has been operated to date is 1750 U.S. gpm. The operators believe it could achieve 2000 U.S. gpm.

The design called for an operating range between 220 and 2000 U.S. gpm.

The Lectroclear flotation plant capacity is limited to the amount of suspended solids that can be removed. The design called for 750, 750, and 550 U.S. gpm flows at 1000 ppm suspended solids achieving a minimum 97% removal of suspended precipitates in the skimmings. After various innovations were developed by AMAX, the units can now achieve 98% removal of solids from the rated flowrate carrying 700 ppm solids.

CURRENT OPERATING LEVEL

At the time of the Randol visit, the plant was treating 75 gpm pondwater and 270 gpm minewater. This was handled by operating the plant two shifts per day.


CEMENT
SILO
FLUIDIZING
AIR
AIR
AIR/CEMENT

WATER PRODUCT QUALITY

During the period immediately preceeding the Randol visit, the following typical water quality was recorded for the product at discharge:

		Day 1	Day 2	Day 3	Allowable Limit NPDES
pH		7.8	7.8	7.8	6.5-9.0
S/S	ppm	5	5	5	
TDS	ppm	1005	1190	850	N/A
Zn	ppm	0.05	0.1*	0.05	0.6
As	ppm	0.005	0.005	0.005	
Cd	ppm	0.001	0.001	0.001	
Cu	ppm	0.01	0.02	0.01**	
Fe	ppm	0.05	0.10	0.30	
Pb	ppm	0.001	0.003	0.005	
Mn	ppm	0.05			
Hg	Monthly Ave.	LT0.0002		LT0.0002***	0.00005
Mo	ppm	0.01			
Oil	ppm	5			

* Rarely this high

** Detection limit 0.01 ppm Cu

*** Detection Limit 0.0002 ppm Hg

Since startup, the water treatment plant has operated in full compliance with NPDES permit limits.

SCALING

There has been no scale problem at the Mount Emmons plant.

PLANT DESIGN AND CONSTRUCTION

DRAVO ENGINEERING, INC.
Dravo Bldg.
1250 14th Street
Denver, CO 80202
Telex: 45-030
Telephone: (303) 893-4500
Contacts: Terry Amrhein, Sales Manager
Russ Hendrickson,
Project Manager for Mt. Emmons
Augie Clements, Developer of Swift Lectroclear

DRAVO owns the Swift Lectroclear equipment and microflotation process. Dravo also supplies packaged sand filter and coagulation cell packages.

PRECIPITATE DISPOSAL

The precipitated metal hydroxides are skimmed by the Lectroclear flotation process at 1-3% solids. After further dewatering in the filter presses to 12% solids, the cake is mixed with 0.9 lbs. cement per one lb. pressed cake. The cured cement-sludge mix makes the thixotropic sludge both easier to handle and more environmentally stable. The cement stabilized waste meets the EPA leach standards required for landfill disposal.

SAND FILTERS

Four sand filters are installed, and these are used two at a time in series.

The sand filter tanks employed for polishing treated water measure 12' 6" Ø x 17' 4" high. There are four of them. The filters are loaded with sand filter media which was purchased for the initial installation as follows:

171	tons	1-2 mm Graded Silica Filter Media Spherical Mark #4.3
9	tons	1½" x 3/4" Silica Gravel in 100 Lb. Bags
4.5	tons	3/4" x ½" Silica Gravel
17.5	tons	½" x ¼" Silica Gravel
9.0	tons	¼" x 1/8" Silica Gel

So far, since the plant was started up in 1980/81, the sand has not required replacement. Occasionally mudballs are removed from the surface of the filters, however.

Suspended solids in the feed to the sand filters typically run 10 ppm. After polishing in the filters, the suspended solids is reduced typically to less than 1 ppm which is well below that required to meet the suspended solids effluent limit. However, such low levels of suspended solids are needed to meet the limits on total amounts of various metals allowed in the effluents (both dissolved and suspended as a precipitate.)

Compressed air for backflushing the sand filters every 45-minute cycle is supplied by a Sutorbilt Blower made by:

SUTORBILT PRODUCTS
Compton, CA 90224

and fitted with Goddard Silencers.

The sand filters are downflow but fed through an enclosed tank. Two pumps are installed for the backflush cycle.

Ingersol Rand Centrifugal pumps withdraw washdown water and glandwater from a filtered water sump ahead of the discharge point.

GROUNDWATER MONITORING

Groundwater is not monitored at the Mount Emmons Site.

CAPITAL COSTS

The capital cost for the water treatment system including the plant, collection system, and diversion ditch was $10,900,000 in 1976.

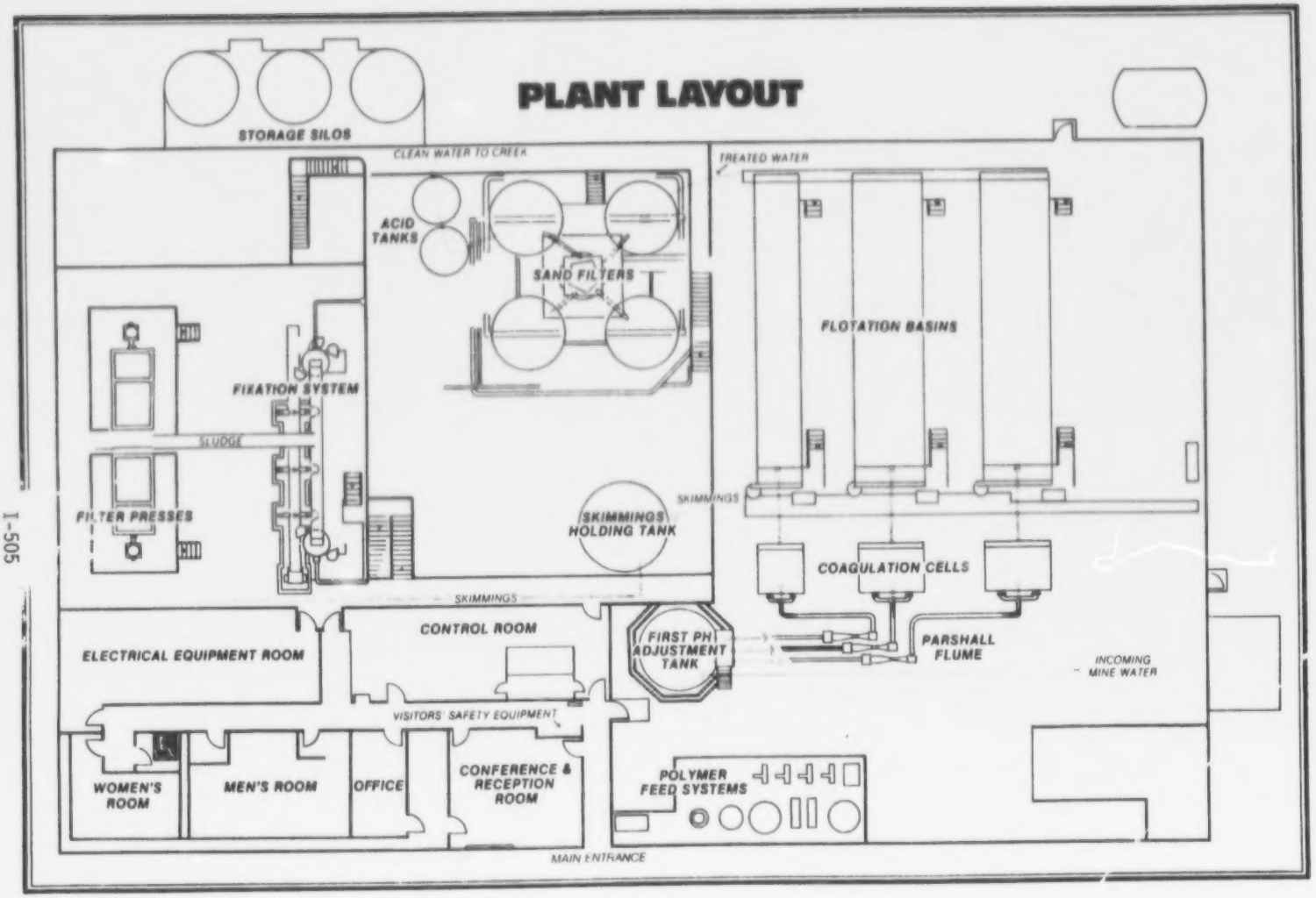
According to AMAX, INC., the total capital spent on the site for water management and treatment is close to $14 million.

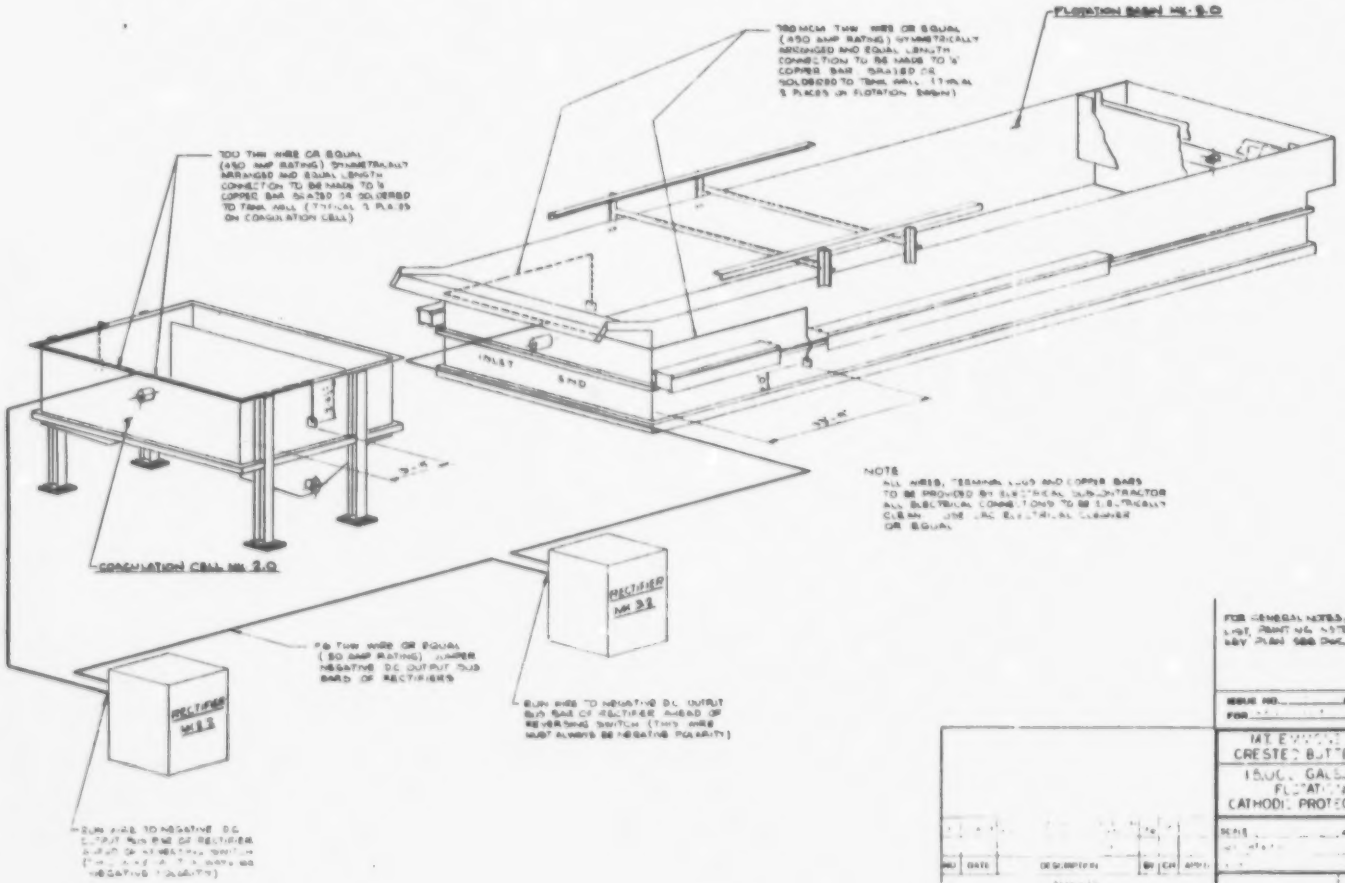
Some cost items included in this are:

Stabilizing and Covering Keystone Tailings Dams	$ 358,000
Outside Design Engineering	$2,400,000
Plant Building 120' x 200'	$1,706,000
Equipment, Piping for Process and Underground from Discharge Area to Storage Pond, Electric Instrumentation, and Erection	$6,441,000

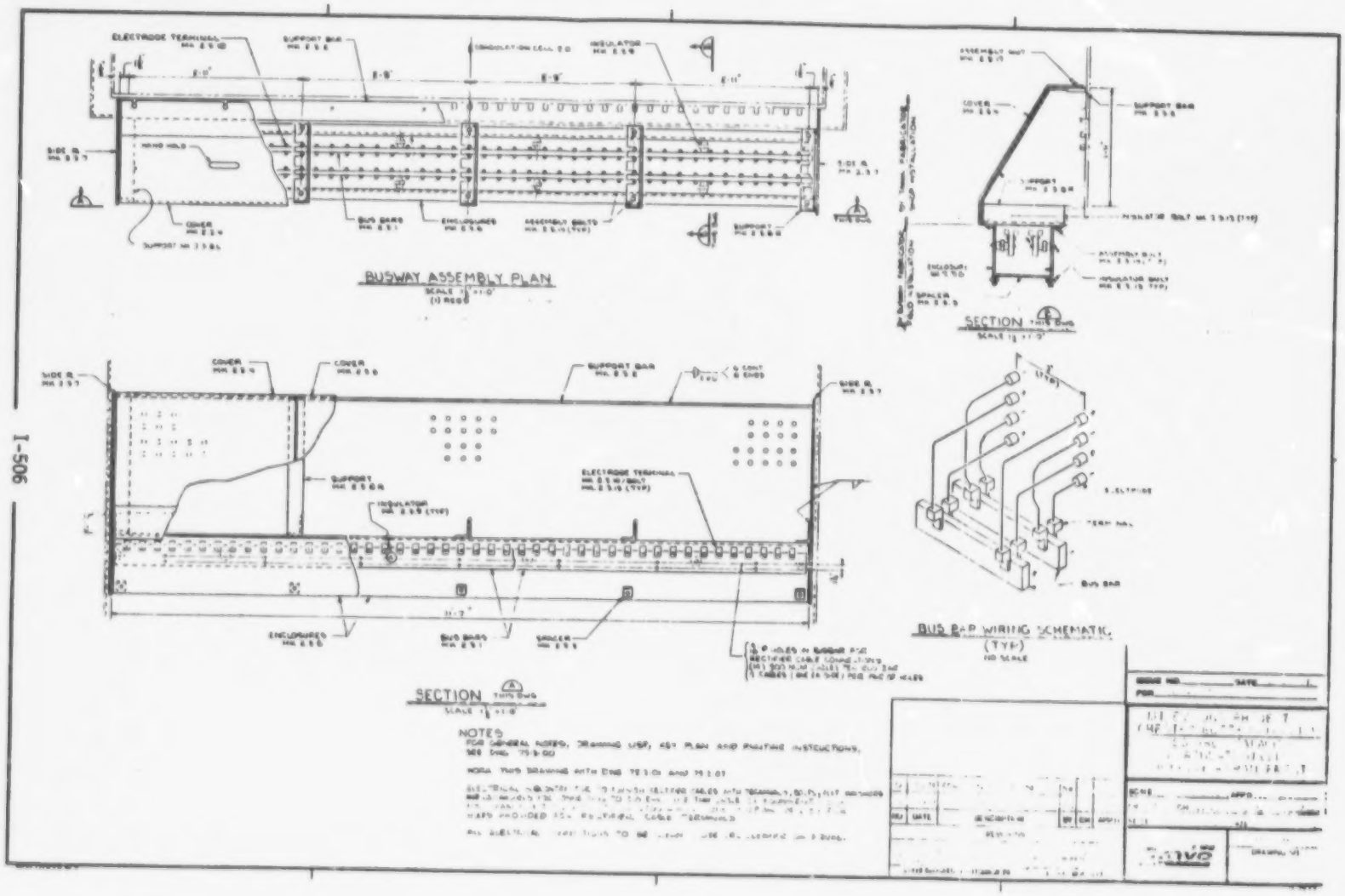
OPERATING COSTS

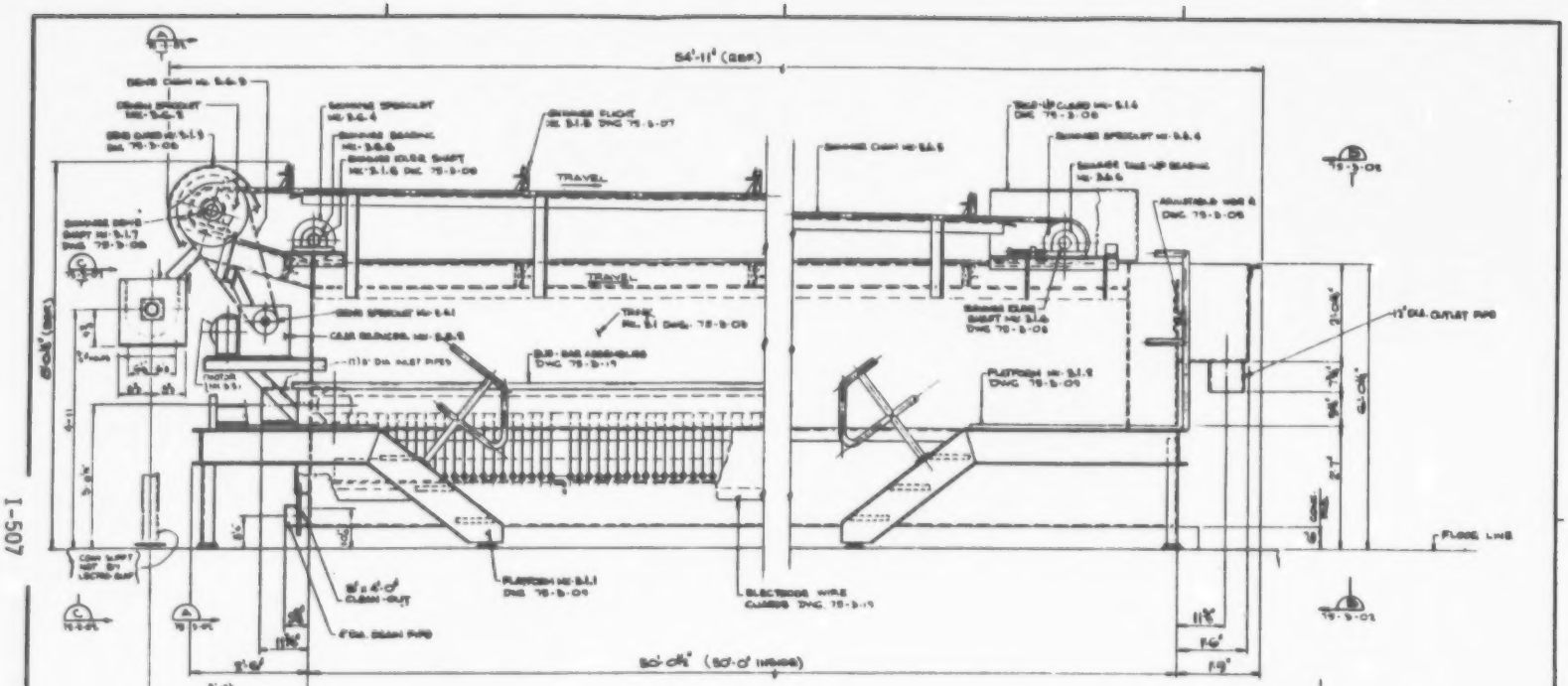
Power Costs	$180,000
Labor	$180,000
Supplies	$105,000
Direct Cost Non Supply Items (Sales Tax, Freight, Insurance, Medical Exams, Telephone, Travel, Road Maintenance, Analyses, Etc.)	$260,000
Hauling Waste Sludge	$ 80,000
	$805,000


PLANT LAYOUT
STORAGE SILOS
CLEAN WATER TO CREEK
TREATED WATER
ACID TANKS
SAND FILTERS
FLOTATION BASINS
FIXATION SYSTEM
SLUDGE
FILTER PRESSES
SKIMMINGS HOLDING TANK
SKIMMINGS
COAGULATION CELLS
SKIMMINGS
CONTROL ROOM
ELECTRICAL EQUIPMENT ROOM
FIRST PH ADJUSTMENT TANK
PARSHALL FLUME
INCOMING MINE WATER
VISITORS' SAFETY EQUIPMENT
WOMEN'S ROOM
MEN'S ROOM
OFFICE
CONFERENCE & RECEPTION ROOM
POLYMER FEED SYSTEMS
MAIN ENTRANCE


FLOTATION BASIN NO. 2.0
INLET
END
CONGULATION CELL NO. 2.0
RECTIFIER NO. 2.2
RECTIFIER NO. 2.1
NOTE
FOR GENERAL NOTES, DWG. LIST, PRINTING INSTRUCTIONS, AND REV PLAN SEE DWG. 90-5-00
MT. EMMONS PROJECT
CRESTED BUTTE, COLORADO
ISUCL. GAS CAPACITY
FLOTATION BASIN
CATHODIC PROTECTION DIAGRAM

I-505a


ELECTRODE TERMINAL
SUPPORT BAR
INSULATOR
SIDE RL
HAND HOLD
COVER
BUS BARS
ENCLOSURES
ASSEMBLY BOLTS
SUPPORT
BUSWAY ASSEMBLY PLAN
SECTION
ASSEMBLY NUT
INSULATOR BOLT
ASSEMBLY BOLT
INSULATOR BOLT
SPACER
SECTION
ELECTRODE
TERM. NAIL
BUS BAR
BUS BAR WIRING SCHEMATIC
(TYP)
NO SCALE
NOTES
FOR GENERAL NOTES, DRAWING LIST, KEY PLAN AND PAINTING INSTRUCTIONS, SEE DWG. 75-5-00
NOTE THIS DRAWING WITH DWG 75-5-01 AND 75-5-07
HARD PROVIDED AS ELECTRICAL CABLE TERMINALS
ALL ELECTRICAL CONNECTIONS TO BE MADE FROM SIDE RL. SERVICE IN 3 DWG.



ELEVATION
FLOTATION BASIN NO. 3.0

NOTE CONCRETE BASE PAD TO BE POURED TO A LEVEL TOLERANCE OF 1/8" IN TWELVE (12) FEET, AND 1/4" MAXIMUM DIFFERENCE OVER THE TOTAL LENGTH OF THE BASIN.

NOTES

1. FOR GENERAL NOTES, DRAWING LIST AND KEY PLAN, SEE DWG. 75-3-00
2. WATER VOLUME = 8,000 CU. FT. (APPROX.)
3. APPROXIMATE BASIN HEIGHT EMPTY (INCLUDING ELECTRODES) = 5'-4.0 AIPS
4. CARBON STEEL SHALL BE ASTM A-1 OR A-36. MINIMUM PLATE THICKNESS AND MINIMUM NOMINAL STRUCTURAL SHAPE THICKNESS SHALL BE 1/4". GALVANIZED AND NON-FERROUS MATERIALS SHALL BE AS DESCRIBED ON THE DRAWINGS OR BILLS OF MATERIALS.
5. WELDING SHALL CONFORM TO THE LATEST AWS D1.0 SPECIFICATIONS. MINIMUM FILLET WELD SHALL BE 1/4". WATERTIGHT WELDS SHALL BE FULL PENETRATION.
6. SHOP PRIMT
   SURFACE PREPARATION: REMOVE RUST, SCALE, DIRT, GREASE, MILD WASHOUT, ETC., FROM CARBON STEEL SURFACES IN ACCORDANCE WITH SSPC-SP3-63 POWER TOOL CLEANING

   PRIMTING: INTERIOR OF TANK PLATES SHALL NOT BE PRIMTED. ALL OTHER STEEL SURFACES, EXCEPT EXTERIOR SURFACE OF TANK BOTTOM PLATE, SHALL RECEIVE ONE (1) COAT OF KOPPERS CO. "PLIG PRIMER", 1.5 MILS MINIMUM DRY FILM THICKNESS. THE EXTERIOR SURFACE OF THE TANK BOTTOM PLATE SHALL RECEIVE ONE (1) COAT OF KOPPERS CO. "BITUMASTIC SUPER DURIFICE BLACK", 15 MILS MINIMUM DRY FILM THICKNESS PER COAT.

   ALL PRIMT MATERIALS SHALL BE APPLIED PER MANUFACTURERS INSTRUCTIONS. DO NOT PRIMT GALVANIZED AND NON-FERROUS METAL SURFACES.

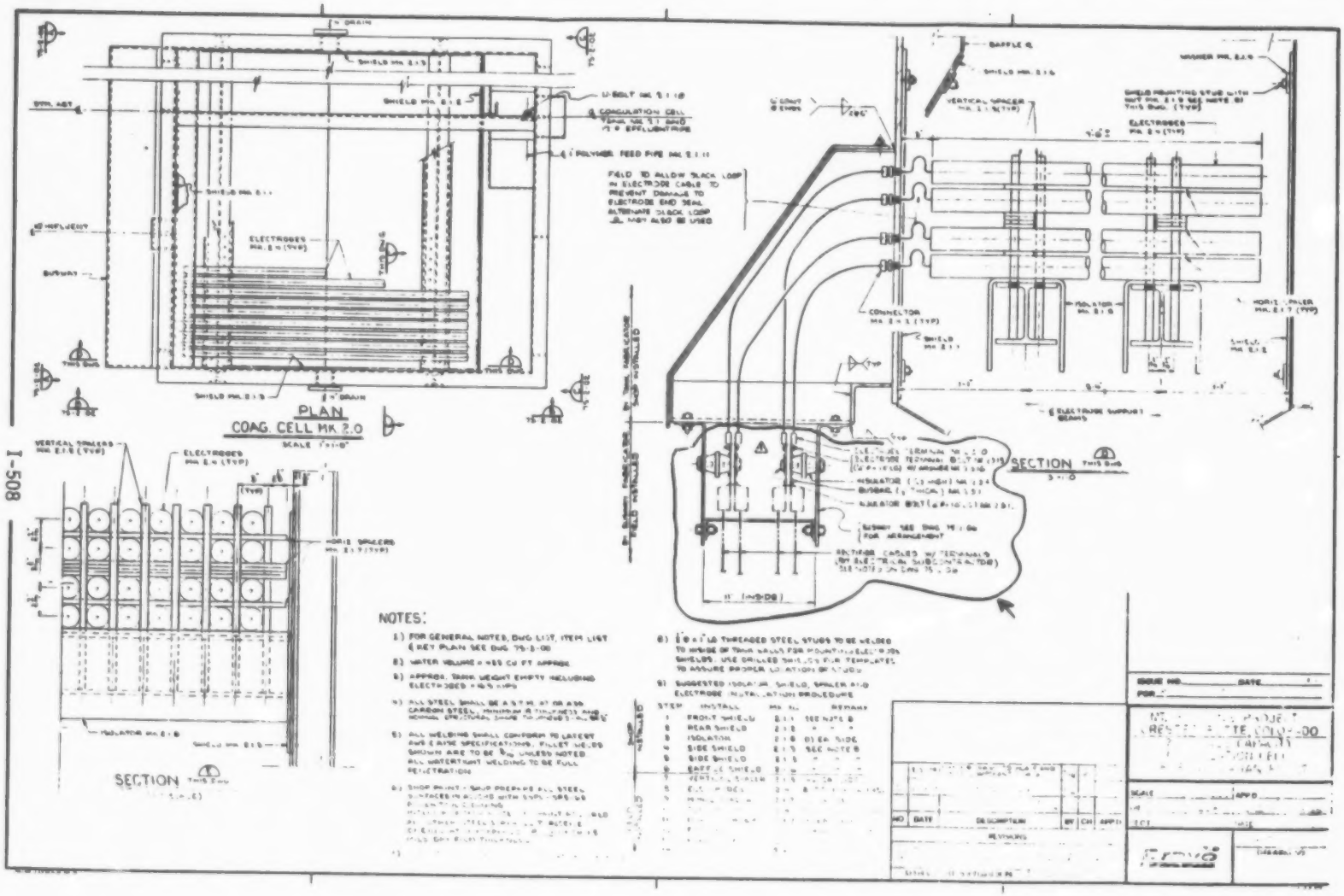
7. TAG ACCOUNT NO. 0.00780 AND 0.00740

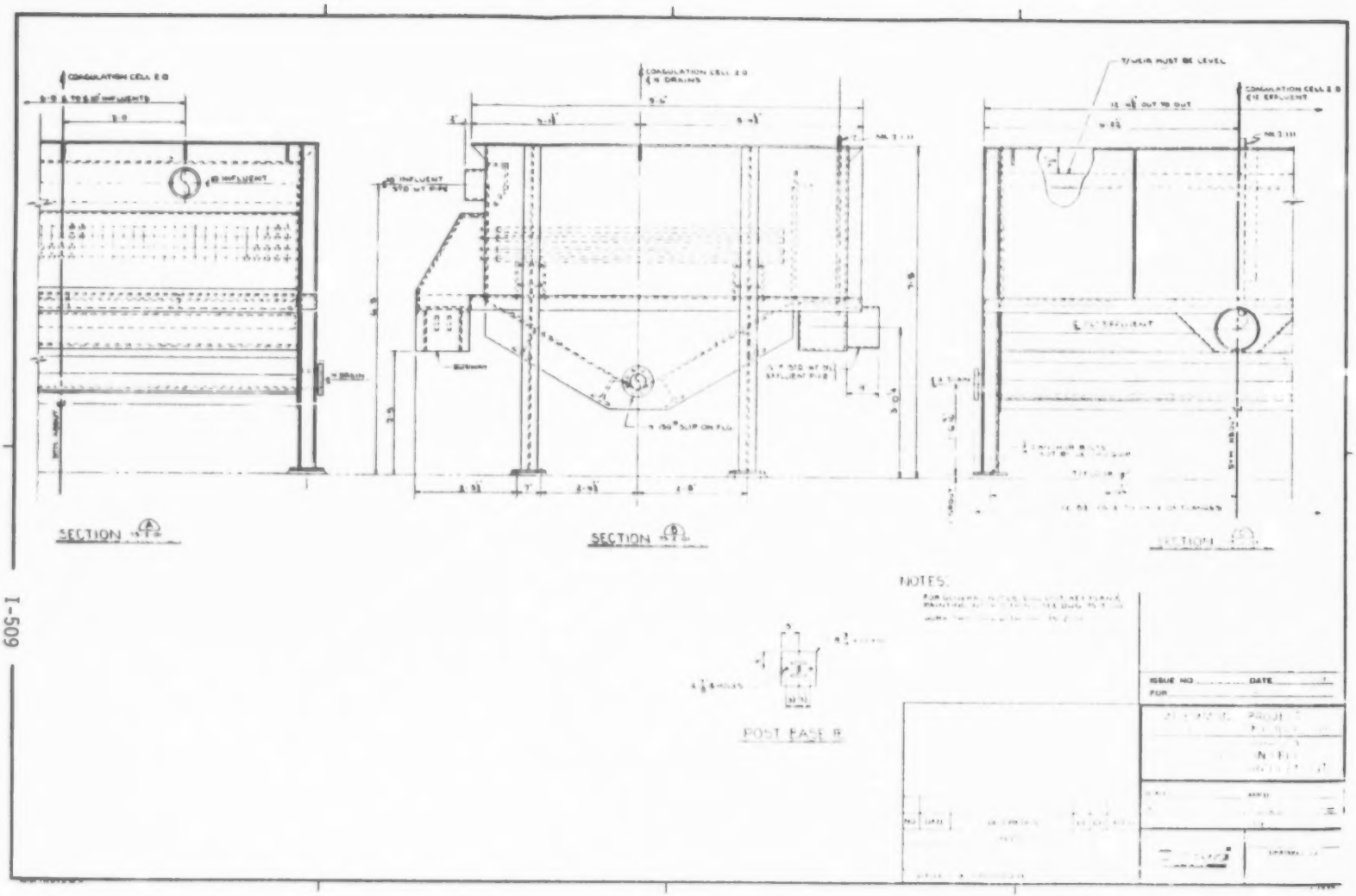
NO	DATE	DESCRIPTION	BY	CH	APP'D
		REVISIONS			

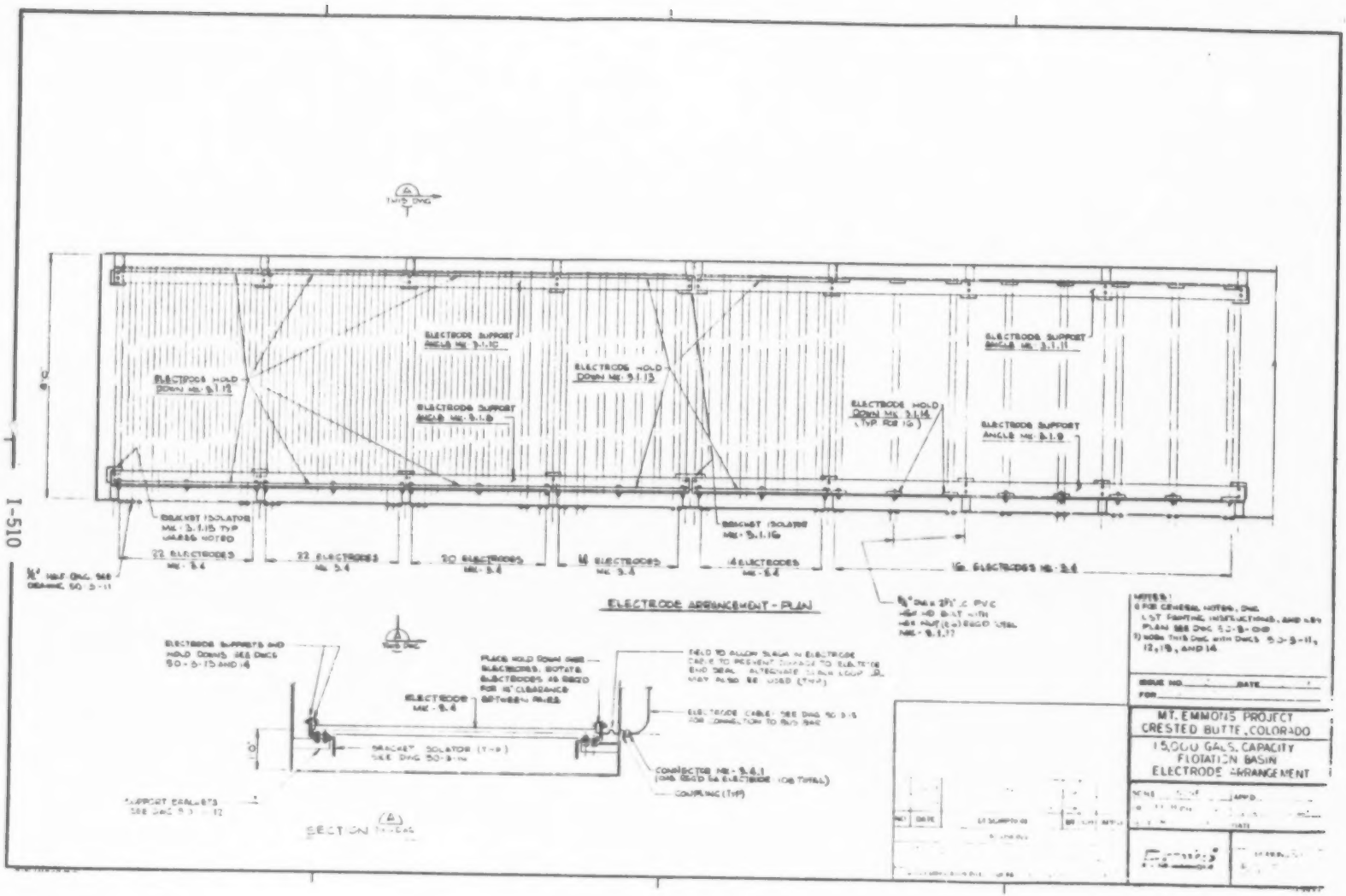
MT. EMMONS PROJECT
CRESTED BUTTE, COLORADO
22,500 GALS. CAPACITY
FLOTATION BASIN
GENERAL ARRANGEMENT

SCALE NONE APPD.

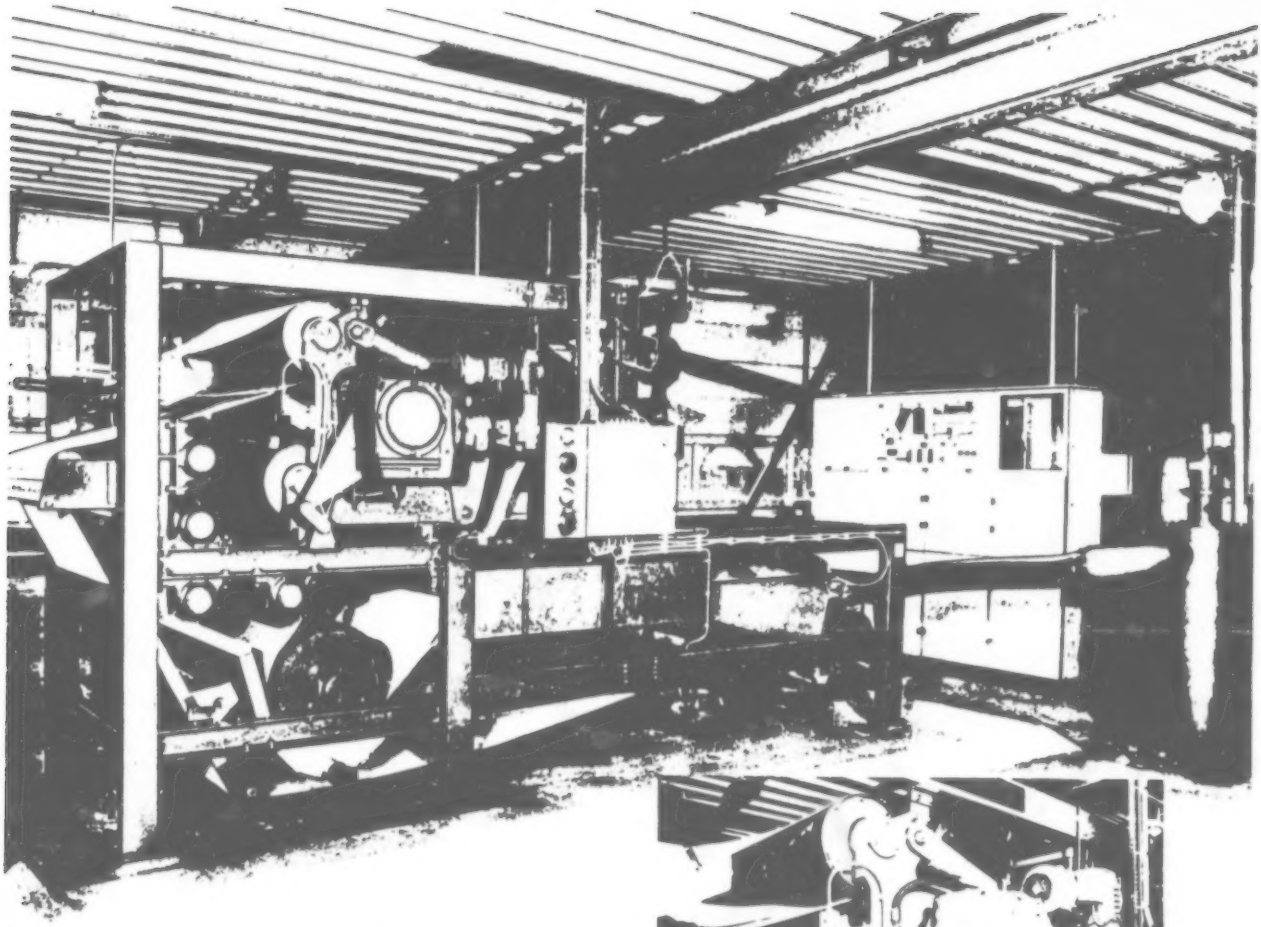
DRAWING NO. 75-3-01


PLAN
COAG CELL MK 2.0
SCALE 1"=1'-0"
SECTION
SECTION
NOTES:
1) FOR GENERAL NOTES, DWG LIST, ITEM LIST & KEY PLAN SEE DWG 79-3-00
2) WATER VOLUME = 485 CU FT APPROX
3) APPROX. TANK WEIGHT EMPTY INCLUDING ELECTRODES = 16.5 KIPS
4) ALL STEEL SHALL BE A 37 M, AT OR ASM CARBON STEEL, MINIMUM 3/16" FILLETS AND NORMAL DIMENSIONS SHOWN TO BE ALL 3/16"
5) ALL WELDING SHALL CONFORM TO LATEST AWS & AISC SPECIFICATIONS. FILLET WELDS SHOWN ARE TO BE 3/16 UNLESS NOTED. ALL WATERTIGHT WELDING TO BE FULL PENETRATION
6) SHOP PAINT - SHOP PREPARE ALL STEEL SURFACES IN ACCORD WITH SSPC-SP6 OR
8) 1/8 x 1" LG THREADED STEEL STUDS TO BE WELDED TO INSIDE OF TANK WALL FOR MOUNTING ELECTRODE SHIELDS. USE DRILLED SHIELDS FOR TEMPLATES TO ASSURE PROPER LOCATION OF STUDS
9) SUGGESTED ISOLATOR, SHIELD, SPACER AND ELECTRODE INSTALLATION PROCEDURE
STEP INSTALL MK NO REMARKS
1 FRONT SHIELD 2:1 SEE NOTE 8
2 REAR SHIELD 2:1 8
3 ISOLATOR 2:6 8) ON SIDE
4 SIDE SHIELD 2:5 SEE NOTE 8
5 SIDE SHIELD 2:5 8
6 BAFFLE SHIELD 2:4 8
7 VERTICAL SPACER 2:5
8 ELECTRODES 2:4
9 CONNECTOR 2:3
10 2:1
11 2:1
12 2:1
13 2:1
14 2:1
15 2:1
16 2:1
17 2:1
18 2:1
19 2:1
20 2:1
NO DATE DESCRIPTION BY CH APPD
REVISIONS
ISSUE NO DATE
FOR
SCALE APPD
DATE
DRAWING


SECTION
SECTION
SECTION
POST BASE B
NOTES:


ELECTRODE SUPPORT ANGLE NO. 3.1.10
ELECTRODE HOLD DOWN NO. 3.1.12
ELECTRODE HOLD DOWN NO. 3.1.13
ELECTRODE SUPPORT ANGLE NO. 3.1.11
ELECTRODE SUPPORT ANGLE NO. 3.1.8
ELECTRODE HOLD DOWN NO. 3.1.14 (TYP. FOR 16)
ELECTRODE SUPPORT ANGLE NO. 3.1.9
BRACKET ISOLATOR NO. 3.1.15 TYP UNLESS NOTED
BRACKET ISOLATOR NO. 3.1.16
22 ELECTRODES NO. 3.4
22 ELECTRODES NO. 3.4
20 ELECTRODES NO. 3.4
16 ELECTRODES NO. 3.4
14 ELECTRODES NO. 3.4
16 ELECTRODES NO. 3.4
ELECTRODE ARRANGEMENT - PLAN
ELECTRODE SUPPORTS AND HOLD DOWNS SEE DWGS 50-3-13 AND 14
ELECTRODE NO. 3.4
BRACKET ISOLATOR (TYP) SEE DWG 50-3-14
CONNECTOR NO. 3.6.1
COUPLING (TYP)
SECTION (A)
MT. EMMONS PROJECT
CRESTED BUTTE, COLORADO
15,000 GALS. CAPACITY
FLOTATION BASIN
ELECTRODE ARRANGEMENT

I-510



Typical Magnum Press installation (without side covers).

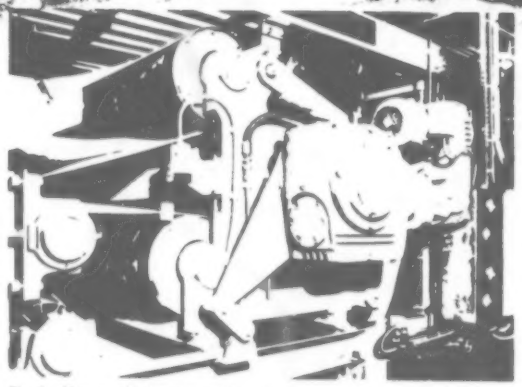


Fig. 1 - Magnum high-pressure Stage 3.

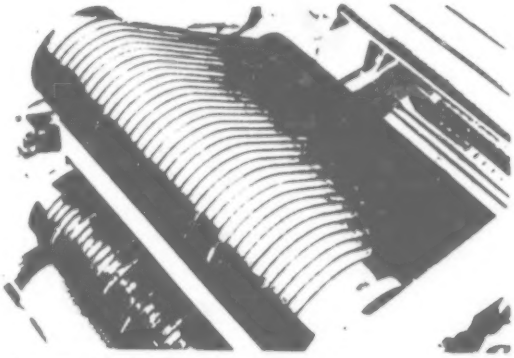


Fig. 2 - Detail of high-pressure belts.

INTRODUCTION

Disposal of large volumes of wet sludge produced in water and wastewater treatment processes is a serious problem, and is best solved through the use of a dewatering device that will reduce the water content effectively and efficiently.

In general, belt-filter presses are rapidly becoming accepted as effective dewatering devices, due to low energy and maintenance requirements. Also, belt-filter presses operate continuously and do not generally need lime or precoating to assist in the dewatering process. The only limitation of current belt-filter presses is the amount of pressure that can be applied . . . with the result that final sludge cake solids content is not high enough for incineration or economical transportation to a landfill. Parkson offers a new solution to eliminate this limitation . . . the Magnum Press, a belt-filter press with the Third Dimension.

The Magnum Press utilizes a new and unique approach to sludge dewatering in that it provides three functionally separated steps in the dewatering process: draining, low-pressure pressing, and finally a very high-pressure pressing for a sustained period of time (see Figures 1 and 2). The sludge cake produced with this process has a very high dry-solids content (close to that achieved with a plate-filter press) and is of a consistency that allows easy handling and transportation.

© 1977 - Parkson Corporation

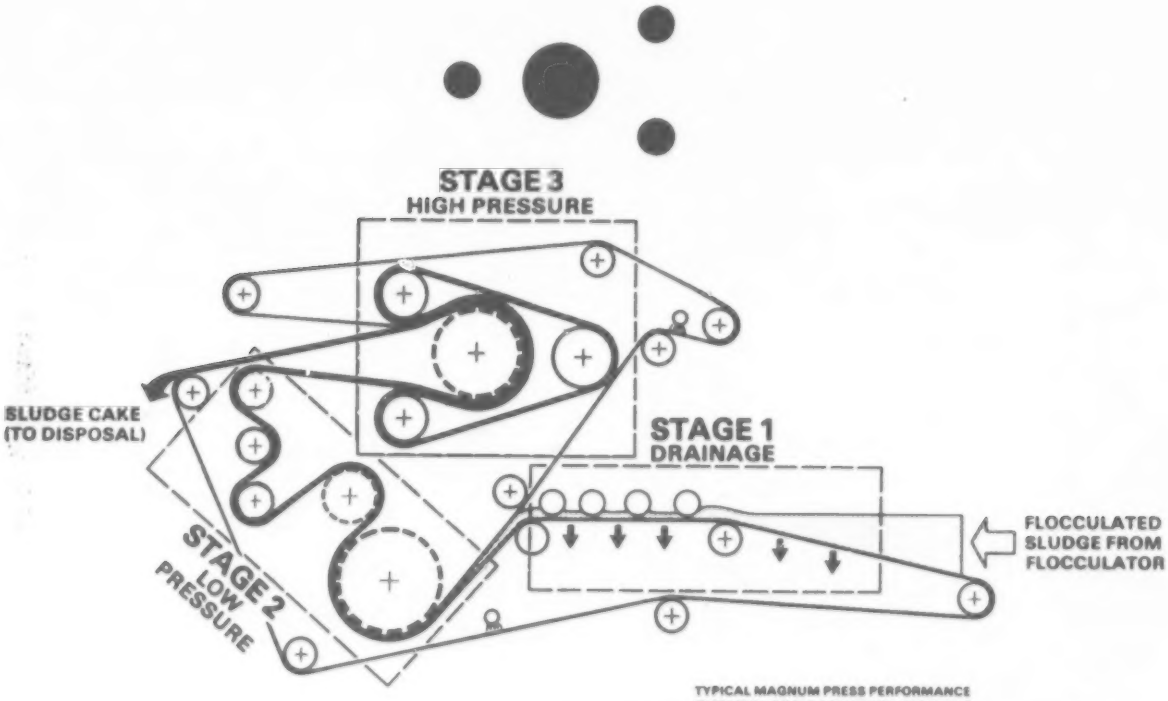


Fig. 3 - Schematic view of sludge flow through Magnum Press.

TYPICAL MAGNUM PRESS PERFORMANCE FROM FULL-SCALE DEMONSTRATION UNIT

Application	Cake % Dry Solids	Capture Rate %	Polymer Dose Lbs./Ton Dry Solids
Pulp & Paper			
• Kraft Pulp	27 32	99	4 5
• Sulphite and Mechanical Pulp	30 35	99	7 12
• Fine Grade Printing Papers	45 50	98 99	0.5 1.0
• Tissue	35 40		
Municipal Wastewater			
• Primary and Activated Sludge Anaerobically Digested	30 42	95	4 7
• Primary and Bio Tower Anaerobically Digested	35 40	98	3 6
• Primary and Activated Sludge Aerobically Digested	19 28	98	1/1

How the MAGNUM PRESS works

The press functions in three stages: (1) Draining; (2) Low-Pressure Pressing, and (3) High-Pressure Pressing (see Figure 3 above). A flocculant (usually an organic polyelectrolyte) is added to the sludge before entry into the press, and the mixture is pumped to a flocculator. There, while being mixed, the sludge forms flocs whereby free water is released. This flocculated mixture then flows to the feed box and onto the drainage screen (Stage 1). During transport to the low-pressure section, the majority of free water is drained off. To increase the drainage, the sludge can be subjected to a light pressure provided by rollers and be turned by plows (both optional).

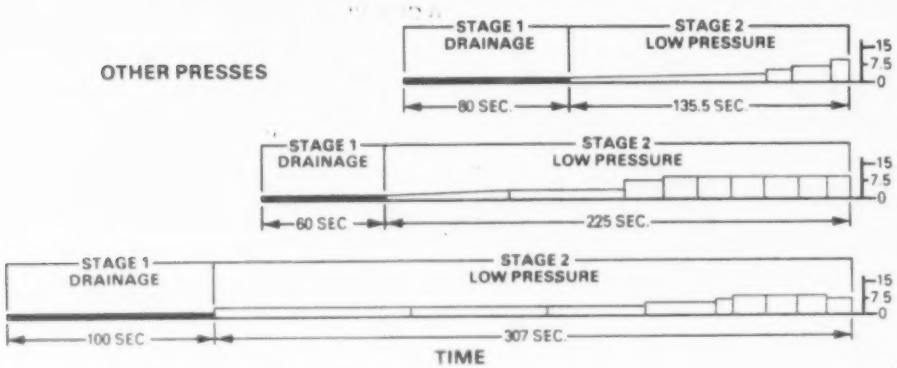
The consistency of the sludge is now such that it can be fed to the low-pressure area (Stage 2) where perforated press rollers of decreasing diameter subject the sludge to continuously increasing pressures. After this careful low-pressure pressing, the sludge is fed into the high-pressure area (Stage 3).

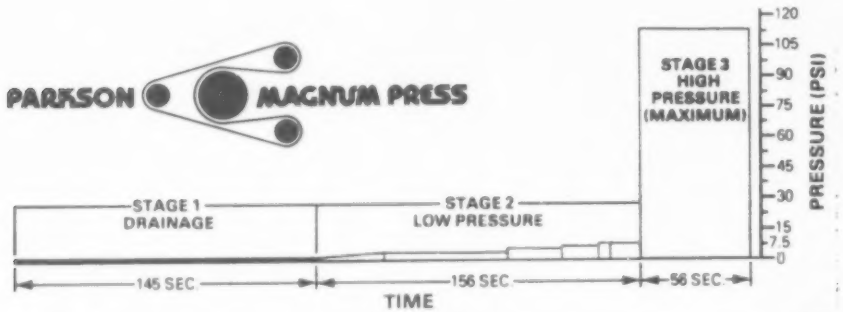
In this last and most important stage the sludge is subjected to very high pressure that is adjustable, depending on the application. This high pressure is generated by a series of 1 inch wide flat belts (see Figure 2) that press the screens against a perforated roller uniformly from side to side. It is this major design advantage that allows the sludge to be subjected to high pressure for a long period of time without producing an excessive load on the screens.

The dewatered sludge is discharged as a pressed sludge cake (see Figure 4).

Fig. 4 - Typical sludge cake from Magnum Press.

PRESSURE/TIME COMPARISON*





*NOTE: AT EQUAL SCREEN TENSION (5KP/CM) AND SCREEN SPEED (1M/MIN.)

Fig. 5 · Graph of pressure/time relationship comparison of Magnum Press and three competitive presses.

The relationship between PRESSURE/TIME and DRY-SOLIDS content

Figure 5 above illustrates the pressure/time relationship of the Parkson Magnum Press as compared to three competitive "high performance" press configurations. Note that the pressure reached in the third stage of the Magnum Press approximates that of a plate-type filter press. Thus, the resulting cakes are almost as high in dryness without the expense and inconvenience of a batch-type dewatering process. It is also important to consider the type of solids and the relationship between pressure/time and resultant dry-solids content. If the pressure is gradually increased, the sludge is effectively dewatered. If the pressure increase is too rapid, the drainage channels by which the water normally leaves the sludge are blocked and dewatering is impaired.

The Magnum Press provides an optimum relationship between pressure/time and resultant dry-solids content (see Figure 6 to the right). Note how the dry-solids content of the sludge increases after each roller, and the dramatic increase in dry-solids content in the Magnum high-pressure Stage 3. The horizontal axis shows the relative time during which the sludge is subjected to pressure.

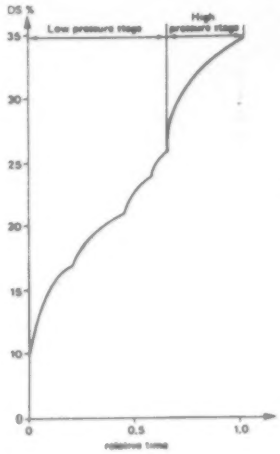


Fig. 6 · Relationship between dry-solids content and relative pressing time.

Parkson
CORPORATION
5601 N.E. 14th Avenue
P.O. Box 24407
Fort Lauderdale, Florida 33307
Phone: (305) 772-6860

REFERENCES

GOTT, R. D., and LAFERTY, JOHN M. (1977) A Discussion and Review of the Development of Wastewater Treatment at the Climax Mine, AMC Meeting, San Francisco, California.

RAMIREZ, E. R., and GIANNINI, A. P. (1977) Removal of Heavy Metals from Mining Tailings Wastewater by Electrocoagulation - 3rd Annual Conference on New Advances in Solid-Liquid Separation/Expo III, Cherry Hill, New York, October 1977.

RAMADORAI, GOPALAN (1978) Treating Tailings Water from Moly Operations - A Review, Mining Engineering, September 1978, pp1302-1306.

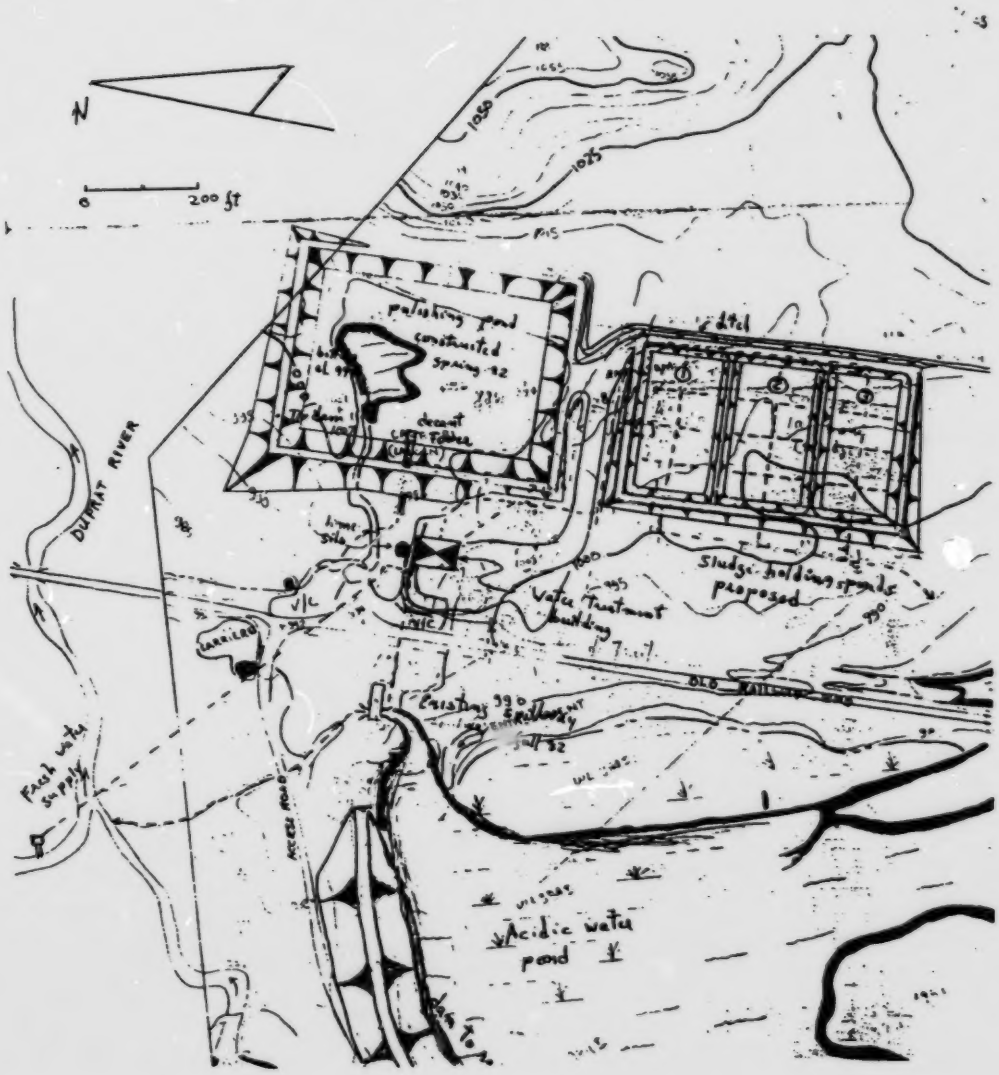
E. R. Ramirez formerly worked for the Swift Company and played a role in developing the Electrocoagulation and Lectroclear Flotation Process. J. M. Laferty currently works for AMAX, Inc. as does G. Ramadorai. R. B. Gott formerly worked for AMAX.

OPERATION	NORANDA MINES LTD. HORNE DIVISION BP 4000 NORANDA QUEBEC CANADA J9X 5B6	
TELEPHONE	(814) 762-7764	
CONTACT	Bernard W. Brooks P. Guillemette	Chief - Waste Water Management Civil Projects Engineer
COMPANY	NORANDA INC. P.O. Box 45 Commerce Court West Toronto Ontario M5L 1B6	
TELEPHONE	(416) 867-7111	
TELEX	065-24231	
CONTACTS	Frank Frantisak Hennie Veldhuizen	Vice President Environmental Services Chief Environmental Engineer
RESEARCH	NORANDA MINES LTD. 240 Hymus Blvd. Pointe Claire, Quebec Canada H9R 165	
TELEPHONE	(514) 697-6640	
CONTACTS	Ken Wheeland	Head Environmental Technology

INTRODUCTION

There are two particularly interesting aspects of the Waite-Amulet site restoration and maintenance program. First is the HDS efficient treatment plant and secondly the revegetation of high sulfide acidic tailings.

FIG 6. PROPOSED WATER TREATMENT PLANT AT WAITE AMULET
APPROXIMATE SITE ARRANGEMENT



HDS EFFLUENT TREATMENT PLANT

This operation is designed to treat 4320 m^3/d (660 lgpm) acid mine drainage from 8,000,000 tons sulfide tailings on a 100 acre pile and mine drainage from a restored zinc mining site near Noranda Quebec. This plant was designed and constructed after examining all the HDS plants then operating in Canada. Actual construction detail varies somewhat from the proposed layout illustrated below. It therefore represents the best of Canadian experience. Features of the plant that started up in 1984 are:

WATER TREATMENT PERFORMANCE

	Plant Feed	Plant Discharge	Polishing Pond Discharge
pH	2.8	9.7	9.3
Acidity mg/l $CaCO_3$	922.00	0.00	0.00
Alkalinity mg/l $CaCO_3$	0.00	20.00	20.00
Conductivity u MHOS	2740.00	1964.00	2104.00
Cu mg/l	3.1	.02	.01
Zn mg/l	19.2	.02	0.02
Cd mg/l	0.04	LT .005	LT .005
Mn mg/l	5.3	LT .02	LT .02
Fe (total) mg/l	246.00	2.2	0.5
$SO_4^=$ mg/l	1940.00	1050.00	1100.00
Pb mg/l	.05	LT .05	LT .05
Ni mg/l	.06	LT .05	LT .05

- Capital Cost: Estimated C$1.7 million 1983

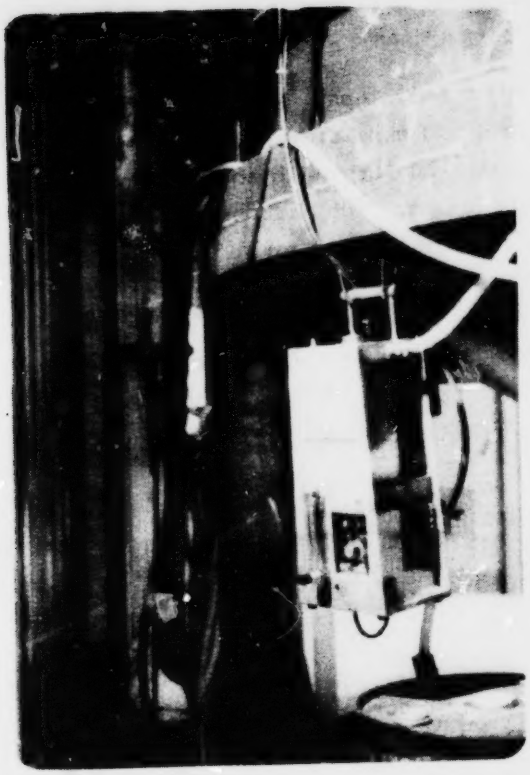
- Operating Cost (1983 Projection)

Lime	C$231,000	C$0.100 /$m^3$
Polymer	C$ 12,000	C$0.005 /$m^3$
Labor	C$ 55,000	C$0.023 /$m^3$
Power	C$ 32,000	C$0.041 /$m^3$
Total	C$330,000	C$0.142 /$m^3$

- Water treatment costs were significantly cut by reducing the watershed that drains into the affected area from 1000 acres to 313 acres through various diversion projects. Through successful revegetation of the sulfide rich dumps an attempt has been made to reduce the rate of acid and dissolved metal generation.

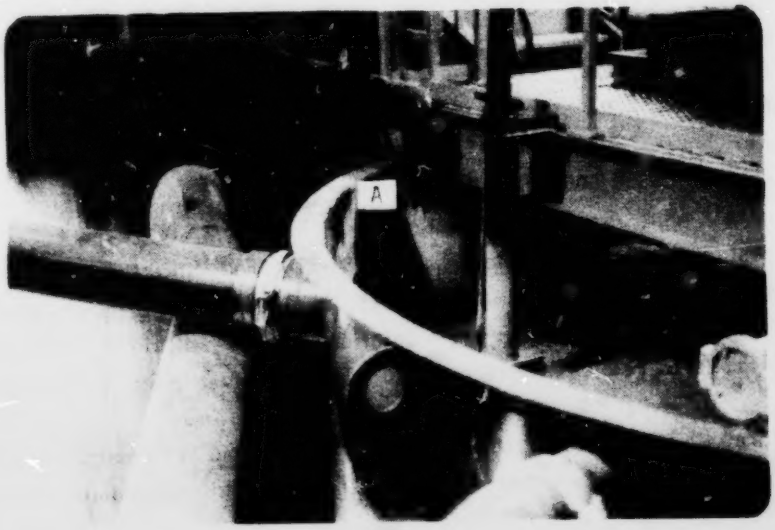
- Being located in a cold climate, the Waite Amulet treatment plant including thickeners is installed indoors in a 2730 ft^2 building measuring 42' wide x 65' long x 34'.

- To accomplish the compact plant a lamella platepack thickener is used inside a small indoor clarifier tank.



Liquid Polymer Metering Pump
Note Aging Coil in Rear

Innovative Lime Addition Line
Can be moved from one tank to another very easily.



Polymer Dosing Line to Overflow Upcomer at A

FIG 8. PROPOSED WAITE AMULET WATER TREATMENT PLANT BUILDING
GENERAL ARRANGEMENT TOP FLOOR

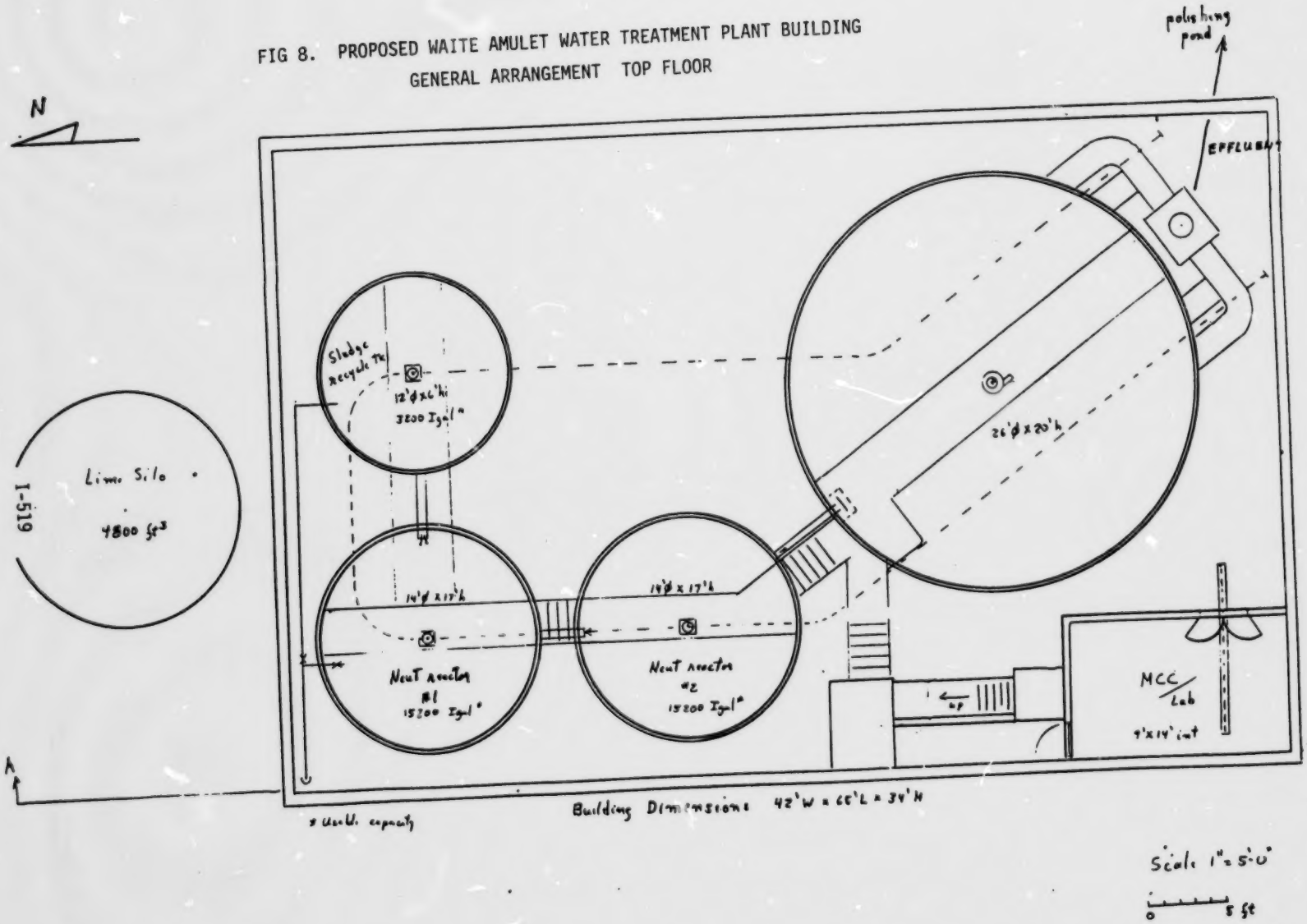
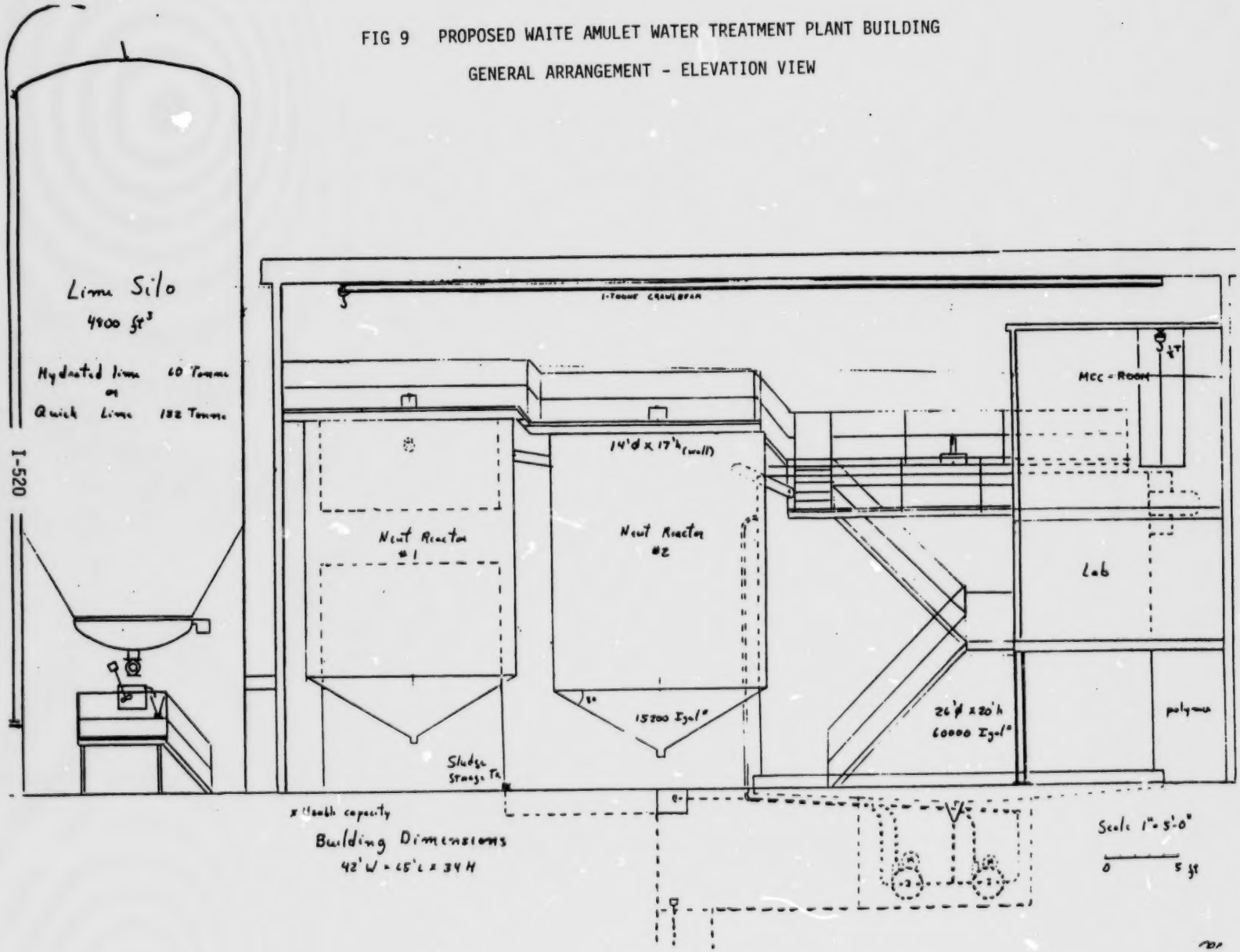


FIG 9 PROPOSED WAITE AMULET WATER TREATMENT PLANT BUILDING

GENERAL ARRANGEMENT - ELEVATION VIEW



- The Waite-Amulet system includes:

  - Acidic water retention pond - adequate for one in 25 year rainfall containment. 242 acre-feet.
  - Water treatment plant for 660 lgpm allowing 20% margin over the required one in ten year maximum flow rate of water needing treatment.
  - Polishing pond for treated effluent
  - Three division sludge storage and dewatering ponds with porous sand floors.
  - Provision to add lime at the decant point to any excess effluent over and above the capacity of the treatment plant that might have to be released in an emergency to Lake Default.

- The HDS plant consists of the following:

  - Lime storage. 60 ton skirt supported outdoor lime silo.
  - Lime slurry preparation system 1/3 HP Lightnin mixer, 3-4 minute retention, deep vortex mixing, Schutte & Koerting water jet eductor, lime slurry pump.
  - Lime-recycle sludge mixing tank. Prochem 10HP mixer.
  - Two neutralization reactors each 15,200 l gallons mixed by Prochem agitators with baffles and air lances at 7 psi.
  - One 26'Ø X 20', 60,000 l gal. thickener fitted with an Axel Johnson LGS-T3200-55 Lamella Plate Pack. The thickener has a rake mechanism to bring sludge to a central discharge point.
  - 12'Ø X 15'6" h. sludge storage tank, 10,400 l gal.
  - 400 cfm blower system 15 psi.

- The HDS plant at Waite-Amulet was required to reduce the volume of precipitate sludges generated. A 3.3 active acre lagoon would have been adequate storage for only 3-6 months sludge generated by conventional neutralization.

- Preliminary test work was conducted by P. W. Shipley of P. W. Shipley Associates.

- Cost of lime at the Noranda, Quebec site is $144/st in bulk. Lime demand in 1984 was 12 lbs per 1000 l gallon or 1.2 Kg lime/m^3.

- The Waite-Amulet HDS plant is designed to be completely automatic. Controls and sensors place the plant on hold when there is a shutdown and signal a problem at at the Horne Division Control Room.

- The plant is operated at a steady flow of 800 lgpm provided by a pump at the pond. This steady flow feature is one of the keys to trouble-free operation. When there is inadequate water in the pond to achieve this flowrate, the plant shuts itself off.

- Flowrate is measured using an ultrasonic device on a Parshall flume, which measures flow and solids density of the underflow, made by:

  Marig, Inc.
  #230, 3300 Boulevard Cavendish
  Montreal, Quebec H4B 2M8

  Telephone: (514) 487-1024
  Telex: 055-66305

- For the automated plant, hydrated lime was selected over quicklime to avoid the need for a slaker or storage reservoir and to minimize operator and maintenance requirements. At the time of the visit NORANDA had not yet reached a final conclusion on the relative merits of quicklime vs. hydrated lime.

- Lime discharge from the feeder is connected to a totally enclosed polyethylene mixing tank. Makeup water is piped through the lid of the tank at a constant flow rate to produce 30% slurry at maximum lime demand of 20 lbs/minute. The water nozzle is positioned to induce a deep vortex in conjunction with a 1/3 HP Greey-Lightnin mixer. Lime flowing into the vortex is carried to the downdraft impeller where it mixes instantaneously to produce a lime slurry. The mixing tank has a 3-4 minute retention time providing a fast response to the control loop.

- A submerged overflow from the lime mixing tank flows into an enclosed funnel which discharges to the suction port of a "Schutte and Koerting" type 264 carbon steel water jet eductor. Even though a 1½" water jet eductor can handle 5/16" particles, the submerged overflow at the mixing tank prevents any non-dissolved lime from reporting to the eductor. The system requires only 21 gpm at 60 psi to carry 8 gpm of 30% lime slurry against 15 psi back pressure. The system has proven itself to be simple and reliable to convey a lime slurry for the short distance with only 22 ft lift to the reactors.

  By enclosing the rotary feeder discharge the lime mixing tank and the eductor funnel, and by operating the eductor so that the air is drawn from inside the sytem, a slight negative pressure is created in the lime system and the escape of lime dust is minimal. This system is installed at both Geco Division and Waite-Amulet with successful results.

- <u>Sludge-Lime Mixing</u>

  Sludge is recycled to the lime-slurry mixer fitted with a Prochem 10 HP Type 640 ft/s agitator at 44.6 RPM. The baffled sludge recycle tank measures 12'Ø x 6' high with 3200 lgal. (14.5m³) storage capacity, designed for 15 minutes retention. This modifies the sludge solids from a fluffy slime to an almost particulate texture.

- Neutralization Reactor Tanks

  Two reactors each 15,200 I gallons (69 m^3 each) are sized for 23 minutes residence time not counting sludge recycle and 20 minutes including sludge recyle, indicating 27.3 m^3/h sludge recycle.

  The tanks are of mild steel with mixing and discharge baffles and a cone bottom discharge. All wetted parts are coal-tar-epoxy coated. One Prochem agitator is installed in each tank.

- In the original design air was to be injected in the primary neutralization reactor at 15 psi and 400 scfm (0.6 scfm/Igpm) to convert ferrous to ferric. The idea was to minimize gypsum scaling by keeping an accelerated motion of the particles while they formed.

  In the operating plant, however, air was injected at 7 psi via four removable air lines per tank inserted to below the Prochem mixers.

  To prevent spillage, and to contain any foam that might occur, the tanks are provided with 2.5' freeboard which makes an obvious difference to the cleaniness of the plant.

Polymer System

Liquid polymer is used which is much simpler to use than a dry polymer makeup system. Liquid polymer systems are currently in use at two INCO plants and at NORANDA MINES LTD. GECO DIVISION.

Alchem HC35 flocculant was in use at the time of the visit, although Alchem 8C26, 8C35 and 87079 had been tested.

In the original design, liquid polymer was to be introduced via a variable speed "Liquid Metronic" model D73 pump. However, a Stanco Polyblend Bradley Illinois polymer pump was installed. The flocculant is mixed into thickener o/f water bleedstream via a T static mixer and then passes through a 300' clear plasic 1"Ø pipe acting as an aging coil before being injected into a 5gpm stream for a second dilution which carries it to the delivery point which is achieved by inserting the end of the diluted flocculant solution delivery line into the overflow upcomer at the discharge of the second neutralizing tank allowing flocculant to disperse in the water as it cascades down the trough leading to the clarifier.

The use of flash mixers for flocculant mixing was dispensed with after Noranda staff visited several installations where the static mixers or propeller mixers had been removed.

Solid/Liquid Separation

Noranda measured clarification rates for hydroxide thickeners at 0.2 - 0.5 lgpm/ft^2 (0.54-1.36 m/h). To enable the clarifier to operate indoors a lamella clarifier was selected. Conventional thickeners operated in Canada experience interference due to surface currents on the sludge blanket. A circular thickener 26 ft Ø x 20' high walls sides is installed and fitted with an Axel-Johnson LGS-T3200-55 Lamella plate pack and a rake mechanism to bring sludge to the central discharge point.

Sludge level is detected using a Sensall device supplied by:

National Sonics Division
Sensall Control
Xertex Corporation
Hauppauge, NY 11787

The Lamella plate packs are made by:

Axel-Johnson Ltd.
Montreal

Clarifier overflow is pumped via a Sclairpipe line to a 2.5 acre polishing pond which overflows to the creek system at pH 8.5-9.5.

Sludge Handling

Based on experience at Noranda Mattabi Division where the original Moyno pump was replaced by a SRL type centrifugal pump, the latter was installed at Waite-Amulet. Positive displacement pumps normally prefered for this job require so much maintenance that the benefits do not offset the greater reliability of SRL centrifugal pumps. Flocc breakage can be overcome by a little extra flocculant dosage.

At Cominco's Kimberly BC plant two SRL Allis Chalmers pumps are installed, each capable of recycling 850 lgpm sludge. At Kimberly the pumps are fitted with DC variable speed motors, and one pump operates at a time. Cominco reportedly initially experienced problems with constantly changing polymer dosage requirements created by the solid mass flow not being uniform. The RPM of the motor is now controlled to draw a constant amperage. In this way a change in sludge viscosity or density caused by a sudden slide of material to the thickener discharge cone is taken care of by a change in pump rpm.

To achieve 25-30% sludge density, 95-98% of the sludge must be recycled. At Waite-Amulet two Worthington 3" X 3" horizontal rubber lined slurry pumps were installed as slurry recycle and sludge waste pumps. One heavy duty AC motor and a single controller were selected for the variable speed sludge recycle pumps.

The sludge recycle pump and sludge waste pump are located in a pit under the thickener which minimized the length of the suction line to the pumps. One Galligher sump pump acts as a backup for either the recycle or waste sludge pump. The sump is designed to discharge its overflow to the clear water overflow ditch.

Recycle flow monitoring is by a Taylor mag-pipe flowmeter installed on the sludge recycle line. The purpose of the sludge flow measurement is to be able to optimise the flocculant/recycle ratios and to shut the plant down automatically if the recycle sludge volume drops below a preset limit.

Sludge Disposal

Once sludge density has been reached the sludge waste pump is activated for a timed period by an ultrasonic sludge level detector supplied by National Sonics Division, Happauge, NY (address given above.)

To minimize the amount of spare parts, this pump is identical to the recycle pump but with a standard AC motor which is feasible because the sludge pond is only 300-400 ft from the treatment plant and at the same elevation.

The sludge disposal line is insulated and has a 1½% slope back to the treatment plant. After every sludge purge the line is be flushed. The waste pump header is connected to the upper part of the clarifier and by means of automated knife valves, some of the clear water will be used for the flushing of the line by the waste pump. After the flushing sequence has been completed an automated knife dump valve will be activated to drain the line.

Sludge production is estimated at 2.6 acre-ft/year and a 10 acre-ft sludge disposal pond has been constructed adjacent to the plant.

The sludge impoundment system has a porous base of sand and cobble to drain the sludge to 50% solids.

The sludge pond consists of sand beds fitted with buried pebble size slag drains. The impoundment is divided into three sections which are cycled to provide maximum drying before being covered with fresh material.

During winter dewatering is limited but as the spring thaw arrives the drainage characteristics of the once frozen material is greatly enhanced. In summer drying will remove additional moisture causing shrinking and cracking which allows air to come into contact with the sludge. There will be some conversion from ferric hydroxide to the carbonate too. This results in a very stable dry sludge. It was still too early to determine whether metals leach from this sludge although it is considered highly unlikely.

A similar sludge leach tested by Cominco at Kimberly BC was said to have resulted in virtually no dissolution of heavy metals but more information on this could be requested from:

Mr. Walter Kuit
Cominco Ltd.
200 Granville Street
Vancouver, BC
V6C-2R2

Telephone: (604) 682-0611

At Waite-Amulet, the storage ponds are about 300 ft x 500 ft long divided into three sections with clay dikes with a usable storage height of 5 ft.

Dry sludge production rate is estimated at 4000 tpa or 2.6 acre-ft/year. Utimately dry sludge will be hauled to one of the tailing sites for final disposal.

Drainage lines from the sludge impoundment exit to a drain for gravity flow to the acid feed water reservoir. In future this water could be diverted to the clear overflow ditch once its good quality has been confirmed.

Control System

A very innovative automatic control system has been installed at the Waite-Amulet water treatment plant. The heart of the system is a programable Texas Instruments micro-processor which is equipped to handle on/off analogue input/output as well as timing, counting and arithmetic functions. The input/output configurations are simple and easily traceable in the event of malfunction or logic error.

The micro-processor has three prime functions:

- generating temporary shutdown on critical alarm
- monitoring and recording of plant operation
- restarting the plant after power failure

The plant is also wired for manual operation at the central control panel although it is intended to be operated as a remote unmanned automatic unit except when the unit is being worked on or optimized.

The microprocessor is programmed to handle signals from a variety of contact switches associated with field instruments:

- High pH at neutralization tank #1
- Polymer delivery line pressure
- High sludge bed level
- High efficient turbidity
- High clarifier rake torque 70% of maximum rated torque
- Medium high clarifier rake torque at 40% of maximum rated torque
- Low pH in neutralization tank #1
- Low water supply pressure
- Low compressed air pressure
- Low raw water pond level
- Low sludge recycle flow

A Leeds & Northrup 5 channel recorder continuously records the following parameters:

- Turbidity of Overflow
- pH of Reactor Tank #1
- pH of Reactor Tank #2
- Inlet Flowrate
- Sludge discharge Flowrate

Services

The water treatment plant facility operates at 150 HP installed power and 75 KW for heating at the coldest period. Cost of installing a 25KV line for the installation was $55,000.

The microprocessor is connected by telephone line to the Horne Division to continuously transmit plant operating status and for communications with the plant operator.

The plant also needs 60 Igpm fresh water to operate. This is supplied by installation of one two stage Flygt pump alongside the Duprat River about 1500 ft from the plant to provide fresh water for polymer preparation, lime slurry preparation and transport, pump glands and for floor washing.

More information on this excellent installation can be obtained from:

Noranda Mines Ltd.
Horne Division
BP 4000
Noranda, Quebec
Canada J9X 5B6

Telephone: (819) 762-7764
Contact: Bernard W. Brooks

Details on the excellent programable control system for an automated plant can also be requested from the engineer that developed the system first.

Noranda Mines Ltd.
Geco Division
Manitouwadge, Ontario
Canada P0T 2C0

Telephone: (807) 826-3211
Contact: Walter Sencza
Mill Environmental and Control Engineer

TAILINGS AND SITE REVEGETATION

The Waite-Amulet tailings are one of the very few high sulfide tailings which to date have have successfully been revegetated with a self-sustaining cover.

The 7-8 million ton No. 2 dam tailings consist of 50-60% pyrite (60% - 325#) and a smaller swampy pond area were active acid generators. Samples of water from the seepage collection ditch run pH 2.8.

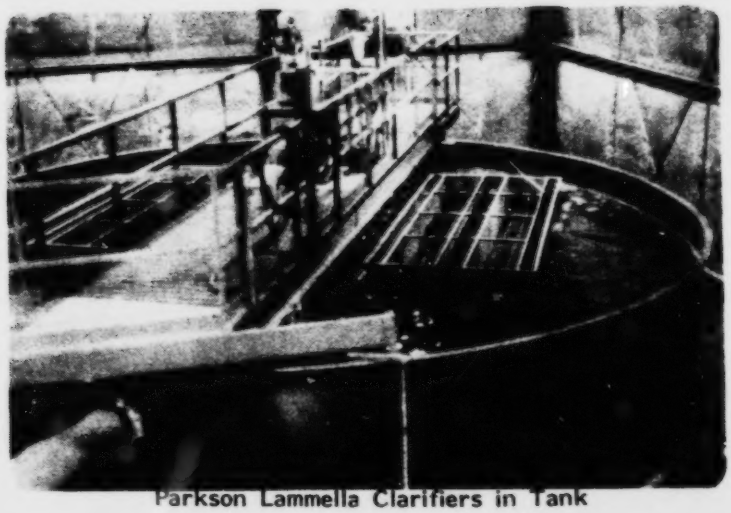
Mine water drains from the old underground workings at around pH 7.2-7.4, and the only deleterious contaminant is iron. This water is divereted in an open ditch around the tailings area and by the time it is discharged to Duprat Creek, it meets discharge limits.

There are two tailing dumps known as the No. 1 and No. 2 dams. Of these, the No. 2 dam is by far the largest.

An important aspect of restoration of the mine and tailings site has been the diversion of water from several watersheds that used to drain into the tailings area.

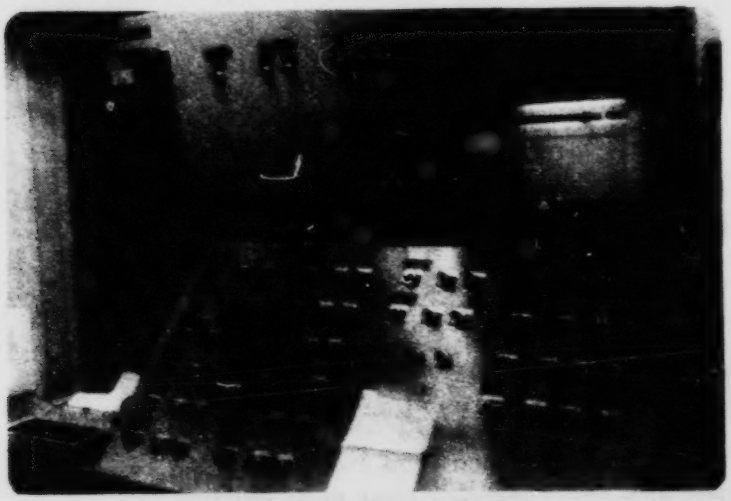
The No. 1 tailings dam which was was laid down prior to 1929 has been clay covered and revegetated. There are one or two acid springs in the vicinity from which water at pH 2.9 is emitted, but the cause or source of this water is not known.

The No. 2 sulfide tailings dam has been successfully revegetated with birdsfoot trefoil, a nitrogenous legume after spreading 25-40 tons per acre lime and one ton per acre fertilizer over the surface of the material. The tailings were, however, not capped by a clay layer.



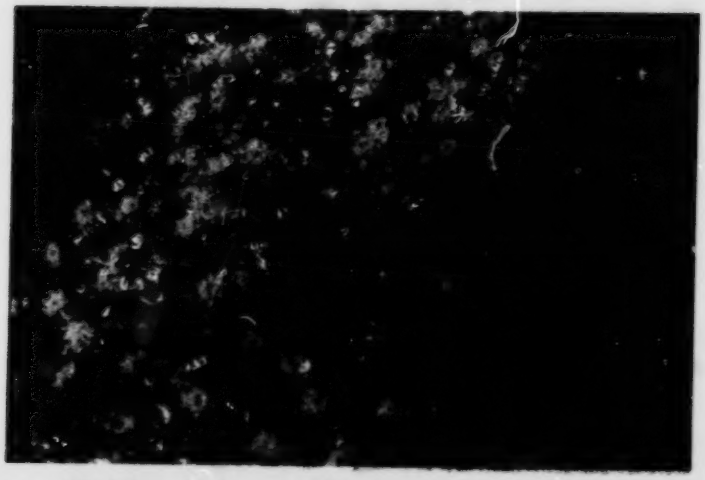
Parkson Lammella Clarifiers in Tank

HDS Precipitate Disposal - Rapidly Dries to a Stable Solid



Control Room of Plant Designed for Automatic Remote Control

Surface of Waite Amulet Reclaimed Tailings
(Note Volunteer trees in distance)



Thriving Self-sustaining Birdsfoot Trefoil Legume
on Waite Amulet Tailings

Solution Holding Pond and
New HDS AMD Treatment Plant in background

The tailings revegetation program for Waite-Amulet was initially started under the direction of W.J. (Bill) Marshall, a Noranda Environmental Coordinator who has subsequently retired.

BIOASSAY TECHNIQUE

During the past decade of research, trial, and error, the Horne Division of Noranda, which is responsible for the Waite-Amulet site, has developed a concept that is unique in the field of reclamation of sulfide tailings. This concept involves using bioassay techniques to determine the vegetation potential of the wastes to find out whether and what species can be directly seeded, and developed into a maintenance free plant cover. The aim is to find a way of direct seeding of sulfide waste without the need for overburden cover, capillary barriers, or additional topsoil covers.

A two year university investigation by the University of Guelph proved that chemical soil analyses are unsuitable as a means of developing a reliable field reclamation program.

The bioassay technique reveals any wide differences within and between sites as far as dosages of agricultural limestone and fertilizer needed to sustain plant growth. It also indicates where an overburden application is necessary.

ORIGINAL REVEGETATION PROGRAM

The first attempt by Noranda to revegetate the Waite-Amulet tailings disposal area was undertaken in 1969. A reclamation contractor with experience in this field gave Noranda a written guarantee before discing the stable primary tailings area and applying lime, 650 lbs.t 10-10-10 fertilizer, and seeding with 256 lbs/acre of perennial rye and New Zealand Fescue grasses. This approach, which had worked in the Sudbury basin and at Timmins was a complete failure on Waite-Amulet tailings.

Even after applying 7 tons lime per acre to the tailings in a second attempt, the results of a second seeding were a complete failure.

Noranda commenced a test program in 1972 to find a way to revegetate the Waite-Amulet tailings. Bottle tests of tailings material indicated that 25 tons lime would be needed to sustain a pH that would support plant growth. The 1972 test plot program using 50 tons lime/acre, and 1200 lbs/acre of 5-20-20 fertilizer with a seed mixture of equal proportions of birdsfoot trefoil, Canada bluegrass, Timothy, Red Top, and creeping Red Fescue with 100 lbs/acre of a nurse crop of barley or oats in some cases demonstrated that vegetation could be grown on high sulfide tailings, but at a high cost.

UNIVERSITY OF GUELPH - CHEMICAL ANALYSIS

In 1974, a 5-year research program was started between Noranda and the University of Guelph, one of the foremost agricultural research centers in North America. Two principal aspects were investigated:

a) To determine the degree of variation within and between high sulfide tailings and its effect on plant growth.

b) To improve or develop techniques to establish permanent vegetation cover on high sulfide tailings.

None of the many analyses revealed any consistent relationship between the various parameters. Analyses for total and water soluble components, relationships between sulfur and sulfate in non-oxidized and oxidized tailings and for iron, heavy metals and sulfur concentrations all provided inconclusive.

Although attempts to predict vegetation supporting ability from chemical composition data proved futile, the use of empirical practical growth experiments in a growth room under different additive conditions proved to be useful.

Using the growth room, results that might require three or four years work in the field can be obtained in four to six months. Growth room investigations were performed through the winter months.

The growth room tests were tested in the field in 1975 and experiments were undertaken to find more economical pH modifiers than limestone. Anhydrous ammonia raised the pH from 3.4 to 7.2 instantaneously but the seeds failed to germinate. Fly ash proved an excellent pH amelioration material but transportation costs were prohibitive.

Noranda-Guelph next undertook a comprehensive evaluation of the entire Waite-Amulet tailings in the growth room using the biossay technique developed in the previous 5 year program. Over twenty samples of Waite-Amulet tailings were obtained for the study and these represented a wide range of variations in color, granulometry, location and surface moisture content. The tests proved that although a single fertilizer application rate was suitable for the entire dam, limestone requirements varied from 10 to 75 tons/acre. Surface plans were developed to indicate contours for limestone rates to be applied at various areas of the dam.

As Noranda's knowledge of the Waite-Amulet area increased, so did its awareness of the fact that reclamation of a tailings area was just one facet of a complete ecological program.

A schedule for application of agricultural limestone, fertilizer, and seed was started in the fall of 1978 when the tailings surface was dry enough to allow large agricultural equipment to operate, but before the surface moisture had evaporated due to the extremes of summer heat and the tailings texture and color. It was known that contrary to popular belief, photosynthesis of plants is not continuous while the sun is shining. Photosynthesis may almost completely stop at the height of summer heat. Light colored tailings reflect excessive radiation to the plant surfaces and intensify physiological stress. INCO has measured under leaf temperatures as high as 140°F.

WAITE-AMULET REVEGETION TECHNIQUE

The technique used to revegetate the Waite-Amulet dam followed the following procedure:

1) Where a hardened crust or hard-pan had formed as a result of oxidation of the tailings, the surface was ripped or disced depending on the thickness of the hardpan.

2) Agricultural limestone was applied using a rotary spreader on a 10 ton capacity wagon.

3) An 18-foot rotovator was passed over the area which resulted in a well mixed and level seed bed.

4) Next, fertilizer was spread using a standard box fertilizer spreader. The Waite-Amulet required a blend of 1,500 pounds of 5-20-20 and 500 pounds of 0-46-0 fertilizer per acre. Fertilizer without filler material was used to reduce shipping costs.

5) Fertilizer was incorporated using the adjustable teeth of a culti-packer. The machine also compacts the tailings to form a firm seed bed. A harrow was attached to the culti-packer to prepare the seed bed for mechanical seeding--it is not needed for hydroseeding.

6) The area was then seeded using:

   a) A split-box Brillion seeder on areas which were relatively flat and able to retain some surface moisture.

   b) A hydroseeder on areas which would not retain adequate moisture, which were prone to wind disturbance, or which were crested or sloped. A Canadian-made straw and cotton waste mulch was applied at 1400 lbs/acre to all areas which were hydro-seeded.

7) Two seed mixtures were used:

a) For wet, fine-grained areas:
30 lbs per acre of tall fescue (K31)
20 lbs per acre birdsfoot Trefoil.

b) For relatively dry, coarser grained areas:
30 lbs per acre creeping red fescue
20 lbs per acre birdsfoot Trefoil.

Excellent results were obtained with 90% coverage after the initial growing seasons. More than 6 years later in 1984, the area continues to support a lush growth up to three feet high which requires no additional care or maintenance.

The smaller secondary tailings dam at the Waite-Amulet property is located in a low-lying swampy area which is unsuitable for heavy farm equipment. This area was reclaimed by placing a clay capping over the tailings and surrounding swamp prior to seeding. This could only be done during the winter months. The cost of this technique is four to five times higher than direct seeding.

All major fresh water streams running through the swampy tailings area were diverted prior to placing the clay cover over the area. The largest creek was ditched to a new receiving stream almost a mile to the north while a smaller tributary was piped through the area in an 18-inch polyethylene pipe.

CONCLUSIONS

Noranda's efforts to establish vegetation on highly acidic mine tailings and swamps have been successful so far. The ability to establish maintenance-free vegetation cover on acidic mine tailings has been demonstrated.

The bioassay method using growth rooms has provided a new and useful method of selecting appropriate soil conditioning and seed mixes for a given site.

At Waite-Amulet a successful self-sustaining vegetation cover consisting largely of birdsfoot trefoil was established, but this is being successfully invaded by indigenous species as evidenced by the appearance of many trees on the Waite-Amulet site. Many of these trees were over 15 feet in height by 1984, and a florishing wildlife habitat has been established over the area.

The dense vegetation cover over tailings achieves the following:

1) Vegetation appears to have reduced the volume of acid seepage from the dam. Vegetation utilizes very large quantities of water in its life processes and loss through transpiration. The plants intercept much of the precipitation which evaporates into the atmosphere before reaching the acidic tailing surface.

2) Dense vegetation has eliminated the previous serious dusting problem.

3) The aesthetics of the area have been greatly improved. Organic matter from seasonal plant decay and growth has developed into a soil layer.

4) Noranda is still evaluating whether or not vegetation has an effect on the quality of seepage water from the area. Noranda has concluded that revegetation is just one part of a multi-faceted program in restoration of abandoned minesites.

An important aspect of the successful Noranda project is that a capillary barrier is not always necessary between vegetation and high sulfide tailings.

Consultants and service companies that were involved with Noranda in this successful project include the following:

Consultants:

Mine Waste Reclamation Ltd.
565 Massey Road
Guelph, Ontraio
Canada

(519) 823-2060
Edward M. Watkin, Ph.D.
Jo-Ann Watkin

ERO-MAT
Verdyol Plant Research
R. R. #1
Cookstown, Ontario LOL ILO

(705) 458-9601
Contact Joe Dol

Noranda has undertaken several additional experiments in an effort to find better ways to restore mine tailing sites. In one of these a lazer-controlled subsoil plough was tested to lay slotted pipes in the tailings in an attempt to drain them. This type of subsoil plough is used by drainage contractors and is offered by a company known as Big-O (Canada) Ltd. Slotted pipe installed into a test area in 1979 is still producing water in 1984. More information on this test is available from:

Professor Bob Broughton
Department of Hydrology
McGill University
Montreal, Quebec

The area around the water treatment plant at Waite-Amulet and all earthworks were seeded to provide a grass cover using a hydroseed mulcher at a cost of C$1100/acre.

In Canada there is more than one revegetation contractor who offers patented mulch mixes.

A good review paper on revegetation of sulfide tailings ponds is provided by WATKIN & WATKIN (1982), Tailings Reclamation in Eastern Canada, World Mining, December 1982.

REFERENCES

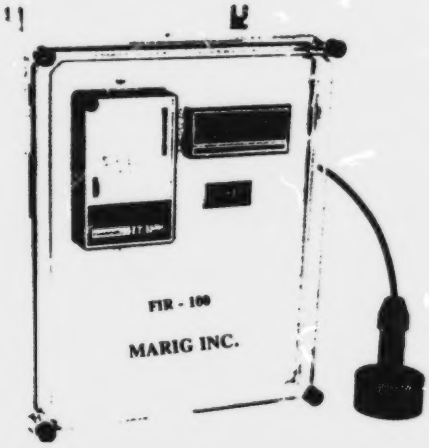
WATKIN, EDWARD M. & WATKIN, JO ANN (1982) Tailings Reclamation in Eastern Canada, World Mining, December 1982.

MARIG INC.

SUITE 230, 3300 BOUL. CAVENDISH
MONTREAL, P.Q. H4B 2M8
TEL: (514) 487-1024 TELEX: 055-66305

UNIT #52, 1000 WINDMILL ROAD
DARTMOUTH, N.S. B3B 1L7
TEL: (902) 463-1680 TELEX: 019-31697

ULTRASONIC FLOW METERS



Monitoring of liquid flows in open channels can be accomplished reliably and economically through the use of the MARIG series of ultrasonic flow meters. Each meter is completely solid state, microprocessor based, and pre-calibrated for a wide range of flumes and weirs.

Field selection of alternate primary elements is provided through two BCD switches. Totalizing, flow and range are also BCD adjustable. Solid state temperature compensation is available with an accuracy of 0.1%.

FLOW MEASUREMENT

FLUMES — PARSHAL / PALMER-BOWLUS / LEOPOLD-LAGCO
WEIRS — RECTANGULAR / V-NOTCH / CIPPOLLETI

LEVEL MEASUREMENT

RESERVOIRS / TANKS / BINS / PUMPING STATION CONTROLLERS

SPECIFICATIONS:

Repeatability	0.1%	Minimum Range	18"
Linearity	0.1%	Maximum Range	12'
Accuracy	1 %	(Dependent upon flow)	

Temperature — Electronics −20° to +50°C
— Transducer −40° to +70°C
Approximate weight 20 lbs.

FEATURES:

- Flow totalizer
- Sampler relay
- Instantaneous flow rate indicator
- Strip chart recorder (F.I.R.-100)
- Programmed flow curves
- NEMA 4 plastic enclosures c/w clear covers are standard for Model F.I.R.-100
- NEMA 12 enclosures are standard for Models F.I.T.-50A and F.I.T.-50D
- 6 digit totalizer totals in 100, 1,000 or 10,000 unit increments
- Sample rate adjustable. Samples every 1 to 99 units of totalization
- 0-1 mA output for analog meter (50A)
- 0-10 V. output
- 4-20 mA output (ground referenced, into 750 ohm max. load)
- Echo loss indication
- Temperature compensation - compensates for temperature change at the sensor.
- Standard cable length 20'

TRANSDUCER:

Barium titanate element in C.P.V.C. outer housing. (optional: 316 SS)

MODELS:

F.I.R.-100

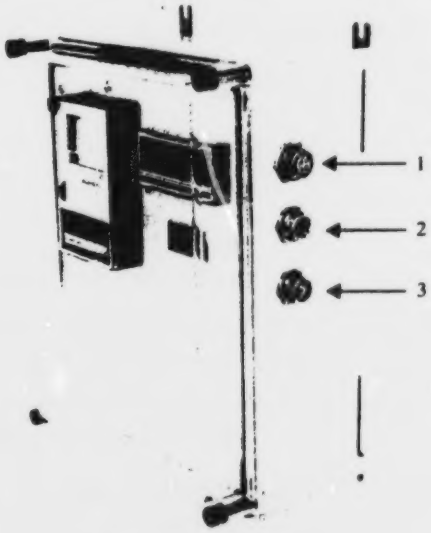
- Flowrate Indication (digital)
- Flow Totalizer
- Strip Chart Recorder
- Sampler Relay
- Programmed Flow Curves

F.I.T.-50A(D)

- 0-100 percent Analog (F.I.T.-50A)
- 0-100 percent Digital (F.I.T.-50D)
- Flow Totalizer
- Sampler Relay
- Programmed Flow Curves

CONNECTIONS:

1 — Transducer cable
2 — A.C. Power, Twist Lock 6' cable
3 — Output Signal, Twist Lock



11.81" × 14.56" × 8.25"

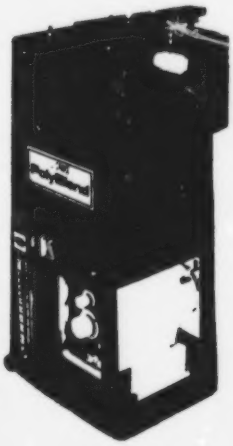
MARIG INC.

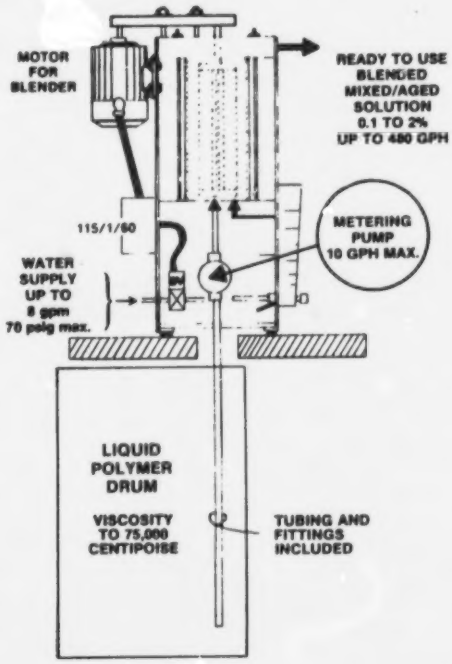
SUITE 230, 3300 BOUL. CAVENDISH
MONTREAL, P.Q. H4B 2M8
TEL: (514) 487-1024 TELEX: 055-66305

UNIT #52, 1000 WINDMILL ROAD
DARTMOUTH, N.S. B3B 1L7
TEL: (902) 463-1680 TELEX: 019-31697

POLYBLEND - FOR LIQUID POLYMERS

Eliminates Mix Tank, Storage Tank, Rotameter and Metering Pump.





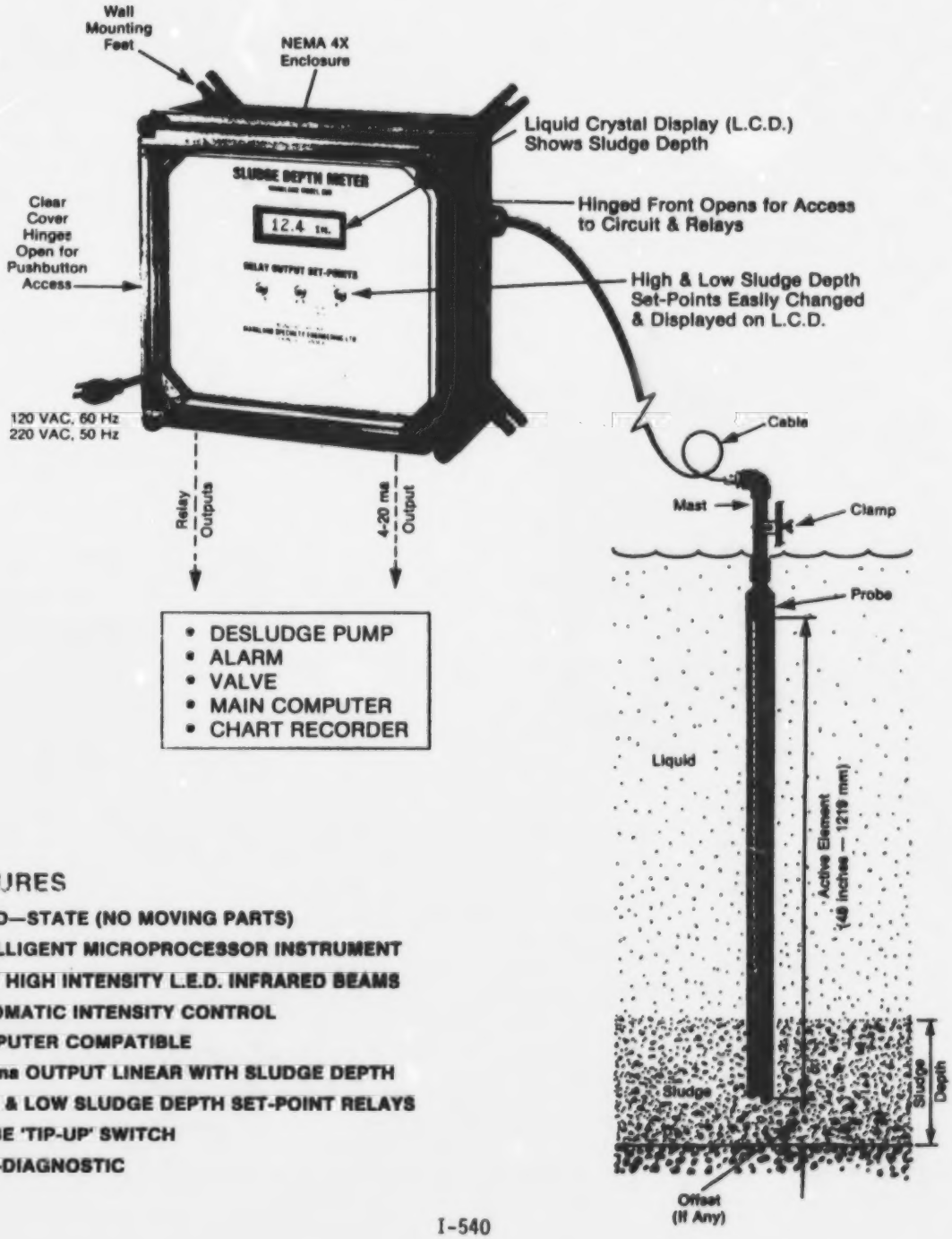
Reduce Polymer consumption by 30% to 70%

WEIGHT: — PB-1 & PB-2 — 70 lbs. PB-4.5 – 130 lbs.

MODEL	LIQUID POLY METERING PUMP		WATER SUPPLY		SOLUTION FLOW RATE	
	MIN. GPH	MAX. GPH	MAX. PSIG	MAX. GPM	Concentration	Max. GPH
PB-1	.02	1.0	70	2	.1%	100
					2%	50
PB-2	.04	2.0	55	2	.1%	100
					2%	100
PB-4.5	.09	4.5	55	8	.1%	480
					2%	225

SLUDGE DEPTH METER

MARKLAND MODEL 600



FEATURES

- SOLID—STATE (NO MOVING PARTS)
- INTELLIGENT MICROPROCESSOR INSTRUMENT
- VERY HIGH INTENSITY L.E.D. INFRARED BEAMS
- AUTOMATIC INTENSITY CONTROL
- COMPUTER COMPATIBLE
- 4-20 ma OUTPUT LINEAR WITH SLUDGE DEPTH
- HIGH & LOW SLUDGE DEPTH SET-POINT RELAYS
- PROBE 'TIP-UP' SWITCH
- SELF-DIAGNOSTIC

MICROPROCESSOR CONTROL

A microprocessor scans the Probe elements and locates the sludge bed if there is one, and displays this on the L.C.D. Any bottom offset is automatically incorporated into the reading. Out of range, or zero readings are displayed if there is no sludge/liquid interface. Error trap routines identify and reject bad scans. To lessen the impact of short term events such as passing 'clouds', the Meter accumulates a running-average of several good scans, which dampens the response and smooths the output. If after several attempts, the Meter can not obtain good scan data (i.e. broken wire, etc.) the L.C.D. reads "SIGNAL LOST", both Relays are de-energized, and the 4-20 ma output goes to zero indicating *fault*. During a fault condition the Meter continues trying to find good scans and resumes normal operation as soon as good data is obtained. Using techniques borrowed from computer photographic enhancement, the microprocessor disregards individual beam signals which are not consistent with those on either side; thus, spot fouling, or floating clumps are ignored, and minor failure in Probe elements merely creates a 'dead spot'. The entire Probe does not have to be replaced. Automatic intensity control adjusts the L.E.D. firing power to the correct level for each particular sludge/liquid. Progressive slime buildup on the Probe merely results in the instrument boosting its own power to the intensity required to shoot through the scum. An integral self-diagnostic routine displays the Microprocessor's memory on the L.C.D., and makes troubleshooting easy.

PROCESS CONTROL

A desludging pump can be operated automatically from the Low Set-Point along with a Pump Run-Interval Timer, and the High Set-Point used as an alarm for excessive sludge depth. Alternatively, the desludge pump can be turned ON at the High Set-Point, and OFF at the Low Set-Point. The Meter is useful for decant control, resin level monitoring, and slurry inventory assessment. Online real-time computer monitoring of sludge depths is accomplished through the 4-20 ma output.

OTHER MARKLAND SYSTEMS

Markland's portable sludge level detector, the SLUDGE GUN®, is a valuable operating tool for manual sludge bed detection. Markland also manufactures ultrasonic Meters for controlling sludge levels or monitoring suspended solids. Markland DUCKBILL® wastewater Samplers operate without mechanical moving parts for reduced maintenance and high reliability. Write for a complete catalog of Markland products.

SPECIFICATIONS

Materials	Probe — PVC Mast — PVC Pipe Clamp — Stainless Steel & Polypropylene Cable — Vinyl Jacketed Enclosure — Fiberglass Body & Clear Plastic Cover
Dimensions	Probe: Overall Length 1330 mm (52¼ in.) Active Element Length 1219 mm (48 in.) Cross Section 64 mm (2½ in.) x 38 mm (1½ in.) Gap — 25 mm (1 in.) Mast — 3½ metres (12 ft.), 1 in. Sch. 80, shipped in 3 pieces with fittings Cable: Probe Pigtail — 10 metres (33 ft.) Enclosure: Width 350 mm (13¾ in.) • Height 350 mm (13¾ in.) • Depth 200 mm (7⅞ in.)
Cable Length	10 metres (33 ft.) pigtail supplied (measured from top of Probe). Maximum cable length 150 metres (500 ft.). Order extra cable separately if pigtail length not sufficient.
Active Element Spacing	64 pairs infrared L.E.D./Phototransistor, spaced vertically on 19 mm (¾ in.) centers
Accuracy	± 2 cm (± 1 in.)
Bottom Offset	Switch adjustable, 0 - 99 cm, or, 0 - 99 in. (Note: For Model 600-DAF, this is TOP OFFSET)
Depth Units	Switch selectable, inches or centimeters
Temperature	Maximum 50° C (120° F)
Power	120 volts, 60 Hz, or, 220 volts, 50 Hz, 15 watts
Outputs	• Liquid Crystal Display (L.C.D.), 16-Digit Alphanumeric • 4 - 20 ma output signal, linear with sludge depth • Two DPDT, 5 Amp. Relays, independently adjustable set-points
Response Time	30 seconds
Microprocessor	6809 with one EPROM and one EEPROM

MANUFACTURED BY

MARKLAND SPECIALTY ENGINEERING LTD.
BOX 145, ETOBICOKE, ONTARIO, CANADA M9C 4U2

MARIG INC.
SUITE 230, 3300 BOUL. CAVENDISH
MONTREAL, P.Q. H4B 2M8
TEL.: (514) 487-1024 TELEX: 055-66305

OPERATION	ROOIBERG MINERALS DEVELOPMENT CO. LTD. P.O. ROOIBERG TRANSVAAL
GROUP	Gold Fields of South Africa Ltd. P. O. Box 1167 Johannesburg 2000
TELEPHONE	(011) 639-9111
CONTACT	A. W. Pullen

INTRODUCTION

Rooiberg operates three mines in the northern Transvaal between Warmbaths and Thabazimbi in an area which is short of water. The available underground water in this area is also high in fluorides and the available minewater contains 6-10 ppm F^- which is considered to be detrimental to healthy teeth formation in growing children.

Of interest at Rooiberg is the new fluoride removal process that has been designed based on tests by the NIWR (National Institute for Water Research) in Pretoria, and which uses activated alumina to remove fluoride. Two identical processes have been installed, one at the A mine and another at the C mine. The plants produce 500 m^3/d of drinking qualtiy water which contains less than 1.5 mg/l of fluoride in the product water.

MINE LOCATION There are three mines in the Warmbaths, Transvaal area:

- A Mine
- C Mine
- Vellefontein Mine

A and C Mines are 21 km apart.

WATER SUPPLY

A Mine has an irregular water supply and has often been short of water.
C Mine has adequate fissure water available, which contains 6 to 10 mg/l of fluoride.

In order to supply water to A Mine, water is pumped from C Mine by pipeline. Several tapping points along the line provide water to farmers for livestock. The pipeline was installed by late 1982, it is a 10" (250 mm) line which cost R1.0 million.

A Mine has some boreholes which do not yield an adequate supply.

WATER CONSUMPTION

At the Rooiberg operation net consumption of water by the mine community works out to 0.8 m^3/person/day which is considered higher than average in South Africa. Water consumption by the flotation plant was not obtained, although water is reclaimed for reuse from the tailings dam.

WATER QUALITY

Minewater from fissures in C mine contains 6-10 ppm F^-. This fluoride level is detrimental for growing children, especially in early growth stages during tooth development even though a seriously impacted health case was never found in the area. World Health standard for F^- is 1 ppm in drinking water.

A study investigated the possibility of distributing defluoridation systems to each household so that only potable water would be treated. Eventually it was found more practical to install a central plant. The CSIR conducted a literature search on the subject of fluoride removal.

The minewater is also relatively high in dissolved silica (12-14 ppm) and has 30-70 ppm NO_3 contributed by explosives used in the mine and small amounts of Cu, Sr, Ba, Fe and Mn.

FLUORIDE REMOVAL PROCESS

The process selected for defluoridation of Rooiberg water is adsorption onto activated alumina. When the F^- adsorption capacity of the alumina bed is exhausted; i.e., when the product water contains 1.5 mg/l of F^-, the alumina is reactivated with 1% NaOH solution. After reusing and neutralization with dilute H_2SO_4 the full adsorption capacity is restored.

A regeneration cycle effluent containing high fluoride and salt levels is to be disposed of by using it as a vehicle to pump tailings onto the tailings dam.

TESTWORK AND PROCESS DESIGN BY:

National Institute for Water Research
CSIR
P. O. Box 395
Pretoria 0001

Telephone: (012) 86-9211
Telex: 3-630SA

Contacts: Gerrit R. Botha
Japie Schoeman

FINAL DESIGN AND CONSTRUCTION: Prentec (Pty) Ltd.
P. O. Box 1433
Edenvale 1610

Telephone: 609-5216
Contact: John A. Buchanan, Managing Director

It was mentioned that the actual plant will be much more conservatively designed than the parameters supplied by NIWR which are shown in the data and diagram presented here.

CAPITAL COST Plant plus Reticulation System R0.75 million
Includes Reticulation System
Two Plants, One at A Mine, one at C Mine

PLANT SIZE 518 m^3/d for each plant

OPERATING COST R0.33/m^3 treated US \$0.20/m^3

PROCESS SELECTION

The CSIR carried out a literature search and found several approaches to fluoride removal from water.

- Reverse Osmosis Works well and gets F^- down lower than needed. Costs 50% more than alumina process. Fouling by Cu, Sr, Ba, Fe, Mn and membranes need weekly citric acid cleaning. Estimated R. O. cost R0.55/m^3.

- Chemical Addition
  - Lime addition - cannot achieve below 8 mg F/l.
  - With additional $MgSO_4$ and alum can achieve below 1.5 ppm F^-, by coagulation and flocculation but requires costly reagents and sludge disposal.

- Ion Exchange
  - Several ion exchange processes are employed including activated carbon, strong base ion exchange resins, bone char, tricalcium phosphate and activated alumina.

A disadvantage of activated carbon is that it works best at pH 3 which would require too much reagent also for raising pH of product water again.

Advantages of Activated Alumina:

1) Activated alumina is very specific.
2) Has a high capacity for F^-. In South African tests 3.2 F^-/l of Settled Al_2O_3 was achieved. 5 g F/l under special conditions is achieved in the USA.

3) Al_2O_3 is not friable, attrition losses are low.
4) Al_2O_3 is not affected much by Cl^- and $SO_4^=$.
5) Regeneration is simple using NaOH.

Based on the above, the activated alumina process was selected.

FLUORIDE REMOVAL PROCESS

The process and design criteria are described in the following information sheet provided by the CSIR National Institute for Water Research.

NIWR INFORMATION SERVICE
NATIONAL INSTITUTE FOR WATER RESEARCH

UDC 628.162.081.38

I WAT 11
March 1983

Fluoride removal from drinking-water by activated alumina adsorption

INTRODUCTION

Fluoride in drinking-water may be beneficial or detrimental to health (particularly of infants and young children), depending on its concentration. In excess of 1,5 to 2,0 mg/ℓ fluoride is known to cause permanent grey or black mottling of tooth enamel and the longterm intake of 3 to 10 mg/ℓ may result in abnormal bone growth in both humans and animals[1,2,3]. On the other hand a fluoride level of about 1 mg/ℓ has been shown to reduce dental cavities in children significantly[1,2], and this concentration level is widely recommended for the growth and maintenance of strong, healthy teeth.

Many groundwaters in the Republic of South Africa are unfit for human consumption because they contain more than the maximum allowable limit of 1,5 mg/ℓ fluoride recommended by the S.A. Bureau of Standards. Fluoride concentrations in groundwater vary from about 2 to 20 mg/ℓ, with levels up to 10 mg/ℓ being fairly prevalent.

DEFLUORIDATION METHODS

Fluoride removal methods can be divided into two categories - those based on the addition of chemicals to cause precipitation or co-precipitation during coagulation and those based on ion exchange or adsorption.

Chemical addition includes the use of lime and magnesium and aluminium salts. Theoretically, lime can reduce fluoride to no lower than 8 mg/ℓ, while fluoride levels of less than 1,5 mg/ℓ can be attained using aluminium and magnesium sulphate. However, excessive and therefore costly dosages are required to remove small amounts of fluoride and the resultant sludge disposal problem makes chemical addition unattractive.

Adsorbents that have been evaluated include activated carbon, strong base anion exchange resins, bone char, tricalcium phosphate and activated alumina[3,4,5,6].

Of these adsorbents, activated alumina appears the most promising because it is specific for fluoride, has a relatively high fluoride exchange capacity, is not affected by chloride and sulphate concentrations normally found in water, and is easy to regenerate. In addition adsorption onto activated alumina is a proven, reliable, safe, simple process.

THE ACTIVATED ALUMINA PROCESS

Activated alumina (Al_2O_3) functions as an anion exchange material in the removal of fluoride. The process, which is carried out in a suitable column or vessel, may be represented as follows:

Loading (fluoride adsorption)

$$\text{Alumina.}H_2SO_4 + 2NaF \rightarrow \text{Alumina.}H_2F_2 + Na_2SO_4.$$

Loading is usually best performed under slightly acidic conditions (pH 5-6) to optimize fluoride adsorption. The product water is, therefore, slightly acidic but can be stabilized with either caustic soda, soda ash or lime.

Backwashing

This is carried out upwards to expand and redistribute the bed and prevent short-circuiting.

Regeneration (using a dilute caustic soda solution)*

$$\text{Alumina.}H_2F_2 + 3NaOH \rightarrow \text{Alumina.}NaOH + 2NaF + 2H_2O.$$

Neutralization

$$2\text{Alumina.}NaOH + 3H_2SO_4 \rightarrow 2\text{Alumina.}H_2SO_4 + Na_2SO_4 + 2H_2O.$$

The Alumina.H_2SO_4 is now ready for another adsorption cycle.

EVALUATION PROGRAMME

The activated alumina process was evaluated by the National Institute for Water Research using a pilot plant (32 m^3/d) on an underground water containing approximately 8 mg/ℓ of fluoride in order to -

- compare regeneration methods (caustic soda vs alum);
- determine the importance of feedwater pH adjustment before loading on process performance;
- establish design criteria for general use; and
- determine the economics of the process.

---

*Aluminium sulphate (alum) may also be used as a regenerant but, although this is a simpler process, it has been shown to result in a lower capacity for fluoride removal and is, therefore, not recommended[7].

CONCLUSIONS

- Fluoride can be reduced from approximately 8 to less than 1 mg/ℓ by the activated alumina process.
- Approximately twice as much product water of a better quality can be produced with soda than with alum as regenerant.
- The precipitation of a sparingly soluble aluminium-silica complex when using alum for regeneration appears to have an adverse influence on the adsorption capacity of the alumina.
- Silicate and hydroxyl ions compete with fluoride for exchange sites on the activated alumina when the pH value of the feed water is greater than 7. This effect is remedied by pH adjustment of the feed water to between 5 and 6.
- A water recovery of more than 90% is possible.
- Provision has to be made to dispose of the regenerant and rinse waters, which amount to about 10% of the water treated and contain high concentrations of fluoride, caustic soda and sodium sulphate.

DESIGN CRITERIA

The following design criteria are based on the use of ALCOA type F-1 activated alumina. They were derived from a pilot plant with a capacity of about 32 m^3/d of defluoridated water.

Activated alumina (ALCOA type F-1*)
Grading: 0,5 to 1,0 mm
Fluoride (F-) exchange capacity: 3,2 g/ℓ
Bed depth: 1,0 to 1,5 m

Feedwater retention (contact) time in column: 5 min minimum

Backwash (50% bed expansion desirable)
Flow rate (adjust as required): 980 $\ell.m^{-2}.min^{-1}$
Duration: 10 min (approx.)

Regenerant (aqueous caustic soda solution): 10 kg/m^3
Regenerant volume: 5 bed volumes**
Regenerant upflow rate: 100 $\ell.m^{-2}.min^{-1}$

Rinsing (after caustic soda regeneration)
Flow rate (downwards): 200 $\ell.m^{-2}.min^{-1}$
Period: 30 min (approx.)

Acid used for neutralization of alumina: 1,53 kg sulphuric acid (1,836 kg/ℓ) per m^3 feed water
Volume of dilute sulphuric acid required: approximately 15 BV (until pH is about 8)
Neutralizing acid flow rate (downward): 200 $\ell.m^{-2}.min^{-1}$

pH Adjustment of feed water to exchange column using dilute sulphuric acid
The amount of dilute (or concentrated) acid required must be determined by calculation or experimentally for each feed water. This may change from time to time and automatic pH control is therefore preferable

*The activated alumina used was obtained from ICI, 1 Leyds Street, Braamfontein, Johannesburg. (This firm is not necessarily the best supplier and any other firm may be approached.)
**1 bed volume = volume of alumina in column.

The output of defluoridated water per regeneration cycle depends on the fluoride concentration of the feed water. At a fluoride concentration of 8 mg/ℓ, approximately 400 bed volumes are produced.

The activated alumina deteriorates with time, due to abrasion and irreversible exchange reactions. A lifetime of about 4 years may be assumed, i.e. approximately 25% fresh alumina may have to be added annually.

COSTS

Total defluoridation costs for a 500 m^3/d (approx.) plant were determined at R0,33/m^3. These include amortization of R146 000 capital over 20 years at 10%/a interest. Also included are the costs of product water stabilization equipment, chlorination and labour, but excluded are those of product water storage and brine disposal. Costs are also affected by factors such as plant size, required regeneration frequency and safety factors. In the case quoted, regeneration was performed after 67 h loading (two regeneration cycles per week) and 25%/a alumina replacement was assumed. However, with more frequent regeneration, smaller equipment may be used for the same output, with a concomitant reduction in cost.

REFERENCES

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2. BISHOP, P.L. and SANCOUCY, C. (1978). Fluoride removal from drinking water by fluidized activated alumina adsorption. *J. Am. Wat. Wks Ass.* 70, (10), 554-559.
3. SORG, T.J. (1978). Treatment technology to meet the interim primary drinking water regulations for inorganics. *J. Am. Wat. Wks Ass.* 70, (2), 105-112.
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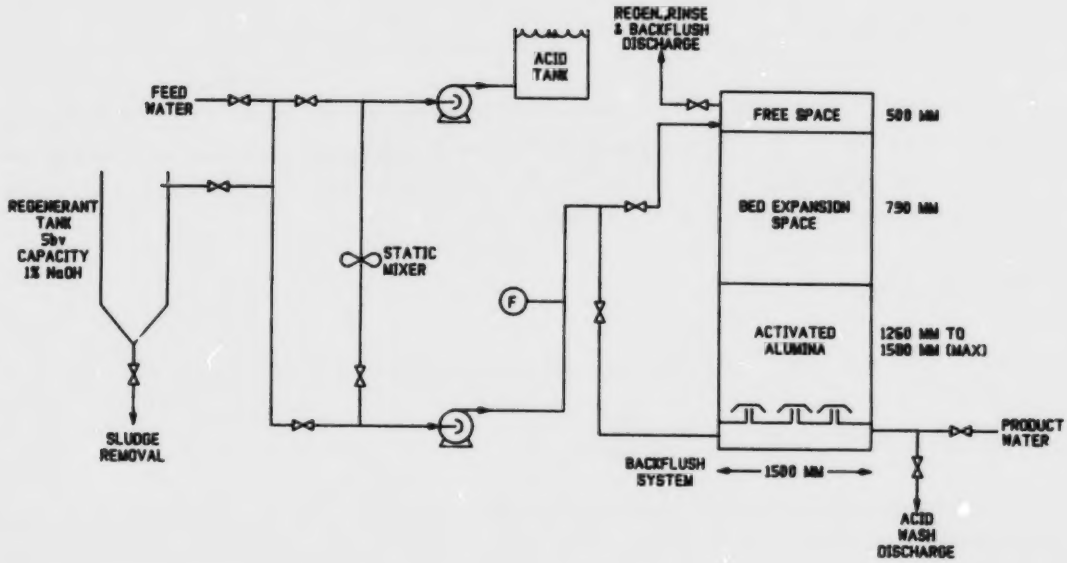
GAcsv 621/0868/8003

DEFLUORIDATION PLANT



In practice two columns were being installed so that one could be regenerated while the second was in the adsorption mode.

OPERATING PROCEDURE

1. Adsorption in fixed bed downflow mode with pH control by H_2SO_4 addition to maintain pH 5.5 at influent end. Adsorption capacity depleted when F^- at outlet is 1.5 mg/l of F^-.

2. Backwash to remove suspended solids accumulated in alumina bed.

3. Regenerate with 1% caustic solution.

4. Rinse, 30 minute upflow at 200 l/min/m².

5. Neutralize alumina with acid.

6. Back to Step 1.

SOURCE OF ALUMINA

Alcoa type F-1 supplied by ICI in South Africa. Alumina is also available from Alusuisse.

WASTE VOLUME

Waste volume is about 10% of the flow of feed. However, an opportunity to make recovery more efficient is the possible reduction of caustic regenerant solution from 5 bed volumes to 3 bed volumes which was shown in the pilot tests to be adequate. The effluent is used to transport tailings into the tailings dam.

PRODUCT QUALITY

Product with less than 1.5 ppm F^- is achieved consistently

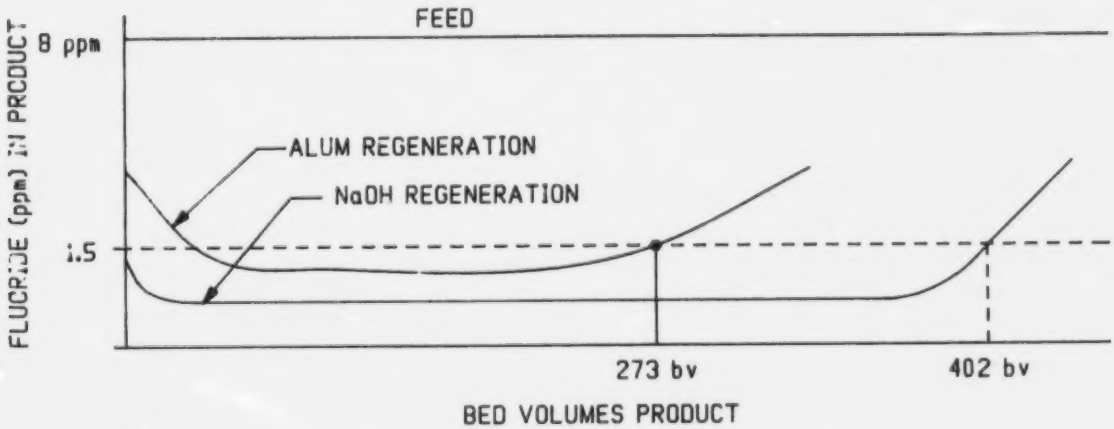
OTHER FLUORIDE REMOVAL PLANTS

An alumina-based fluoride removal plant was designed and installed at the Leeupoort Recreation Farm near Rooiberg Mine at a cost of around R80,000. The owners of the farm needed a good water supply to be able to sell real estate.

The Leeupoort Recreation Farm installed the process without provision for acid dosing to adjust pH and CSIR staff predict that the system will fail.

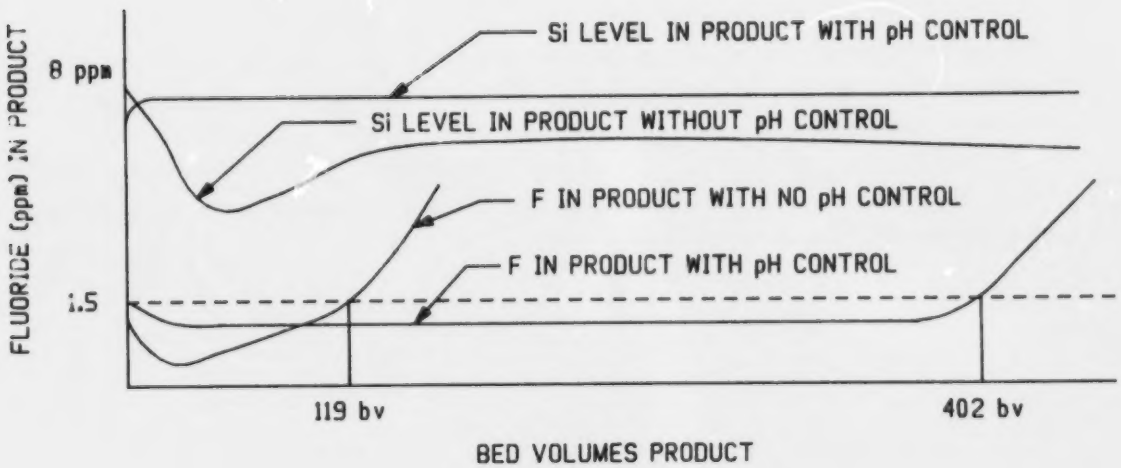
Alumina-based fluoride removal plants are believed to be installed at Gila Bend, Arizona and at Bartlet, Texas. There is believed to be at least one other such plant in California.

PILOT PLANT PERFORMANCE



(Diagrams sketched and not to scale)

402 bv of product at less than 1.5 ppm F^- was recovered per cycle using NaOH regeneration compared with only 273 bv using alum to regenerate the alumina.



(Diagrams sketched and not to scale)

Silica adsorbs onto the alumina granules unless the pH is dropped to below 6. There is enough silica in the feedwater (12-14 ppm) to affect the F^- adsorption capacity of the alumina unless pH is dropped.

CHEMISTRY SENSITIVITY OF ALUMINA F^- REMOVAL

1. If NaOH is added to the raw water, magnesium hydroxide precipitates and flocculates out. The raw feed is scale forming.

2. Arsenic is adsorbed by the activated alumina and it adsorbs irreversibly so it is important that the feed should have no arsenic in it.

3. The activated alumina treated water at reduced pH 5-6 is very corrosive. NaOH is injected at the outlet of the process to maintain slightly scaling conditions.

Note on R. O. Pretreatment

The Leeupoort water is scale forming, and would foul an R. O. membrane. By using alum coagulant, diatomaceous earth and cartridge filters, plugging index can be reduced from 95% to 20%.

CONCLUSIONS

1. An effective and easy to operate activated alumina adsorption and regeneration pilot plant process has been developed and demonstrated for fluoride removal from water.

2. The performance of the actual commercial scale 500 m^3/d plant has not yet been fully evaluated. All indications are, however, that performance will meet the expectations in every single respect.

3. Interesting chemistry sensitivity and mechanisms are identified which must be taken into account in F^- removal by this process.

OPERATION SHULLSBURG MINE
SHULLSBURG, WISCONSIN
(CLOSED SINCE 1979)

COMPANY EAGLE PICHER INDUSTRIES, INC.

LOCATION Southwestern Wisconsin

INTRODUCTION

This minesite was not visited but is reported here based on a description by HOFFMAN (1984) because of the somewhat surprising water quality effects that closure of this mine seems to have had on the quality of the local aquifer.

Exploration and mining operations have been undertaken in this part of the Upper Mississippi Valley zinc-lead district since the 19th century. Extensive underground mining occurred for about 25 years south and west of Shullsburg until the closure of the Bearhole Mine in 1978 and the Shullsburg Mine in 1979. Groundwater quality deterioration was noted by nearby area residents about nine months after closure of the Shullsburg Mine.

Changes in groundwater chemistry believed to be the result of acid mine drainage mechanisms were construed to be responsible for altering associated private water supply quality.

NATURE OF GROUNDWATER CHANGES

Groundwater quality in the Galena-Platteville dolomite aquifer deteriorated due to significant increases in dissolved sulfate to 3500 mg/l. Other impacts were noted with an increase in iron to 65 ppm and lesser quantities of zinc, lead and arsenic.

IMPACT OF WATER QUALITY CHANGE

Water quality impact is primarily due to the high sulfate, some of which reached levels rendering the water impotable to humans and livestock. Dairy farms were especially susceptible.

GEOLOGY

The Shullsburg Mine complex is located in the Driftless area of Wisconsin. Glacial deposits are absent and the surface is characterized by rolling hills with local relief of 100-200 ft. Surface drainage patterns are controlled by geologic structure. Drainage divides are influenced by structural highs, minor folding and joint patterns.

Surface geology is characterized by Ordovician shale overlying the Galena dolomite. Subsurface geology includes the Galena, Decorah and Platteville dolomites overlying the St. Peter sandstone.

All the Ordovician units serve as aquifers, with the majority of wells finished in the Galena-Platteville dolomite or the St. Peter sandstone.

HYDROGEOLOGY

The hydrologic system is a combination of water table and artesian system. The water table system is present in all of the Shullsburg area, but local confinements may produce artesian conditions. Generally, groundwater divides follow surface divides; exceptions occur when pumping activities associated with mine dewatering alter the potentiometric surface. Groundwater flow in the shallow Galena-Platteville dolomite is fracture and joint controlled, typical of carbonate terrains. Groundwater which is recharged throughout the area discharges to streams and through springs.

Mine dewatering was necessary for operations in the Shullsburg region. The lead-zinc sulfide ores occur in the Galena-Platteville dolomite and thus are intimately associated with this upper bedrock aquifer. Large scale dewatering began in the 1950's and continued until closure in 1978-9. It is significant that the Shullsburg Mine was developed in close proximity to the groundwater divide that separated flows between the Galena River and Apple River basin. The development of a large cone of depression resulted in movement of the divide 2-3 miles northwest and southeast of the mining site.

Up to 20 million gpd were pumped during development phases of the 1950's. Flows of 8000 gpm were reported when mining proceded into new fracture systems. Pumping rates just prior to closure were 6.5 million gpd.

GROUNDWATER QUALITY

The groundwater was characterized in 1973 as a calcium-magnesium bicarbonate type, very hard, but suitable for most purposes. TDS were typically between 300-400 mg/l with total hardness accounting for about 90% of the dissolved load. Sulfate averaged 40 mg/l with a maximum reported value of 470 mg/l.

SHULLSBURG MINE

The Shullsburg Mine was the largest and most productive of the underground mines in the area. Sphalerite was the primary ore mineral with associated pyrite, marcasite, galena and calcite, typical of the fracture filling type of orebodies in the region.

Mineralization was not restricted to joints and fractures but also occurs as disseminated replacements up to 400 ft from the primary fracture filling. The mining excavations resulted in drifts following the productive veins. Access was by inclined shafts so ore was trucked from the working faces of the mine to the mill. Ore bodies were drilled, blasted and then worked with front end loaders. Many of the older mined out areas were reached with vertical shafts some of which are still open. Numerous springs and seeps have been noted in the fractured dolomite and it is likely that many or most fractures would yield water under recharge conditions.

Underground inspection in 1978 revealed that several fractures contained abundant sulfides, primarily pyrite and marcasite. A number of these were seen to be actively oxidizing with deposits of an orange gelatinous precipitate. Classic acid oxidation of FeS_2 as discussed in the chapter on Acid Mine Drainage, was occurring in the carbonate environment.

ACID MINE GEOCHEMISTRY

The chemistry of acid mine drainage is discussed in the chapter on the subject. BARNES & ROMBERGER (1968 reference uncertain) stressed the chemical aspects of acid mine drainage and suggest that special problems can occur if the acid product of the reactions are neutralized by dolomite.

Oxidation of sulfide minerals under conditions observed in the Shullsburg area can be described as follows:

Initial Reaction

$$FeS_2 + 2H_2O + 7O_2 = 2Fe^{2+} + 4H^+ + 4SO_4^{=}$$

This reaction is accompanied by minor amounts of metastable thiosulfate which also oxidizes to yield sulfuric acid. Under acid conditions iron sulfides are the most reactive followed by zinc and lead sulfides. The reaction for marcasite and pyrrhotite can be nine or ten times as fast as for pyrite.

In the presence of sulfuric acid and oxygen, ferrous sulfate oxidizes to form water soluble ferric sulfate.

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe(SO_4)_3 + H_2O$$

The kinetics of this reaction is greatly increased by the presence of T. ferroxidans bacteria.

The ferric ions react with water to form ferric hydroxide which yields additional sulfuric acid:

$$Fe^{3+} + 3(SO_4^{2-}) + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4$$

The ferric ion can also oxidize additional iron sulfide to yield sulfuric acid and ferrous ions which energize the T. ferroxidans bacteria.

Ferrous sulfate can react with water to form melanterite $FeSO_4 \cdot 7H_2O$ and copiatite $Fe(OH)_2\ Fe_4\ (SO_4)_6 \cdot 20H_2O$.

The final major reaction involves neutralization of the sulfuric acid by the dolomitic host rock.

$$H_2SO_4 + CaMg(CO_3)_2 = MgSO_4 + Ca^{2+} + 2HCO_3^-$$
$$MgSO_4 = Mg^{++} + SO_4^=$$

The reaction is slowed by the coating effect of precipitated hydroxides and the slower reaction rates of dolomite with acid compared with calcite. This results in micro-environments within the dolomite fractures where acid mine drainage reactions could persist over extensive areas in the underground workings in the Shullsburg Mine.

An important consideration for water quality impacts is that $MgSO_4$ or epsom salts is almost 200 times as soluble as gypsum $CaSO_4$. Therefore, neutralization by dolomite can produce much greater levels of dissolved sulfate than might result from neutralization of calcite or limestone. Evidence of reaction between dolomite and acid mine drainage would be an increase in Mg^{2+} ions relative to calcium as well as elevated sulfate levels.

Water chemistry in the Galena-Platteville dolomite and in the underground workings as determined by C. L. R. HOLT of the U. S. Geological Survey are as follows.

	Fe (ppm)	Ca (ppm)	Mg (ppm)	HCO_3^- (ppm)	$SO_4^=$ (ppm)	Cl^- (ppm)
Galena-Platteville Aquifer	0.6	-	-	374	33	4.6
Galena-Platteville Mineworkings	0.14	113	61	395	203	4.4

SHULLSBURG

Within a year of closure of the mines some area residents noticed deteriorating water quality. Several dairy farms close to the Shullsburg Mine noted a significant drop in milk production. Water samples collected in response to complaints by the Wisconsin Dept. of Natural Resources confirmed elevated sulfate concentrations and associated magnesium, calcium, bicarbonate and iron. High levels of sulfate in the drinking water had both the human and dairy cow victims "on the trot."

Neither the mining company nor the Wisconsin Dept. of Natural Resources anticipated the possibility that cessation of pumping and reflooding the mine would adversely affect nearby private water supplies. Local residents claimed damages against the mining company for an amount in excess of $200,000 in the United States District Court.

Many of the sulfate values for samples of wells in the area exceed the 250 mg/l National Secondary Drinking Water Standard (Federal Registor 7-19-79) by an order of magnitude. Review of the data is believed to support the claim that the increased sulfate levels resulted from the flooding and solubilization of acid oxidation products precipitated in the dolomite fracture system.

Water Quality Impact Data

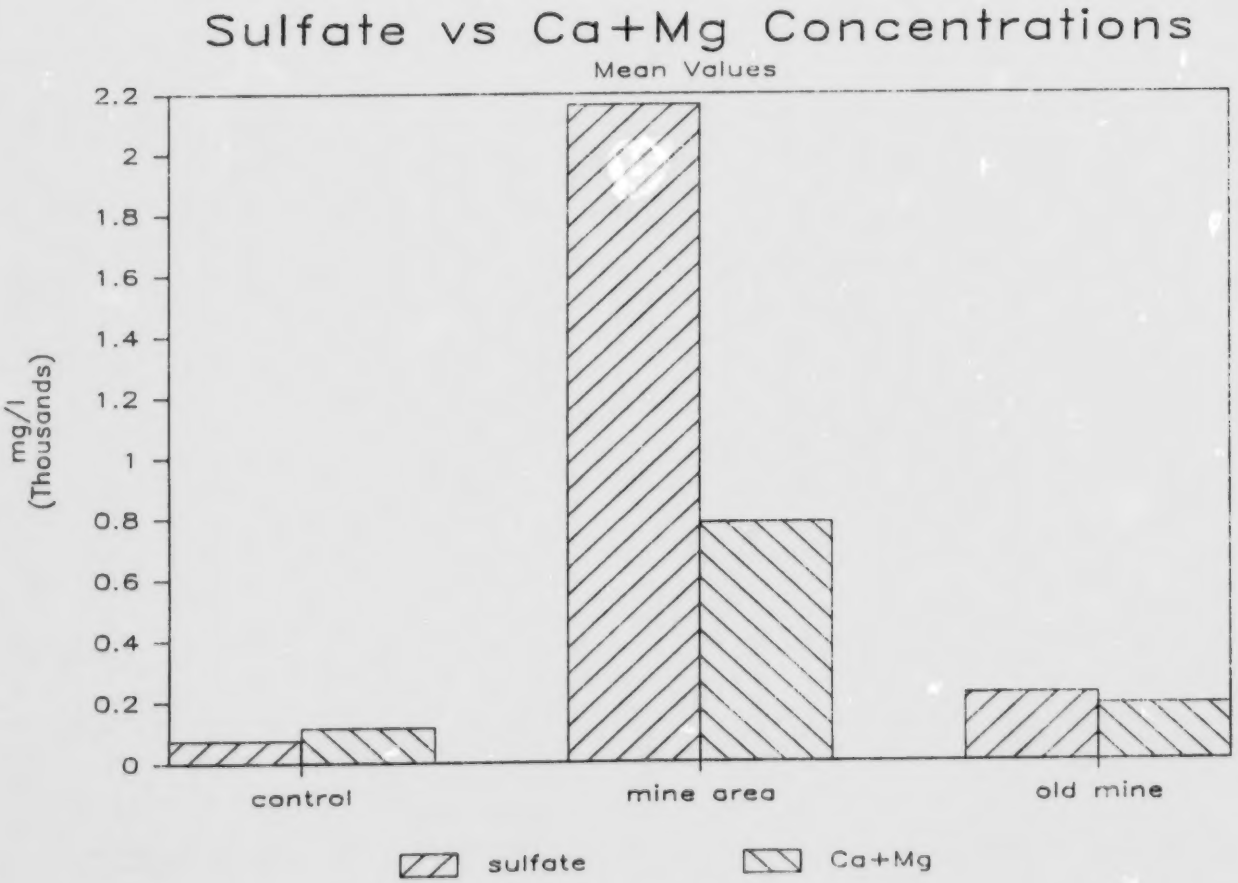
Well #	Sulfate	Calcium	Magnesium	Iron	Zinc	Date
1	1800	498	285	20	-	10/10/80
2	1260	320	160	0.1	18	9/24-80
3	1400	378	261	-	4	12/22/81
4	2800	551	525	8	3	10/10/80
5	2325	380	450	6.8	10	9/24/80
6	900	325	148	6.9	4	10/24/80
7	800	260	121	6.6	14	12/11/80
8	3500	370	820	13	5	9/25/80
9	3000	556	481	0.06	2	12/22/81
23	2300	498	432	0.05	4	12/22/82
25	2100	436	396	0.07	1	12/22/82
Mineshaft	3500	452	590	10.1	15	12/22/82

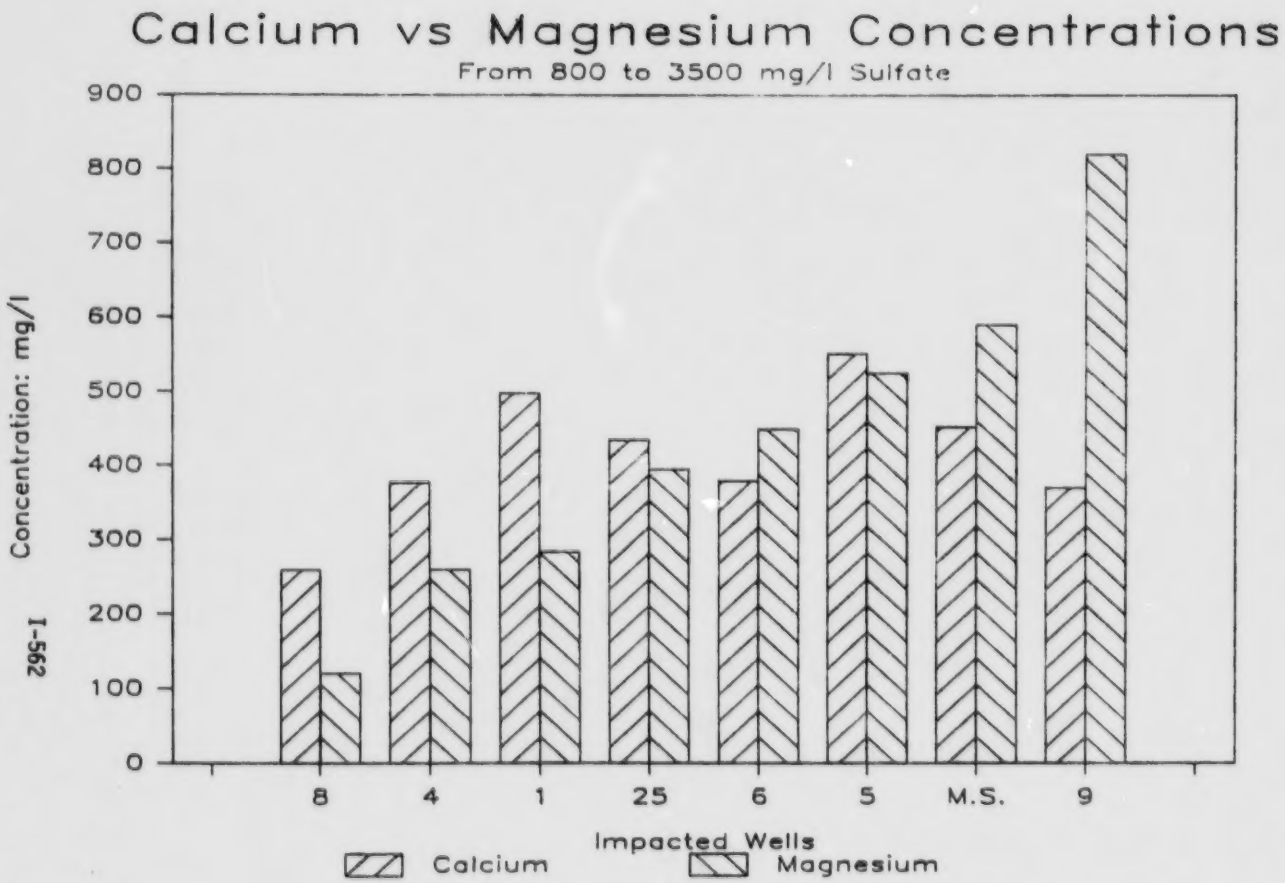
TABLE 3

Shullsburg Ground Water Mine Problem

Wells		Chemical Parameters					
Control Area		Sulfate	Calcium	Magnesium	Iron	Zinc	Date Sampled
	13	120	94.6	60.2	0.01	0.05	3/12/82
	11	45	73.4	40.7	0.01	0.21	3/12/82
	12	32	62.5	34.4	0.01	0.05	3/12/82
	14	85	88.3	53.8	0.01	0.14	3/12/82
	15	95	91.6	48.8	0.01	0.58	3/12/82
	mean	75.4	82.1	33.9	0.01	0.21	
Recent Mine Area							
	4	1400	378	261	0.04	3.68	12/22/81
	25	2100	343	359	1.19	9.24	3/12/82
	17	3000	346	481	0.05	1.68	12/22/82
	mean	2166	422	367	0.43	4.87	
Older Mine Area							
	19	130	81.7	42.6	0.04	0.01	3/12/82
	20	280	147	66.8	0.02	0.19	3/12/82
	21	260	150	71.2	0.02	0.65	3/12/82
	mean	233.3	126.2	60.2	0.03	0.29	

Table 3 represents data from Evans, (1983), grouped according to location with respect to the recently active Shullsburg and Bearhole Mines, older mine areas, and the City of Shullsburg background area. This data was collected either in December of 1981 or March of 1982. It have been chosen because it represents the widest area distribtion of wells sampled in a reasonably close time frame. It is possible that the March data may be influenced by spring recharge conditions; however, given the magnitude of the differences between the control wells up gradient in the City of Shullsburg area, with the impacted wells in the mine area, the influence probably was significant.


Sulfate vs Ca+Mg Concentrations
Mean Values
mg/l
(Thousands)
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
control
mine area
old mine
sulfate
Ca+Mg


Calcium vs Magnesium Concentrations
From 800 to 3500 mg/l Sulfate
Concentration: mg/l
900
800
700
600
500
400
300
200
100
0
8
4
1
25
6
5
M.S.
9
Impacted Wells
Calcium
Magnesium

1. The high sulfate concentrations in ground water associated with dolomitic aquifers in Southwestern Wisconsin appears to be the direct result of acid mine drainage associated with mines in the area.

2. Dewatering of the fractured rock exposed pyrite, marcasite and sphalerite to oxidation in non-saturated flow conditions.

3. Neutralization of sulfuric acid by dolomite produced highly soluble magnesium sulfate.

4. When mining stopped and pumping of water from the workings stopped, the workings were flooded and the exposed sulfates dissolved. Locally sulfate concentrations were increased to 100 times regional background levels rendering the affected groundwater non potable for human and livestock consumption.

5. Water quality data for the older mine area indicates a much lower level of sulfates and AMD products, probably due to the salts having been flushed out of the system which is now flooded.

6. The State of Wisconsin enacted a comprehensive ground water quality protection law in May 1984, and similar types of legislation have been enacted, proposed or planned for other states and the federal government. Ground water quality protection based on numerical standards such as the primary and secondary federal drinking water standards, or the suggested no-adverse response level of the federal EPA have been or are likely to become the basis for regulatory decision making.

   Formal programs of reference sample testing, quality control and chain of custody records will be subject to regulatory control.

   The Wisconsin approach has been to set two tier performance boundaries based on preventative action standards and enforcement standards. Implementation of these standards will require detailed water quality monitoring prior to the new activities in order to establish background conditions. Some fraction of Federal Drinking Water Standards are expected to become the litigation level. Water quality standards will have to be achieved within the property boundaries of new solid waste disposal facilities, and monitoring is likely to be required for all parameters which may be impacted.

The Shullsburg case of mineral rights and water rights raises an interesting situation. It would appear that in Wisconsin a mining company paying royalties to a landowner for mineral extraction will have to guarantee that associated groundwater will not be impacted or of supplying an alternative water supply. This burden will be carried by the company into post mining situations. The above is the opinion of Professor James I. Hoffman whose paper this description summarizes.

Important impact will be felt by long established mines when closure and reclamation applications are made. The Shullsburg litigation was settled out of court.

More details and information on the Shullsburg Mine case study can be obtained from:

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INTRODUCTION

Rehabilitation of the Wedge Mine is one of the pioneering cases where acid mine drainage damage has been prevented, and a sulfide ore minesite restored to an extent that it can be abandoned permanently. The need for perpetual operation of a treatment plant to treat acid mine drainage has been avoided.

Wedge Mine ore was treated at the nearby Heath Steele concentrator so there were no sulfide bearing mill tailings on the site. This simplified the task considerably. High pyrite wasterock on the site was disposed of however in the old mine excavation.

KUIT et al. (1977) described the challenge that presented itself at the Wedge and the measures that were taken to solve the problem. At the time the paper was written the rehabilitation project was not yet complete. The projected steps were in fact carried out in 1978/9 bringing total expenditures to $2 million.

KUIT (1984 personal communication) visited the site in 1984 and found that the natural revegetation over the clay cap and till cover has progressed beautifully.

This is one of the earliest first really successful mine, mill-waste restoration programs and it serves as a good example of what can be achieved. At a cost of $1 per ton ore removed, it indicates that today through proper planning the same results could be achieved at a much lower cost, if implemented as part of the operation. Finally, it does not provide much help in finding an answer to the bigger problem of permanently disposing of acid generating tailings from concentrates which is a subject deserving special attention in Canada today and in the future.

KUIT, W. J.; JACKSON, H. E. & MATTSON, R. M. (1977) Treatment of Acid Water at the Wedge Mine, New Brunswick. CIM Bulletin, October 1977.

Treatment of Acid Water at the Wedge Mine, New Brunswick

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R. M. Mattson, Senior Mining Project Engineer,
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Abstract

Since closure in 1968, the Wedge Mine, situated adjacent to the Nepisiguit River in New Brunswick, has been flooding with acidic water containing toxic levels of heavy metals. Cominco Ltd. has undertaken a series of pollution control measures to mitigate the threat posed to the river quality. Included has been a successful treatment campaign in 1976 which discharged in excess of 30 million gallons of high-quality effluent from the accumulated volume of mine water.

The sources of contamination have been identified as actively leaching waste dumps. A comprehensive program of permanent corrective measures has been prepared which will culminate in mine backfilling. Once completed, the unacceptable burden of water treatment in perpetuity at a non-producing property will be removed.

Introduction

THE WEDGE PROPERTY, located about 30 miles inland from Bathurst, New Brunswick, was discovered in 1956 and mined by Cominco Ltd. from 1962 to 1968. Development and mining operations at the site and ore concentration in the Heath Steele mill 10 miles to the southwest have been described by Douglas.[1] Until exhaustion of ore reserves forced closure, total production amounted to 1.5 million tons at an average rate of 750 tons per day. The main production value was 3% Cu as chalcopyrite, but the total sulphide content was about 95%, with the bulk of the ore being fine-grained massive pyrite, a characteristic feature of much of New Brunswick's base metal mineralization.

During the operating life of the Wedge, environmental control requirements were relatively simple as compared with current standards, which are becoming more demanding. A relatively small flow of acidic mine drainage, averaging 50 gpm, was treated with lime from an underground station and pumped to the surface, where sludge composed principally of fine drill cuttings was settled in ponds. Decanted water then flowed into the Nepisiguit River, which is only about 1,000 feet down slope from the production shaft. The main purpose of this measure was to prevent river contamination by the drilling fines. The ponds containing this material were covered with lime, surface till and gravel when the mine ceased operations in 1968.

Subsequently, however, a mined-out stope began subsiding to the surface and a large open cave developed. This was accompanied by a sustained rise of water level within the underground workings and increasing soluble metal concentrations. In effect, closure was just the beginning of environmental problems originating with earlier mining activity, but the property was far from being left abandoned (as have many hundreds of similar short-lived operations across the country).

A critical element in the case of the Wedge has been the close proximity of the mine, its functional openings and the subsidence cave to the Nepisiguit River, as Figure 1 illustrates. The importance of defending this watercourse from contamination by uncontrolled, heavy-metal-containing acid mine drainage was recognized early by the New Brunswick and Federal authorities and Cominco Ltd. Prior to construction of a hydro-electric installation and other industrial development downstream from the mine, the river and its tributaries were a significant migratory spawning area for Atlantic salmon. The protection of the river is becoming a more acute requirement, as the Federal Department of Fisheries are planning to develop the

Walter J. Kuit was born and educated in British Columbia and since graduation in chemistry in 1966 has been employed by Cominco Ltd. He has conducted a range of chemical and metallurgical research assignments which, since 1972, have been mainly related to process development for effluent control from mining and metallurgical operations. He is currently a research chemist at Cominco's Technical Research Centre in Trail, B.C.

Harry E. Jackson graduated with an Honours degree in chemistry from London University, England, in 1939 and was with I.C.I. until he moved to Canada and joined Cominco Ltd. in 1952. In various assignments, he has had extensive experience in the research, development and application of various chemical and fertilizer products. He is currently senior research chemist at Cominco's Technical Research Centre in Trail, B.C., with main responsibility for effluent treatment and electrometallurgical research.

R. M. (Matt) Mattson was born in Greenwood, British Columbia and grew up in the mining camps of that area. Following graduation in mining engineering from the University of Idaho in 1942, he joined Cominco Ltd. and has held a number of positions in that company's mining operations in the Northern Territories and British Columbia, including that of senior mine engineer at the Sullivan Mine in Kimberley. He is currently senior mining project engineer in Cominco's Central Mines Group in Trail, B.C.

Keywords: Environmental control, Wedge Mine, Cominco Ltd., Acidic water, Effluents, Water pollution, Backfilling, Liming, Waste dumps, Dewatering.

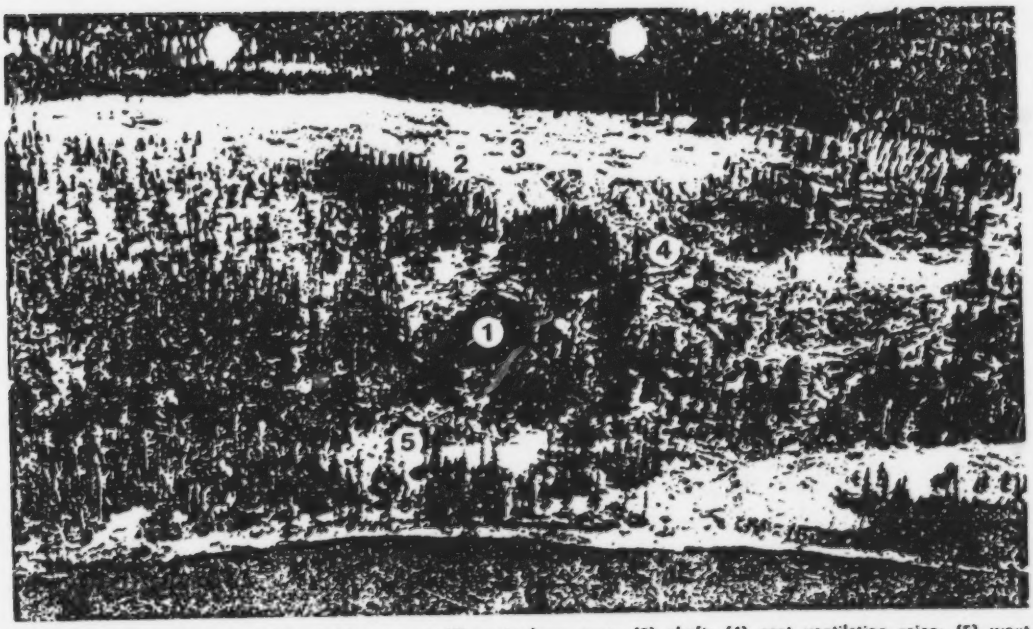

FIGURE 1 — Wedge Mine Site: (1) subsidence cave; (2) waste-dump area; (3) shaft; (4) east ventilation raise; (5) west ventilation raise.

Nepisiguit's potential contribution to salmon resources provided that the interfering downstream factors can be overcome.

This paper provides a review of the various control measures that have been undertaken at the mine site to the end of 1976, an assessment of major factors contributing to post-production environmental problems and an outlook toward the implementation of a permanent corrective solution. The only alternative to this last item is the unacceptable situation of intermittent water treatment operating in perpetuity.

Ventilation Raise Sealing

Water infiltration to the mine and the leaching processes which solubilize toxic heavy metals continued since closure, but were without impact on the river until 1971, when site inspections revealed that seepage from the west ventilation raise (Fig. 1) was reaching the river. This increased during the spring runoff of 1972 to about 45 gpm and was at pH 2.9, containing 850 mgpl Zn and 7 mgpl Cu. It was at this time that New Brunswick and Federal authorities together with Cominco Ltd. agreed on the location of sampling stations above and below the mine on the Nepisiguit to monitor the impact of metals-containing drainage on river quality. Routine sampling commenced in May 1972 and data collected to the end of 1976 are discussed later in the paper.

An unsuccessful attempt was made to seal the raise in July 1972, but a second effort in December of that year resulted in the emplacement of a concrete plug with encased pipe and a valve that effectively prevented any drainage from the mine. This action only served to contain the problem, as the mine cavity was then a water-tight reservoir in which infiltrating volumes of contaminated drainage continued to accumulate. By the summer of 1973, the full magnitude of the problem became apparent and Cominco was requested to prepare contingency measures to deal with uncontrolled mine discharge that could possibly occur over the low point of the subsidence cave rim. Monitoring of the water accumulation indicated that level increases of more than 20 feet per year were experienced, with the bulk being in the spring months. Although the average annual precipitation in the area is less than 2.5 feet, the mine cavity must intercept surface and ground water originating some distance from the mine. The effective mine catchment area capacity is in the order of eight times (20 ft/2.5 ft) that provided by the underground workings.

In-Situ Liming Attempt

In the spring of 1974, the cave water level rose to 10 feet below the low point (total depth approximately 85 feet), and it was estimated that at least 60 million U.S. gallons had accumulated since closure in 1968. Following the consideration of various options, an operation (schematically illustrated in Fig. 2) was undertaken with the objective of neutralizing the contained mine water to about pH 8.5 by the addition of hydrated lime. This would effectively precipitate dissolved metals as a hydroxide sludge within the mine. To achieve efficient circulation, the water was pumped from the shaft, limed and returned to the mine via the subsidence cave. Based on the premise that leaching of heavy-metal sulphides would not occur at a significant rate in the flooded mine due to the slow availability of oxygen and high pH, it was expected that this program would:

— permit any immediate mine discharge to be of safe quality;

— afford a measure of sustained protection for several years.

The criterion for discharge related to the incipient lethal effects of Cu on salmonoid species,

was stipulated by the New Brunswick authorities as being that it should not cause a toxicity increase in the Nepisiguit River of more than 0.1 Toxic Unit of Cu. This system of definition arose from studies during the Northeastern New Brunswick Water Quality Program, which has been reviewed by Bell and Nancarrow.[3]

Although substantial metals reductions were achieved, the final project results, summarized in Table 1, demonstrate that the operation fell short of complete in-situ treatment. A total of 772 tons of hydrated lime were added, but it was subsequently estimated that to reach pH 8.5 and about the 1-mgpl level for all heavy metals, in the order of 1,800 tons would have been necessary. Various operating problems impeded the campaign, of which the most severe was corrosion by the cementation reaction of the soluble Cu in the raw water. A six-week shutdown was caused by the virtual destruction of mild steel lineshaft pump columns.

Following the operation's termination, it became apparent that reversion of the water quality was a confirmed trend. From depth sampling conducted by the Environmental Protection Service to April 1975, the average values for pH and Cu concentration given in Table 2 indicate that even complete treatment would have been only a temporary success. This phenomenon was believed to be caused by infiltration from sulphide-containing waste dumps above the mine and not by leaching from the flooded broken and in-place ore that remained underground, an interpretation indirectly supported by the following analysis of a surface dump puddle which collected after heavy rains.

pH	Cu	Zn	Fe
2.0	1,700 mgpl	2,000 mgpl	20,000 mgpl

Controlled Discharge and Treatment Progress in 1975

In order to avert a massive uncontrolled mine overflow during spring runoff, permission was obtained to conduct a limited discharge of accumulated water from the valve in the previously sealed west ventilation raise. The restriction on this emergency measure was that the combined impact of Cu and Zn was not to result in greater than 0.1 Toxic Unit in the Nepisiguit below the mine. This required that regulation of the rate of discharge be based on the metals concentration and the actual river flow. With daily discharge flow adjustments and increased river monitoring, the program was started on April 30 with the subsidence cave level at 7 feet to overflow and concluded June 7 after discharging 5.7 million U.S. gallons of mine water and lowering the water level to about 14 feet from overflow. Average heavy metals concentration of the discharge was:

Cu	Zn
60 mgpl	670 mgpl

Total river flow over the period was estimated at 13.8 $\times 10^{10}$ U.S. gallons, which yields a dilution factor of 24,000:1. Owing to channeling, average measured metals concentrations in the river, as shown in Table 3, indicated undesirable effects immediately below the mine, which caused fish kills in test cages, but the program had negligible over-all impact on downstream quality. In spite of this action having relieved the immediate pressures, it was evident that a further reduction of accumulated water was required in order to contain the mine infiltration anticipated in the spring of 1976. For this purpose, an operation (outlined in Fig. 3) was rapidly mobilized using essentially the same major facilities as in 1974, with the inclusion of a 200,000-gallon settling pond, 3,000 square feet in surface area, complete with a sludge pumping system. The plant was located on the waste dump near the mine shaft. By lime neutralization of raw water to pH 9.5, the objective of the campaign was to discharge 10 million gallons of treated pond overflow to the river, with metal hydroxide sludge return to the subsidence cave. Essentially, this plant was a rough field attempt at what is now considered conventional mechanized drainage treatment.

The main project parameters, given in Table 4, show that only 35% of the discharge objective was achieved over the 23-day operating period from September 5

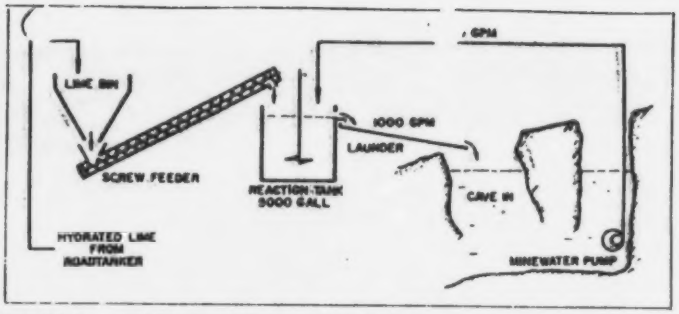

FIGURE 2 — 1974 Treament Plant — in-situ liming.

TABLE 1 — 1974 In-Situ Treatment Results

Parameter	Start, July 2	Final, October 5
pH	3.5	6.7
Cu	64 mgpl	0.25 mgpl
Zn	780 mgpl	365 mgpl
Fe	2,800 mgpl	1,480 mgpl

Total volume circulated: 44.8 million U.S. gallons
Lime added: 772 tons

TABLE 2 — Water Quality Deterioration — Post-1974 Treatment

Date of Sampling	pH	Cu, mgpl
October 8, 1974.....	6.7	0.25
November 7, 1974....	5.8	1.60
December 11, 1974...	4.1	5.5
April 23, 1975.....	3.2	32.8

(Values averaged from E.P.S. subsidence cave depth surveys)

TABLE 3 1975 Controlled Discharge Program River Monitoring Results

Sampling Station	Cu, mgpl	Zn, mgpl
A (above mine)	.006	.065
B (1/2 mile below)	.036	.285
D (3 miles below)	.008	.059
*Calculated (below mine).....	.0085	.093

*Based on dilution of discharge metals concentrations added to A values

to September 28, which [illegible]ered the subsidence cave water level to 20.5 feet from overflow. **Massive sludge volumes were a severe problem and this effect was reflected in plant efficiency, as only 24% of the water volume treated was actually discharged to the river.** Effluent quality was less than expected, but it was reported that a continuous bioassay by the placement of a fish cage directly in the discharge over the last 11 days showed 100% survival.

Hydrogeological and Waste-Dump Studies

Concern over continuing difficult treatment requirements at the Wedge property led Cominco Ltd. in early 1976 to retain Montreal Engineering Co. Ltd. for the purpose of conducting a hydrogeological assessment of the mine area and to recommend the most viable long-term solution to the problem. In their report to the company, this firm concurred with Cominco's conclusions that the major sources of the over-all hydraulic and leached metals accumulation, illustrated by Figure 4, were respectively:

— direct surface runoff and relatively shallow ground-water flow from a catchment area immediately up gradient from the mine;

— pyritic waste and development waste dumps immediately above the mine.

The recommendation submitted was that Cominco's program of mine backfill be undertaken, which, in summary, would include:

— submersion of chemically active surface dumps in the deepest accessible part of the mine;

— ground caving above the shallow stopes by drilling and blasting;

— substantial mine dewatering by treatment;

— backfilling with inert till and gravel;

— fill sealing with a compacted clay layer and placement of surface till.

From the standpoint of contaminant production, confidence was expressed that this course of action would recreate a hydrogeologic regime analagous, or even preferable, to the natural pre-mine situation. This would also satisfy concerns for public safety that had been expressed regarding the open subsidence cave.

The key element in the rationale on which the proposal was based was that the waste dumps were the source of water-soluble metals. Confirmatory leach studies were done in Cominco laboratories and these substantiated the contention. Both the estimated 18,000 tons of pyritic waste and the 65,000 tons of development waste in surface dumps were found to readily generate acidity and significant metals concentrations. Based on moisture content and contained soluble metals, Table 5 indicates the volume and quality of the water in the respective dumps at the time the samples were taken. The continuing impact of the dumps on the mine water quality would be controlled by the cyclic features of natural leaching. Alternating periods of precipitation or runoff and dry weather would be expected to flush and replenish the soluble metals. In an extensive study of abandoned New Brunswick tailings dumps, Boorman and Watson[9] concluded that seepage metals concentrations were largely controlled by availability of oxygen for sulphide oxidation. The exposure and permeability of the Wedge dumps

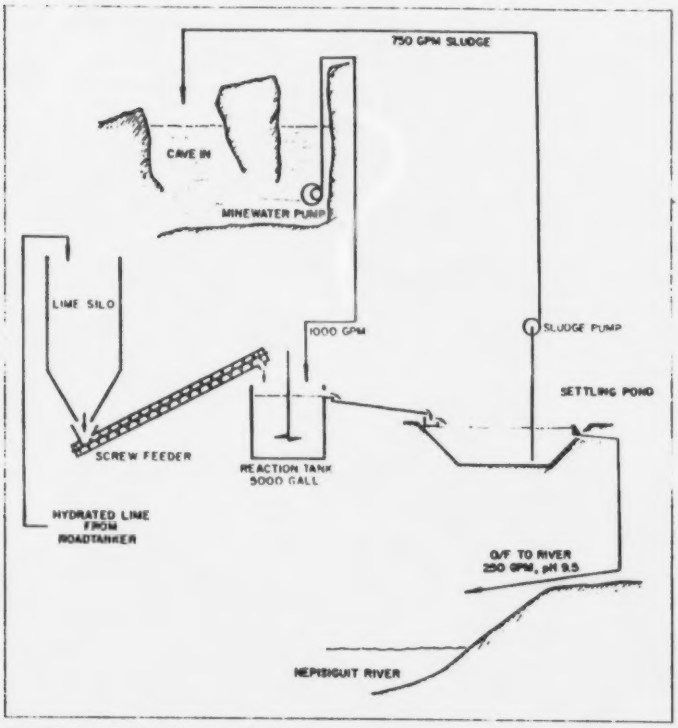

FIGURE 3 — 1975 Treatment Plant.

TABLE 4 — 1975 Treatment Operation Results

Parameters	Raw Mine Water, Avg.	Treated Water, Avg.
pH	4.2	9.4
Cu	55 mgpl	0.25 mgpl
Zn	580 mgpl	1.6 mgpl
Fe	2,100 mgpl	3.0 mgpl

Water volume treated: 15 million U.S. gallons
Water volume discharged: 3.6 million U.S. gallons (24% of total)
Lime consumption: 230 tons

TABLE 5 — Wedge Surface Waste Dumps — Contained Water Quality

Parameter	Pyritic Waste	Development Waste
Weight	18,000 tons	65,000 tons
Moisture	15.1%	7.5%
Contained Water Volume	543,000 gallons	975,000 gallons
pH	2.1	2.3
Cu	346 mgpl	180 mgpl
Zn	771 mgpl	184 mgpl
Fe	7,600 mgpl	760 mgpl

would provide adequate ventilation for the production of highly contaminated drainage.

1976 Dewatering and Treatment Program

Previous water treatment experience at the site demonstrated that a substantially improved plant was a prerequisite to meet the continuing threat of massive mine overflow and to support the several stages of complete rehabilitation that were being planned. Research and engineering studies were made of several alternatives which would overcome the most severe operating problems encountered in 1975 and permit a reasonably high rate of good-quality discharge from the mine.

A target objective for the 1976 campaign was set at 30 million U.S. gallons discharge, and a plant was designed and constructed to operate on the basis of the simplified flowsheet shown in Figure 5. In addition to diesel electric power generation and the lineshaft pump system (250-ft depth) in the mine shaft, major process components were:

— hydrated lime slurry preparation and storage incorporating a jet mixer, 10,000-gallon rail tank, air agitation and submersible pump for lime supply — no plant handling of dry lime;

— two 10,000-gallon reaction tanks in series (nominal retention time 20 minutes), equipped with aspirating pumps for mixing and partial oxidation of ferrous iron (Fe^{++});

— organic flocculant solution preparation followed by dilution prior to application in the reaction tank discharge launder;

— 200,00-gallon, 3,000-square-foot primary settling pond with an installed static underflow collection and pumping system with sludge return to the mine;

— a 30,000-gallon polishing pond before effluent overflow discharge to the river.

The total installed plant horsepower was 175 and primary settling pond effluent was used for all process water requirements.

Treatment commenced on July 12, 1976 and over the 78-day operating period achieved a total discharge volume of 30.6 million U.S. gallons, exceeding the objective. This lowered the mine water level by 46 feet, as illustrated in Figure 6. Based on the total volume treated of 64.6 million U.S. gallons, the average discharge efficiency during the campaign was only about 45%, but improved greatly from 30% at the start to about 80% at the end.

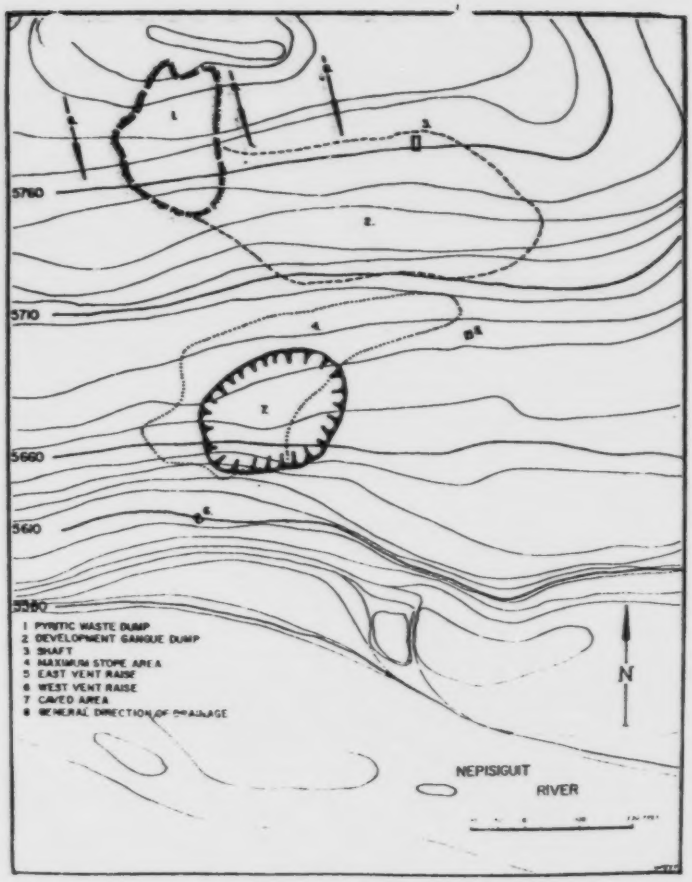

FIGURE 4 — Wedge Mine surface plan.

Although sludge flocculation was satisfactory, the high volumes collected in the primary settling pond (70% of total flow) during the early stages of operation were a severe problem and the original underflow pumping system had to be supplemented with a 4-in. diesel-driven unit. Treatment was intermittent, but sludge pumping was continuous to reduce pond accumulations. A second serious difficulty, common with most facilities treating water with high metals concentrations, was gypsum scaling throughout the plant following contact of lime with the raw water. This necessitated substantial maintenance downtime for manual descalling of equipment and piping. The system for supplying treated water to the plant was found to be particularly sensitive.

The quality of plant effluent discharged to the Nepisiguit River is shown by daily total metal concentrations of Cu, Zn and Fe over the 78-day operating period in Figure 7. Average pH was 9.8 and additional analyses showed Pb to be consistently less than 0.1 mgpl. Sampling by relatively untrained personnel under highly contaminated field conditions may have been a factor in the occasional high values, of which the most unfavourable were 1.5 mgpl Cu, 2.2 mgpl Zn and 14 mgpl Fe. Including these, however, the over-all treatment performance is regarded as being excellent, with the average effluent quality of:

Cu	Zn	Fe	Pb	pH
0.24 mgpl	0.58 mgpl	1.6 mgpl	<0.1 mgpl	9.8

These parameters compare well with the objectives set forth in the "National Guidelines/Regulations" for existing mining operations, which are (Fe not specified):

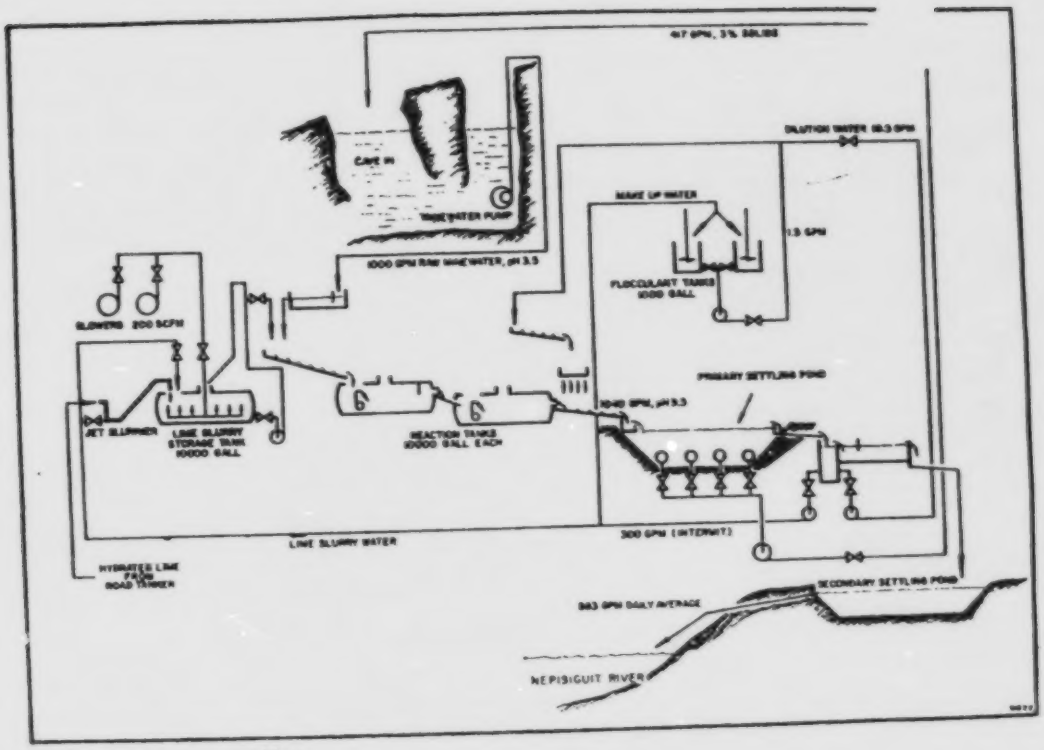

FIGURE 5 — 1976 Treatment Plant.

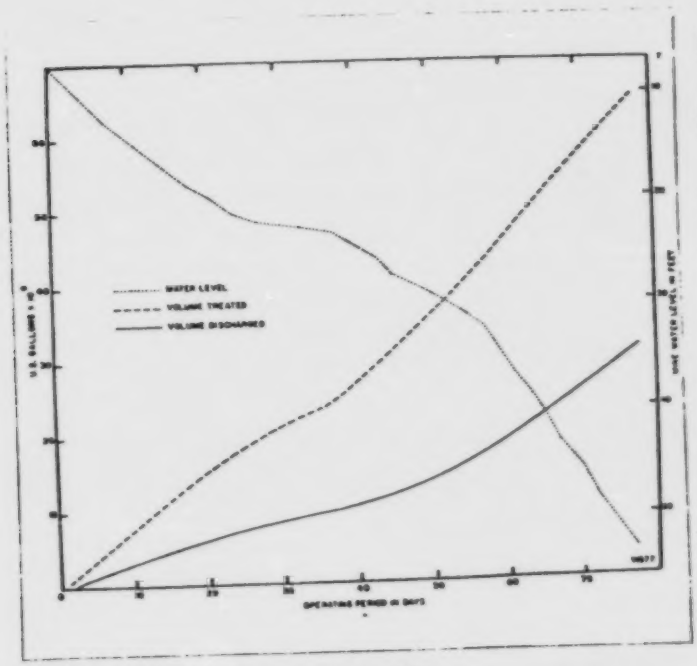

FIGURE 6 — 1976 operation — progress summary.

	Cu	Zn	Pb	pH
Daily Maximum	0.45 mgpl	0.75 mgpl	0.3 mgpl	minimum 5.5
Monthly Average	0.3 mgpl	0.5 mgpl	0.2 mgpl	minimum 6.0

In addition, the above requirements are accompanied by respective suspended solid standard levels of 37.5 and 25 mgpl, which in reality could not be tolerated if the metals parameters are to be satisfied in a treatment operation of this type. Soluble metals concentrations less than the objective levels can readily be attained by pH control at 9.5, but treatment sludge solids are metal hydroxides that will reflect in total metals analyses, usually proportionate to the corresponding raw water concentrations. Preparatory research studies indicated that the Wedge plant effluent had to contain consistently less than 5 mgpl suspended solids in order to satisfy the daily maximum metals parameters.

Total hydrated lime consumed over the 78-day operation was 940 tons, but actual process consump-

tion declined dramatically from 25 to 7 tons per million U.S. gallons of water treated, which corresponded to reduced metals concentrations in the mine water, as illustrated in Figure 8. This factor was of primary importance in greatly improved plant efficiency in the latter stages of the campaign, because sludge production, lime demand and metals concentrations are directly interrelated. Accompanied by increased pH from 3.5 to 7.5, the improved raw water quality was attributed to the dilution effects of the high volume of low-density sludge, which was about 95% treated water. Without being intended, the objective set for the previously discussed in-situ liming operation in 1974 came close to being attained.

Pyrite Waste Disposal and Future Rehabilitation

The substantial reduction of accumulated water volume achieved by the successful 1976 treatment campaign permitted Cominco Ltd. to start implementing corrective actions addressed to causes of the mine water problem. In October, a 90-foot-long drop raise of about 70-degrees inclination was driven from safe ground near the east ventilation raise (Fig. 1) to the deepest part of the stoped area. The 18,000 tons of pyritic waste were then placed under the surface of the remaining water using the drop raise as a chute. Submersion of the waste is expected to have a moderate impact on the metals content of the contained mine water, but fresh leaching will be prevented.

This action represents the start of the permanent rehabilitative measures to which Cominco Ltd. is committed. During this paper's preparation, planning of the subsequent stages was in progress and it was expected that a substantial portion of the project could be completed by the end of 1977. When concluded, this costly mine filling and surface restoration program will remove the potential threat to the Nepisiguit River and relieve the difficult burden of water treatment in perpetuity.

River Quality Monitoring

Since May 1972, Cominco Ltd. has conducted routine monitoring in the Wedge area, which has included the use of stations immediately above the mine and about ½ mile below on the Nepisiguit

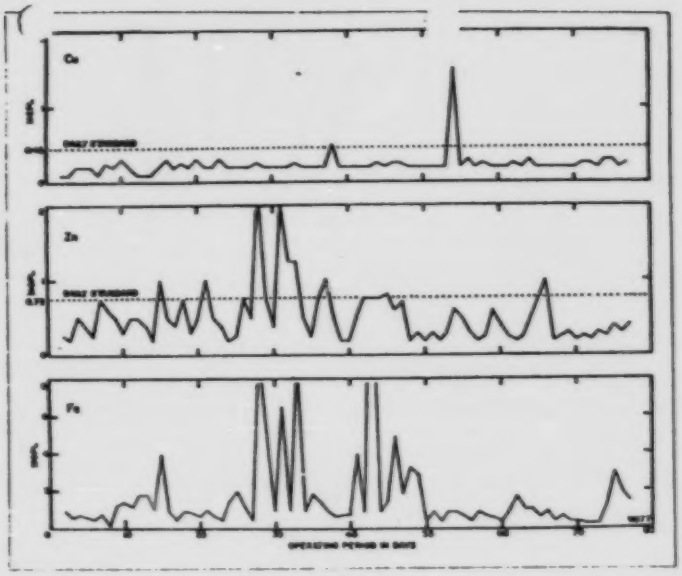

FIGURE 7 — Treated water quality — 1976 operation.

TABLE 6 Nepisiguit River Quality Monitoring Summary

Period	Station A (Above Mine) Cu, mgpl	Station A (Above Mine) Zn, mgpl	Station B (Below Mine) Cu, mgpl	Station B (Below Mine) Zn, mgpl
May-June 1972	.005	.010	.005	.375
July-Dec. 1972	.005	.030	.005	.075
Jan.-June 1973	[illegible]	.028	.006	.030
July-Dec. 1973	[illegible]	.018	.011	.025
Jan.-June 1974	.005	.050	.005	.040
July-Dec. 1974	.010	.077	.010	.023
Jan.-June 1975	.007	.085	.010	.120
July-Dec. 1975	Nil	.011	<.001	.021
Jan.-June 1976	N/A	N/A	Nil	.070
July-Dec. 1976	<.001	.011	.001	.022
Averages 1972-1976	.0052	.036	.0054	.086

TABLE 7 — Wedge Mine — Pollution Control Expenditure Summary

Period	Project	Effect	Cost, $
Dec. 1972	Ventilation Raise Sealing	Problem Deferment	$40,500
July-Oct. 1974	In-Situ Liming	Unsuccessful	153,000
May-June 1975	Controlled Discharge Program	Mitigation of Drainage Impact	12,000
Sept. 1975	Water Treatment	Modest Discharge of 3.6 Million Gallons	66,000
Dec. 1975-Oct. 1976	Research, Design, Consultants		47,000
July-Sept. 1976	Water Treatment	Successful, 38.6 Millions Gallons Discharged	274,000
October 1976	Pyrite Disposal	First Phase of Mine Rehabilitation	49,000
1972-1976	Monitoring		62,000
Total to Date			$703,500
Mine Rehabilitation Estimate			750,000
Total Costs			$1,453,500

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above the confluence with Forty Mile Brook. Analytical data for Cu and Zn in the river water to the end of 1976 are presented in Table 6 as averages over six-month intervals, with anomalous values being rejected. The latter include samplings when significantly higher metals concentrations were apparent upstream and others where contamination caused obvious discrepancies.

With the exception of channeling problems in the 1975 controlled discharge program, which have been discussed, there has been no evidence since the sealing of the west ventilation raise that the mine has had significant downstream effects on water quality. Cu, the most toxic element, has been consistently low at both sampling stations. The averaged data shows Zn concentrations to be higher downstream, but most of the difference is due to the pre-raise sealing period. In any case, the over-all impact of the mine in this period is not believed to have been harmful to aquatic life in the Nepisiguit River.

Pollution Control Expenditures

Since closure of the mine in 1968, Cominco Ltd. has spent more than $700,000 on the various projects and support functions directed either to water treatment or to mitigating the pollution threat posed by the Wedge Mine. These are summarized in Table 7, and, including estimates for the remaining stages of mine rehabilitation, the total expenditure will amount to about $1,500,000, equivalent to $1.00 per ton of total production. It is noteworthy that these costs have come after the fact that production termination measures satisfied requirements existing at that time. If they could have been anticipated during the mine feasibility stage, the decision on property operation may well have been seriously affected.

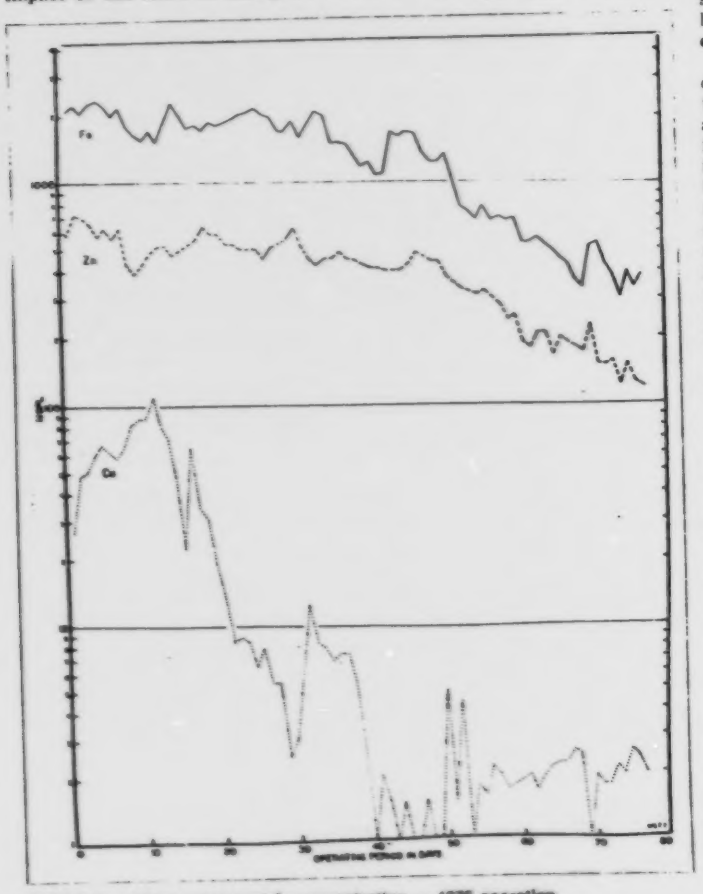

FIGURE 8 — Mine water metals concentration — 1976 operation.

Summary

Since closure of the Wedge Mine in 1968, Cominco Ltd. has undertaken a series of pollution control measures at the site addressed to the problem of highly contaminated mine water. These have successfully protected the quality and aquatic life of the Nepisiguit River by either prevention of the uncontrolled discharge of highly toxic drainage or treatment to produce effluents of low metals content. The 1976 treatment campaign, in which 30.6 million gallons of accumulated water was discharged, is significant in that conventional liming treatment technology was viably adapted to a self-contained operation at a site without normal plant services. The high quality of effluent produced demonstrates that the objective levels of the National Guidelines/Regulations standards for existing mines can be satisfied at abandoned properties.

The source of the contaminated drainage problem has been identified as surface waste dumps that are actively leaching, and a plan for permanent mine rehabilitation is being implemented. This includes burial of the surface wastes in the mine and total backfilling of the accessible stopes. It is expected that once this course of action is completed the generation of contaminated drainage will be prevented and the burden of water treatment in perpetuity will be removed.

Acknowlegments

The authors gratefully extend appreciation to Cominco Ltd. for permission to submit this paper. Acknowledgment is also made to L. Tozer of Tozer Construction Ltd., Bathurst, New Brunswick, for his many contributions to the projects undertaken at the Wedge Mine.

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(3) Boorman, R. S., and Watson, D. M.; Chemical Processes in Abandoned Sulphide Tailings Dumps and Environmental Implications for Northeastern New Brunswick, *CIM Bulletin*, August 1976.

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INTRODUCTION

St. Joe Minerals operates a large electrothermic zinc refinery at Monaca , PA. This trip report describes a water treatment program brought into effect for this plant that achieved a 95% reduction in metals released to the environment in effluents from this plant.

A description by CULICK & BROCKMILLER (1980) outlines the program from 1970 to 1980. It is somewhat out of date because since it was written the Monaca operation has been trimmed considerably. Nonetheless, their paper is of importance because it shows what can be achieved using conventional lime precipitation and settling techniques. It also shows the importance of cutting back on water use and of segregating water flows to keep non-contact water separate from water that has been contaminated by metals.

In March-April 1984 a new regulation package governing non-ferrous metal smelters appeared in the Federal Register under the title: "Final Effluent Limitation Guideline, Non Ferrous Manufacturing - Non-Point Source Category." These Best Available Technology regulations under RCRA would require technology beyond lime-settle-filter. The new regulations placed restrictions on both the mass of metal that may be released in effluents and maximum allowable concentrations for these metals.

St. Joe Minerals Corporation together with other non ferrous metals producers filed a complaint and were in the process of supporting American Mining Congress litigation against the U.S. EPA.

Because of the sub-judice status of regulations governing non-ferrous smelters, the company was understandably not free at that time to discuss the subject in detail.

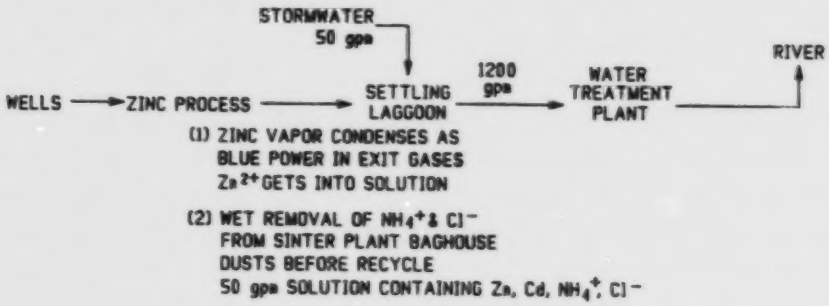
For non-ferrous metals refinery operations consisting of several consecutive processes, the total amount of metal contaminants that may be released in effluents is computed building-block fashion from a series of allowances for each part of the metal processing sequence. Since the regulations are interpreted to have been written for electrolytic plants, it was felt that several processing steps applicable to pyrometallurgical processing had been left out and that the net allowable levels of metals in effluents from plants such as at Monaca were impossibly low.

METALLURGICAL OPERATING UNITS : Roaster and Acid Plant
Sinter Plant
Electrothermic Zinc Plant
Chloride and Ammonia Removal Plant
Treating Sinter dusts

PROCESS WATER FLOWRATE : 1200 USgpm

FUTURE AIMS : St. Joe aims to be able to recycle more water within the plant, thereby reducing the amount of effluent requiring treatment.

WATER BALANCE



Water for use in the process is obtained from wells on the property which supply 1120 USgpm. About 80 gpm (average) stormwater is added to yield a total of 1200 USgpm to the settling lagoon and treatment plant.

Water is used in the metallurgical processes in two main places:

1) In the zinc vapor condensors where exit gases are scrubbed. Blue powder is formed and some chloride and zinc goes into solution.

2) In the sinter process bagfilter dust containing zinc and cadmium is treated at pH 10.5. About 50 gpm liquor is generated containing dissolved Zn, Cd, NH_4^+ and Cl^-.

TYPICAL EFFLUENT COMPOSITION (BEFORE & AFTER TREATMENT)

	Element	Mean	1 Day Max.	10 Day Max.	30 Day Max.
St. Joe - Influent	Zn	14.5	77.2	30.0	21.3
	Cd	2.4	16.7	6.2	3.9
	Pb	2.6	16.0	6.0	4.0
St. Joe - LS&F	Zn	0.55	3.34	1.24	0.75
	Cd	0.19	1.02	0.39	0.22
	Pb	0.07	0.45	0.17	0.12
	Flow	1200 gpm			

Note: All analyses expressed in ppm except as otherwise noted.

TREATMENT PROCESS

The water treatment process installed by St. Joe consists of the following steps:

1. Settling Lagoon with 2.5 million gallon surge capacity. Min 4' depth to 9.5' level.

2. Lime addition tank - Reactor 1

3. Lime addition tank - Reactor 2

4. CBI - Thickener - Clarifier

5. Overflow filtration units

6. Clarifier sludge recycle to the sinter plant

Settling Lagoon

The plastic lined settling lagoon is fitted with a center boom to provide a longer residence time for effluents. Three floating pumps are installed at the outlet end of the lagoon. At any one time two may be in use with one standby. Plant effluents as well as drainage and spills drain directly to the lagoon. Feedwater is usually at pH 7.5.

Chemical Contactor No. 1

Settled effluent water is pumped to mechanically agitated reactor No. 1 (12,000 gallon capacity) which is baffled. A magnetic flowmeter controls the flow to the reactor No. 1 and is regulated by the liquid level therein. A 5% lime slurry is added to maintain pH 8.8 in Reactor No. 1. Lime addition is controlled by a BIF Splitter made by BIF Division of General Signal Corporation, Warwick, R. I. which is pneumatically controlled.

Chemical Contactor No. 2

Overflow from Reactor No. 1 flows into Reactor No. 2 to which lime slurry is added via another BIF Splitter to bring the pH to 9. Sludge from the clarifier is returned to this tank. Overflow from Reactor No. 2 flows to the clarifier which is outdoors. Reactors 1 and 2 and reagent as well as flocculant makeup tanks are housed indoors.

Flocculant Addition

Calgon 3100 flocculant is added to the feed launder at 1 ppm dosage.

Clarification

The precipitated effluent is clarified in a 65' Ø 15' wall depth Walker Division of Chicago Bridge and Iron clarifier with radial launders. Sludge is either recycled to Reactor 2 or discharged to filters for further dewatering before being added to the sinter plant feed.

Initially the clarifier failed to achieve a clear overflow. Tests with bentonite addition to the lime to provide an aid in clarification were abandoned in favor of underflow sludge recycle as the overflow still contained too much suspended solids.

Initially underflow was recycled to increase sludge density but the sludge compacted to form a cake that could not be pumped.

The clarifier operation was modified to use a very shallow sludge blanket - just enough to feed the recycle pump. Thickener underflow recycle now achieves a very clear overflow effluent.

LIME SLURRY SYSTEM

Every day a new batch of flocculant is made up by dissolving 10-15 lbs of dry flocculant powder in stainless steel 400 gallon batch tanks. Two tanks are in use for this purpose. One tank is mixed and aged for 24 hours while the other tank is in use as a dispenser. Calgon 1P3100 flocculant costing $2.30/lb was being used in June 1984. The flocculant dosage is varied by changing the amount of dry polymer added to the 400 gallon mixing tank each day depending on the flow of effluent.

Milton Roy diaphram pumps are used for flocculant solution dosing and are found to be reliable.

It has been found that if the polymer addition system fails, a problem develops rapidly with the overflow clarity.

pH CONTROL

Lime addition is controlled by measuring the pH automatically. Solutions are usually saturated with carbonate and as the pH is increased $CaCO_3$ coats the electrodes. When this happens the slowdown in response can be observed in the pH chart recorders. Electrodes are then simply immersed in hydrochloric acid to clean them which immediately speeds up their response and brings the pH back under tight control.

UNILOC pH electrodes have been in use at the plant and have proven satisfactory.

FILTER PRESS

Six loads per week are typically dewatered in a Perrin filter press. Two loads on Mondays, Wednesdays and Fridays.

The dry cake contains about 50% moisture. On a dry basis the cake contains about 10% Zn and 1% Cd. The cake is returned to the roaster plant as secondary feed.

About 12 tons/week of wet sludge is generated.

MULTIMEDIA POLISHING FILTERS

Three Envirotech Multi-media 10' Ø filters using anthracite coal and sand media are employed in the plant. Two are in use and one on standby at any time. Each filter is backwashed every 8 hours. The biggest problem encountered is buildup of $CaCO_3$ on the media support grid, with the result that the filters have to be rebedded every 2-3 years. Possibly inhibited hydrochloric acid would make it possible to clear the calcite scale buildup more easily.

FLOW REGULATION

A Leeds and Northrup magnetic flowmeter is used to regulate the valve at the inflow to the system.

OPERATORS

The plant is unattended. A utility man from the acid plant passes through every 2 hours. Several alarms signal in the plant control room and also at the utility room to alert when the operation of the plant is out of balance.

The daylight shift utility man comes to operate and clean the filter press as needed to dewater the sludges.

SLUDGE PUMPS

Warren Rupp pumps are installed to pump the clarifier underflow to the filter presses. Two lines are installed. These require 90 psi compressed air.

DORRCO recessed impellor pumps are used to recirculate sludges to the #2 Reactor tank at about 50 gpm.

St. Joe Minerals Corporation, Monaca PA
Achievement Record

		1970		1979	1984
		Ave.	Range		
Effluent					
Flowrate		46,000 m^3/d		32,700 m^3/d	
Total Suspended Solids		6.5 ppm	3.6-39 ppm	1.12	
Zinc	Total	8.3	4.2-27	0.48	0.30
Zinc	Soluble	5.2	1.8-15		
Cadmium	Total	0.3	0.2-0.8	0.04	0.02
Cadmium	Soluble	0.3	0.1-0.7		
pH		7.2	3.0-8.1		

St. Joe Minerals Corporation, Monaca PA

NPDES Effluent Limits

Parameter	1975-1977 Daily Max	1975-1977 30 d Ave	1977-Jan 2, 1980 Daily Max	1977-Jan 2, 1980 30 d Ave	Proposed New Regs 1984
Cadmium Kg/d	13.1	5.73	6.50	3.25	0.05
Zinc Kg/d	874	219	85	28.4	0.15
Suspended Solids (ppm)	528	132	161*	81*	
Arsenic	0.05	-	0.05	-	
Mercury	0.005	-	0.005	-	
pH	-	6-9	-	6-9	6-9
Temp °C	40.6	-	40.6	-	

* Limits for total solids applies only to process water discharge stream.

CONCLUSIONS

1. The Monaca plant of St. Joe Minerals is an excellent example of how metal contaminant levels in effluents can be reduced by careful housekeeping and segregation of flows. Water management must take into account both process water and runoff drainage as well as plant washdown all of which is likely to contain dissolved metals in the vicinity of an older pyrometallurgical plant.

2. The success achieved at Monaca is the result of adopting a systems approach to identify and analyze all streams of water that contribute metals to the effluent, and then rerouting them, reducing flows through controlling the use of water and segregating the flows as necessary. Ongoing efforts will result in further improvement.

3. St. Joe uses sludge recycle to achieve a clear overflow from the water treatment plant. Use of a deep sludge bed in the clarifier was found not to be possible due to compaction of the flocs into a cake that could not be pumped. For new installations RANDOL recommends that a high density sludge process be tested. The HDS process described elsewhere in this report requires recycled sludge to be mixed with lime ahead of lime addition to the feed water.

4. The proposed new BAT regulations for discharges from primary zinc under 40 CFR part 421 in the Federal Register March 8, 1984 were reviewed and main gist was grasped, the precise computation of allowed metals content from a typical plant was not clear. The main thrust is that sulfide precipitation and filtration would be required under BAT for primary zinc producers as well as further effluent volume reductions..

5. The proposed new regulations which would require, depending on how the building block formula is calculated, maximum daily discharges of 0.2-0.3 lb Zn/d and 0.1 lb Cd/d total in effluents appears to be extremely ambitious if not impossible for a plant of the size of St. Joe's Monaca facility. Even if more water is recycled and possibly more advanced precipitation methods applied e.g., HDS, coprecipitation and possibly polishing with sulfide precipitation or ion exchange it is questionable whether this target could be achieved. This would require new technologies and there are legitimate questions as to the cost/benefit to society as a whole of taking effluent limits quite so far especially as the new BAT regulations would also result in the generation of a hazardous waste sulfide precipitate which may or may not be recyclable in the process.

6. Reduction in cadmium levels to the very low sub ppm levels in the effluent is ascribed to carbonate precipitation rather than hydroxides. There is normally adequate carbonate in the water but after periods of heavy rain soda ash may be added to the effluent.

7. Industry representatives interested in reducing metal levels by water treatment are advised to contact St. Joe Minerals staff at Monaca, PA direct to discuss a variety of alternatives that have been considered and tested over the years.

8. Attention of designers of new effluent treatment plants is drawn to the NORANDA application of HDS; e.g., at Waite-Amulet described in this Appendix and also to the very much simplified flocculant makeup system employed by NORANDA acid mine drainage treatment plants.

LEAD-ZINC-TIN '80

Proceedings of a World Symposium on Metallurgy and Environmental Control sponsored by the TMS-AIME Lead, Zinc, and Tin Committee at the 109th AIME Annual Meeting, February 24-28, 1980, in Las Vegas, Nevada

MODERN WATER TREATMENT PRACTICE AT THE ZINC SMELTER OF THE ST. JOE ZINC COMPANY

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Charles A. Brockmiller
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The St. Joe Zinc Company completed in early 1979 a "lime and settle" water treatment plant for controlling zinc and cadmium metal discharges in the process water stream from the zinc smelting operation located near Pittsburgh, Pennsylvania. The successful start-up of the treatment facility was the last step in a complex 8-year program to bring zinc smelter discharges into compliance with EPA NPDES effluent limits. The compliance effort also required upgrading existing process equipment, installing settleable solids removal and spill control facilities, segregating "clean" water discharges from contaminated discharges, and closing the loop on an existing effluent quality control facility.

The problem of achieving compliance was approached in an orderly manner and solved in five phases by applying time-proven technology to specific aspects of a complex and challenging problem. The St. Joe effluent compliance effort demonstrates the significant environmental improvements which can be achieved by "older" metallurgical facilities when given challenging but achievable compliance schedules and when the governing regulatory agency has some flexibility in setting effluent limits so that the goals set can be attained. The overall zinc smelter compliance program resulted in a 30% reduction in the quantity of effluent discharged, a 90% reduction in the total suspended solids and cadmium discharged, and a 95% reduction in zinc discharged to the Ohio River.

Introduction

St. Joe Zinc Company operates a primary zinc smelter employing the electrothermic process to recover zinc from zinc sulfide ore concentrate (1). The smelter, located near Pittsburgh, Pennsylvania, has a rated capacity of 226,800 metric tons per year (MTPY) of zinc equivalent production. The primary products are zinc metal in various sizes of slabs, ingots and anodes, and multiple grades of zinc oxide produced by both the American and French processes. In 1978 a modestly sized zinc dust plant, employing the Imperial Smelting Corporation Ltd. electrothermal process, was started up at the zinc smelter to provide a domestic source for a zinc product with a rapidly expanding market (2). Major by-products include 317,500 MTPY of 66° Baumé sulfuric acid and about 450 MTPY of cadmium metal. The wide variety of pyro and hydrometallurgical and chemical processes employed in the zinc smelter provide many challenging environmental problems.

Recently the zinc smelter started up a "lime and settle" effluent treatment plant as a final step in bringing smelter effluent discharges into compliance with effluent limits set by the United States Environmental Protection Agency's (EPA) National Pollutant Discharge Elimination System (NPDES) program (3). The program to achieve compliance spanned about eight years and was carried out in five main phases. The basic steps in the phased compliance program were:

1. Installation of a facility to minimize total suspended solids discharge and to control spills which would adversely impact the quality of the effluent being discharged.

2. Segregation of the smelter sewer system so that slightly contaminated process water (noncontact cooling water) could be handled separately from severely contaminated process water.

3. Installation of new shell-and-tube heat exchangers in the acid plant scrubber liquor circuit to replace cascade type lead tube coolers thus decreasing the potential for noncontact cooling water contamination resulting from process liquor leakage from the old style coolers.

4. Minimization of process water discharges by installing an electrothermic furnace off-gas washer system recycle water facility.

5. Installation of a "lime and settle" facility to treat the process water effluent which could not be recycled or eliminated.

A detailed description of the design and operation of the "lime and settle" facility will be presented. However, since the compliance program evolved over a period of time, a review of the steps in the development of the compliance program will first be made to provide perspective for other industrial dischargers with similar problems.

Background

Under mandate from the Clean Water Act, the EPA was charged with developing a national program for control of effluents from municipal and industrial sources. Formulation of the program occurred in the early 1970's. To provide a clear reference point for evaluating the compliance program executed by the zinc smelter, 1970 will be used as a base year.

In 1970 the zinc smelter used a total of about 113.6 million liters per day (lpd) (30 MGD) of process water. Through the use of closed-loop recirculating systems and multiple uses of single pass water, the 1970 zinc smelter effluent discharge was limited to about 45.4 million lpd (12 MGD). All process water to be discharged flowed through a single sewer system which also collected and discharged storm water runoff. The typical quality of the zinc smelter effluent discharged in 1970 is summarized in Table I. While the 1970 zinc smelter effluent quality was far less than our present effluent limits, the 1970 effluent quality was substantially in compliance with ORSANCO* limits as administered by the Commonwealth of Pennsylvania Department of Environmental Resources (DER).

Table I. Typical Zinc Smelter Effluent Quality - 1970
Concentrations in mg/l

Parameter	Average	Range
Total Suspended Solids (TSS)	6.50	3.6 - 38.4
Zinc - Total	8.33	4.2 - 27.1
Zinc - Soluble	5.19	1.8 - 14.8
Cadmium - Total	0.32	0.17 - 0.75
Cadmium - Soluble	0.26	0.10 - 0.70
pH	7.2	3.0 - 8.1

In January 1971 the zinc smelter was informed of revisions in ORSANCO limits. Two of the revised limits significantly impacted zinc smelter effluents. The effluent limit for cadmium was decreased to $\leq$0.01 mg/l from a level of $\leq$0.50 mg/l. And all dischargers were to "substantially complete removal of settleable solids." This latter restriction was defined only as "removal to the lowest level attainable with current technology." Since cadmium discharges at the time averaged about 0.30 mg/l, the zinc smelter was presented with a formidable challenge in the area of effluent quality control.

To meet the challenge, St. Joe extensively reviewed zinc smelter water uses and discharges and studied effluent quality control alternatives available. The investigation of effluent quality control alternatives was focused in three areas:

1. Development of an end-of-line treatment process to control cadmium discharges and total suspended solids.

2. Development of design criteria for additional facilities to minimize total suspended solids discharges.

3. Assessment of the feasibility of converting the existing zinc smelter water supply- and-discharge system to a closed loop total recycle system.

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*ORSANCO - Ohio River Valley Water Sanitation Commission - An organization whose members were states bordering the Ohio River and whose purpose was to develop uniform standards for sanitary and industrial discharges so that all users of the Ohio River would have equal opportunity for the use of good quality water and equal responsibility for the maintenance of that quality.

None of the effluent quality control investigations provided the zinc smelter with a clear path to compliance with the cadmium and total suspended solids limits imposed by ORSANCO.

Because of the large volume of effluent, end-of-line treatment focused on chemical addition systems. Laboratory treatability studies indicated that a form of the "lime and settle" process used for years in the mining industry was the most likely candidate for controlling cadmium discharges (4, 5). Operation of a 3.15 liter per second (lps) (50 GPM) pilot plant in 1971 to treat a slip-stream from the zinc smelter discharge resulted in significant decreases in both zinc and cadmium discharges. However, cadmium concentrations of $\leq$0.01 mg/l were not routinely achieved (see Table II) and the overall effluent quality varied greatly, most likely as a result of extreme variations in the quality of the zinc smelter effluent at the time. Two additional problems associated with the operation of a full-sized "lime and settle" treatment facility were foreseen. First, the high pH (>9.0) required for cadmium removal required neutralization with sulfuric acid prior to discharge--such sulfuric acid neutralization would increase the effluent sulfate content above specified limits. Second, if equalization facilities prior to the treatment plant were not installed, the plant would have to be able to respond instantly to a wide variation in flow since the process sewer system also served as the storm sewer system for the zinc smelter.

Table II. Typical "Lime and Settle" Pilot Plant Effluent
Quality Concentrations in mg/l

Parameter	Average	Range
Total Suspended Solids	No Data	
Zinc - Total	0.41	0.04 - 0.55
Zinc - Soluble	0.13	<0.01 - 0.44
Cadmium - Total	0.04	<0.01 - 0.28
Cadmium - Soluble	0.02	<0.01 - 0.08
pH	9.6	7.7 - 11.4

Development of design criteria for additional settleable solids control involved constructing a pilot settling pond with the same proportions as the anticipated full-sized facility and evaluating available filtration equipment. The results of tests conducted utilizing a slip-stream from the zinc smelter effluent discharge indicated that a pond with six hours' retention time provided optimum solids removal effecting about a 60% reduction in total suspended solids. Increasing the retention time or filtering the pond effluent did not measurably increase the removal of solids from the zinc smelter effluent.

Ideally the best form of effluent quality control is to eliminate the discharge. On this basis a detailed study of the zinc smelter water uses and effluent discharges was conducted to assess the feasibility of converting the existing distribution-discharge system to a total recycle system. The conclusion of this study was that the wide variety of metallurgical and chemical processes employed in the zinc smelter could not be accommodated in a closed loop system without significant revisions to many smelter processes. The concept, although perhaps technically possible, was not economically feasible. Data collected relative to the quantity and quality of discharges from various elements in the zinc smelter process, however, provided the key to achieving effluent discharge quality compliance.

Analysis of effluent discharges from various elements in the zinc smelter process (Table III) revealed that about 297 lps (4700 GPM) of the existing 536 lps (8500 GPM) smelter discharge was essentially noncontact cooling water and, thus, should require no treatment prior to discharge. Of the remaining 240 lps (3800 GPM), 202 lps (3200 GPM) was discharged from process gas washers used to scrub the last traces of zinc from electrothermic furnace off-gases. The washer stream already passed through a series of settling ponds for recovery of the metal values prior to discharge to the sewer system. The effluent from the furnace washer settling ponds accounted for about 57% of the total suspended solids, 90% of the zinc, and 47% of the cadmium discharges in the smelter effluent.

Table III. Typical Stream Analyses of 1970 Zinc Smelter Effluents

Parameter	Noncontact Cooling Water	Process Water: Furnace Washers	Process Water: All Others
Flow, lps	296.5	202	37.8
Zinc, mg/l	<0.5	20	10
Cadmium, mg/l	<0.05	0.40	2
Total Suspended Solids, mg/l	<1	10	31

Investigation revealed that with the installation of a clarifier ahead of the existing settling ponds--with polymer addition to accelerate settling--and then using the existing ponds to polish the clarifier effluent, the furnace washer system could be close looped with only about a 9.5 lps (150 GPM) blowdown stream to the existing sewer system. Therefore, if the furnace off-gas washer system was close looped and the 297 lps of clean water was discharged through a separate sewer system, a 47.3 lps (37.8 lps all other + 9.5 lps blowdown) stream of process water would remain which would require treatment prior to discharge.

Utilizing the information developed in the studies, St. Joe proposed a four-phase compliance plan to the DER as follows:

Phase 1

Immediately construct a settling pond to reduce the total suspended solids discharged from the smelter. The facility would consist of a 16 million liter (4,225,000 gallon) capacity primary pond to settle suspended solids and a 7.6 million liter (2,000,000 gallon) auxiliary pond into which the smelter discharge could be diverted in the event of a spill which would adversely affect effluent quality (9<pH<6).

Phase 2

Segregate the sewer system into noncontact cooling water discharges and process water discharges. The noncontact cooling water discharges would bypass the settling facility installation. (The Phase 1 and 2 proposals are shown schematically in Figure I.)

Phase 3

Install necessary clarification and pumping facilities to substantially remove the furnace off-gas washer system effluent from the zinc smelter effluent discharge.

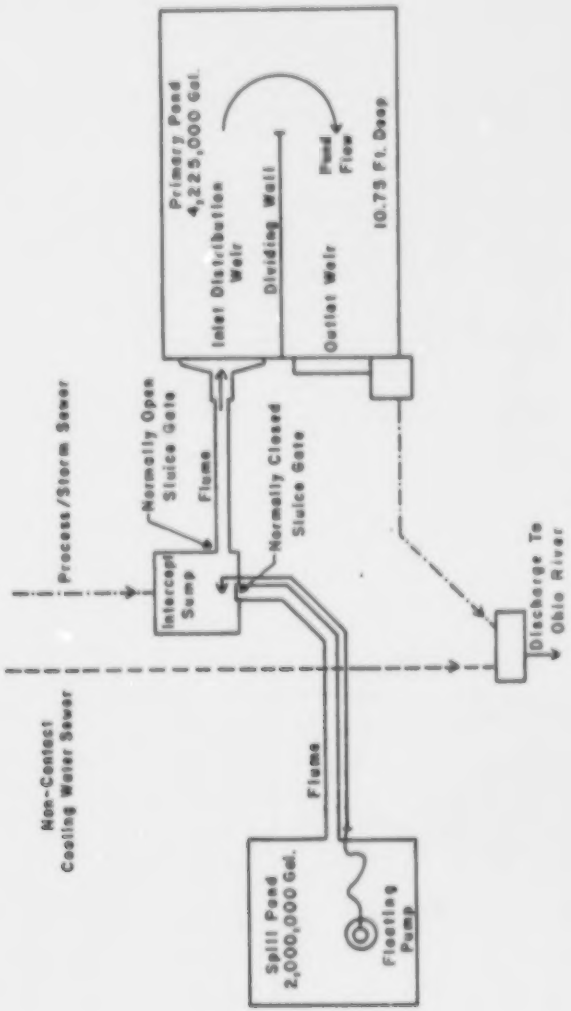

FIGURE I. ZINC SMELTER EFFLUENT SOLIDS REMOVAL AND SPILL CONTROL FACILITIES

Phase 4

At the conclusion of Phases 1, 2, and 3, perform treatability studies on the process water discharge and install a treatment process using the best available technology to reduce cadmium levels to the lowest achievable concentration.

It was anticipated that the proposed program would take three to four years to complete. The DER accepted the compliance plan and St. Joe began construction. The impact of the completion of Phases 1, 2, and 3 on zinc smelter effluent quality is shown in Table IV. The actual facilities are shown in Figures II, III, and IV. The revised pond inlet and discharge pumping facilities to accommodate the "lime and settle" treatment plant are visible in Figure III.

Table IV. Improvement of Zinc Smelter Effluent Quality With Completion of Phased Compliance Program

	1970 Quality		At Completion of Phases 1 & 2			At Completion of Phase 3		
Parameter	mg/l	kg/d	mg/l	kg/d	% Red.	mg/l	kg/d	% Red.
Total Suspended Solids	6.50	301.2	2.52	116.6	61	2.28	67.6	78
Zinc - Total	8.33	385.6	5.65	261.7	32	1.90	56.2	88
Cadmium - Total	0.32	15.0	0.30	14.1	6	0.10	3.2	79
Zinc Smelter Discharge, lps	536		536		0	344		36

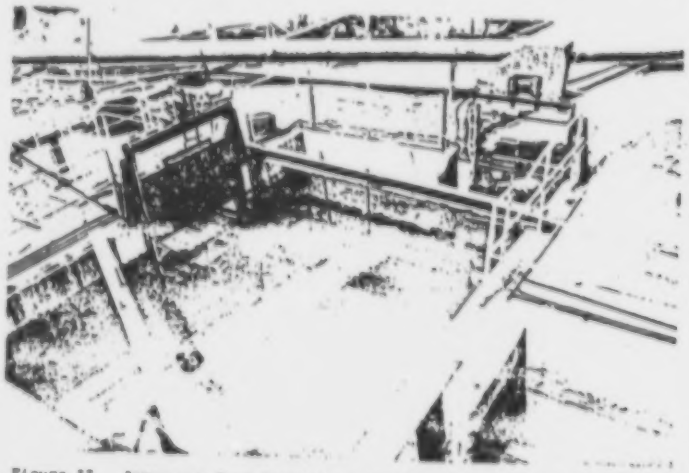

Figure II. Intercept Sump Facility - Discharge to Primary Pond at Upper Left; Discharge to Spill Pond at Upper Right

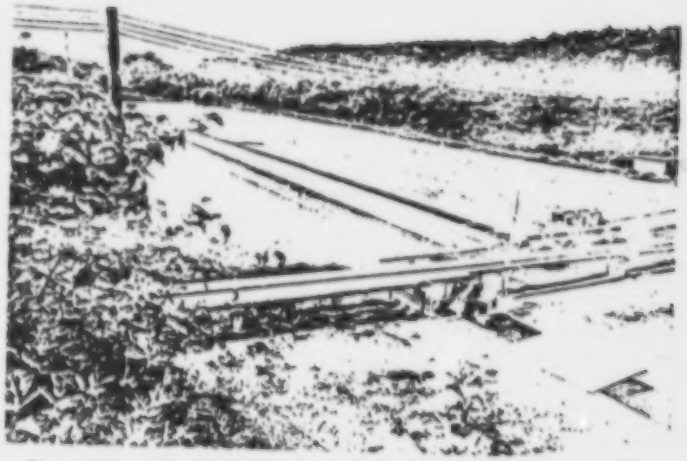

Figure III. Primary Settling Pond for Control of Settleable Solids

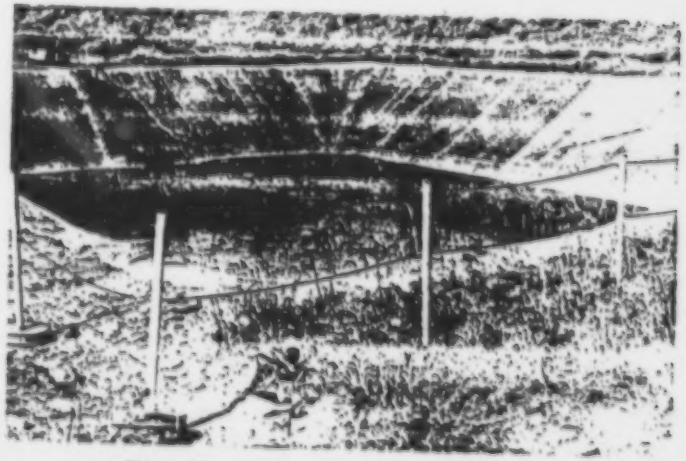

Figure IV. Auxiliary Pond for Spill Control

Through this same period in time, the EPA under mandate from the Clean Water Act was formulating effluent limits and guidelines for various types of municipal and industrial dischargers. The zinc smelter participated in a number of surveys and studies relating to nonferrous smelter water usage and effluent quality. A lengthy period of negotiations followed during which NPDES effluent limits for the zinc smelter were evolved. The final form of the zinc smelter effluent limits with two stages of compliance is shown in Table V. During the negotiations with EPA, the zinc smelter continued with the compliance program developed for the DER. At the end of Phase 3, the anticipated reductions in contaminants had been achieved. One additional problem which became evident was inconsistent quality of non-contact cooling water. The cause of this was traced back to the periodic leaking of coolers in the acid plant operation. As a result of this discovery, the zinc smelter proceeded with a program to replace the old coolers with new shell-and-tube heat exchangers, which had a leak-free operating history, as part of the overall compliance effort. With Phases 1, 2, and 3 of the original compliance plan completed and an NPDES permit with fixed effluent limits and phased compliance dates in hand, the zinc smelter now began the Phase 4 program to determine the most effective treatment for the process water stream and bring the zinc smelter effluent quality into compliance with NPDES limits.

Table V. St. Joe Zinc Company Zinc Smelter NPDES Effluent Limits

	Time Interval			
	January 2, 1975-June 30, 1977		July 1, 1977-January 2, 1980	
Parameter	30-Day Average	Daily Max	30-Day Average	Daily Max
Cadmium, kg/d	5.73	13.1	3.25	6.50
Zinc, kg/d	219	874	28.4	85
Total Suspended Solids, kg/d	132	528	81*	161*
Arsenic, mg/l	-	0.05	-	0.05
Mercury, mg/l	-	0.005	-	0.005
pH	6-9	-	6-9	-
Temperature, °C	-	40.6	-	40.6

*Limits for total suspended solids only applies to process water discharge stream.

Process Water Treatment Plant Design

An intensive study was again conducted in 1976 to characterize zinc smelter effluents so that the best available technology could be defined for control of the process water stream. To complement the efforts of St. Joe personnel, an engineering consulting firm with a strong background in industrial effluent treatment was retained to conduct treatability studies; recommend a treatment process; and participate in the preparation of equipment specifications. After the treatability studies were completed, the consensus of those involved in the investigation was that a "lime and settle" process was the best available at the time. Cadmium removal was still proving to be a problem so cotreatment with sodium sulfide was recommended to improve cadmium removal.

Theory of "Lime and Settle" Process

Lime treatment has been the standard in the mining industry for many years and is, thus, extensively documented. In general lime is added to the effluent stream being treated until a pH of 9.0 or higher is achieved. At the elevated pH, the solubility of zinc and cadmium is reduced and metal hydroxides are formed. By the addition of flocculating agents to promote agglomeration, large particles can be formed which are amenable to settling.

In the case of cadmium, the solubility is not sufficiently reduced at a pH of 9.0 to achieve mandated effluent limits. The addition of sodium sulfide was recommended so that additional cadmium could be precipitated as a metal sulfide. Extensive literature exists indicating that, at or near neutral conditions, metal sulfides have much lower solubilities than the metal hydroxides (6, 7). Subsequent operating experience indicated that the precipitation of cadmium as cadmium sulfide was not effective in decreasing zinc smelter cadmium discharges.

External Factors Affecting Treatment Plant Design

Since the "lime and settle" process involved pH adjustment and clarifier operation, the need for relatively constant treatment plant flows to achieve consistent pH values and stable clarifier operation was recognized. At the time the zinc smelter process water discharge had increased to an average of 56.8 lps (900 GPM). Instantaneous flows throughout a day might vary from 25.2 lps (400 GPM) to 75.7 lps (1200 GPM), depending on the cycles of various operations within the smelter. Additionally, the zinc smelter process water sewer system also served as the storm sewer system. This necessitated the additional design criteria that the treatment plant be able to handle the rain water runoff from a 100-year storm.

To provide the constant flow necessary for good treatment plant operation, the primary settling pond, installed in Phase 1 of the compliance program, was to act as a surge facility between variations in the process/storm sewer water flow and the treatment plant. As originally designed, influent to the pond was distributed uniformly into one side of the pond, flowed around a dividing wall, and overflowed a 12.2 meter (40 ft) weir at the discharge of the pond (see Figure I). The head over the weir was about 1.5 centimeters. The nominal depth of the filled pond is 3.3 meters (10.75 ft). Therefore, at the start-up of the water treatment plant, flow to the plant would be at the maximum design rate until the pond level was lowered to a depth of 1.2 meters (4 ft). At that time the plant flow would be reduced to the average process water flow rate.

With the pond level at 1.2 meters of depth, approximately 10.7 million liters (2,830,000 gallons) of storage capacity is available. When heavy rains occur, the pond level will rise while the treatment plant flow is gradually increased in step-wise increments until the rain stops or the pond level starts to fall. As the pond level again approaches the 1.2 meter depth, treatment plant flow is decreased gradually to match process water flow. In the event of problems in the water treatment plant requiring a shutdown for maintenance, the pond storage capacity provides about two days of effluent retention at normal flows.

To protect the treatment plant from low pH excursions, the spill pond, also part of Phase 1 in the compliance schedule, was retained. If a pH of less than 6.0 is detected in the intercept sump, process water sewer flow is automatically diverted to the spill pond until the cause of the excursion is found and corrected. Caustic soda is then added to the spill pond until the pH rises to 7.0 or higher. The contents of the spill pond are then pumped back to the intercept sump for discharge into the primary pond.

Figure V shows the primary pond at the start-up of the water treatment plant. Note that the water level is already about 1.5 meters below the original discharge weir on the left so that all process water is passing through the treatment plant prior to discharge. Also note the floating inlet flume extending into the pond being used in place of the original inlet distribution weir. As the pond level is lowered, hypalon pond liner material cushioned by a sand bed is exposed. If the original inlet distribution weir were continued in service, the impingement of pond influent onto the exposed liner might result in displacement of the underlying sand bed which could lead to rips or tears in the liner material. The floating flume prevents direct impingement and thus protects the watertight integrity of the pond. The waste transfer pumps were also placed on a floating platform as a means of keeping the pond in operation during water treatment plant construction.

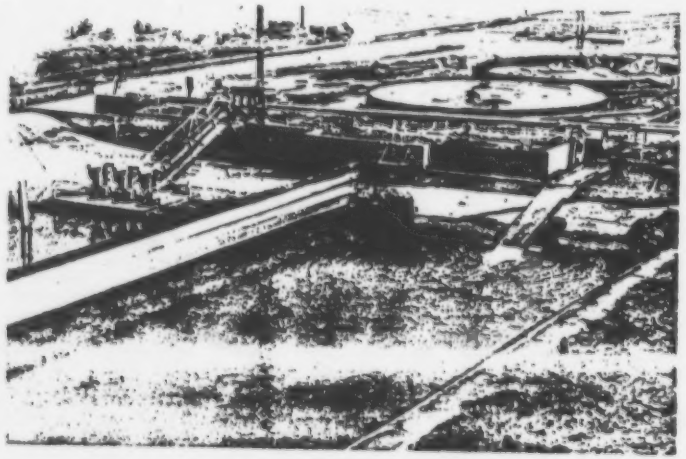

Figure V. Water Treatment Plant Waste Transfer Pumps

General Treatment Plant Operation

As shown in Figure VI, process water is pumped from the primary pond at a rate of 37.8-75.7 lps (600-1200 GPM), as conditions warrant, to the first of two 22,700 liter (6000 gallon) capacity continuously agitated neutralization tanks. The pH is raised to within about 0.2 pH units of the desired pH level by the addition of a 5% lime slurry. The first tank overflows by gravity to the second neutralization tank where a 5% lime slurry is added until the final pH level required is achieved. To provide nuclei for particle growth, a 1.6 lps (25 GPM) stream of underflow solids slurry is pumped from the clarifier to the second continuously agitated neutralization tank. The overflow of the second neutralization tank goes to the clarifier.

Prior to entering the clarifier, a polymer solution (coagulant aid) is injected into the process water stream to promote particle growth and settling. The clarifier is a solids contact design with a process stream retention time of 5 to 10 hours, depending on the treatment plant flow rate. The effluent from the clarifier flows by gravity into a 22,700 liter (6000 gallon) capacity filter feed tank ahead of the multimedia filters. The filter feed tank is used to smooth out variations in flow to the filters and also provides an overflow bypass in the event of a filter failure. From the filter feed tank, water is pumped through the multimedia filters into a 60,600 liter (16,000 gallon) capacity effluent storage tank. Two of the three multimedia filters are in use at the same time with the third on standby. Filter switching is done automatically on a timed cycle. The effluent storage tank provides a source of clean water for backwashing the multimedia filters, general treatment plant washing, lime slurrying, and polymer batching. Overflow from the effluent storage tank is discharged to the Ohio River. Filter backwash water as well as general wash-down water is discharged to the primary pond for retreatment prior to final discharge.

The plate and frame filter press is operated as necessary to maintain a uniform depth sludge bed in the clarifier. Current operation requires 3 to 4 filter press cycles per week. The filtrate is returned to the clarifier while the filter cake is discharged into a mobile container for disposal in a licensed industrial landfill. Figures VII, VIII, IX, and X show key pieces of water treatment plant operating equipment.

Unit Operation

Lime Storage System. Hydrated lime is delivered in 16-18 metric ton (18-20 short tons) loads by trucks with pneumatic unloading capability. Prior to initiating the truck unloading cycle, sufficient water is added to the lime storage tank (71,900 liter capacity) to result in a 40% lime slurry. During the unloading operation, water sprays are operated in the tank to prevent dusting. The lime storage tank (center foreground Figure VII) is continuously agitated. Care must be exercised in mixing the lime slurry since a slurry of >45% solids results in a paste which does not mix or flow predictably.

Lime Slurry System. For neutralizing the incoming process water stream, a 5% lime slurry is used. The lime slurry batches are made automatically in 1140 liter (300 gallon) units. A low level probe in the continuously agitated lime slurry dilution tank activates the cycle. A valve in the pipe from the lime storage tank opens and allows 40% lime slurry to enter the pump tank. When the equivalent of approximately 45 kilograms (100 pounds) of lime has been timed into the dilution tank, the valve is closed. Water is then added to the dilution tank until a high level probe is satisfied. Each time the batch cycle is activated, the event is recorded on a counter.

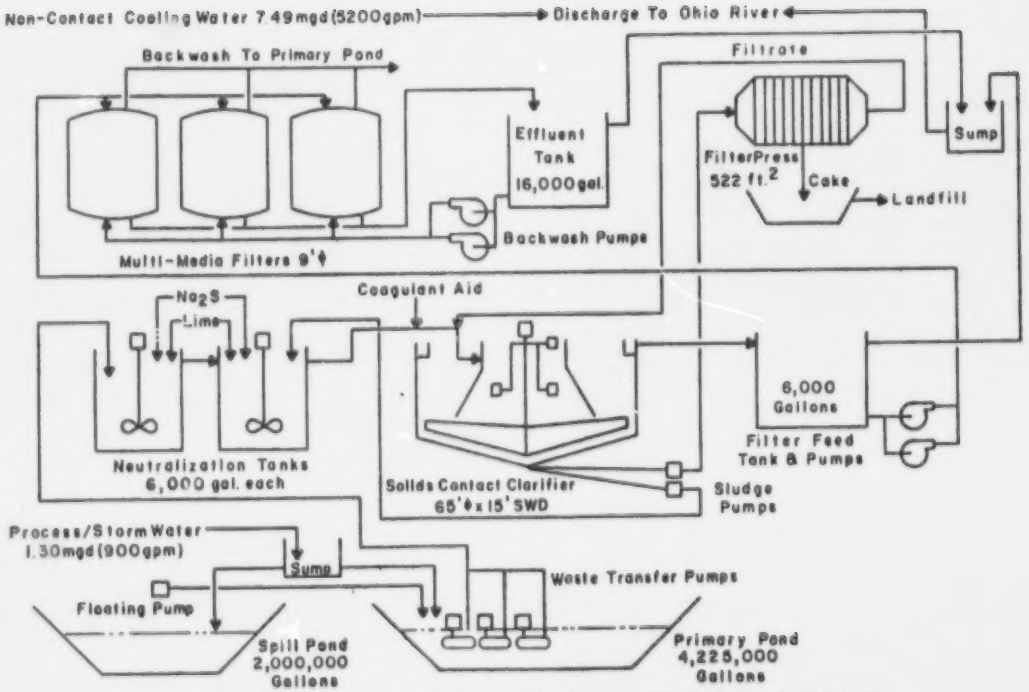

FIGURE VI. WATER TREATMENT PLANT PROCESS FLOW SCHEMATIC

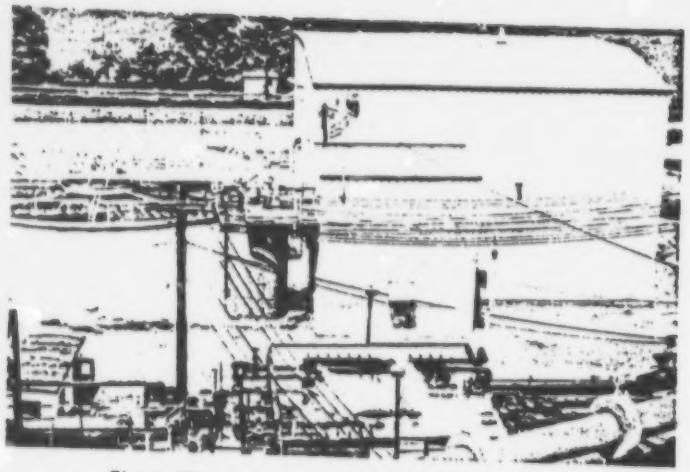

Figure VII. Process Water Treatment Plant Facility

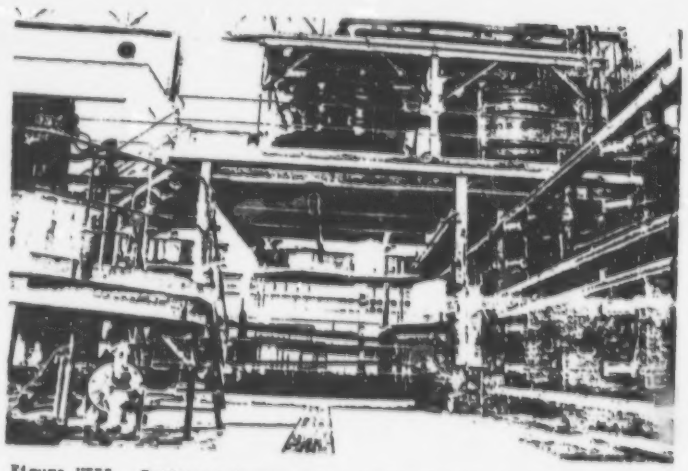

Figure VIII. Equipment Arrangement - Neutralization Tank in Upper Right - Control Room in Upper Left - Multimedia Filters in Lower Right

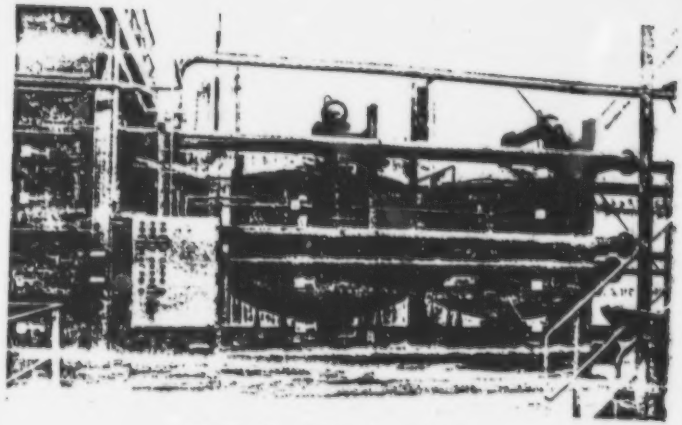

Figure IX. Multimedia Filters

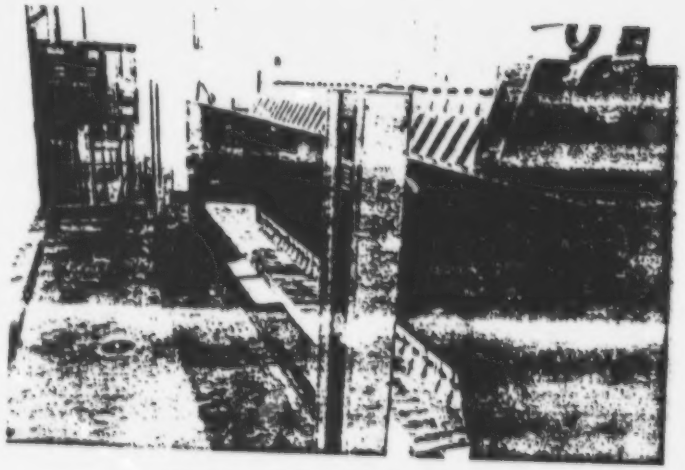

Figure X. Plate and Frame Filter Press

By recording each lime slurry batch, a lime-use record is maintained. Current levels of operation require the use of about 320 kilograms (700 pounds) per day of lime.

Polymer Addition System. A batch of polymer solution (coagulant aid) is prepared daily by the treatment plant operator. The strength of the solution is determined by the water treatment plant flow rate. Extensive jar tests have indicated that Calgon WT-3100 polymer is the most effective coagulant aid for treating zinc smelter effluents. In preparing a polymer solution, no more than 9 kilograms (20 pounds) of polymer is diluted in 1520 liters (400 gallons) of water as a higher concentration of polymer results in a highly viscous solution which cannot readily be handled by the injection system. The polymer solution is injected into the neutralization tank effluent at a constant rate of one liter per minute. The desired dosage for optimum particle growth is in the range of 1.0-1.5 mg of polymer per liter of process water.

Clarifier Operation. Acceptable clarifier operation has been achieved by maintaining the sludge bed at the lowest practicable level. If an underflow sludge recycle stream were not required to provide nucleation material for the process water stream being treated, the clarifier could be operated with no sludge bed. The underflow sludge recycle system requires the clarifier to be operated with a sludge bed of sufficient depth to keep the clarifier underflow cone full of sludge.

Multimedia Filter Operation. Three multimedia filters, each about 3 meters (9 ft) in diameter, are utilized to polish the clarifier effluent. Two filters are on line at a time with the third being backwashed or on standby. Provision has been made in the existing multimedia pipe header system to accommodate additional filter equipment in the event additional process water treatment plant capacity should be required. The filter media consists of a 30.5 centimeter (12 inches) deep bed of sand covered by a 45.7 centimeter (18 inches) deep bed of 24 mesh anthracite coal. The filters may be backwashed on a regular cycle or whenever a specified filter pressure drop is reached. The filters are currently being operated on a 16-hour time cycle with a pressure drop override in the event a clarifier upset causes solids carryover to prematurely plug the filters.

Clarifier Sludge Filter Press Operation. The operating cycle of the filter press is determined by sludge accumulation in the clarifier, which can be correlated with lime usage. Presently one filter press cycle is required for every 11 lime slurry batches prepared. The filtrate is returned to the clarifier. The filter cake, about 0.85-1.0 cubic meters weighing 1590 kilograms (30-35 cubic feet - 3500 pounds) of 50% by weight solids material, is dropped into a mobile container for disposal in a local licensed industrial landfill. The filter cake, which contains about 35% zinc on a dry basis, is not recycled to the zinc smelter because the water treatment chemicals used are not compatible with the electrothermic process.

Staffing. The operation of the process water treatment plant is the responsibility of the zinc smelter acid plant personnel. No additional personnel have been required to support the operation of the water treatment plant. The acid plant operator makes a regular walk-through inspection of the water treatment plant about four times per shift as part of his normal routine. The acid plant control room has a remote annunciator panel to alert the operator to any abnormal conditions. Since stable operation has been achieved, the process water treatment plant has required only minimal attention.

Water Treatment Facility Start-up Problems

When the process water treatment plant was started up at the beginning of 1979, effluent quality was not good enough to comply with NPDES limits. The problem seemed to be the result of solids carryover from the clarifier since the floc did not attain sufficient size for settling. This was related to insufficient particulate matter in the influent stream for proper nucleation. Initially there was no underflow sludge pumping back to the clarifier influent stream since no provision had been made for sludge recycling in the original treatment facility design. The carryover from the clarifier resulted in short multimedia filter cycles due to filter bed plugging.

In an attempt to provide material for nucleation, a bentonite slurry was made using the lime slurry solution as a carrier. The addition of the bentonite material resulted in an incremental improvement in effluent quality, but the improvement was not sufficient to achieve NPDES compliance. Finally by using a spare clarifier sludge filter press feed pump, clarifier underflow sludge recycle was initiated and the improvement in water treatment plant effluent quality was immediate and dramatic.

After initiating clarifier underflow sludge recycle, cadmium control remained a modest problem. Increasing the sodium sulfide dosage did not achieve any recognizable incremental reduction in effluent cadmium concentrations over lower dosages. Finally acting on speculative comments in the report summarizing the operation of the pilot "lime and settle" treatment plant many years before, the addition of sodium sulfide was terminated. Although cadmium in the water treatment plant effluent was then reduced, several other changes were made at the same time, so it is difficult to assess how much impact terminating the sodium sulfide had on reducing cadmium levels. Even if the sodium sulfide was not interferring with the reaction taking place, it offered no benefit in achieving additional reduction in cadmium levels in the zinc smelter effluent and, therefore, was not required. The precipitation of cadmium carbonate appears to be the primary reaction for the removal of cadmium from zinc smelter process water discharges. The carbonate ion is available for reaction since the zinc smelter water supply is relatively hard. In periods of heavy rain, the addition of a soda ash to the incoming process water may prove necessary to maintain the concentration of carbonate ions at a level sufficient to control cadmium discharges.

During the first few months of process water treatment plant operation, problems also occurred in determining the proper sludge depth to be maintained in the clarifier to achieve optimum unit operation. On the basis of jar tests and experience with similar installations, the consultant had recommended a 2.1 meter (relative to the clarifier side wall) bed depth. The purpose of this was to provide solids contact with the incoming effluent to promote particle growth and eliminate the need for underflow recycle. The 2.1 meter sludge bed depth was thought possible because the treatability studies found that the resulting settled material remained light and fluffy with minimal bed compression. In actual operation, however, the bed not only compressed, but formed a cake which the clarifier rake could not break. After the first four months of operation, it was necessary to drain the clarifier and manually remove the cake. Since then the clarifier has been operated maintaining only a bed of sufficient depth to provide material for underflow recycle. The differences in the predicted sludge characteristics and the actual sludge are most likely the result of the actual influent containing lower concentrations of contaminants than the water used in the treatability studies. The inference is that the clarifier is conservatively sized and is probably capable of handling an equal volume process stream with substantially higher concentrations of contaminants.

Treatment Plant Performance

Since stable operation has been achieved, the process water treatment plant has proved very effective in reducing zinc and cadmium levels as indicated by typical analyses shown in Table VI.

Table VI. Typical Process Water Treatment Plant Performance Concentrations in mg/l

Parameter	Influent	Effluent
Zinc - Total	22.3	<0.66
Cadmium - Total	0.61	<0.06

The treatment plant effectively removes >97% of the incoming zinc and >90% of the cadmium. The "lime and settle" process is capable of achieving consistent zinc concentrations in the treatment plant effluent regardless of zinc loading in the influent stream. Extremely high levels of zinc, however, tax the capacity of the neutralization equipment and require excessive sludge filter press operation. Control of cadmium has been sufficient to consistently meet NPDES permit requirements, but the quality of the effluent relative to cadmium has been more variable than that of zinc. This is because cadmium solubility is more sensitive to variations in pH than zinc in the pH range in which the water treatment plant operates. The "lime and settle" process has proven to be an extremely versatile operation for controlling zinc smelter process effluent quality. With a properly controlled feed stream, the "lime and settle" process appears capable of consistently meeting current zinc smelter effluent limit requirements.

Smelter Compliance

With the changes in cooling equipment in the acid plant operation and the completion of the water treatment plant, the smelter effluent discharge was brought into compliance with current EPA NPDES effluent limits as shown in Table VII. Total suspended solids discharges have been reduced by nearly 90% from 1970 levels while zinc and cadmium have both been reduced by greater than 90%. As a result the smelter effluent discharges are well within current NPDES limits. To effect these reductions, considerable effort was necessary requiring a complex five-phase program to achieve compliance:

1. Installation of a facility to minimize total suspended solids discharges and control spills (Figure 1).
2. Segregation of the zinc smelter effluents into noncontact cooling water and process/storm water sewer systems.
3. Installation of new heat exchangers in the acid plant operation to minimize the potential for noncontact cooling water contamination.
4. Minimization of process water discharges by installing a furnace off-gas washer recycle water facility.
5. Installation of a "lime and settle" process to treat remaining process water.

Table VII. Typical Zinc Smelter Effluent Quality

	1970 Smelter Effluent		1979 Smelter Effluent			Current NPDES Limits
	mg/l	kg/d	mg/l	kg/d	% Red.	Avg
Cadmium	0.32	15.0	0.04	1.31	91	3.25 kg/d
Zinc	8.33	385.6	0.48	15.70	96	28.40 kg/d
TSS	6.50	301.2	1.12	36.63*	88	81.0 kg/d*
Arsenic	<0.05	-	<0.005	-	-	0.05 mg/l Max
Mercury	<0.005	-	<0.0002	-	-	0.005 mg/l Max
pH	7.2	-	7.8	-	-	6-9
Temp, °C	<40.6	-	<40.6	-	-	40.6 Max
Smelter Discharge, lps	536		378		29	

*Current NPDES limit applies only to process water discharge; smelter effluent value reflects combined zinc smelter discharge.

The zinc smelter NPDES compliance effort required a capital expenditure of about $4,780,000 with the "lime and settle" process/storm water treatment facility accounting for $2,160,000 of the total. The estimated annual operating and maintenance cost for the "lime and settle" facility is $150,000. The total zinc smelter annual direct operating and maintenance costs for all the facilities installed as part of the NPDES compliance program are about $450,000. To insure continuous compliance with NPDES limits, an extensive effluent discharge monitoring system is operated which adds an additional indirect cost of $150,000 per year to the cost of compliance.

The installation of facilities to control zinc smelter effluent discharge quality may be complete, but the maintenance of compliance requires a continuing effort on the part of many groups. Operating departments within the smelter must wisely use water and insure discharges go into the proper sewer system. Engineering personnel must carefully review water uses in new projects and incorporate water use conservation measures into new facilities and minimize discharges through reuse of process water. Water treatment plant operating personnel must maintain the physical plant in good operating condition; optimize the process to achieve maximum contaminant reduction; and, along with environment control personnel, continuously monitor the actual performance of the treatment facility.

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OPERATION	ZINC CORPORATION OF S. A. LTD. P.O.BOX 218 SPRINGS TRANSVAAL	
TELEPHONE	(011) 818-2121	
CONTACTS	Richard Beck	General Manager
	Gert Schoonraad	Works Manager
	Alan Norton	Zinc Plant Superintendent
GROUP	Gold Fields of South Africa Ltd. P. O. Box 1167 Johannesburg 2000 South Africa	
TELEPHONE	(011) 639-9111	
CONTACT	D. A. Viljoen	Consulting Metallurgist
DATE OF VISIT	29 February 1984	

INTRODUCTION

Zincor treats a zinc concentrate from Black Mountain, Prieska and Rosh Pinah located in the northern Cape Province and Namibia/South West Africa. Concentrates are roasted and then leached in sulfuric acid followed by electrowinning after electrolyte purification.

Although acid is recycled, there are residues which must be disposed of or stockpiled and liquid effluents to be disposed of, as any runoff or spillage is pumped to an effluent treatment plant.

Of interest in this investigation is the Zincor experience with gypsum scaling and how to live with it.

PRODUCTION RATE

Zincor is a small electrolytic zinc refinery by world standards. Capacity is 8,000t Zn slab per month.

WATER CONSUMPTION

Current water consumption is 15 m^3 water per ton of zinc slab produced. Formerly the water needs were 22 m^3/t Zn but these were reduced through recyling of water. A water consumption as low as 13 m^3/t Zn has been achieved at times but operating staff find 15 m^3/t Zn to be more comfortable.

WATER UTILIZATION

Much of the water consumed is used for evaporative cooling in the plant both in the acid plants and the cell house. Solution is bled also to reduce the gypsum loading.

WATER COST R0.23/m^3 R29,200/mo R350,000/year

METALLURGICAL PROCESS

Zinc sulfide concentrate is roasted in a series of Lurgi fluid bed roasters. Two older units at 117 tpd each and two newer units at 200 tpd each make sulfuric acid in two Monsanto acid plants.

The calcine is leached in recycled H_2SO_4 spent electrolyte with added H_2SO_4. The acid strength is maintained at 1.5 gpl in the first leach tank. Above that concentration excess iron leaches. The acid rides out to a basicity of 0.5 in the last leach tank. The leached slurry is thickened to yield a zinc solution which is filtered and then purified to remove copper, cobalt and cadmium in successive steps prior to electrowinning.

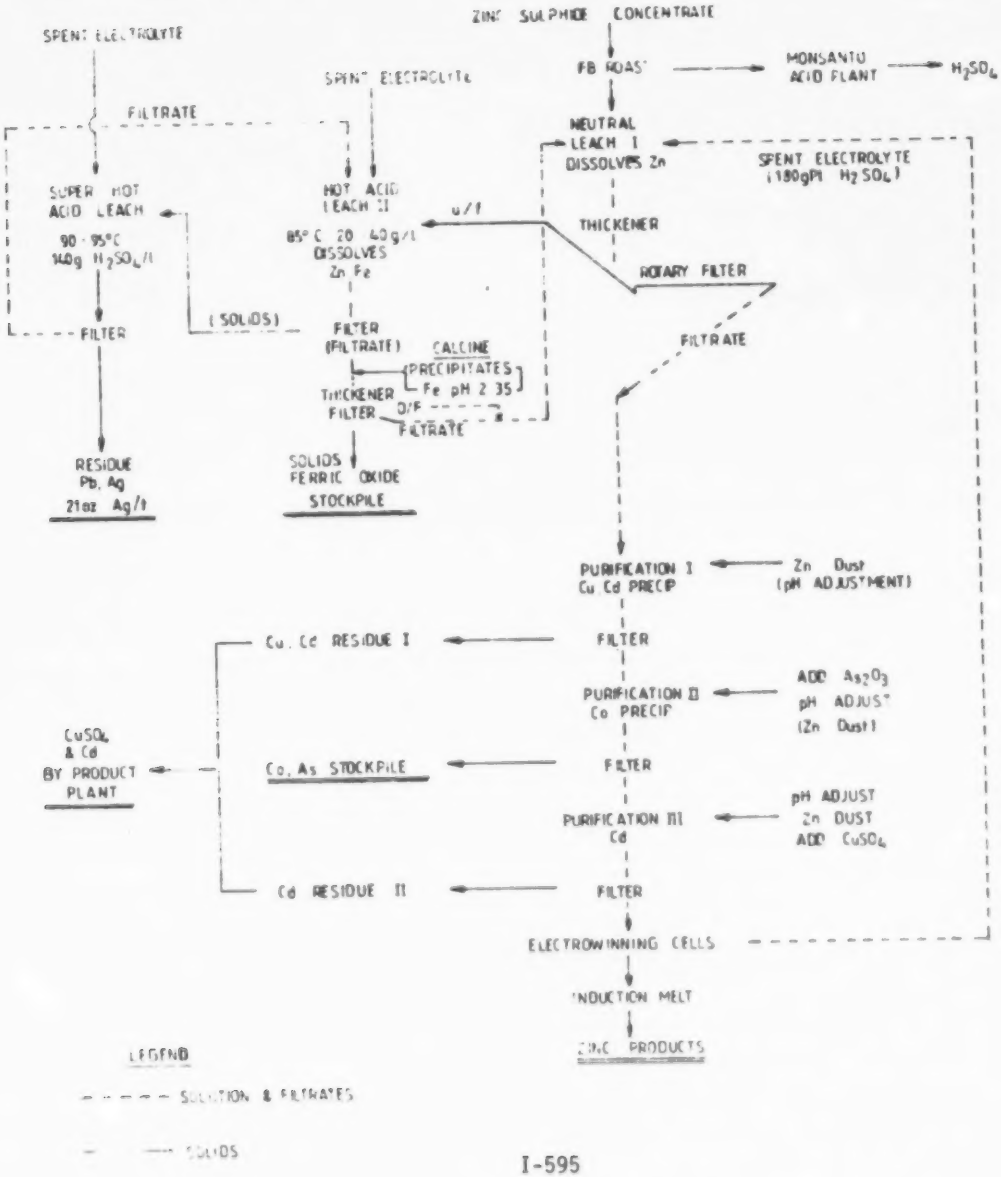
The primary thickener underflow is leached in hot sulfuric acid at 80°C and 20-40 g H_2SO_4/l to dissolve residual zinc and iron from the zinc ferrites that did not dissolve in the primary leach. The hot acid leach pulp is filtered and by adding calcine to the filtrate, iron is precipitated at pH 2.35 which requires close control. This is a Zincor patent. The precipitated iron oxide residue is stockpiled - it is potentially suitable as a catalyst for SASOL. The solution filtered from the iron oxide is recycled to the first stage neutral each tank.

The remaining leach residue is next treated by a super hot leach at 90-95°C and 120-140 g/l H_2SO_4 to recover some additional zinc values which are filtered and recycled to the hot leach step. The residue containing 0.07% (21 oz) Ag/t and lead is stockpiled.

The zinc solutions after iron oxide removal is treated in three purification stages. Firstly copper and cadmium is precipitated with zinc dust. pH is controlled at 4.5.

Next cobalt is precipitated by adding zinc dust, arsenic oxide and spent electrolyte to maintain pH at 4.5. Finally cadmium is precipitated by zinc dust and $CuSO_4$ addition. pH is maintained at 4.5 by spent electrolyte addition.

ZINCOR ELECTROLYTIC ZINC PROCESS
BASIC PROCESS



The stage II cobalt-arsenic sludge is stockpiled. The Stage III cadmium is mixed with the Stage I Cu-Cd residue to obtain a 50-60% Cu-Cd cake which will be used to make a $CuSO_4$ product and cadmium metal sponge which is compacted and melted.

PLANTSITE

The Zincor electrolytic zinc plant is located at the old Vogelstriusbult gold-uranium plantsite. Effluents and tailings are discharged to an effluent site located within the old gold mine tailings dump. The Pb-Ag decant dams are located on top of the old gold plant slimes dam.

ROASTERS

There are four Lurgi fluid bed roasters. Two older 117 tpd units and new 200 tpd units.

WASTE HEAT RECOUPERATION

Waste heat recouperation boilers are installed. Two were installed by Deutsche Babock which use gradual cooling in series and experience less SO_4 formation. These have a rapping mechanism and Air Lance.

These are Oschatz units in parallel. These are scale free with low solids buildup.

SO_2 SCRUBBER

A normal open tower humidifier followed by a plastic packed gas cooling tower is used. In this weak concentration of H_2SO_4, zinc, fluorides and total dissolved solids are controlled by a continuous bleedoff that is pumped to the effluent plant.

GYPSUM CONTROL

The whole circuit is saturated with gypsum. Once a month the tank house circuit is shut down to remove gypsum accumulations from launders, pipes, etc. Typical solutions run 2500 mg $CaSO_4$/l. Cooling towers are de-scaled on a scheduled program.

Zincor was investigating the use of polyurethane pigs and sequestering agents for gypsum control in the pipes. "Pigs" are offered by:

1) Amforce Pty Ltd. offered through R. J. Spargo (Pty) Ltd.
2) RSA Pipe Cleaning (Pty) Ltd., Potchefstroom

In acid circuits the gypsum is soft as opposed to gypsum scale in alkaline circuits.

Formerly more water was jetisoned from the circuit to control scaling but subsequently water has had to be conserved because of the drought and a reduction from 22 m^3/t Zn to 15 m^3/t zinc production has been achieved.

One way to remove gypsum scale has been to burn scrap rubber in the steel pipes but this is "labor intensive." This is no longer done at Zincor due to air pollution considerations.

ANIKEM 4370 sequestering agents as used at East Driefontein Gold Mining Company was under consideration to help control gypsum. This reagent has a crysilic acid base. Another gypsum scale reducing reagent has been offered by:

Watercare Technical Services
P. O. Box 312
Gallo Manor 2052

Telephone: (011) 802-2320
Contact: Brian Bignam

Zincor metallurgical staff described previous experience at West Driefontein in raffinate pumping after neutralization which had a bad scale problem until the steel pipe was replaced by HDPE. The plastic pipe was supported at intervals and due to expansion/contraction the pipe would flex and become self-cleaning.

Soft rubber pipes are used from the V-M header tanks. When these scale up, the problem is solved by turning the flow off and collapsing the pipe to break the scale.

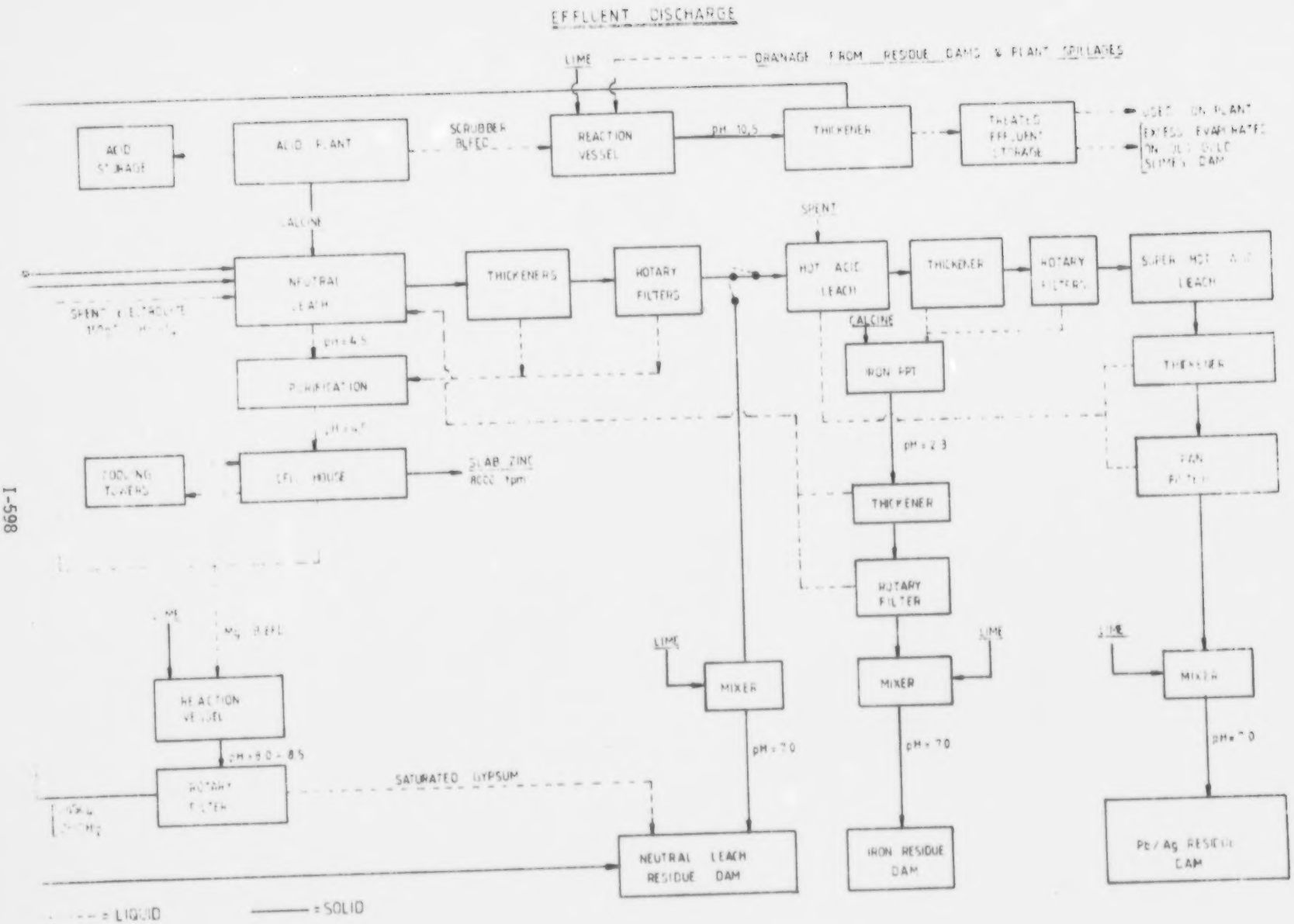
In West Germany, Ruhrzink uses pinchvalves on the cooling towers which are self cleaning. The cooling towers are used to cool down the electrolyte during electrowinning.

At Zincor forced updraft cooling towers are used. Heavy gauge PVC flaps are suspended on the sides. Gypsum forms in sheets on the plastic and slides off the slippery plastic surface. Prior to using plastic flaps there used to be a heavy gypsum buildup requiring a heavy support structure. About 14% of the water in the electrolyte solutions is lost to evaporation.

EFFLUENT DISCHARGE

After lime treatment to recover $Zn(OH)_2$ from the magnesium bleed spent electrolyte, the solution is pumped to the effluent treatment plant and together with other effluent solutions, it is treated to precipitate metals. A portion of the treated effluent is reused in the plant and the rest irrigated to the surface of the old gold tailings to dispose of it.

Stormwater goes to a stormwater drain fitted with a pH probe and automated gates. If the pH is within a dischargeable range the stormwater is discharged to Blesbokspruit which ultimately flows into the Vaaldam. If the pH is low, the flow is directed automatically to the emergency dam from which it is returned to the effluent treatment plant.


EFFLUENT DISCHARGE
LIME
DRAINAGE FROM RESIDUE DAMS & PLANT SPILLAGES
ACID STORAGE
ACID PLANT
SCRUBBER BLEED
REACTION VESSEL
pH 10.5
THICKENER
TREATED EFFLUENT STORAGE
CALCINE
NEUTRAL LEACH
THICKENERS
ROTARY FILTERS
SPENT
HOT ACID LEACH
THICKENER
ROTARY FILTERS
SUPER HOT ACID LEACH
CALCINE
IRON PPT
THICKENER
pH = 4.5
PURIFICATION
COOLING TOWERS
CELL HOUSE
SLAB ZINC
pH = 2.3
THICKENER
ROTARY FILTER
LIME
MIXER
LIME
MIXER
LIME
MIXER
REACTION VESSEL
pH = 8.0 - 8.5
ROTARY FILTER
SATURATED GYPSUM
pH = 7.0
pH = 7.0
pH = 7.0
NEUTRAL LEACH RESIDUE DAM
IRON RESIDUE DAM
Pb/Ag RESIDUE DAM
= LIQUID
= SOLID

WATER BALANCE

Attempts to develop an accurate water balance have not been successful. A considerable quantity of water could not be accounted for. Accurate measurement is virtually impossible because of the lack of suitable instrumentation.

NUMBER OF WORKERS

The semiskilled worker compound houses 630. This is hooked up to the municipal sewage treatment works at Springs.

WATER SOURCE

In early 1984 Rand Water Board was supplying Zincor. A promising effort was being made to replace RWB water with Springwater from their own property. Two wells have been sunk which yielded reasonable quality water.

Note: Considering high TDS seepage in the effluent disposal area it would be interesting to see whether the water quality remains good from these wells.

RECYCLE

The iron residue filtrate is repulped using effluent water. Reclaimed effluent water is also used for cooling the roaster bed and for road dust control. Calcium and magnesium may be added to the calciner and it ends up in the magnesium precipitation plant.

Several cooling systems have been installed on the plant to cool and recycle water locally. Steam condensate is now returned to the acid plant where it is used to heat up zinc solutions. There is some concern about copper contamination. Pb-Ag residues from final stage leaching are repulped with reclaimed effluent water.

WATER TREATMENT

Zincor employs two water demineralizers using ion exchange following lime-soda softening to produce water for special applications.

Filtomat units were installed to clean cooling water in the acid plant to remove suspended solids (mainly unreacted ZnS, calcine, etc.). The filtomats gave lots of trouble and wasted "too much" water with the discharge of solids.

Excess water from the lined emergency water dam is treated in the effluent treatment plant with lime to pH 10.5 which precipitates Mg, Fe and everything else except $CaSO_4$.

ENVIRONMENTAL

Monitor wells are installed around the effluent and tailings area over which effluents are spray irrigated. Monitor well samples are regularly sent to the Department of Environment's slimes dam inspector so far with always low metal values.

There has been some request for a seepage collection drain to collect runoff and seepage before it can reach an adjacent bird sanctuary.

Effluent water after lime treatment to pH 10.5, thickening is sprayed onto the East Daggafontein slimes dam which practice has been approved by the Dept. of the Environment. Galvanized irrigation pipes and rainbird sprinklers are used. These pipes tend to corrode rather than clog up due to the pumping of this solution.

The slimes dam inspector with jurisdiction over the Zincor operation is Mr. Greenblatt from the Government Mining Engineer's office in Heidelberg.

Monitor well samples are taken by Zincor and analyzed in-house before being reported. Half the monitor wells are dry so no samples are collected.

CONCLUSIONS

Due to the recent concern in South Africa about the effects of high TDS effluents contaminating groundwater, it remains to be seen what effects disposal of tailings and high TDS effluents - (albeit low in metal values) have on groundwater in the local aquifers below the tailings piles. The missing water in the water balance attempts may be searched for in seepage.

Gypsum problems may be resolvable together with a much enhanced water recycling program by using seeded slurry R. O. desalination, but this is unlikely to be competitive with adding fresh water as long as it is available at R0.23/m^3 and as long as excess water can be bled with high TDS.

Stormwater drainage release to the spruit and the Vaaldam deserves careful in-house scrutiny from the point of view of pointsource contribution of dissolved solids and metals. Details of effluent discharge regulations were not scrutinized.

It is remarkable that such a large hydrometallurgical base metal plant can operate with such minimal environmental problems as indicated by Zincor. Generally jarosite residues are known to be difficult to contain without experiencing metal contamination. Zincor's water conservation program has made big improvements but it is believed that they will ultimately develop a water management plan that consumes less than the current 15 m^3 H_2O per ton zinc produced, but a careful water balance model is needed to devise such a plan.

Sulfates in the presence of magnesium can get to very high levels in water without precipitating $MgSO_4$. Water is generally unusable for agriculture or human consumption when the $SO_4^{=}$ levels get high enough . Treatment of excess water that accumulates in the lined "emergency" dam with lime to pH 10.5 is one way to remove all TDS except $CaSO_4$ and alkali metals.

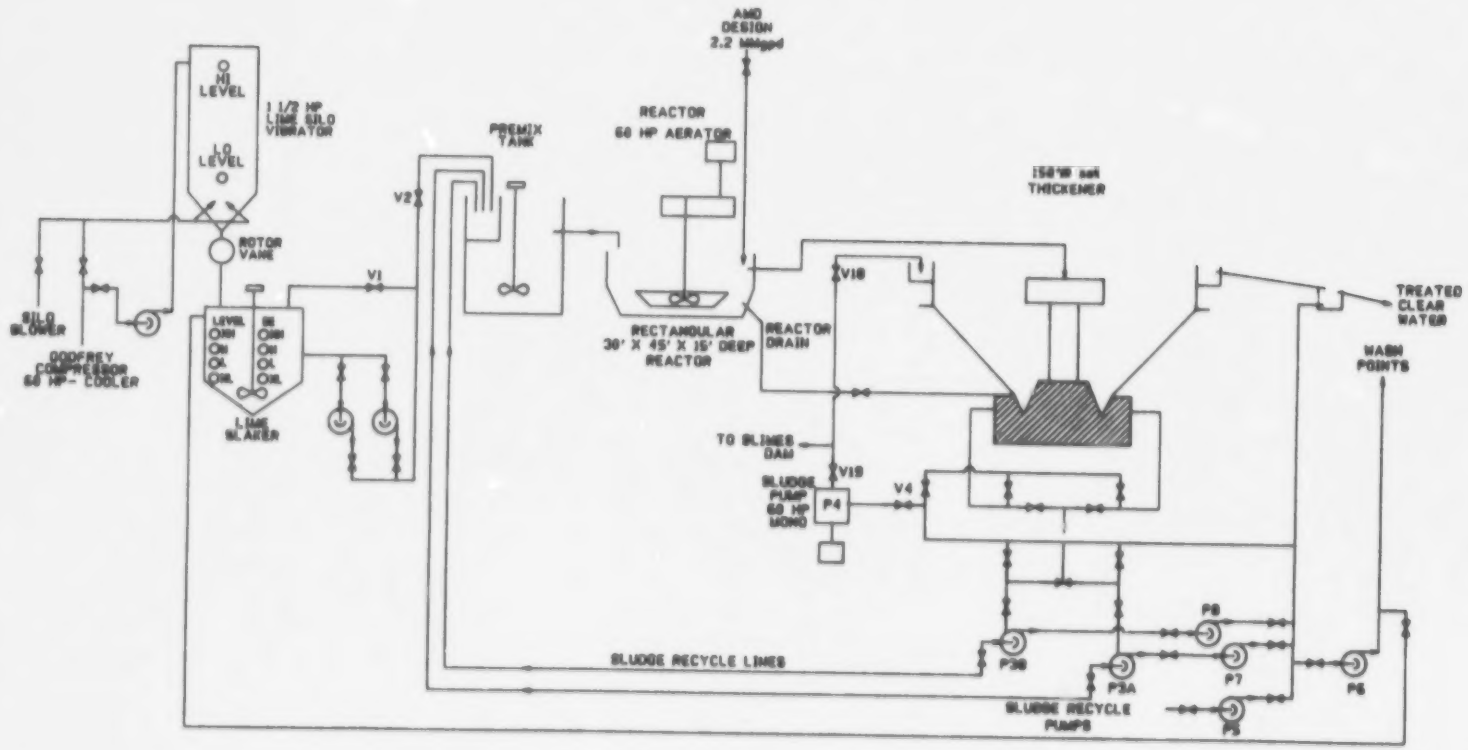
In general, considering the large flows of high TDS solutions and disposal of precipitates and residues in the tailings area divided into "acid valley" for iron residues, "lead valley" for Pb-Ag residues and the evaporation area, it would be surprising if there were not serious groundwater contamination potentials - These may not be regulated for the time being, but judging by US trends the time is likely not too far off when groundwater protection becomes an important issue in South Africa as well.

MINE (CLOSED)	KROMDRAAI COAL MINE OLD CORONATION MINE P. O. BOX 2 WITBANK 1035
OPERATING UNIT	New Largo Colliery Private Bag Voltargo 2226 South Africa
CONTACT	Mr. Trevor Wilmot Manager Telephone: Voltargo (0135332) No. 3
PARENT ORGANIZATION	Anglo American Corporation of South Africa 44 Main Street Marshalltown 2107
TECHNICAL RESPONSIBILITY	Amcoal Central Coal Laboratories P. O. Box 2774 Witbank 1035 Brian Peacock Telephone: (01351) 2201 Anglo American Research Laboratories P. O. Box 106 Crown Mines 2025 Danie J. Bosman Telephone: (011) 835-3251
LOCATION	About 20 minutes by car from Witbank, Transvaal due north of the Highveld Steel Plant.
DATE OF VISIT	20 December 1983

INTRODUCTION

The Old Coronation Coal Mine at Kromdraai, Transvaal ceased production around 1970. The minesite was restored but significant volumes of acid mine drainage (AMD) water flowed to the surface at pH 2.2-2.4. In 1974 the flow of AMD was 3.0 mm Igpd (14,000 m^3/d) with a total dissolved solids level of 1750 ppm and conductivity of 180 mS/m.

HDS PLANT
OLD CORONATION MINE, KROMDRAAI



Numerous methods were evaluated for the disposal of this water as described by BOSMAN (1974). Initial attempts at lime neutralization and settling yielded a precipitate with a volume equal to 10% of the feedwater with further densification possible to 4% of the original volume of water treated. Since the mine was estimated to contain 10,000 tons of precipitable solids the volume of the sludge at 2.5% solids would be 400,000 m^3 requiring a costly surface dam. Disposal of the sludge underground was also unwise as it was not known how much of the sludge would redissolve and because this practice would interfere with possible future open cast mining of the pillars.

After pilot tests described by BOSMAN (1974) to test the high density sludge process (HDS) originally developed by Bethlehem Steel Corp. as described by KOSTENBAEDER & HAINES (1970) and the NALCO Water Treatment Handbook, a plant was installed at the Kromdraai site to treat 14,000m^3/d of acid mine drainage. This plant is described by BOSMAN (1983).

The HDS plant at Kromdraai was visited on 20 December, 1983 with a view to learning more about the performance, design and operation in practice of such a plant. A flow sheet showing pumps, meters and valves is provided. Detailed accounts of the pilot testwork and performance of the plant are provided in the Chapter on Acid Mine Drainage Treatment.

OBSERVATIONS

1. The plant in 1974 originally treated 3 million gallons of acid mine drainage per day (14,000 m^3/d). Initially the plant was operated 24 hours/day seven days a week but after three years the mine had been dewatered and it was necessary to operate the plant only one third of the time. At the time of the RANDOL visit the plant needs to be operated only 8 hours per week indicating that water inflow to the mine is drying up.

2. Lime neutralized sludge drawn from the mixer settles at the following rate:

Time :	0	5 min.	10 min.	15 min.	30 min.	1 hr.
Sludge height :	1000	800	680	420	280	170

3. Samples drawn from the side of the thickener indicate excellent one hour settling rates:

Sample Point :		1	2	3	4
Suspended solids :	ppm	clear	clear	20	40

4. Water from the thickener overflow used to be discharged via three settling dams to a spruit which flows via the Wilge River eventually to the Loskop Dam. Now, however, overflow water is pumped to the 93 AD army base adjacent to the old minesite for use in lavatories and as washwater. Attempts to use thickener overflow as drinking water had the army "on the trot" on account of its saturated gypsum level.

5. Sludge underflow from the thickener is pumped to a disposal dam about 4 miles away using a 60 HP Monopump. The monopump has worked exceptionally well for the duration of the operation. Thickener underflow density has never been higher than 34% solids.

6. Inspection of the sludge disposal site indicated that of the four earth dams provided for the purpose, the total amount of sludge generated to date could be accommodated in about 50% of the volume of the first dam. The dried sludge is stable and can be walked on. It takes the form of a very low density yellow cake and dries to a very low moisture content, bonedry to the touch.

7. The operator pointed out that the sludge pipe should have been constructed with flanged couplings to allow the pipe to be broken into sections when necessary to unclog it.

8. Lime consumption at full operation (10,000 m^3/day) amounted to about 750 tons per month (based on lime cost of R15,000 per month at R18-21/t).

9. Lime is purchased from Marble Hall (Pty) Ltd. If there is too much sand and grit in the lime then the lime lines clog. Lime is delivered by road tanker and conveyed pneumatically into a bin feeding a lime slaker. Conclusion: Lime with a low sand content should be selected.

10. The original plant was installed with an underground 3"Ø line to feed slaked lime slurry from the lime slaker tank to the sludge premix tank. This line was too large in diameter with the result that downhill flow velocity was too slow to keep the lime slurry in suspension. The line clogged up. The problem found a practical solution by installing a 1½"Ø flexible plastic line above ground level to transfer lime slurry to the premix tank.

11. The original plant was designed for automatic operation, but it proved more practical to operate it by manual control.

12. The plant is currently operated by one superintendent with two unskilled assistants who also preform minor maintenance tasks. Major maintenance is carried out by the New Largo Collieries mine staff.

Geomembranes manufactured by the above processes are produced in rolls approximately 1.5 m to 10 m (5 to 33 feet) in width. Geomembranes that are produced in wide rolls, typically 5 to 10 m (16 to 33 ft), and heavy geomembranes such as asphaltic geomembranes are commonly transported to the field site where they are seamed together. Geomembranes that are produced in narrow, lighter rolls are first transported to a fabrication factory where they are seamed into large blankets. Blankets can be fabricated to any designed shape and are limited only by handling weight and dimension. They are commonly less than 2000 m^2 (20,000 ft^2). Blankets are packaged and transported to the construction site where they are seamed together. Small facilities can often be lined with a single blanket, thereby eliminating the need for field seaming.

Seaming methods depend upon the composition of the geomembrane. Some geomembranes can be seamed by several different methods. The most common seaming methods for polymeric geomembranes are: (i) methods involving heat only, such as electronic (dielectric) bonding, hot air bonding, hot wedge (or knife) bonding; (ii) methods involving supply of hot base product, such as extrusion (or fusion) welding; (iii) methods involving solvents and/or cements, such as solvent bonding, bodied solvent adhesive, solvent cements, contact cements; and (iv) methods involving vulcanizing tapes or adhesives. Methods involving heat are applicable only to geomembranes made with base products sensitive to heat, ie, thermoplastics, cristalline thermoplastics and thermoplastic elastomers. All seaming methods can be used in a plant or in the field, except the dielectric method which is not used in the field because it is sensitive to dust and humidity and the equipment is cumbersome. Extrusion welding is used only for high density polyethylene. Asphaltic geomembranes are typically seamed using flame or hot wedge, with or without supply of hot liquid asphalt.

Geomembranes made in situ (ie, at the construction site) are usually continuous (ie, with no seams) and are made by spraying or otherwise placing a hot or cold viscous material onto a substrate. The geomembranes made by spraying are commonly referred to as "spray-applied geomembranes" or "spray-on geomembranes". The base product of the sprayed material is commonly asphalt, an asphalt-elastomer compound (eg, asphalt-latex, asphalt-butadiene-styrene, etc), or a polymer such as polyurethane. The sprayed material forms a continuous flexible film with little or no tack after curing. If the material is applied onto an existing surface (ie, earth or concrete) the spray-applied geomembrane is non-reinforced. If the material is applied onto a fabric or geotextile,

13. It was pointed out by Anglo American Research Laboratories that at Kromdraai the plant had excess capacity and there had proven to be more than enough available dam storage for neutralization sludges. Consequently it had never become necessary to optimize the HDS process to achieve the densest possible sludge.

14. Most of the HDS plants in the world have been constructed by Bethlehem Steel Corporation, at Bethlehem Steel installations. At ERPM the HDS plant was designed with Bethlehem Steel knowhow purchased in 1974 and subject to a secrecy agreement valid until March 1984. The Kromdraai plant demonstrates that HDS can successfully be applied based on available published information and appropriate testwork.

15. A point of interest is the high level of suspended solids in the thickener overflow of the pilot unit at Kromdraai compared with the full scale operation; the improvement believed to be due to an improved aeration device in the full scale plant.

16. No excessive scaling was observed in the Kromdraai HDS plant. Recirculation of sludges in the HDS process and the low gypsum concentrations appear to successfully avoid scale problems.

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KOSTENBAEDER, P. D. & HAINES, G. F. (1970) High Density Sludge Treats Acid Mine Water. Coal Age, September 1970, p. 90.

OPERATION	PHOSPHATE DEVELOPMENT CORPORATION P. O. BOX 1 PHALABORWA 1390	
TELEPHONE	(01524) 2155/2261	
CONTACTS	E. H. Roux	Production Manager
	J. G. Goodey	Assistant Manager Research
	J. A. Visser	Assistant Production Manager
DATE OF VISIT	21 December 1983 2 March 1984	

INTRODUCTION

The huge ore deposit at Phalaborwa, in the lowveld of the Eastern Transvaal is one of the world's great orebodies and mines. FOSKOR faces challenges with respect to water management and future treatment needs.

Foskor operates an open pit mine and mill to recover phosphate, copper, magnetite baddeleyite from a pyroxenite-carbonatite pipe complex.

FOSKOR also treats tailings from the adjacent operation of Palabora Mining Company after primary removal of copper by PMC to recover a phosphate concentrate.

Large amounts of water are used in the process much of which is recycled. Recycling results in a buildup of ions in the water which have an effect on the process and also on the amount of reagents required and even the selection of flotation reagents.

Environmental aspects of effluents from large flotation plants such as this are also of interest, as well as possible effluent treatment steps.

LOCATION

At Phalaborwa in the North Eastern Transvaal on the western edge of the Kruger National Park

CLIMATE

Subtropical lowveld with summer rainfall and intense heat, mild winters with no frost.

DESCRIPTION OF OPERATION

FOSKOR's mineral processing operations are summarized in the following flowchart which is straightforward.

FOSKOR processes 25,000 tpd of ore mined and stockpiled by a neighboring mine; i.e., the Palabora Mining Company and a further 25,000 tpd of tailings from this company's adjacent operations.

The basic processing steps consist of crushing and grinding followed by a sequential flotation of a copper sulfide concentrate and phosphate minerals followed by heavy mineral recovery of baddeleyite.

The second processing stream receives tailings from Palabora Mining Corporation and recovers phosphate minerals.

WATER BALANCE

The water balance is illustrated in a diagram below showing the movement of water and solids within the FOSKOR plant and tailings. Please note that this water/mass balance includes a third processing stream for treatment of ore from Foskor's own mine. This section of the plant is not currently in operation.

The macro water balance can be crudely summarized as follows:

Water Intake		Water Discharge/Loss	
Industrial Water supply	28,000 m^3/d	Discharge to Creek	39,800 m^3/d
Water in PMC tailings	22,000 m^3/d	Loss with Phosphate Conc. to Fedex	1,800 m^3/d
		Loss with Phosphate Conc. stockpiles	700 m^3/d
		Loss with magnetite Concentrate	3,400 m^3/d
		Net Evaporation and Seepage over precipitation Drainage collected	4,300 m^3/d
	50,000 m^3/d		50,000 m^3/d

WATER SOURCES

Foskor's water comes primarily from the Olifants River from which it is pumped 7 km to the plantsite at a rate of close to 30,000 m^3/d. It is used directly without treatment except settling in the Industrial Water dam.

A further 22,000 m^3/d water is received with the slurried PMC tailings which are treated by FOSKOR to recover apatite. This water contains relatively high levels of dissolved solids which comprise part of the water quality challenge.

A dam was built on the Olifants River to ensure an adequate water supply to the Phalaborwa community and industry.

WATER COST

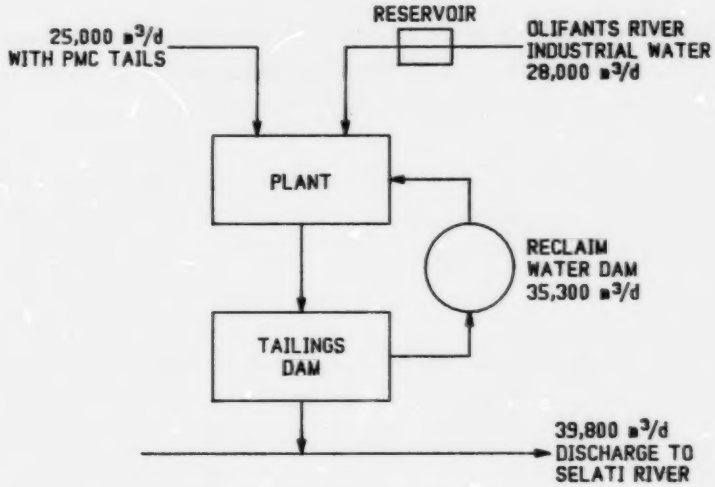
Industrial water from the Olifants River is supplied by the Phalaborwa Water Board at a cost of a few cents per m^3.

WATER ANALYSES

Water Type	Industrial Water	Reclaimed Water I	Reclaimed Water II	PMC Feed Water	Tailings Effluent
Sampling Location See Water Flow Diagram	A	B	B	C	D
pH	8.3	8.4	8.1	8.3	8.0
TDS (ppm)	300	3450	3350	5100	3300
Total Hardness (ppm Ca CO_3)	138	1468	1368	3408	1370
Ca (ppm)	54	514	454	1260	430
Mg	84	954	914	2148	940
Alkalinity (ØØ)	20	6	0	0	0
(MO)	132	134	134	58	134
Chlorides	38	260	276	324	270
Na	30	330	345	130	355
K	5	120	125	138	125
F	0.4	3.1	3.9	5.4	3.9
P	0.2	0.3	0.4	0.2	0.3
SO_4	-	-	-	3031	1635
S/S	-	-	-	-	21

EFFLUENT STREAMS

About 38,000 m^3/d of effluent is released from the FOSKOR tailings dam. Further losses of water occur through evaporation, seepage from the tailings dam and with copper and magnetite concentrates.



INTERNAL RECYCLE OF WATER

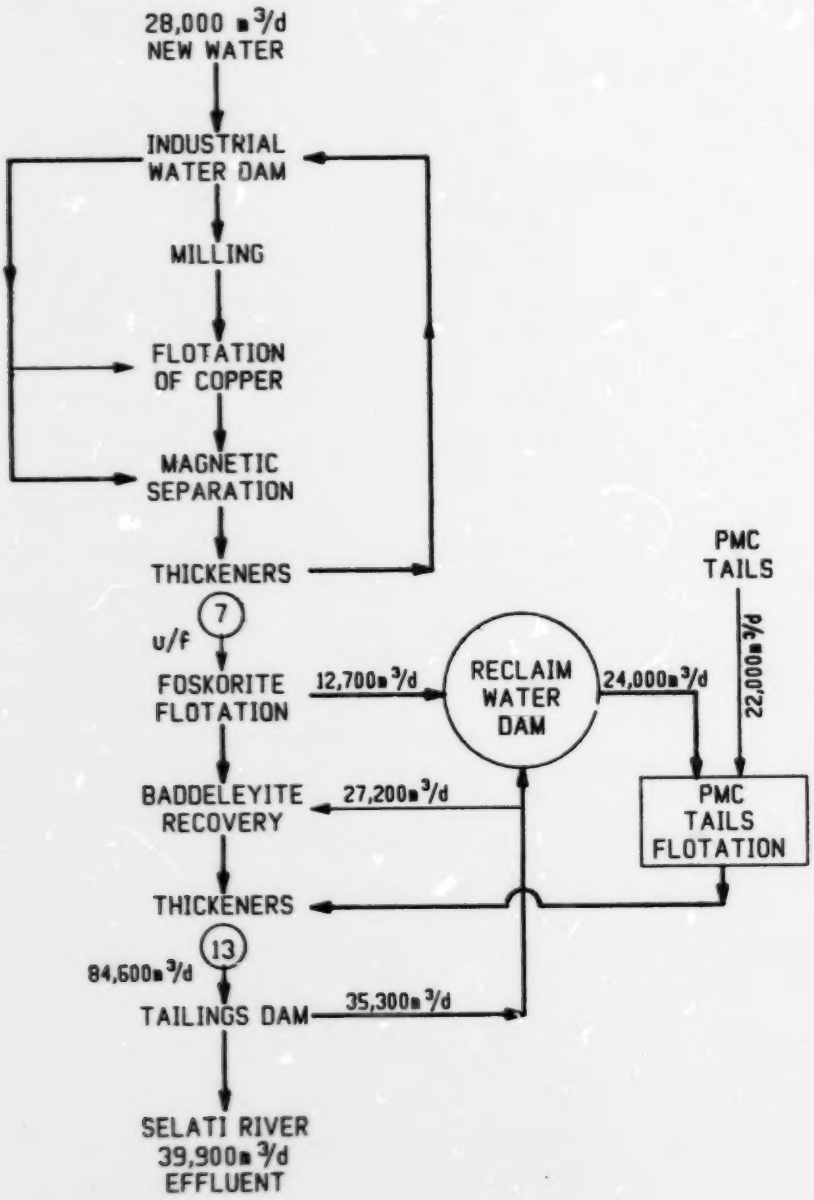
The FOSKOR operation recycles considerable quantities of water and the recycling flow pattern is relatively complicated as evident from the diagram. In addition water received with the PMC tails is a bleed from PMC's water recycling system and the effect of their recycling of water is seen on its quality.

The main recycle water loops observed in the FOSKOR flowsheet are as follows:

1) New water is added to the Industrial Water Dam which supplies water for grinding (26,000 m^3/d), 9000 m^3/d to the flotation circuit and a further 15,300 m^3/d to the magnetic separation plant. Final tailings are thickened prior to foskorite flotation, and an estimated 22,300 m^3/d thickener overflow is recycled to the Industrial Water dam.

2) Feed to the Foskorite flotation plant, i.e., underflow from thickener 7 is diluted with 12,700 m^3/d reclaimed tailings water. Finally after recovery of Baddeleyite from apatite flotation tailings they are thickened and pumped to the tailings disposal dam. A total of 84,000 m^3/d thickener overflow and 35,300 m^3/d tailings decant water is returned to the reclaim water dam with a bleedstream of 27,200 m^3/d being recycled to the baddeleyite recovery plant.

FOSKOR
MAIN WATER RECYCLING LOOPS



WATER QUALITY RELATED PHENOMENA AND PROBLEMS

1. Effect of Water Quality on Metallurgical Processing and Recovery

The water that is delivered with the PMC tails is highly contaminated with dissolved salts. Typical Analysis is as follows:

	PMC Tails Water	
pH	8.3	
TDS	5,100 ppm	
Hardness (total)	3,408	
Ca as $CaCO_3$	1,260	504 ppm Ca
Mg as $CaCO_3$	2,148	527 ppm Mg
Alkalinity (ØØ)	6	
M. O.	58	
Chloride	324	
Na	130	
K	138	
F	5.4	
P	0.2	
SO_4	3,031	

This water with combined Ca + Mg at 1031 ppm and 3000 ppm $SO_4^{=}$ has probably not reached equilibrium. The fluoride level at 5.4 is well in excess of that permitted for discharge by FOSKOR which is 1 ppm max.

The FOSKOR flotation process to treat PMC tails has been developed to be able to handle this water. Subsequent tests in which 80% of the water was replaced by "industrial water" did not result in a significant savings of reagent.

The main gangue minerals in the PMC tails feed to Foskor are calcite, dolomite, phlogopite and olivine/serpentines.

The particle size distribution of the flotation feed material is as follows:

Microns	% Mass
+425	9.2
300/425	9.8
150/300	33.3
75/150	25.0
45/75	8.4
-45	14.3

Fine feed containing apatite and calcite in contact with water that is recycled slowly adds Ca and Mg ions to the water.

The hardness of the water interferes with the froth and reacts with the fatty acid collector used to float apatite to form Ca and Mg oleates. These are insoluble soaps and have a detrimental effect on the float system.

To overcome the effect on flotation, increased amounts of gangue depressant has to be used. In the primary flotation circuit poly glycol ether is used as a gangue depressant. In the flotation plant treating PMC tails poly glycol ether plus a modified polysaccharide is used.

Several types of poly glycol ethers have been used including one manufactured by Berol Kemi of Sweden. The one found to be most suitable is a nonyl-phenol tetra glycol ether. Poly glycol ether helps to emulsify the fatty acid and may possibly adsorb on the calcite surfaces to help depress the gangue.

Chemically modified polysaccharide is supplied to FOSKOR by TROCHEM SA (Pty) Ltd.

Modified polysaccharide is manufactured from quar beans and is known as ACROL LG 21 and ACROL LG 31. Typical doses for analagous operations are 120 g per ton solids treated and a typical cost is R2.00-R2.20/Kg according to an independent source.

FOSKOR's annual consumption of flotation reagents is confidential, it is however "substantial" amounting to several million rands.

Flotation of nonmetallic minerals is discussed in the AIME-SME Gaudin Memorial Series, Volume I.

If clean water is used for flotation a carboxylic acid derivative collector such as HOECHST 3309 has been indicated to work well and economically. However, with over 5000 ppm TDS and such high hardness, the consumption of this experimental collector has been found to be excessive as it appears to be precipitated before it can get to the mineral.

Addition of waterglass Na_2SiO_3 has been found to act as a modifier/dispersant and also as a slight depressant for mica. FOSKOR uses about 600g waterglass per ton solids in their flotation reagent mix. In South Africa waterglass costs about R300/ton.

Waterglass addition is found to remove some calcium and magnesium from solution.

Considerable testwork of flotation reagents and the effects on and of ion populations in flotation pulps on flotation reagent consumption and recovery have been carried out by FOSKOR.

In the past, flotation difficulties on the main plant could sometimes be ascribed to a change in the raw water quality. The hardness of the industrial water fluctuated with the seasons reaching a peak before the first summer rains, and was shown to have an effect on apatite recovery from Foskorite ore.

The amount of suspended solids in industrial water when the Olifants River was in flood also was found to have an influence on apatite flotation both in lab tests and in the plant.

FOSKOR investigated the roles of additional ions present in flotation plant water and their interaction with ions from the flotation reagents and from the mineral constituents of pyroxenite and foskorite ore, with particular emphasis on the effects of calcium and magnesium.

Several interesting observations were made as a result of these tests:

1) Foskorite constituents, e.g., phlogopite, olivine, magnetite, calcite and apatite all contributed ions to the water phase of the flotation pulp and an alkaline pulp was obtained in each case.

2) Reagent additions to the ore pulp in dosages giving optimum apatite recovery, constantly caused a removal of ions from the aqueous phase.

3) A significant removal of silicate ions was consistently found. Soluble silicate was removed from solution by gangue minerals calcite, and iron-bearing minerals olivine, magnetite and phlogopite but not by apatite. Sodium silicate addition acts as a depressant of magnetite and olivine, and lowers the iron content of apatite concentrates.

4) Very little flotation depression of calcite was observed in the absence of apatite although in the presence of apatite the same reagent combination gave excellent apatite-calcite separation and selective depression of calcite.

5) Once the mineral mixtures had been milled and conditioned with all essential flotation reagents, the flotation water could be filtered off and be replaced by demineralized water, and the mineral subjected to flotation without any subsequent change in flotation recovery of apatite.

AFFECT OF REAGENTS & ORE ON PULP WATER QUALITY

- Foskorite ore in different stages of weathering contributes calcium and magnesium to the system and an alkaline pulp is always obtained.

- The reagents sodium hydroxide and sodium silicate soften the flotation liquid.

- Less reagents are necessary for successful flotation of apatite when demineralized water is used compared to industrial water.

- The order of addition of sodium silicate and sodium hydroxide affects the flotation recovery of apatite - soluble silicate reagent is removed from solution by the ore.

- Addition of sodium silicate and sodium hydroxide either separately or together caused a reduction in calcium and magnesium in solution in the pulps.

- Phlogopite contributes potassium, calcium, magnesium and sodium to pulp solutions.

- Addition of NaOH to several mineral slurries resulted in a drop in Ca & Mg that went into solution.

- Addition of calcium to a phlogopite slurry resulted in an increase in potassium ions in solution.

V. M. Lovell, formerly employed by the Council for Mineral Technology (MINTEK), is known to have written several papers on the effects of water quality on flotation performance of apatite from the PMC tailings. More information could possible be obtained from:

Council for Mineral Technology (MINTEK)
Private Bag X3015
Randburg 2125
South Africa
Telephone: (011) 793-3511
Contact: Librarian

Randol was unable to reach Dr. Lovell and did not have the opportunity of including his observations in this investigation.

OPTIMUM FLOTATION REAGENT COMBINATION

An optimum flotation reagent combination was found in lab tests to be as shown below. This combination gave apatite recoveries from binary apatite-mineral test mixtures exceeding 80%. All sodium silicate and caustic soda additions were made in the mill. Fatty acid (Unitol O. S. R.) and Berol E. M. U. 26 were added to the flotation pulp prior to the conditioning step.

Reagent	Reagent addition lb/ton ore	meg/l Na^+	meg/l $SiO_2^=$
Sodium Silicate	0.412	1.00	4.00
Caustic Soda	0.25	1.25	
Fatty Acid Unitol D.S.R.	0.6		
Berol E.M.U. 26	0.4		I-617

Berol E.M.U. 26 is a nonionic emulsifier of the alkylphenol poly glycol ether type, proposed as a depressant for calcite.

2. ENVIRONMENT AND EFFLUENTS

The second water problem is the discharge of effluents containing such high TDS values and in particular containing F^- at 3.9 ppm when the effluent discharge limit is 1 ppm F^-. A special dispensation from the Dept. of the Environment allows FOSKOR to discharge effluents at up to 4 ppm F^-.

According to Hendrik Best of the Dept. of the Environment, the high potassium levels in the effluents (due to contact with potassium containing carbonatites) are also toxic to fish. The water in the PMC tail slurry was reported to have 138 ppm K^+, and the reclaim water used in the plant contains around 120 ppm K^+.

This is the one and only reference found during this investigation to the possible toxicity of potassium to fish. This point has been queried for confirmation from:

Hendrik J. Best
Department of the Environment
Private Bag X313
Pretoria 0001

Telephone: (012) 268-402

It is interesting that even though phosphate minerals are one of the principle values recovered by FOSKOR, phosphate levels in recycled water remain well below 1 ppm.

3. SCALE AND CORROSION

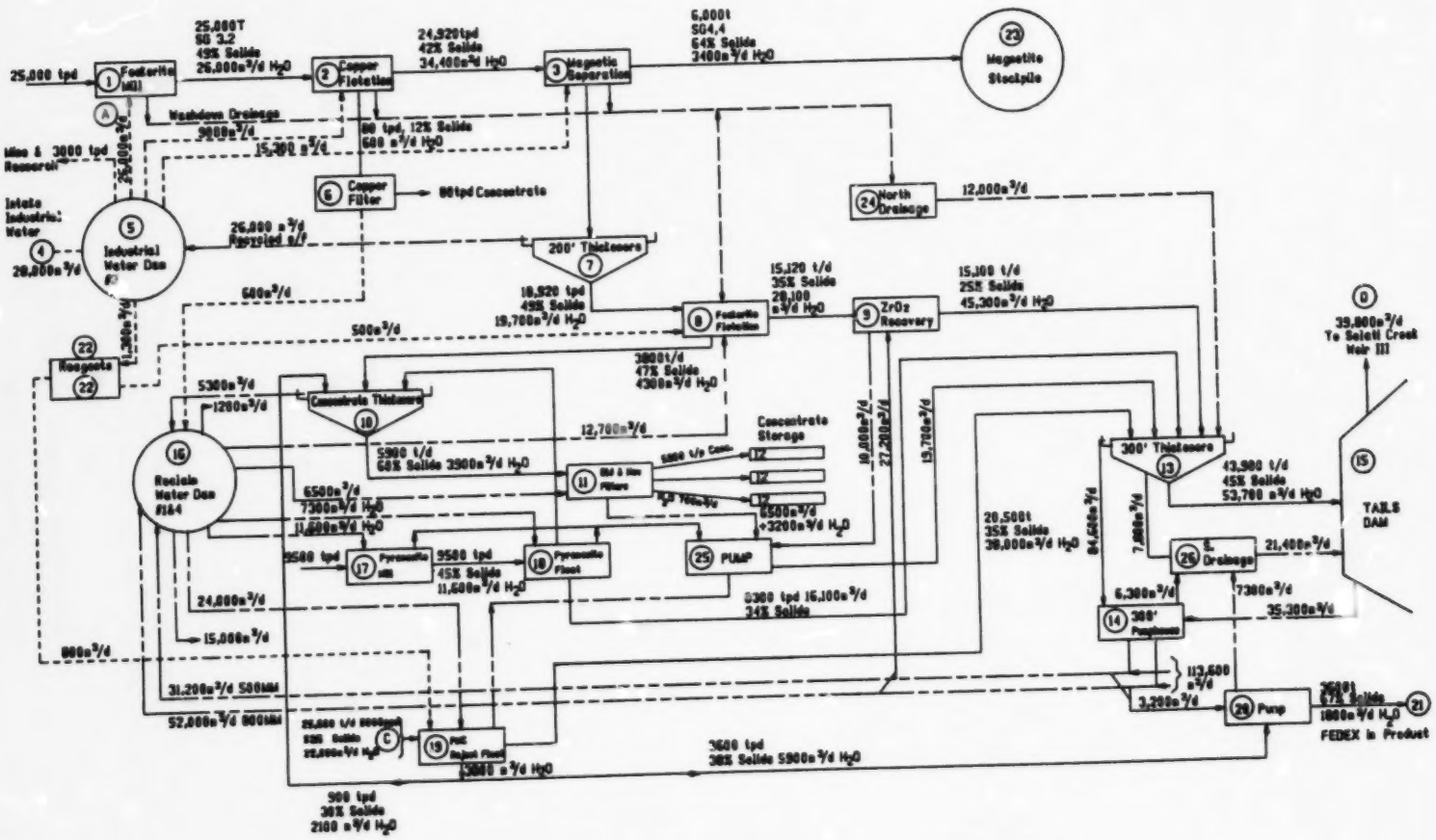
Although the recycled water at FOSKOR is very high in Ca^{++}, Mg^{++} and $SO_4^=$, it is not found to cause scaling nor corrosion in the plant. No scale inhibitors are used. The reason that such a high Ca^{2+} and $SO_4^=$ can be in solution without scale problems seems to be the presence of Mg^{2+} which seems to modify the gypsum solubility.

4. PMC ACID SCRUBBING EFFECTS

In the adjoining PMC plant water is recycled and total dissolved solids build up more than they do in the FOSKOR plant mainly because of their SO_2 gas scrubbing operation. Final tailings material is subjected to classification. The fines fraction is then used for gas scrubbing. Calcite/dolomite reacts with undissolved SO_2/SO_3 gas resulting in high concentrations of Ca^{++}, Mg^{++} and $SO_4^=$ ions in the water phase.

It has been speculated by independent sources that water that has passed through the gas scrubber results in improved flotation recovery of valerlite, a copper mineral. This was not confirmed but is possible since SO_2 can convert oxidized copper to metallic copper which may float better.

FOSKOR WATER FLOW DIAGRAM

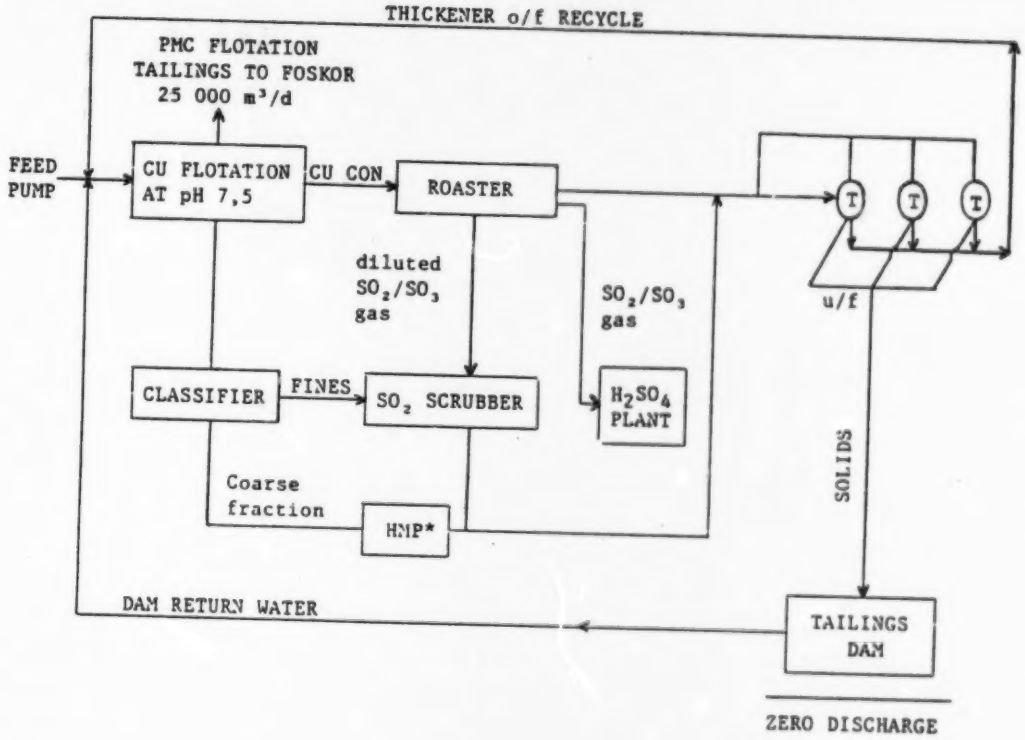


LEGEND

- INDUSTRIAL WATER
- SLURRY
- RECYCLED WATER
- WASHDOWN DRAINAGE

1. FOSKORITE MILL
2. COPPER FLOTATION
3. MAGNETIC SEPARATION
4. INDUSTRIAL WATER
5. INDUSTRIAL WATER DAM #2
6. COPPER FILTER
7. 200' THICKENERS
8. FOSKORITE FLOTATION
9. ZrO2 RECOVERY
10. CONCENTRATE THICKENERS
11. OLD & NEW FILTERS
12. CONCENTRATE STORAGE
13. 300' THICKENERS
14. 300' PUMPHOUSE
15. TAILS DAM
16. RECLAIM WATER DAM # 1 & 4
17. PYROXENITE MILL
18. PYROXENITE FLOAT
19. PMC REJECT FLOAT
20. PUMP
21. FEDEX PRODUCT
22. REAGENTS
23. MAGNETIC STOCKPILE
24. NORTH DRAINAGE
25. "GAT" PUMPS (IN A HOLE)
26. S. DRAINAGE

PMC



*Heavy mineral plant

WATER CONSUMPTION

Net water consumption at FOSKOR is complicated by the additional water that enters the processing system with the PMC feed stream. Examining the treatment of ore mined by FOSKOR in a separate circuit, it appears that net fresh water consumption works out to 26,700 m^3/d to treat 25,000 tpd ore or about 1.07 m^3 water/ton ore.

TAILINGS DAM DESIGN

FOSKOR employs a consulting firm on a retainer to review water management and for engineering aspects of their tailings disposal including dam design.

Watermeyer, Legge, Piesold & Uhlman
P. O. Box 221
Rivonia - Sandton 2128
South Africa

Telephone: (011) 803-3200
Telex: 4-22369
Contact: J. R. G. Williamson

Flow diagram

Sources:

1. Pyrosmite Crown pit - 10 million tonnes of ore per year
2. Feldspar Pan - 3 million tonnes mined by PMC under agreement - 3 million tonnes of ore per year
3. PMC tailings - PMC plant pulp - 3 million tonnes pulp per year

Transport:

1. Pyrosmite 80 km diesel-electric trucks
2. Feldspar 80 km diesel-electric trucks
3. PMC tailings 300 mm pipeline from PMC

Crushing:

1. Pyrosmite
   (a) Primary - 1 100 x 1 800 mm Allis Chalmers gyratory crusher. Ore crushed to 125 mm
   (b) Secondary - Allis Chalmers and Symons cone crushers. Ore crushed to 50 mm
   (c) Tertiary - Allis Chalmers and Symons cone crushers. Ore crushed to 19 mm
2. Feldspar
   (a) Primary - 1 200 x 1 500 mm Blake type jaw crusher. Ore crushed to 250 mm
   (b) Secondary - 1 800 mm Symons cone crusher. Ore crushed to 50 mm
   (c) Tertiary - 1 200 mm Symons standard crushers. Ore crushed to 25 mm
   (d) Final - 1 200 mm Symons short head crushers. Ore crushed to 13 mm

Storing:

1. Pyrosmite
   (a) Primary stockpile - 30 000 tonnes
   (b) Fine ore stockpile - 50 000 tonnes
2. Feldspar 40 000 tonnes fine ore stockpile

Milling:

1. Pyrosmite 5 x 1 2 m x 3 6 m and twelve 2 7 m x 6 6 m ball mills in closed circuit with a hydrocyclone classifier for each mill
2. Feldspar Six 2 4 m x 3 6 m rod mills in closed circuit with a twelve cone classifier for each mill

Copper Flotation:

1. Feldspar Copper flotation is done in 24 8 4 m flotation cells by means of rougher and cleaner stages. The copper concentrate is stockpiled for subsequent despatch to PMC for refining under contract

Magnetic separation:

1. Feldspar After copper flotation the magnetite is extracted by means of magnetic separators and pumped to stockpiles for possible future use. The non-magnetic fraction is pumped to the phosphate flotation plant for flotation of phosphate concentrate

Phosphate flotation:

1. Pyrosmite The pulp from the mills is treated with reagents prior to phosphate flotation. Flotation is carried out in 88 8 678 m³ flotation cells through four stages namely rougher, scavenger, cleaner and re-cleaner
2. Feldspar Prior to phosphate flotation the non-magnetic pulp from the magnetic separators is treated with reagents. The phosphate is then floated in 32 8 678 m³ flotation cells through the same stages as for pyrosmite
3. PMC tailings The phosphate is floated with a combination of reagents in 48 8 4 m³ and 288 1 416 m³ flotation cells through the same stages as already mentioned

Filtering:

1. Feldspar The phosphate concentrates from the pyrosmite flotation and PMC tailings flotations are partly dewatered through a succession of thickeners and disc filters to a moisture content of 10%. After filtration concentrates are removed by a conveyor belt system to stockpiles

Storage of Concentrates:

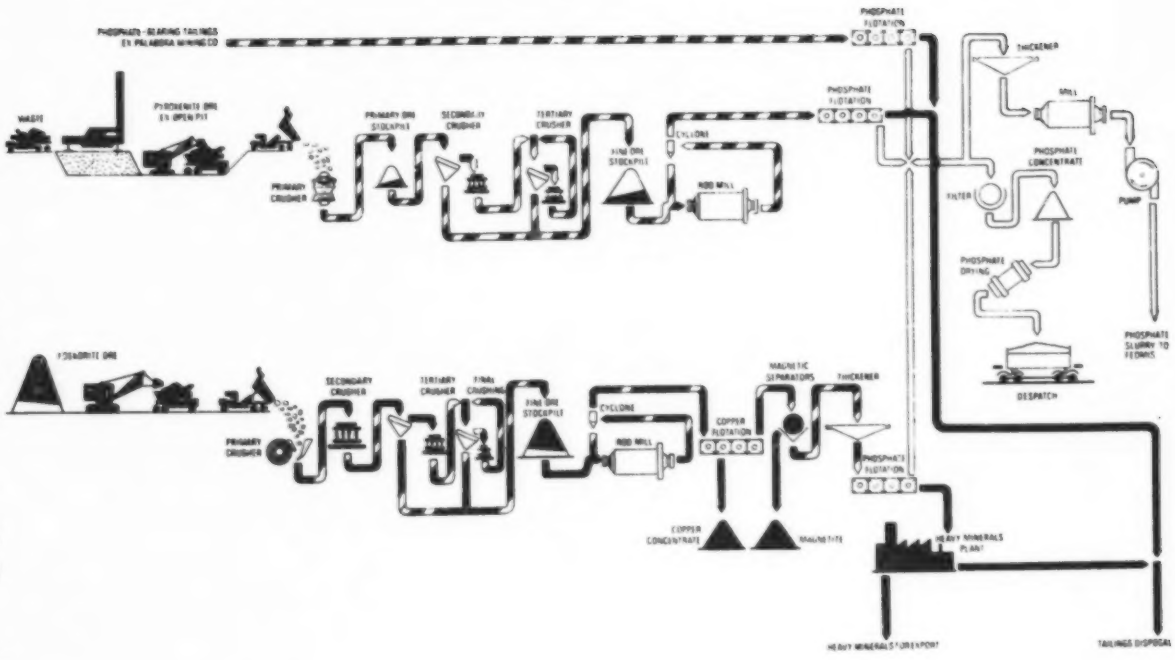
320 000 tonnes with phosphate concentrates can be stored in two bunkers and open stockpiles from where it is reclaimed for drying

Drying:

The phosphate concentrates are dried by means of three 21 m rotary kilns and two fluid bed dryers to a moisture content of approximately 1% and despatched to consumers

Heavy Minerals Plant:

1. After phosphate flotation the tailings are pumped to the heavy minerals plant where baddeleyite is recovered by means of gravity and leaching
   Baddeleyite concentrates are exported



OPERATION	STILFONTEIN SEWAGE WORKS STILFONTEIN MUNICIPALITY POST OFFICE BOX 20 STILFONTEIN, TRANSVAAL
TELEPHONE	(018) 41471
CONTACT	Andre Kilian — Acting Engineer Cornelius Bezuidenhout — Retired Town Engineer

INTRODUCTION

Inclusion of a discussion of a sewage works in an investigation of water management and water treatment for mining and metallurgical operations is of particular interest because reuse of treated sewage water represents a major potential addition to water that is available for metallurgical processing.

Treated sewage water is used in several gold plants, after being added to the tailings dam to blend with other reclaim water at, for example, Vaal Reefs and at Deelkraal. At Kloof Gold Mining Company and West Drefontein (both Gold Fields of South Africa) reclaimed sewage water is being considered for use in underground refrigeration units. At President Brand treated sewage water is believed to have had detrimental effects on flotation recoveries and on carbon adsorption performance. At Vaal Reefs, treated sewage effluent is used without problems in gold and uranium recovery circuits.

At Hartebeesfontein Gold Mining Company (Anglovaal) laboratory tests showed that treated sewage water from the new Stilfontein Sewage plant could be used for high pH flotation of pyrite and gold, whereas water samples from the old Stilfontein Sewage Treatment Plant showed a negative impact on recovery.

The purpose of a visit to Stilfontein was to find out what the differences in treatment process between the Old and New Stilfontein Sewage Treatment plants are and also what differences in water quality between the products of these two plants could account for the different test results reported by Anglo-Vaal Research Laboratories.

STILFONTIEN SEWAGE TREATMENT PLANT

A visit to Stilfontein Municipality failed to find any knowledgeable engineer who was familiar with the sewage treatment technologies employed. Eventually the retired former municipal engineer was located and he advised that there are in fact three sewage treatment units.

1) The old biofilter plant
2) The new biofilter plant
3) The new activated sludge plant

RANDOL was referred to a firm of consulting water treatment engineers in Johannesburg that is responsible for quality control checks and for civil engineering and process advice.

Stewart Svirdov & Oliver
P. O. Box 784148
Sandton 2146

Telephone: (011) 783-5393
Telex: 4-28044
Contact Philip J. Pybus

It was revealed that the "Old" plant at Stilfontein is a biofilter plant and the "New" plant is a Mark III 5-stage Badenpho activated sludge plant designed in 1977 based on CSIR technology. Incoming sewage water was split on entering the property and would be of essentially the same quality to both sewage plants.

"OLD" PLANT

The old plant using biological filtration to remove organics is overloaded and not performing well according to the consultants.

BIOFILTER SEWAGE TREATMENT

Biofiltration is one of the oldest most established and operator proof sewage treatment processes. Biofiltration uses trickle filters with a high surface area substrate on which the bacteria attach themselves, and is effective for removal of organic materials. However, biofiltration does not come close to meeting modern day PO_4^{3-} and NH_3 removal requirements. For example, in many parts of South Africa a maximum of 1 ppm $PO_4^{=}$ is allowed to avoid utrification of dams. In parts of the USA, e.g., Reno/Sparks the limit is 0.5 ppm for total P. Most phosphorous in effluents is in the form of orthophosphate $PO_4^{=}$ except that bound in cell biomass.

NEW BADENPHO PLANT

The "New" Stilfontein Sewage plant is a Mark III Badenpho plant designed by the CSIR in 1977.

The Badenpho process was developed by the CSIR and more information on the process can be obtained from:

National Institute for Water Research
CSIR
P. O. Box 395
Pretoria 0001

Telephone: (012) 86-9211
Contacts: Andre Gerber Biotechnology Division

in effluents the ratio of nutrients may not be the same as that required by the microorganisms. The aim of the Badenpho (and later Phoredox process) is to trick the bacteria into removing more phosphate than they really need. In the Phoredox process bacteria take up to 10 times the amount of phosphate needed for their metabolism.

Although it is now known how to make the process work, the pathways and mechanisms of "luxury" phosphate uptake have not yet been sorted out, and is the subject of further research.

NH_3 must be removed from recycled sewage water because it stimulates aquatic plant growth and results in an oxygen deficiency in the water. Also where the water is to be used underground in South African mines, it must be rendered potable and for each 1 ppm NH_3, 10 ppm Cl_2 are consumed during chlorination, so it becomes important to remove as much ammonia as possible.

The bacterial processes employed in Badenpho activated sludge processes are:

1) NH_3 oxidation by bacteria to NO_3^-
2) PO_4^{-3} removal in luxury amounts by bacteria
3) NO_3^- denitrification and discharge to air as N_2

In earlier denitrifying processes used in the USA, NO_3^- conversion to N_2 is achieved by adding methane as a carbon source for the bacteria. In the Badenpho and Phoredox processes, this is achieved using the carbon in sewage to provide the energy needed by the bacteria instead of methane.

The 5 stage Phoredox process consists of the following steps:

1. ANAEROBIC DIGESTION Anaerobic microorganisms are introduced in recycled sludges from the final clarifier. The incoming feed is rich in organics, ammonia and phosphates.

2. ANOXIC DENITRIFICATION Sludge is recycled to the primary aerator from the next stage. This step removes most of the NO_3^-. The rich organics provide energy to convert NO_3^- to nitrogen.

3. PRIMARY AERATOR This step oxidizes ammonia to NO_3^- and also results in some PO_4^{3-} uptake. Waste sludge is bled from this stage containing PO_4^{-3} as polyphosphate. Sludges are also recycled to the previous stage.

4. SECONDARY ANOXIC REACTOR This step gets rid of the remaining NO_3^- and consumes nutrients provided by the dying organisms and any residual organic matter.

5. SECONDARY AERATOR Stages 4 and 5 are a polishing step.

6. CLARIFIER The clarifier sludge containing aerobic microorganisms is recycled to the primary anaerobic stage.

In the Badenpho/Phoredox process the recycled sludge serves as an innoculant and affects the degree of stress on the bacteria in the anaerobic stage.

The Badenpho process generates sludges with up to 15-30% P content. It is not yet known how to dispose of these sludges. It may be possible to condition the sludge with lime and ferric chloride and use it as a soil conditioner. More work is needed in this area.

The Badenpho and Phoredox patent is owned by S. A. Inventions Development Corporation, and licenses can be purchased through:

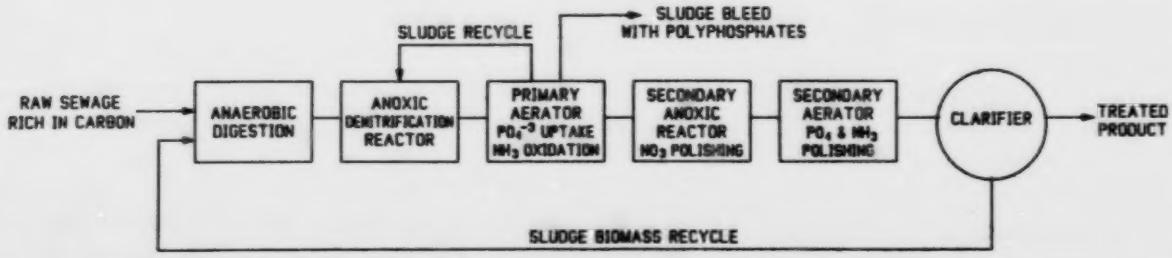
Meiring & Partners, Inc.
Pretoria

Commercial scale Badenpho plants are installed in South Africa, Windhoek, Brazil, Canada and the USA. The US experience is at South Lake Tahoe Water Works where Culp & Culp Brothers have acted as consultants on the process.

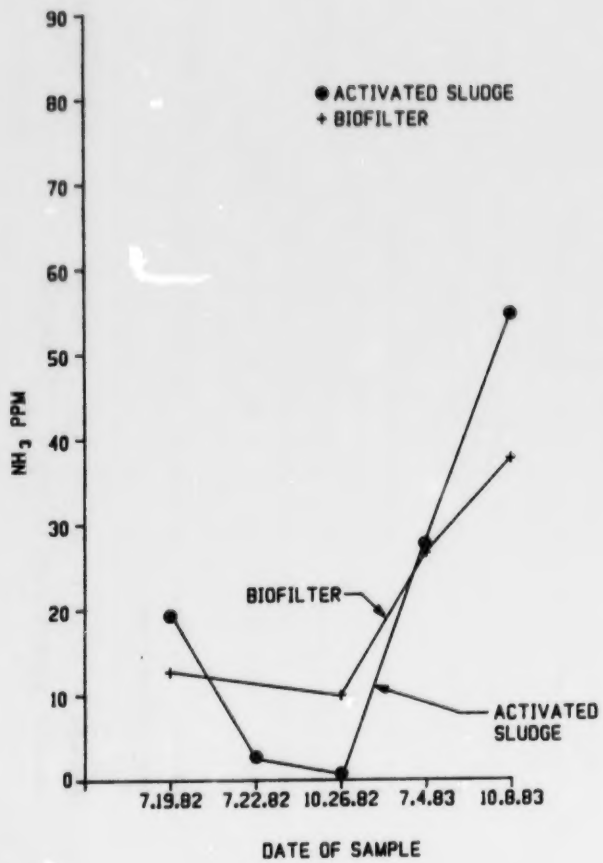
STILFONTEIN TREATED WATER QUALITY

The following analyses of product from the "new" activated sludge plant and the "old" biofilter plant taken on five different days from midwinter to early summer indicate the variation in quality that can be experienced in this water.

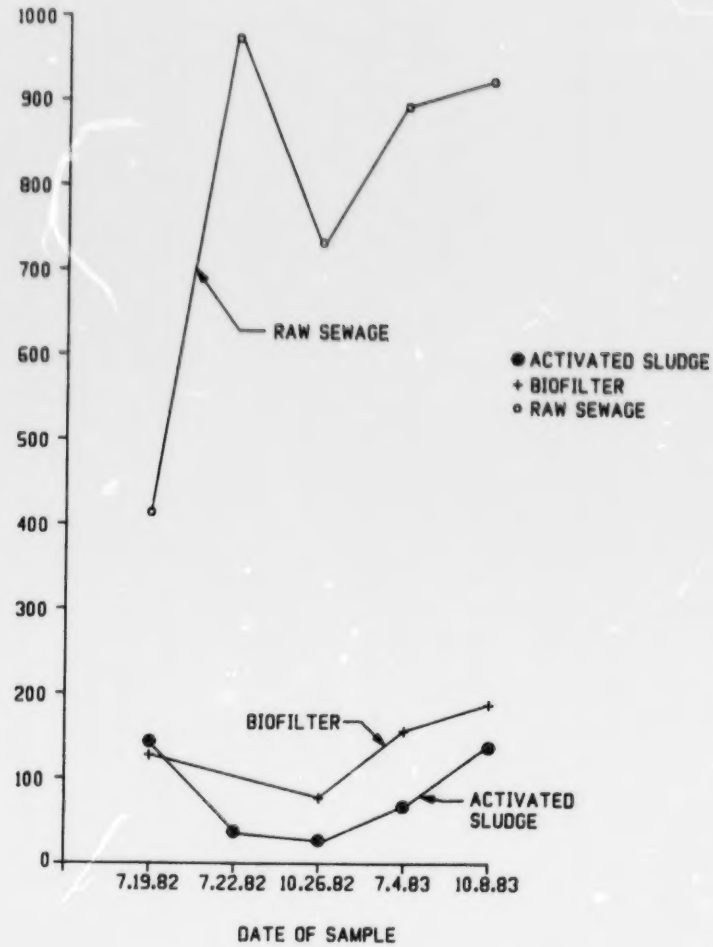
THE 5 STAGE BADENPHO PROCESS



AMMONIA IN
TREATED SEWAGE WATER



CHEMICAL OXYGEN DEMAND IN
TREATED SEWAGE WATER



CONCLUSIONS

1. There is an indication that the Badenpho process yields a water product from sewage that can be used in high pH flotation without adversely affecting recovery - based on tests by Anglo-Vaal Research Laboratories.

2. The Badenpho process is designed to remove NH_3, NO_3^- and PO_4^{-3}, however according to Stewart, Sviridov & Oliver, and as indicated by the Stilfontein plant results, PO_4^{-3} removal does not achieve the 1 ppm target claimed, and no comparative data were reported for PO_4^{3-} removal by the biofiltration plant.

3. If Stilfontein is a typical sewage treatment operating environment, then such operations are subject to wide performance fluctuations and relatively primitive operating controls.

4. When drawing water samples for flotation tests from biological sewage treatment plants it is important to analyze the water samples used to characterize its quality. Although the results are encouraging it remains to determine whether flotation results will remain as good through the full range of water quality fluctuations experienced in the Badenpho activated sludge water product.

5. Although the Badenpho process treated water has been found to be suitable for use in high pH flotation of pyrite and gold from Witwatersrand ores, the reasons for the improved performance using this water compared with biofiltration are not understood. More research is needed to be able to use this water with confidence and to understand what water quality parameters are important.

6. Consideration can be also given to using RBC's for removal of NH_3 from treated sewage water for use as recycle water in underground refrigeration.

7. The use of treated sewage water in metallurgical operations, especially flotation plants, is highly contraversial. Gencor and President Brand claim that it causes a reduced recovery. Other plants use treated sewage water in gold recovery (Vaal Reefs and E. Driefontein), and others have shown on a lab scale that if treated by the activated sludge process, it can be used for flotation.

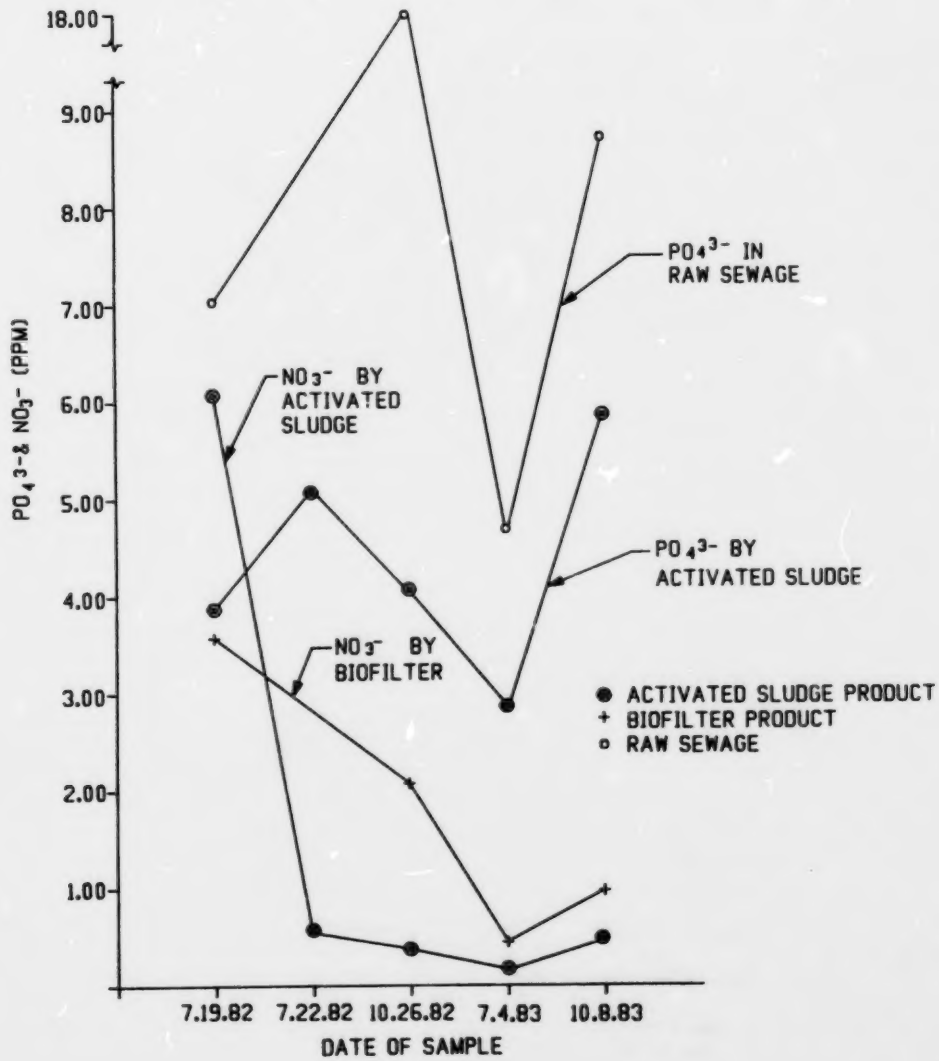
   At Cons. Murchison recycled sewage was formerly used for flotation, but has since been discontinued.

   Elsewhere, Kloof G. M. Co. Ltd. is seeking ways to use treated sewage reclaim water in underground cooling of their stopes.

President Brand G. M. Co. Ltd. has found that after sewage water is used as a coolant in the Peabody Scrubber, then it can be used in flotation without deleterious effects.

8. The performance of the Badenpho and Phoredox Process to remove NH_3, PO_4^{-3} and NO_3^- from sewage water is also contraversial especially for remote locations.

NO_3^- & PO_4^{3-} IN TREATED SEWAGE WATER



STILFONTEIN

EFFLUENT ANALYSES

19 July 1982

Constituent	Sample	Raw Sewage	Activated Sludge Effluent	Biofilter Effluent	General Standard Limits
COD	mg/l	400	128	120	75
PV/OA	mg/l	-	82	76	10
Suspended Solids	mg/l	-	83	92	25
TKN	mg/l	200	-	21	-
NH_4 - N	mg/l	3.7	19.1	12.1	10
NO_3^- - N	mg/l	-	6.0	3.5	-
PO_4^{3-} - P	mg/l	6.8	3.8	-	1.0 +

Mixed Liquor Solids = 6.87 mg/l

+ Special Standard

Return Sludge Solids = 10.50 mg/l

22 September 1982

Constituent	Raw Sewage	Activated Sludge Effluent	Biofilter Effluent	General Standard Limits
Chemical Oxygen Demand	960	36		75
Permanganate value		2		10
Suspended Solids		5		25
Total Kjeldhal Nitrogen	90			-
Ammonia		2		10
Nitrate		0.5		-
Phosphate		5		1*
Mixed Liquor Suspended Solids		6.77 g/l (6.13 g/l)		
Return Sludge Solids		9.25 g/l		

Results in mg/l except as noted.

* Special Standard
Clear Solution

STILFONTEIN

EFFLUENT ANALYSES

4 July 1983

Constituent	Raw Sewage	Activated Sludge Effluent	Biofilter Effluent	General Standard Limits
Chemical Oxygen Demand	876	57	151	75
Permanganate value				
Suspended Solids	-	16	44	25
Total Kjeldhal Nitrogen	77.2	29.1		-
Ammonia	63.8	28.7	27.6	10
Nitrate	-	0.12	0.54	-
Phosphates (P)	4.64	1.68	-	1*
Mixed Liquor Suspended Solids	4.55 g/l			
Return Sludge Solids	5.82 g/l			

26 OCTOBER, 1982

Chemical Oxygen Demand	720	24	72	75
Permanganate value		4	8	10
Suspended Solids		20	70	25
Total Kjeldhal Nitrogen	76	-	23	-
Ammonia		0.1	11	10
Nitrate		0.2	2	-
Phosphate	18	4	-	1*
Mixed Liquor Suspended Solids		4.516 g/l		
Return Sludge Solids		3.046 g/l		

Results in mg/l except as noted.

STILFONTEIN

EFFLUENT ANALYSES

10 August 83

Constituent	Raw Sewage	Activated Sludge Effluent	Biofilter Effluent	General Standard Limits
Chemical Oxygen Demand	904	124.5	173	75
Permanganate value				
Suspended Solids	-	72.4	76	25
Total Kjeldhal Nitrogen	67.2	57.2	-	-
Ammonia	61.5	53.3	36.9	10
Nitrate	0.22	0.22	0.8	-
Phosphates (P)	8.6	5.8	-	1*
Mixed Liquor Suspended Solids		5680		
Return Sludge Solids		6533		

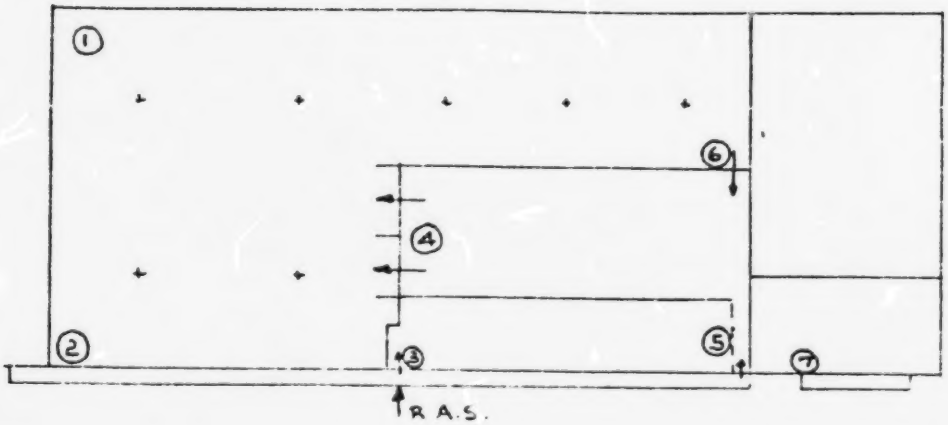
Results in mg/l except as noted.

* Special Standard

MUNICIPALITY OF STILFONTEIN

SEWAGE PURIFICATION WORKS

DISSOLVED OXYGEN MEASUREMENTS



Date	10.9.82	10.9.82	13.9.82
Time	15h30	17h00	-
Point No.			
1	3.3	2.8	1.5
2	3.4	1.5	1.5
3	3.0	0.6	0.9
4	2.7	0.3	0.3
5	2.5	0.5	-
6	2.0	0.5	0.8
7	-	1.5	2.5

Limit Switches

Upper	0	0.05
Lower	0.05	0.10

Note: Decrease in dissolved oxygen within a space of 1 1/2 hours.

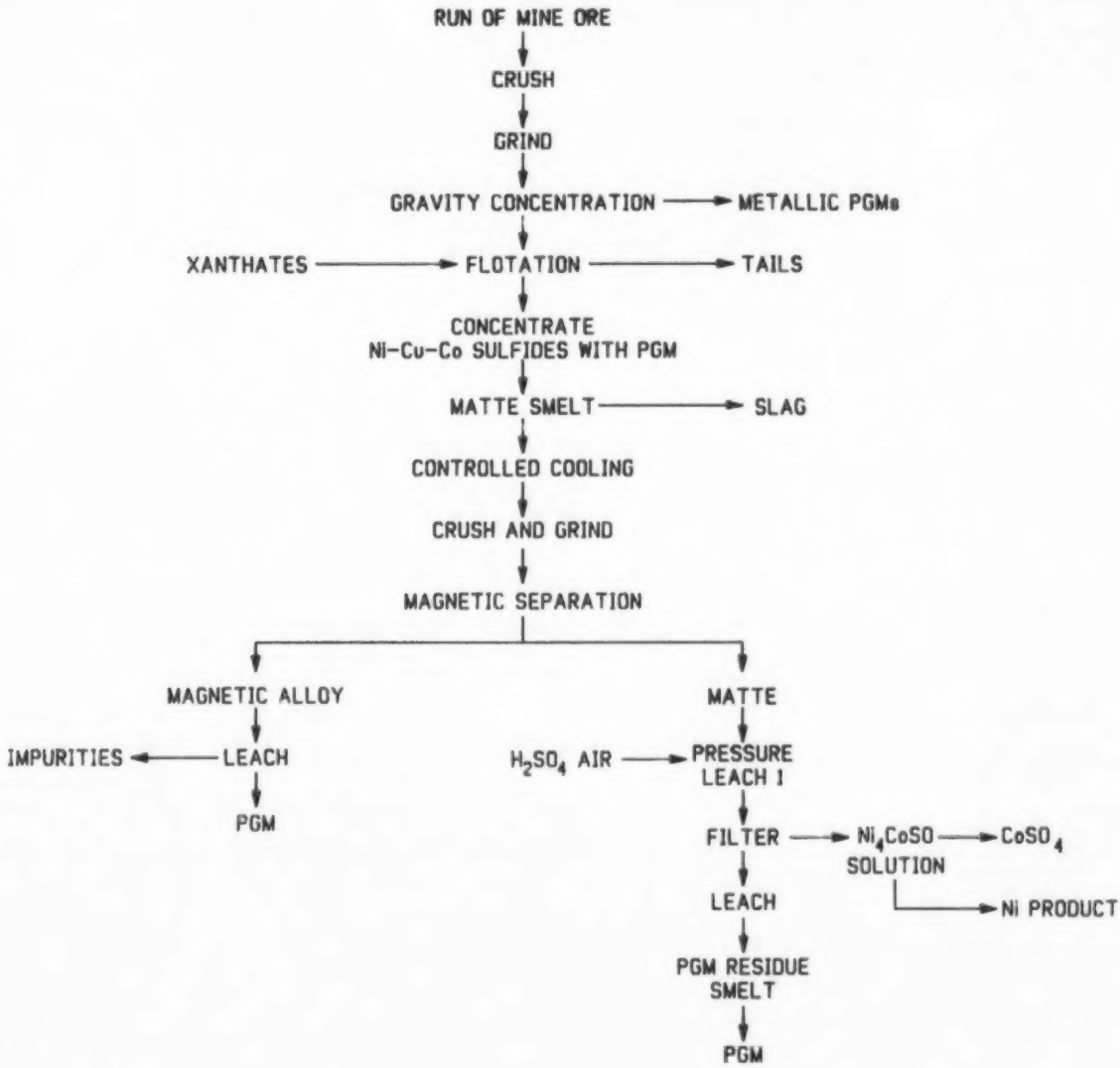
OPERATION	RUSTENBURG REFINERS PTY LTD. P. O. BOX 483 RUSTENBURG 0300 SOUTH AFRICA	
TELEPHONE	(01421) 91141	
CONTACTS	Bruce I. Dewar	Site Manager
	Douglas Haines	Technical Development Manager
MINE	RUSTENBURG PLATINUM MINES LTD. P. O. Rustenburg 0300	
TELEPHONE	(01421) 91011	
CONTACTS	Kennedy M. Maxwell	Managing Director
	Rupert Calcott	Manager of Metallurgy
	Bruce Sutherland	Consulting Engineer
	Ossie Trubie	Flotation Metallurgist
GROUP	JOHANNESBURG CONSOLIDATED INVESTMENT CO. LTD. P. O. Box 231 Johannesburg 2000	
TELEPHONE	(011) 836-2571	
CONTACTS	J. David Parker	Consulting Engineer (Metallurgical)
	John Humphriss	
DATE OF VISIT	February 1984	

INTRODUCTION

During the severe drought conditions of 1982-4 in the Transvaal it became urgently necessary to reduce water consumption by the mines and metallurgical complex. This resulted in the need to recycle more water. Increased water recycling combined with a general deterioration of water quality led to a buildup of TDS which had an impact on metallurgical recovery, corrosion, etc.

Rustenburg Platinum Mines and Rustenburg Refiners undertook an extensive program over an 18 month period to overcome water related problems. At the time of the RANDOL visit, a comprehensive and innovative systems approach was being implemented, from

BASIC PLATINUM TREATMENT PROCESS



which much can be learned. The Rustenburg water management program is an example of the steps that must be taken when drought affects an area. The Rustenburg water management plan is one of the most advanced, if not the most advanced encountered in South Africa for a mining operation.

Platinum mining and recovery processes are considered proprietory and company confidential and this investigation therefore deliberately ignores process details. This was a regretable necessity since in order to fully appreciate the systems approach adopted at Rustenburg, and to see how a change of water quality at one end of the process has an impact at another end of the plant, it would be helpful to have a somewhat detailed understanding of the various processing steps. Nonetheless, even without getting into process details it is possible to gain picture of some of the principles of an advanced water management program.

The focus of this report is therefore on the water management and treatment aspects as they might be applied to almost any hydrometallurgical operation and mine-mill complex.

RANDOL did not ask questions as to how platinum is extracted or refined. A general knowledge rough idea of the process is provided below, but it may be completely incorrect and misleading. It only provides a hypothetical framework within which to discuss water management and treatment steps.

Information released by Rustenburg Refiners Ltd. has had to be rather general.

Items of particular interest at Rustenburg Refiners Ltd. and Rustenburg Platinum Mines Ltd. are:

- Overall salt balance control in recirculated water system.
- Treatment of minewater with 5000 ppm TDS to make a usable domestic potable water
- Affect of water quality on flotation recovery.
- Pretreatment of "fresh" feedwater to reduce the amount of chloride buildup in the plant due to recycling.
- Segregation of high chloride effluents so that only a relatively small volume of water requires desalination, not the complete water inventory.
- Use of R. O. installed to recover water from boiler blowdown and demineralization ion exchange concentrates etc. Operating problems experienced in the use of R. O. for this purpose.
- Proposed use of seeded slurry evaporation to recover water from concentrated effluents.
- Effects of high TDS buildup in minewater on flotation recovery.

BASIC METALLURGICAL TREATMENT PROCESS

Ore is crushed and ground and a concentrate containing all the metal values recovered by flotation, after recovery of any PGM metallics by gravity concentration.

The concentrate is matte smelted. The matte is cooled, then crushed and separated magnetically to yield most of the PGM values in a magnetic alloy. The non magnetic fraction contains Ni, Co and Cu values which are leached sequentially followed by smelting of the leach residue.

In reality the process is very much more complex than this involving pressure leaching in autoclaves and ion exchange separation of cobalt from nickel sulfates. From a water management standpoint it is adequate to know that the process involves a combination of pyrometallurgical and advanced hydrometallurgical leaching and precipitation steps.

Rustenburg Platinum Mines and Rustenburg Refiners' metallurgical facilities are spread over several operating units. There are several separate mining operations some of which have associated milling and flotation plants. Concentrate is shipped by rail to the central matte smelter.

There are two "wet" metallurgical plants that treat the matte smelter products. One of these treats the magnetic PGM concentrate recovered from the crushed matte, the second is a base metal treatment plant that makes Ni, Cu, Co and Na_2SO_4 byproducts from the non magnetic fraction of the ground matte, yielding some incremental PGM values.

Both metallurgical plants treating the matte use fresh water. The new base metal recovery plant which is primarily a nickel refinery was commissioned in 1982 and consumes an order of magnitude more water than the platinum recovery plant.

MAIN AIMS OF WATER MANAGEMENT/TREATMENT PROGRAM

1. To reduce net water intakes
2. To overcome corrosion problems associated with rising chloride levels in feedwater from RWB
3. To achieve zero discharge status by treating effluents and recovering usable water

ZERO DISCHARGE

Rustenburg Refiners is now operated as a zero discharge site. All available water is recovered for recycling. The site has a net evaporation climate.

Rather than build larger evaporation ponds, the water balance has been closed by installing R. O. and by using mechanical evaporation capacity which helps by removing dissolved salts from the system and returning usable water.

WATER SOURCES

The Rand Water Board supplies water to Rustenburg Platinum Mines and Rustenburg Refiners. This water, however, is not the sole source. There is some water from sources other than that used on the Witwatersrand, i.e., from the Boskop Dam, Hartebeespoortdam, Vaalkop Dam and some underground springs.

Rainfall at the Rustenburg site has averaged 627 mm for the last 25 years, and occurs mainly during November to January. Three lined ponds with about 12,000 m^3 capacity contain collected rainwater runoff. This water is returned to the process water system.

Other major sources of water to the mines and mills include underground minewater and treated municipal sewage effluents.

Rand Water Board water was priced at R0.182/m^3 as delivered to Rustenburg Platinum Mines. Normally RWB from the Vaaldam is delivered to Rustenburg Refiners however, during the drought emergency water from another dam - the Bospoort Dam - was being blended into the supply. Bospoort water had a higher TDS and chloride level. The plant requested that only RWB water be delivered, however no sooner had this been achieved than the quality of RWB water deteriorated to 70 ppm Cl^-. There had been an improvement to 30 ppm Cl^- in the RWB water at the time of the Randol visit in February 1984. Bospoort water blended with RWB feedwater had resulted in 150-200 ppm Cl^- in water supplied to the metallurgical plant.

WATER REQUIREMENTS

1. Flotation Plants

   Water for flotation plants is obtained from local sources notably wellwater and underground minewater.

2. Mineworker Hostels require about 2000 m^3/d of potable water.

3. Metallurgical Process Water

PGM Plant	50 - 60	m^3/d
Base Metal Plant	5 - 600	m^3/d
Steam Condensate	150 - 200	m^3/d
Demineralized Water	100	m^3/d
TOTAL	900	m^3/d

The metallurgical process water needs were formerly supplied by Rand Water Board, but is now drawn from the process water recycling loop.

Water Losses

There are three main water losses from the metallurgical processes:

- Evaporation from the base metal plant processing 450 m^3/d
- Balance to Na_2SO_4 crystallization plant also lost by evaporation 250 m^3/d
- Utility area wastewaters 200 m^3/d

About 50% of the evaporated water from the Na_2SO_4 crystallization plant is recovered and returned to the process water system as a very good quality low TDS water at 20-30 uS/cm.

MATERIALS OF CONSTRUCTION

The new base metal plant equipment is constructed mainly from 316L stainless steel.

The new evaporation desalination plant will have titanium tubes and stainless steel 316L sumps.

WATER BALANCE

A key part of the success of Rustenburg Refiners water management program has been their ability to precisely define the water balance for the complex metallurgical facility as a whole, and for each unit operation, without which it would be impossible to design or implement a plan.

The water balance for December 1983 with average figures for the previous six months is shown in the figure as an example of what such a balance looks like. Note the relatively large percentage of process water that is used for utilities.

WASTE STREAMS

1. Utilities water effluents
2. Rainwater runoff from base metal plant site
3. Rainwater runoff from Na_2SO_4 crystallizer site
4. Accumulated effluents in evaporation dams

A processing scheme has been devised to segregate the various waste streams for treatment and recycling of recovered water.

WATER QUALITY EFFECTS

1. Especially during the dry season water available to the flotation plants increases in hardness as Calcium and magnesium levels increase. There have been several studies to examine the effects of this hardness on flotation recovery. Some indicate a decrease in recovery of 0.5-1.0% or so but other tests were unable to confirm this. No data was obtained.

2. Some years ago the sodium sulfate crystallizer plant was owned and operated by an independent contractor prior to the recent acquisition of the plant by Rustenburg Refiners. There has been some mention of Na_2SO_4 in water seeping into the underground workings and interacting with pyroxenite rocks to result in high Mg concentrations in minewater which, it is said, had a negative impact on flotation recovery. This phenomenon was not confirmed, but it was clearly stated that current practice avoids any possibility of Na_2SO_4 in seepage losses.

3. The new base metal recovery plant is constructed from 316L stainless steel. Increased chloride levels in the RWB water used in the plant are reflected in a generally higher concentration of chloride in the process due to in-plant evaporation. New water enters in the copper leach circuit and exits at the nickel circuit during which there is a 200% increase in the salt load. Hence 70 ppm chloride becomes 140 ppm chloride in the nickel circuit if RWB water is used, and more if Bospoort water is used.

   Pitting corrosion was observed in the pressurized leaching equipment and a couple of vessels had to be replaced.

   For this reason it is very important that high chloride levels in feedwater to the plant be avoided. An area of major concern is the future quality of incoming water, particularly with respect to chloride content.

WATER TREATMENT AND RECOVERY PROCESSES AND EFFECTS

1. Sodium Sulphate Crystallizer

   Concentrate leach solutions after recovery of base metals Ni, Cu, Co are acidic and contain high levels of sulfuric acid, which is neutralized by NaOH and then evaporated to remove Na_2SO_4 as a dry product.

   Some 50% of the evaporated water from Na_2SO_4 crystallization is recovered and returned to the process water system. This water is usually of excellent quality with a conductivity of 20-30 uS/cm.

There are occasional deviations but no precautionary measures are taken except for an alarm system which sounds whenever conductivity exceeds 100 uS/cm at which point the flow is automatically diverted.

Until recently the condensate conductivity was much higher due to sulphate content which was solved through repair to the evaporators.

The Na_2SO_4 crystallizer plant has adequate capacity to handle the total flow of solution from the base metal plant which was operating below capacity.

The excess evaporator capacity was being used on a short term basis to treat effluent water that had accumulated in a pond for several years. This water was treated by a lime/soda softening plant ahead of evaporation.

The Na_2SO_4 crystallizer plant was being used to treat the following solutions to yield dry solid salts and water which is returned to the process water circuit:

- Na_2SO_4 solution from base metal plant
- Runoff from the Na_2SO_4 plantsite
- Water recovery from the waste effluent ponds after lime/soda treatment and filtration

Prior to the Na_2SO_4 crystallizer operation being acquired by Rustenburg Refinery, the condensate was lost. Now it is recycled as process water.

The Na_2SO_4 crystallizer plant consists of a 3-stage multi-effect evaporator followed by a centrifuge and air drier to produce a dry solids product.

2. Utility Water Effluent Treatment

Effluents are derived from the utility water system which yield the following effluents:

Water softening IX regeneration liquors	40 m^3/d
Demineralizer regeneration liquors	30 m^3/d
Cooling tower blowdown	20 m^3/d
Boiler blowdown	35 m^3/d
Boiler ash conveying water	10 m^3/d
Total at current production	135 m^3/d

The above effluents had been accumulating in lined evaporation ponds which at the average 760 mm/year net evaporation rate were able to lose an average of 110 m^3 water/day.

The short term answer has been to use temporary Na_2SO_4 crystallizer capacity to evaporate the accumulated excess effluents. The medium term objective is to install evaporator capacity to treat all effluents when the base metal plant is running at full capacity and the Na_2SO_4 crystallizer capacity is needed for that stream.

Resource Conservation International, a South African subsidairy of Resources Conservation Company was consulted to design a short term and a long term plan to conserve water and to avoid any effluents, on the basis of which it has been decided to install an evaporator plant to treat all wastewater arisings.

The old base metal recovery plant used to generate a gypsum effluent which sometimes contained base metal values. This has been avoided in the new base metal plant.

EFFLUENT DAM COMPOSITION

The liquor contains 12,000 ppm Na_2SO_4 with $CaSO_4$ at 95% of saturation. TDS is about 17,000 ppm and Ca concentration is about 600 ppm. The effluent pond water also contains 300 ppm Ni and some Mg.

The effluent dams were lined with Gundle Plastic about ten years ago. The dams are to be emptied and the plastic may be replaced. Activated bentonite will also be considered a replacement lining.

EFFLUENT POND: PROPOSED PROCESS

It had been proposed to treat the effluent pondwater by adding 120% of the stoichiometric dose of lime and soda ash in sequence in separate tanks with 1½ hours residence time each to achieve a lime-soda softening followed by clarification to settle out precipitated $Ni(OH)_2$, $Mg(OH)_2$ and $Ca(OH)_2$.

In the process pH would be adjusted from incoming feed at pH 7.5-8.5 to pH 10.5 by lime addition followed by soda ash addition to pH 11-11.5.

The thickener underflow would be dewatered by rotary drum filter with the filtrate and clarifier overflow advancing to the Na_2SO_4 crystallizer.

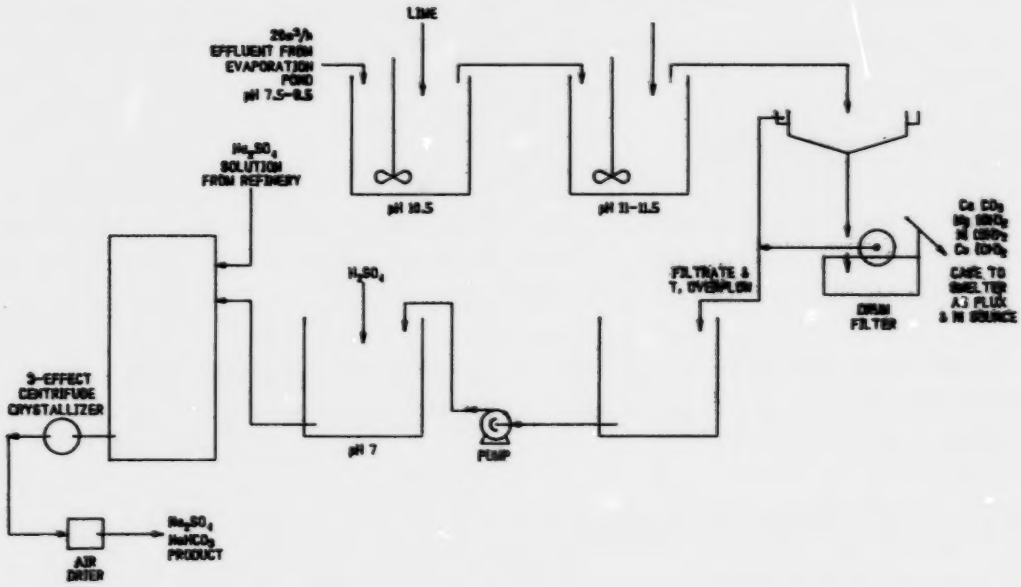
The above lime-soda softening would drop calcium to less than 5 ppm and nickel to less than 3 ppm when working well.

The conversion of the old base metal treatment plant to the above use was achieved to handle 20 m^3/h maximum throughput with clarification to less than 50 ppm S/S.

Through the use of lime for precipitation the settled solids are much denser than if NaOH were to be used, although NaOH is found in tests to give a clearer overflow but a slower settling sludge.

The total cost of this treatment process worked out to R1.50/m^3 with a credit for the nickel values in the precipitate making it possible to recover some of this cost.

EFFLUENT TREATMENT PLANT



Conclusions

1) Lime-Soda softening as a means of reclaiming process water is far from inexpensive.

2) Once the base metal refinery is back in full production the Na_2SO_4 crystallizer capacity will be needed for plant effluent and no extra capacity will be available for effluent treatment.

3) In the base metal plant chloride is converted to chlorine in the electrolyte tankhouse which results in a drop in chloride level in the electrolyte and about 5 ppm Cl_2 in the gas above the cells which is vented using forced air circulation to disperse the Cl_2.

This bleed of Cl^- from the system prevents NaCl from building up in the Na_2SO_4 crystallizer circuit.

4. Desalination R. O. - Utility Effluents

A reverse osmosis plant has been installed to treat some of the effluent water streams instead of pumping them to the effluent pond. A relatively small R. O. unit using spiralwound membrane modules was supplied and installed by:

Cass Africa (Pty) Ltd.
P. O. Box 51051
Randburg 2125

Telephone: (011) 789-2908
Contacts: Tom deLange

Only those effluents which are compatible with R. O. are being treated:

1) Boiler blowdown
2) Cooling tower blowdown
3) Low salinity (less than 4000 uS/cm) end of the demin plant regeneration selected by a conductivity meter activated valve.

In February 1984 the R. O. installation was being commissioned in this application - not without startup problems due to potential fouling of the membrane. More information may be available by now on the ultimate performance of the R. O. plant for treatment of utility wastes from Rustenburg Refiners or from Cass Africa.

Description of R. O. Plant

A combination of the effluent streams listed above is mixed in a 63m^3 sump located near the utilities section of the plant.

Step 1 These solutions at pH 9 are recirculated constantly to provide good mixing.

Step 2 The mixed feedwater is next settled in a 140 m^3 settling dam to cool the blowdown effluent to below 35° C which is the maximum tolerable by the R. O. membrane. Cooled effluent next passes via a 4 m^3 tank at pH 8.5.

Step 3 Next is pretreatment of R. O. feed including acidification to pH 5.6. If alum is used for coagulation then the pH must be below pH 6.5. Purpose of acidification is to convert carbonate to bicarbonate to avoid scale fouling of the membrane.

Step 4 Dechlorination by 5 ppm Na_2SO_3 addition.

Step 5 Coagulation. Alum has been tested as a coagulant and found to work. Because of dispersants in the cooling tower a dose of 100 ppm alum is needed. RANDOL suggested the use of activated bentonite and an anionic polyelectrolyte at B and organopol at C.

Step 6 Sand filtration to yield a filtrate with zero measurable suspended solids or less than 1 ntu.

Step 7 Addition of 4 ppm Flocon 100 scale inhibitor supplies by Pfizor Chemicals.

Step 8 Cartridge Filtration using a polypropylene 5 micron filterite cartridge supplied by Chemilite.

Step 8 Feed to R. O. modules via Tonkflo 27 stage centrifugal pumps supplied by Tonkflo Corp., Minneapolis, Minnesota.

Step 8 R. O. System consisting of two systems each using 3 modules. Each stream is capable of 70 m^3/d. UOP 4600 pA modules were installed in February. These were thin film polyamide composite membranes which are chlorine sensitive.

R. O. Feedwater Quality:

TDS	1,500 ppm
Ca	75 ppm
Cl^-	200 ppm

R. O. Performance

80% Recovery of water was possible in theory from this feedwater before gypsum scaling would occur, allowing a safety margin.

Conclusions:

1. The number of pretreatment steps to be attended to in treating water of this kind by R. O. makes the overall system complicated.
2. Recovery even from relatively low TDS water with low calcium is only 80%.
3. Even with the pretreatment steps, problems were experienced in removing foulants ahead of R. O.
4. This application appears to be suitable for seeded slurry reverse osmosis.

5. Desalination R. O. Feedwater

Because one of the problems experienced as a result of water recycling and deteriorating feedwater quality has been chloride corrosion, Rustenburg Refiners was considering the installation of a R. O. plant to treat feedwater as an alternative to the brine concentrator. No details were available and at the time of the RANDOL visit, no order had yet been placed for such an R. O. plant.

6. Demineralization

Rustenburg Refiners produce about 340 m^3/d demineralized water using ion exchange. This plant yields about 20-40 m^3/d of regen solution. One of the purposes of the new small R. O. plant mentioned above was to remove the contained salts.

7. Brine Concentrator

Rustenburg Refiners had set the objective of emptying the existing effluent dams and then to treat collected runoff water.

Tenders had been called for an evaporation plant of 240 m^3/d capacity.

The proposed process was to adjust pH to 6.0 to control corrosion and to keep all carbonate in the non-scaling bicarbonate form.

The brine evaporator was to be constructed with titanium HE tubes. The sump was to be stainless 316L.

The effluent dam contains about 40 ppm SiO_2 and almost saturated $CaSO_4$. The limiting factor on concentration was Na_2SO_4 crystallization in the concentrate. It was proposed to use a seeded slurry process such as that installed at several plants in the USA by:

Resource Conservation Company
3101 NE Northrup Way
Bellevue, WA 98004

Telephone: (206) 828-2400
Telex: 350-160
Contact: Russel Vandenberg

Resource Conservation Company International
P. O. Box 47041
Parklands 2121
South Africa

Telephone: (011) 788-5070

Evaporation desalination plants and equipment are discussed in a separate chapter of this report. Although Resources Conservation Company International have installed more of seeded slurry evaporators than anyone else, their tender for this installation was significantly more expensive than the other tenderers of falling film, vertical tube vapor compression evaporators. Six companies tendered evaporators for this job including more than one offering seeded slurry evaporation.

The Rustenburg seeded slurry evaporator will have a recovery of 95% at less than 10 ppm TDS.

Capital cost order of magnitude for this installation works out at R4000 per m^3/d capacity or around R1 million for a 250 m^3/d plant. One of the suppliers offered a plant for R1.8 million which indicates the wide range in cost of these plants. Several suppliers of evaporator desalination plants are listed in the chapter on the subject. This plant had been commissioned by the end of 1984.

8. Potable Water

Rustenburg Platinum Mines has set a target of becoming self sufficient in potable water for the semi-skilled labor hostels at the mine. Water available from underground includes two mine service water sources with 5000 ppm TDS and 93% $CaSO_4$ saturation i.e., around 2000 ppm.

The process selected to make this water potable is as follows:

Lime/Soda softening

↓

Clarification

↓

Chlorination

↓

Sand filtration

(Conventional downflow)

↓

OPERATION	PREMIER MINE DIVISION DEBEERS CONSOLIDATED MINES LTD. P. O. BOX 44 CULLINAN PRETORIA 1000 SOUTH AFRICA
TELEPHONE	(012132) 17
CONTACT	Robin Sutter Metallurgical Superintendent
GROUP CONSULTANTS	Diamond Service Division Anglo American Corporation of South Africa Ltd. 45 Main Street Johannesburg 2000
TELEPHONE	(011) 638-9111
CONTACT	Johan F. Slabbert Consulting Metallurgist, Diamonds East

INTRODUCTION

Diamond recovery technology details are proprietory so only the most general information was released by Debeers. Diamonds are often found in areas where water is in short supply so water recovery and management is an important aspect of the feasibility of several projects.

Diamond recovery is by physical processes. The ore is relatively coarsely crushed and screened to liberate diamonds up to ¼ inch in size so it would be expected at first that water recovery would be an easy task, but it is not. The problem is that Kimberlite ores contain a large percentage of ultra fine minus 1-micron ultrabasic particles which, similar to phosphate slimes in Florida, simply do not want to settle out.

Points of interest in this trip report include:

1. A statement of the problem. If a low cost answer could be found to water recovery from Kimberlite slimes, this would be of significant interest to diamond mines.

2. There is room for improvement in water management in diamond mines that requires upgraded technology.
   - Reduced flocculant costs
   - Higher density thickener underflow
   - Reduced pumping costs
   - Availability of water

3. A highly innovative but simple use of poor quality decant water to prewash crushed ore has made it possible to reduce flocculant consumption substantially.

KIMBERLITES

There are 39 different types of Kimberlite. Most Kimberlite contains large quantities of a weathered product called Saponite which is a fine clay. The Kimberlite slimes are high in calcium and magnesium. Kimberlite slimes raise the pH of water in which they come into contact to around 9.0-9.5.

COST OF WATER

Water is drawn from a dam below Bronkhorstspruit 40 km to the east. The only cost is for pumping which amounts to around R0.07/m^3. However, the development of a new African Homeland for the Kwa N'debele may result in a competing need for water during the remaining life of the mine, which is about 50 years. Despite a major search no alternate water sources have been found.

OPERATING COSTS

Diamond mines treat large volumes of feed to recover a relatively small volume of product. Treatment costs must be kept low and are said to be much lower than for gold-uranium recovery operations. Debeers claims that their diamond mines are more conscious of water that other mining industries.

The principal operating cost components of a Kimberlite processing plant are:

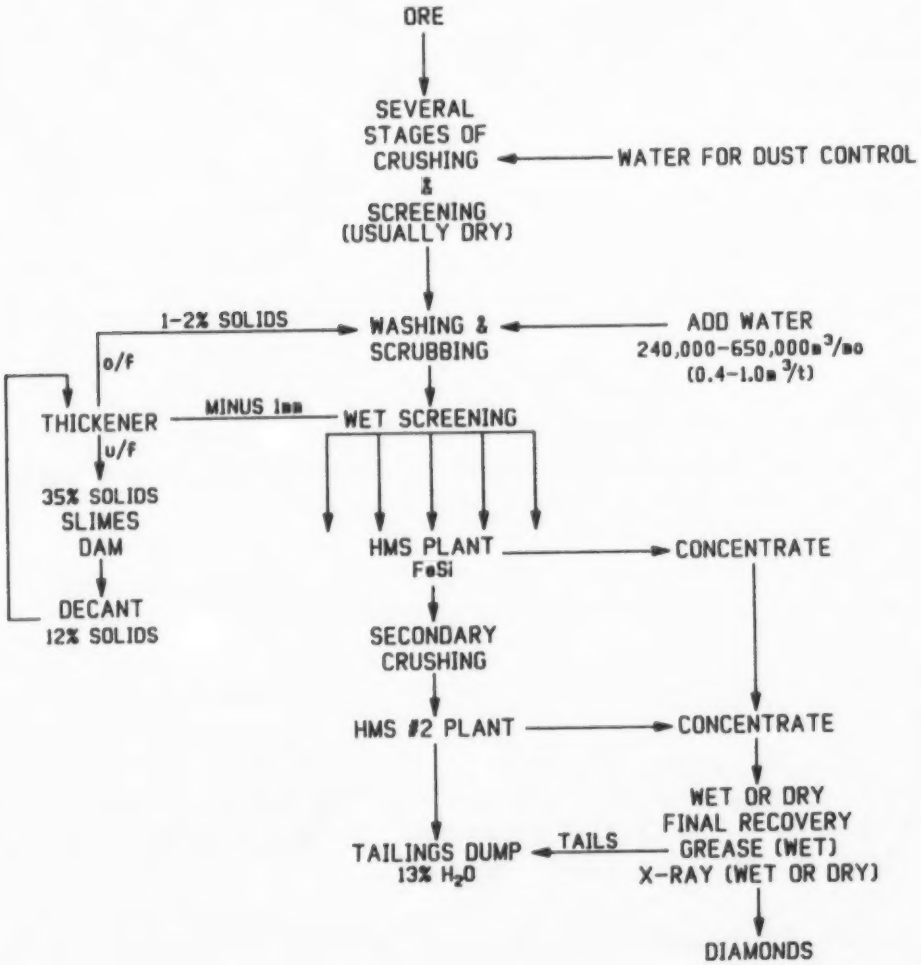
Water	
Power	
Reagents :	Flocculants
	FeSi HMS Media
Labor	

WATER PROBLEM/CHALLENGE

The main problem with water is that it is not generally available in the desired quantities, so it must be reclaimed from the tailings. However, slimes which are abundant in Kimberlites are of such a nature that only about 25% of the water contained in slimes sent to the slimes dams can be reclaimed.

Slimes on thickening historically never gave an overflow with better than 8-9% solids. Through improved flocculant development, Premier Mine now achieves 1-2% solids in the overflow which they "can live with" comfortably.

GENERALISED FLOWSHEET FOR DIAMOND RECOVERY



Attention has been focused acutely on water supply and on conservation of water as a result of the 1982-4 drought. Water resources are subject to reallocation which could deprive some mines of their traditional supply as an emergency measure and in other mining operations there simply is not enough water for a large mine and concentrator to operate without recycling.

GENERALIZED RECOVERY PROCESS

Premier Diamond Mine uses dry crushing which allows improved control of water management. Dust is controlled using a scrubbing system which consumes water to wet down the dust that is collected. Generally gyratory crushers are preferred because they break less diamonds than jaw crushers.

After crushing the ore is washed and scrubbed using 0.4-1.0 m^3 new water per ton ore in addition to the overflow recovered from the thickener at 1-2% suspended solids which is recycled to the scrubber.

At Premier Telsmith scrubbers are installed and a 100' Ø thickener yields 3000 m^3/h overflow water.

After scrubbing the ore is screened to separate it into several size fractions. The minus 1 mm fraction is sent to the thickener. Underflow at 35% solids is pumped to a slimes dam and overflow is returned to the scrubber with 1-2% moisture.

The scrubbed, screened and sized ore is next concentrated by Heavy Media Separation HMS using ferrosilicon. The density of diamonds is 3.5 compared with the gangue at 2.7.

Finally the HM plant concentrate is further concentrated across grease belts or by X-ray fluorescence ore sorters.

At Premier Diamond Mine the main plant has two 100' Ø thickeners for slimes water reclamation. However, a second plant is installed for secondary recovery of diamonds from older tailings which also employs two 100' Ø thickeners.

The thickener underflow is pumped to the slimes dam at 35% solids and decant solution with about 12% solids is used to dilute the thickener underflow to reduce their viscosity for pumping to the dam. Some of the 12% solids decant water is used for a prewash scrubbing step. The slimes dam is located 4 Km downhill from the plant and flow must be kept at 3m/s downhill to prevent coarse solids from settling and 2m/s for the uphill flow.

The slimes dam at Premier is 300 hectares in size and is covered by water running 12% solids. The site has very high humidity and is hot. If a mine manages to reclaim 40% of the water sent to the slimes dam it is doing very well indeed - or it may be putting too much water in the slimes dam in the first place.

WATER CONSERVATION IDEAS

- Since 25% of the ore ends up as slimes which are responsible for a major part of the water loss from the plant, one way to reduce water consumption is to reduce the amount of slimes.

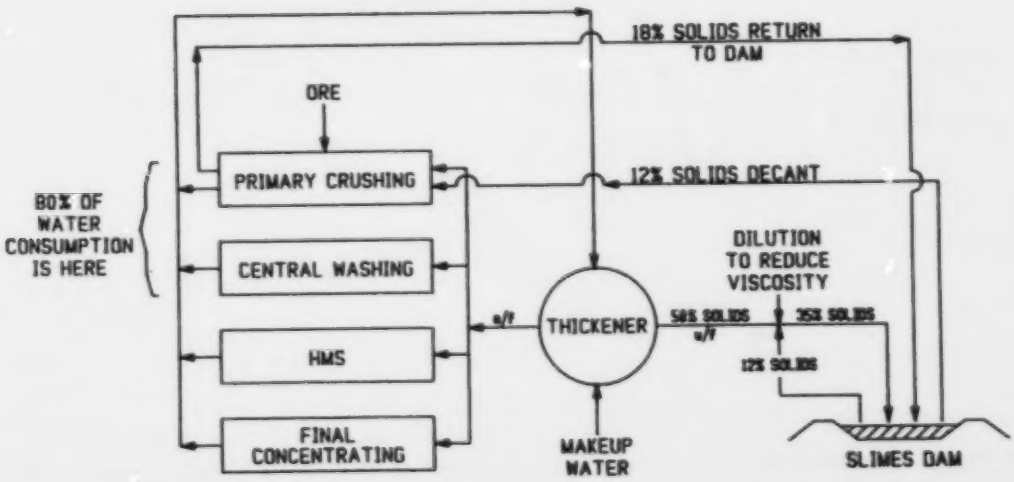
- For planning purposes the net water requirements are equal to the weight of slimes generated.

- Hence less water will be required if it is possible either to reclaim more water from the slimes dam or if a way can be found to generate less slimes in the first place.

A SYSTEMS APPROACH

1. Examining a schematic for a hypothetical diamond recovery plant treating 10,000 tpd ore, the water flow will be as shown in the diagram below

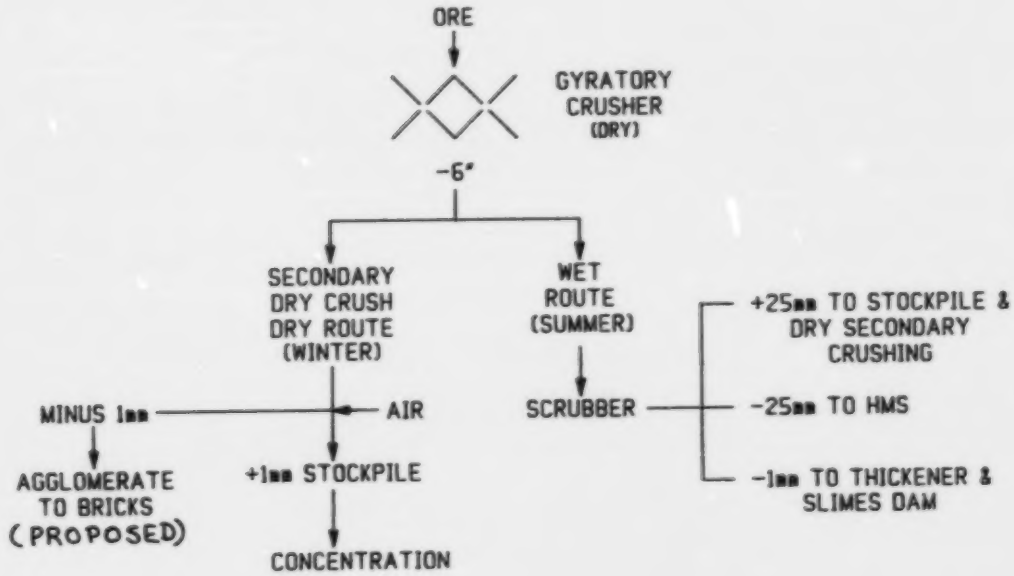
GENERALISED WATER FLOW CHART



2. Selection of Dry/Wet crushing

ROM ore is tipped directly into a large gyratory crusher and reduced to minus 6". Primary crushed ore on a large conical stockpile with 3 draw points works well during 8 dry months, except for lots of dust. However, during the 4 wet months ore hangs up in the stockpile. Most diamond plants are designed for the worst conditions, i.e., the wet months, and operated that way yearround.

If water supply really becomes critical, then a dual process has been proposed which would operate dry during the dry months and wet during the rainy months.



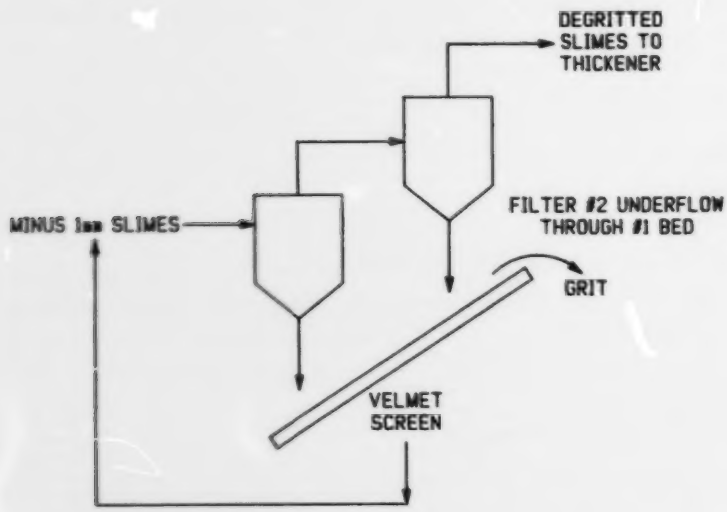
In using the above scheme, as much as possible of the minus 1 mm particles would be separated dry for disposal by a water efficient agglomeration process. Only when the secondary crushers clog in the wet months would the system be switched over to a wet crushing step.

The underlying principle of the proposed system is to avoid using water at all in the diamond recovery process except when it cannot be avoided. Whereas in the past

diamond recovery plants have been designed for the worst case, in the new concept they would be designed for flexibility with the objective of using the minimum amount of water.

If the amount of wet slimes sent to the slimes pond were to be correspondingly reduced, then more expensive water recovery processes could be afforded.

3. Special dewatering screens could be employed to recover more water from the slimes fraction by removing grit and reducing the volume of material sent to the thickeners.



By removing grit from the "slimes" fraction a smaller pump will be needed e.g., 2 X 4 Warman may replace 6 X 4 Warman as only 30% of the weight of solids will now need to be removed to the thickener. An Austrian Lamella thickener is being tested for its degritting ability which looked promising.

4. Water Treatment in the Thickener

Innovative new flocculants and innovations in the way they are used has cut down flocculant costs from R800,000 in 1980 (would be R1.00 million in 1983 due to

inflation) to R200,000 actual 1983 budget. Flocculant purchases dropped form 289 tpa at their peak to 30 tpa.

This has been achieved by:

i) Prewashing the crushed ore with the worst quality water and sending it back to the dam without the use of the thickener.
ii) Appropriate flocculant selection. 5 years ago an Allied Colloids product was used, however today an improved flocculant has been found generally by using empirical test.
iii) Operators feel that a thorough study of the fundamental physics of high pH slimes from Kimberlites will lead to further improvements in flocculant selection, cost and performance.

ENVIRONMENTAL IMPACT

Dam Seepage

A seepage collection ditch is installed below the toe of the dam. The dam wall is provided with survey beacons and piezometers to detect any changes which could warn of danger in advance.

Tailings Dump Runoff

The runoff from the tailings appears to be clear but has a pH 9. It is collected and pumped back to the plant. About 960 m^3/year of water is collected from runoff from the 200 million tons of tailings.

Tailings Stabilization

It has been found to be possible to establish vegetation on the dump. "Star grass" which propagates by rizomes grows well and is suitable as cattle feed.

Several very effective flocculants have been tested in various parts of the world. For example polyethylene dioxide has worked on phosphate slimes but the required dosage is too expensive to be considered for Kimberlites so it has probably not been tested.

One observation of interest was made, is that addition of a small quantity of epsom salts together with the existing flocculant gives an immediate reaction and helps to settle the slimes. This was being examined to evaluate its potential economic usefulness.

Another way to enhance the settling of Kimberlite slimes is by adjusting the pH to 7 but this costs too much.

FLOCCULANT SELECTION

PREMIER

The fine particles of montmorillonite in Kimberlite with a high positive charge makes them difficult to settle.

Fresh and weathered Kimberlite circuits require different flocculants.

It has been found that there is a big difference in the zeta potential between fresh and aged "superfines" from Kimberlite.

An anionic flocculant made by Allied Colloids No. 156 & PDM3 is used. A Cyanamid flocculant A150 has also proven satisfactory. There are two flocculant addition points in the feed launder.

A typical dosage of Allied Colloids PDM3 and 156 mixed in a ratio of 3:1 is 5 ppm total. A typical overflow solids content of around 48 is achieved with these flocculants at the main plant.

Cyanamid A150 is used in the retreatment plant where aged Kimberlite is treated.

Flocculants in use at Premier Diamond Mine are supplied by:

Allied Colloids Pty Ltd.
Box 48775
Roosevelt Park 2129

Telephone: (011) 782-5335
Contact: Rob J. Daly

S. A. Cyanamid (Pty) Ltd.
P. O. Box 7552
Johannesburg 2000

Telephone: (011) 538830
Contact: M. J. Reynders
J. Davies
Peter Lambert

CONCLUSIONS

1. It is generally concluded that diamond recovery operations from Kimberlites are in the early stages of learning how to use less water in their operations.

2. Because water has been inexpensive and available in the past there has been no major incentive to invest in water saving equipment or to use expensive reagents to help recover more water.

3. It is concluded that by investing more capital in a more flexible plant which can employ dry diamond concentrating processes during the dry months, and a wet plant during the rainy season, the amount of water can be dramatically reduced. However, water will have to be extremely expensive to justify the capital needed for such a plant.

OPERATION DELTA MANGANESE (PTY) LTD.
P. O. BOX 323
NELSPRUIT

TELEPHONE (01311) 25171

CONTACTS Anthony Dalrymple Technical Director
Lester Sherman Development Manager

INTRODUCTION

Delta Manganese treats Samancor manganese ore fines from Hotazel, Cape Province to produce up to 60 tpd electrolytic manganese flakes and powders. The process outlined below uses a calcine roast followed by sulfuric acid leaching to dissolve the ore, and then several stages of chemical precipitation to remove contaminant metals as hydroxides and sulfides, before electrowinning manganese metal from the purified solution.

In this process 712 m^3/d of effluents are generated of which 405 m^3/d is discharged directly to the river or municipal sewer while the remaining 307 m^3/d is pumped to an industrial water dam, the overflow from which is discharged to the river.

In addition, heavy metal impurities are precipitated and dumped in various dongas in the area as landfill.

Delta Manganese is an interesting example of a metallurgical operation where little or no concern for the environmental impact of their effluents was required in the past. Since South Africa is becoming increasingly conscious of water quality protection and the environment it is clear that steps will have to be taken in future to recover water for reuse at Delta Manganese and to find better ways of disposing of both liquid and solid residues.

LOCATION Nelspruit in the eastern Transvaal not far from the Mozambique border.

ORE Hotazel Manganese Ore fines from Samancor
13 mm x 0 in size

Mn_2O_3	45%	
Ca	4% max	
Fe(total)	11% typical	14% max

PLANT CAPACITY 60 t/d Manganese flake product

PROCESS

The ore is milled and dried (using hot offgases from the calcines) to minus 80 mesh.

Milled ore is calcined for 1 to 1½ hours at 750°C (max) (1000°C external temp) in tube calciners which are screw fed and fitted with spiral flights which provide 6" dams in the tube.

The calcines are electrically heated but fuel oil is added to the charge which breaks down into methane, CO and H_2 and reduces Mn_2O_3 to MnO. The tubes are fabricated from ALS 253MA stainless steel which is high in chrome and nickel. Fe^{2+} is measured in the kiln discharge. By the time all the iron is in the ferrous state, the manganese has also all been reduced to MnO.

After the reduction roast, the ore is leached at pH 6.2 and 120 g/l $(NH_4)_2SO_4$ in recycled spent electrolyte from the cellhouse. This dissolves the 11% Fe content.

The leach pulp is aerated and the pH raised to 6.8 which converts Fe^{2+} to Fe^{3+} and precipitates the iron. This is followed by addition of alum (to control silica) and a flocculant Magnafloc 351, and the slurry is then pumped to a thickener. Thickener underflow containing ferric hydroxide, silica and any undissolved ore is filtered on belt filters.

The filtrate is recycled to the thickener, and thickener overflow is next treated with $(NH_4)_2S$ to precipitate heavy metal sulfides including Ni, Co, Zn and some MnS.

The solution with precipitated metals is settled in a thickener. The sulfide underflow is pumped to a reactor where sulfuric acid is added which converts any manganese sulfide in the precipitate to H_2S and $MnSO_4$. The H_2S is reacted with ammonia to regenerate $(NH_4)_2S$ for use in the metal precipitation step. The residue after H_2SO_4 treatment of the sulfide precipitate is dried in a filter press and discarded with the belt filter cake in the municipal landfill and in dongas.

The thickener overflow solution is clarified by filtration employing two Funde disc filters and three Stellar Filters. It is essential to remove solids from the electrolyte. The solution is next dosed with SO_2 to modify the manganese from β to α crystals before being pumped to the cellhouse where manganese metal is electrolytically recovered on stainless steel cathodes by the following reaction:

$$MnSO_4 + 2e = Mn^{\circ} + SO_4^{=}$$
$$2H_2O = O_2 + 4H^+ + 4e$$

The electrolyte enters the cathode at 33g Mn/l and exits at 11 g Mn/l.
150 m^3/h of electrolyte is recycled back to the electrolyte tank at full manganese production of 3 tph.

The anodes are lead with 1% Ag. Diaphram cells are used because these limit the backmigration of H^+ to the cathode.

The cellhouse requires a 44MVA power source and takes 56kA @ 6.5V for 74 cells.

Manganese is physically knocked from the cathodes which are then taken to a plate treatment area where they are flexed, acid washed and rinsed before being recycled to the cells.

Sodium silicate is added to the electrolyte as a smoothing agent; the solution is made up once a day and the spent solution is purged prior to new solution being made up.

If the cellhouse stops due to a power outage the manganese goes back into solution which costs a minimum of R5000/hour, so a standby generator is installed.

EFFLUENT STREAM COMPOSITION AND DESTINY

Stream		Volume	Destiny	pH	TDS ppm	S/S ppm	Ca^{++} ppm	$SO_4^{=}$ ppm	Mg^{++} ppm	Na^{+} ppm	Mn ppm
1) Cathode Treatment	Na_2SO_4	14 m^3/d	River	9.5		50				1200	
2) Plate Wash	Acid	202 m^3/d	164 m^3/d to sewer 38 m^3/d to river	5.0		50	145	400	110	-	
3) Detergent Solution	detergent	5 m^3/d	Sewer			no data					
4) Metal Wash		88 m^3/d	River and BF wash	8.2		300	150	1140	180		290
5) Belt Filter Cloth Wash		75 m^3/d	Industrial Water Reservoir			100	216	5960	430		1520
6) Cell Frame & Diaphram Wash		144 m^3/d	Industrial Water Reservoir	3.3		350	450	1100	120		300
7) Cooling Tower Blowdown		56 m^3/d	Recycled		1200	140	350	420	240		90
8) Clarifilter Rinse		40 m^3/d	Recycle & River	5.5		no data					
9) Cellhouse Wash		(sporadic 88 m^3/d)	River	6.5		no data					
10) Calciner Cooler		5 m^3/d	Recycle	7.5		100	230	760	180		

GYPSUM SCALING

Most of the solutions in the plant are saturated with gypsum. Every dayshift a gang of 8 laborers plus one foreman work as a pipecleaning gang at a significant cost.

Delta Manganese are wary of using any gypsum scale inhibitors because its effect on the Cellhouse performance cannot be predicted.

ENVIRONMENTAL

The effluents from Delta Manganese are dumped into a small stream on the edge of Nelspruit which flows into the Crocodile River and then to the Komati River which flows through Mozambique to the sea.

Solid wastes are currently dumped at a municipal landfill which will be closed mid-1985 when a new municipal dump is opened 10 k from the townsite. RANDOL expects that sulfide metal precipitates and effluents containing ammonia would be harmful to the environment.

NATURE OF EFFLUENTS

All the effluents are rather similar and contain:

$(NH_4)_2SO_4$
$Ca\ SO_4$
$Mg\ SO_4$
$Mn\ SO_4$
$Co,\ Ni,\ Zn\ (SO_4)$

All effluents run less than 0.1 ppm heavy metals except three streams.

WATER SOURCE

All water used at Delta Manganese originates from the Crocodile River. Potable water is purchased from the municipality after flocculation, settling, clarification and chlorination. Industrial water is purchased after it has been flocculated and settled only.

WATER AND EFFLUENT MANAGEMENT PLAN

Phase I — The first phase of Delta Manganese water recycling plan is to bring all the effluent streams to the industrial water Dam where they will be commingled. About 60% of the present volume can be reused after settling out suspended solids.

Phase II It was planned to cut down on water usage in several possible ways:

1) Counter current plate washing
2) Cross current metal washing

Phase III Plate and metal wash solutions if treated with lime will precipitate all metals except Na, according to Delta tests. It was proposed to treat these streams with lime ahead of the industrial water dam. This stream would then be settled in a high rate thickener with u/f going to the belt filters and o/f going to the industrial water dam.

Of an expected flow of 574 m^3/d into the industrial water dam, Delta expects to use 561 m^3/d which leaves only 13 m^3/d to be bled to the river compared to the present 557 m^3/d discharge.

Phase IV The potential exists to recover manganese from the 574 m^3/d of effluents, and $(NH_4)_2SO_4$. A process scheme has been devised to put manganese back into the process and to concentrate the $(NH_4)_2SO_4$ for use as makeup to replace the ammonia and sulfate lost in the belt filter residue.

Delta was considering a MINTEK ion exchange process for recovering manganese at a low pH. The broadbrush water treatment process concept is as follows:

WATER TREATMENT CONCEPT

1. Reduce pH to 4 by H_2SO_4 addition

2. Recover Mn by IX

3. Adjust pH to 7 which makes the water non-corrosive, and drop out Fe^{3+}, Co, Ni, Mn and Al^{+3}.

4. Settle and send the overflow water to the industrial water dam

5. Water in excess of needs for industrial water, to be treated by a desalination process to recover $(NH_4)_2SO_4$ and H_2SO_4 which can be used to regenerate the resin and strip the recovererd manganese into a $(NH_4)_2SO_4$ solution to be added back to the electrolyte.

Experiments have been performed with commingled effluent solution and showed that lime addition to pH 8.2 achieves the following result:

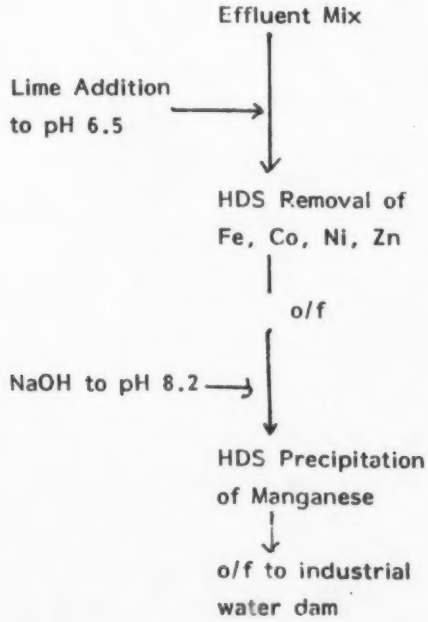
	Raw Commingled Effluent	After pH Adjustment with Lime to pH 8.2
Suspended solids	250	6000 ppm
Mn	380	0
Na	120	140
Ca	340	1080
Mg	135	90
SO_4	1370	1450
pH	7	8.2
TDS	2500	2700

It was conceded that implementation of anything beyond Phase I is still a long way off.

DISCUSSION

1. In the electrolyte purification step, large settling tank capacity is required to remove the finely discarded sulfide precipitates. RANDOL believes that DAF or some modification of an HDS process could make this step easier and more compact.

2. For recovery of manganese, the followng idea may be simpler:



3. Recovery of manganese at low pH by IX in the presence of iron is unlikely to succeed.

4. Recovery of $(NH_4)_2SO_4$ and H_2SO_4 by EDR from the solution after precipitating metals is an area of research both at MINTEK and elsewhere, but no commercial process has been indicated yet.

5. Considering the problems experienced with gypsum sealing and clogging pipes, it is possible that this would justify either looking at sequestering or anti-scaling reagent addition or the use of seeded slurry R. O. treatment of recycle water to remove CaSO and drop the levels in the plant below saturation.

MINE BURNSIDE COLLIERY
P.O. BOX 222
GLENCOE, NATAL 2930

CONTACTS P. J. Buys — Former Mine Manager
Blinkpan Collieries
Glencor Ltd.
P. O. Box
Blinkpan, Transvaal

Telephone: Blinkpan (0132252) No. 7

Mr. Gideon Van Aswegen — Site Restoration Superintendent
Northfield Colliery
P. O. Box 222
Glencoe, Natal 2930

Telephone: (0341) 31137

LOCATION The worked out Burnside Colliery is located on the outskirts of the town Glencoe in Natal about one hour's drive Southeast of Newcastle.

CLIMATE Warm yearround with predominantly summer rainfall.

INTRODUCTION

The original Burnside Colliery operations were granted a closing certificate at least a decade ago before the need to comply with new environment protection regulations (Regulations 513-3 of 1982). The Dept. of the Environment has recently spent R1.5 million on the site to prevent pollution of the Buzi stream which had become contaminated to the extent of being unusable by farms downstream.

The later operations of the Burnside Colliery were incorporated in the Northfield Colliery operations of the Trans Natal Division of General Mining Company, now known as Gencor Ltd.

When the last Burnside Mine was shut down the site had to be restored to comply with current environment protection regulations.

REGULATING AUTHORITY (1) Dept. of the Environment
Private Bag X313
Praetoria 0001

Contact: Hendrik J. Best
Telephone: (012) 268-402

Excerpt from paper by J.O. KEMPE (1983) :

(iii) Burnside Area - Northern Natal

A stream serving a farming community in the Burnside area in Northern Natal was being seriously polluted by underground water which surfaced against a dyke contact and by a small amount of seepage from an old waste dump bordering on the stream. It was decided to divert the stream from the problem area and construct an evaporation dam across the original stream to contain the polluted water. The diversion was 1 200 metres in length. To avoid erosion of the sandstone and soft shale exposed in the 6,5 metre wide channel graded at 1:400 it was necessary to construct four concrete lined stilling bays. The satisfactory effect of the completed project on the quality of the water in the stream is indicated in Table 9.

TABLE 9 Quality of Water at Burnside Stream Diversion Project

	Sampling Position	pH	Total dissolved solids (milligrams/litre)	Sulphates (as SO_4) (milligrams/litre)
1.	Stream above problem area	7,8	95	7
2.	Water surfacing at dyke contact	6,8	4 720	2 350
3.	After confluence of 1 and 2	6,7	3 625	1 450
4.	Same as in 3 after diversion complete and evaporation dam commissioned	8,0	250	15

(2) Government Mining Engineer

MEASURES ADOPTED

Old Burnside Operations

Restoration of the old Burnside Colliery site has been the responsibility of the Department of Environment.

The major problem appears to have been the siting of a coal refuse dump along the course of the Buzi River. The Department of the Environment has spent R1.5 million on diverting the stream to bypass the dump site. A dam has been constructed to retain and evaporate water draining from the dumpsite therby preventing it from reaching the stream.

New Burnside Operations

1. Demolition of all buildings and mine headgear on site. Removal of rubble and foundations to the dump.

2. Removal of scrap metal from mine scrapyard and restoration of the site to grazing land.

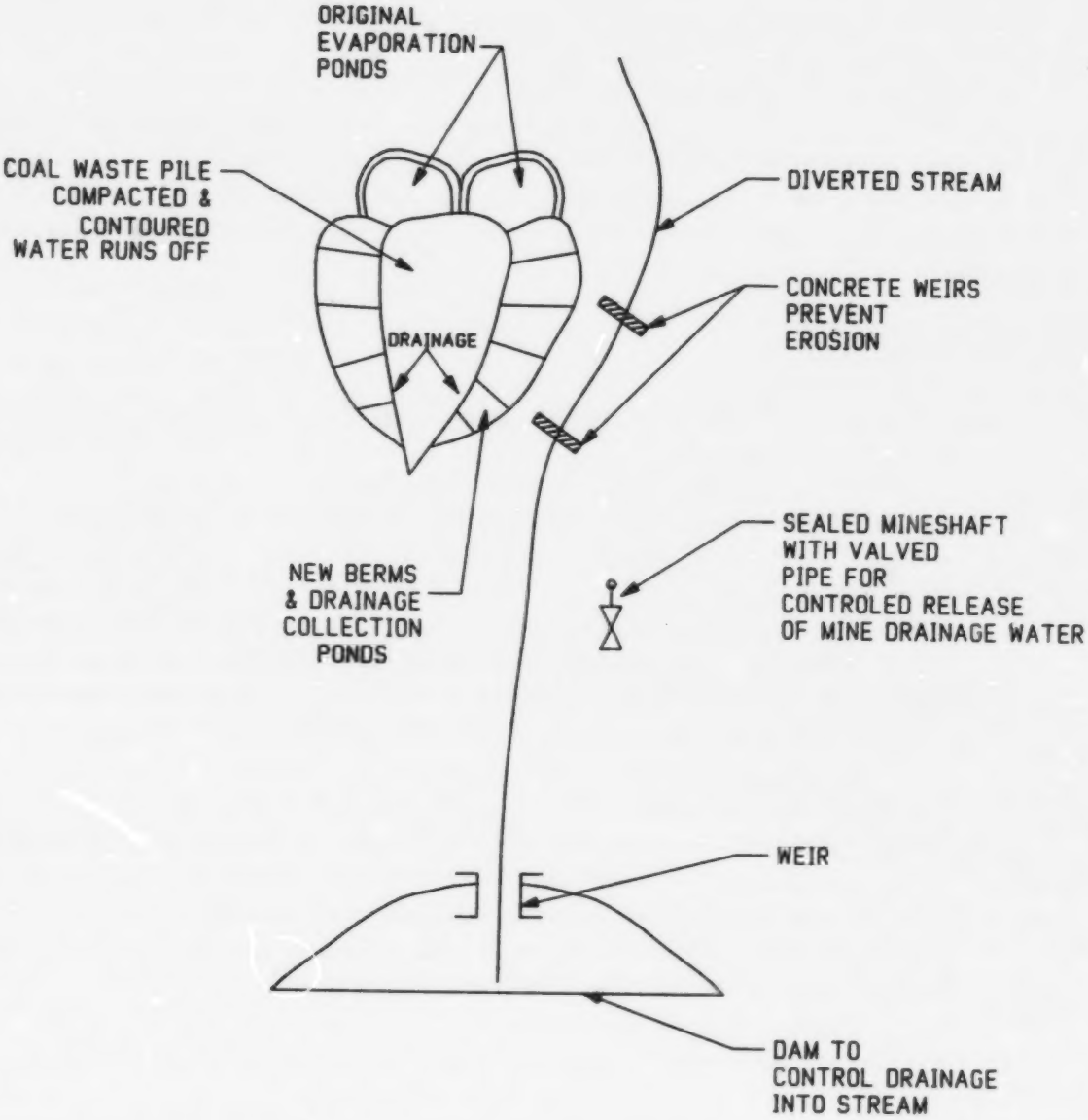
3. Diversion of drainage stream around the coal waste dump which was sited on the stream channel. Construction of an 80,000 m^3 dam to retain runoff water above the tailings pile. Water is allowed to escape at a controlled uniform rate from the dam so as not to erode the dump. Cost of dam and stream diversion: R100,000.

4. The fenced off shaft collar has been sealed with a 2 m thick concrete plug. Wood matpack mineprops underground were treated to prevent rotting so the mine could be reopened in future. A valved pipeline is inserted through the seal in the shaft collar to allow contaminated water to be released if necessary. The collar of the mineshaft has been raised above ground level to prevent drainage water from flowing into the cavity above the seal.

5. A second shaft entrance has also been sealed and fitted with a valved drainage pipe.

   Contaminated water can be released if necessary into the creek during times of flooding when it would be diluted and eventually transported to the sea.

6. The wasterock and reject coal dump was compacted to prevent rainfall penetration and also to seal out air. This extinguished the fires and allows water to runoff rather than penetrate the dump. Runoff water drains to bermed dams around the periphery of the dump.


ORIGINAL
EVAPORATION
PONDS
COAL WASTE PILE
COMPACTED &
CONTOURED
WATER RUNS OFF
DRAINAGE
DIVERTED STREAM
CONCRETE WEIRS
PREVENT
EROSION
SEALED MINESHAFT
WITH VALVED
PIPE FOR
CONTROLED RELEASE
OF MINE DRAINAGE WATER
NEW BERMS
& DRAINAGE
COLLECTION
PONDS
WEIR
DAM TO
CONTROL DRAINAGE
INTO STREAM

7. The dump and shaft areas were fenced. The area around the dump and shaft was planted with grass.

8. Open pit excavations were filled in and available topsoil replaced and the area grassed.

9. Restoring the Burnside minesite was included in a combined budget for Burnside and Northfield of R3.0 mm (1982/3).

Conclusions

1. The principle of releasing contaminated minewater to streams during times of flooding appears to be sound where the streams lead ultimately to the sea, and where adequate dilution is provided by the floodwaters.

2. Shortage of topsoil prevented complete restoration of the open cast minesite area.

3. The minesite as originally abandoned included several brick buildings with corrugated iron roofs. These have since been gutted by looters leaving very unsightly building shells. This justifies the requirement that all buildings on abandoned minesites be demolished except where specific exclusions are granted on application motivated by specific uses for buildings to be left standing.

4. Compaction of the waste dump surface is effective at putting out fires in the dump which has been a major contributor to acidity.

5. The Burnside waste dump will always remain as a stark reminder of mining activity on the site. The dump had been sited on a streambed and had expanded right up to the property boundary which required removal of material to install berm dams for restoration. With foresight and planning in the layout of mines and wastepiles in the initial stages it would be possible to achieve less costly restoration on completion.

6. Gencor Ltd. has retained Mr. P. J. Buys, former General Manager of the mine, to be responsible for the mine restoration over a 3 year period.

   Employment of such a senior man for the task not only expedited the restoration program by allowing more rapid ad hoc decisions to be made, but also has provided an insight into the needs of site restoration which will be valuable in the planning and layout of new operations in future.

7. According to Mr. Hendrik J. Best of the Department of Water Affairs & the Environment, the restoration of Northfield and Burnside Collieries are exemplary of

how things should be done and these sites will serve as models for the South African coal mining industry.

8. Although water quality in the Buzi River was unacceptable due to pollution by minewater and dump drainage prior to restoration, data on water quality before and after was not available. No systematic monitoring program of surface and groundwater of the type required in the USA seems to have been carried out.

9. Despite extremely heavy rains on the night immediately prior to the visit, the berm dam impoundments contained only "very little" water, clearly far less than had flowed off the dump at Burnside. Water had both sunk into the ground and overflowed to banks of one berm dam thereby being lost to the stream. No groundwater monitoring has been required at the site.

10. Mr. P. J. Buys and Mr. G. van Aswegen both emphasize the need to consider post-operation restoration of the site at the initial planning stages of the mine.

11. A wasterock and reject coal dump design that would be less expensive to restore to fulfill the requirements of Regulation 513-3 of 1982 was suggested as follows:

    1) Construct clay berm dam impoundment around the site.
    2) Heap wasterock to no more than 15 ft. (5m).

    Once filled the dump can be smoothed off into a mound and compacted before being covered by the berm material and then a layer of topsoil for Kikuyu planting.

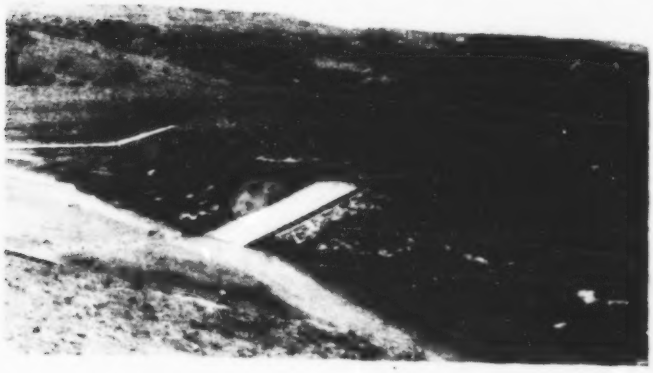
12. Grass (Kikuyu) has been planted on the restored minesties. Kikuyu (used in most South African domestic lawns) propagates by means of rizomes and is ideal for minesite restoration also on account of its hardiness. Most North American grasses for example are less suitable as they grow as individual plants from seed and such grasses will not fill in gaps except through seed propagation.

    At Burnside Kikuyu grass used for restoration planting was taken from as close as possible to the site to obtain plants already adapted to the acidic soil environment.

13. A dam constructed at the open pit restored site is said to contain acid water when allowed to stand.

Collar around old shaft which is now plugged.

Flood damage to runoff catchment ponds alongside compacted coal waste dump. Note incipient grass growth.



Effective drainage diversion around the Waste Pile

OPERATION	Kriel Power Plant Kriel, Transvaal
COMPANY	ESCOM Electricity Supply Commission Megawatt Park Sandhill Park Ext 3 Sandton 2199 South Africa
TELEPHONE	(011) 800-3254
CONTACT	Dr. Godfrey Dalton

NOTE: Most ESCOM staff may possibly be unaware of this trip report and discretion is requested, even though care was taken not to reveal any information that could be sensitive.

INTRODUCTION

In the 1950s Anglo American Corporation operated the largest electrodialysis plant in the world to treat minewater at Welkom. This operation shut down, because the volume of water that required desalination decreased to the extent that the plant was no longer needed.

Since EDR has been advocated as a candidate desalination process for neutralized acid mine drainage on the Witwatersrand, and since there are none installed for this purpose on a commercial scale, there was no option but to visit a commercial EDR plant installed in a different industry to get a feel for this type of process. Accordingly the EDR plant at Kriel power plant was informally visited in the company of the vendor who installed the unit.

Process Systems (Pty) Ltd.
P. O. Box 10142
Johannesburg 2000

Telephone: (011) 802-4230
Contact: Ralph A. Jones Managing Director

MAKE OF EDR PLANT

IONICS INCORPORATED
65 Grove Street
Watertown, MA 02172

Telephone: (617) 926-2500
Contact: W. E. Katz

MODEL OF EDR UNITS Aquamite 100, Two trains installed Kriel

SIZE OF EDR PLANT 6000 m^3/d

PURPOSE OF EDR PLANT

As a rougher desalting for boiler feed water ahead of an ion exchange demineralizer plant which became overloaded when feedwater quality deteriorated from 40 ppm to 300 ppm TDS. The water must be demineralized for use in the Kriel Power Plant boilers. The EDR plant was treating Vaaldam water with 300 ppm TDS to make feedwater for the existing ion exchange demineralizer with 40-60 ppm TDS.

DATE OF INSTALLATION 1983

DURATION FOR INSTALLATION

The EDR plant took 2 months to install from receipt of the order which is a truly remarkable achievement.

DESCRIPTION OF EDR PROCESS

Water is desalinated by removing cations and anions through ion exchange membranes on either side of a layer of water between the reversible anode and cathode of a cell. A description of the EDR process is provided in the chapter on desalination.

SALTS REMOVED

The main salts in the water treated by the Kriel EDR plant are SO_4^+, Ca^{++}, Mg^{++}, $SO_4^=$ and HCO_3^-.

PRETRETMENT

Feedwater is clarified and then filtered in sand filters ahead of the EDR plant which was inserted between the two existing stages of pretreatment at the power plant.

A 10 micron disposable paper cartridge filter is installed in the feed line to each train of EDR stacks.

EDR STACKS AND ARRANGEMENT

The Ionics EDR stacks employed have 500 cells per stack, each consisting of two membranes and a cathode and an anode plate. Each stack of 500 cells costs about $30,000 and can treat about 30 gpm. Each section of the plant employs 4 stacks in series.

REVERSAL CYCLE

Concentrate flow loops around continuously. Flow direction is reversed each cycle by automatically controlled flow reversal values. At each reversal a small amount of makeup water is added to the concentrate and demineralized product is withdrawn. The Kriel EDR plant operates on about a 30 minute reversal cycle because the feedwater has a relatively low TDS level.

DEGREE OF CONCENTRATION POSSIBLE

Concentration of TDS must not be allowed to build up too much. If the Langelier index exceeds 2.3, then acid is added to the system.

When $CaSO_4$ concentration exceeds 180% of saturation a sequestering agent is added to the concentrate stream. Sodium hexametaphosphate is added.

SCALE INHIBITION

$CaSO_4$ scale is inhibited by addition of Na hexametaphosphate. Calcium sulfate precipitation is a lime-controlled phenomenon. By recycling the flow and cell polarity it is possible not to give the crystals time to form. If some $CaSO_4$ crystals should happen to form this occurs against the membrane. The changing polarity and flow helps to move these partially formed crystals out of the system. EDR systems have been demonstrated working with $CaSO_4$ concentrates up to 400% of saturation.

At the Cathode conditions are alkaline and therefore more conducive to scale formation. Water flows over the cathode to provide a continuous electrode rinse.

At the anode conditions are acid and therefore not scaling. The anodes are rinsed intermittently to eliminate gas blanketing.

The concentrate continues flowing in a loop all the time. The reverse flow valves simply reverse the flow at the same time they allow a small amount of new water to enter the concentrate to make up for water lost to the product.

An empirical formula known as the Marshal Slusher formula can be used to predict scaling.

EARTHING SOLUTIONS

Solutions entering or leaving the EDR plant must be earthed. Stray currents would otherwise cause corrosion of the steel parts in the system. Each stack is earthed independently too.

MATERIALS OF CONSTRUCTION

Kriel

The stacks are held in place between two 1" thick plastic end pieces which are bolted tightly together between two 34mm steel framends which weigh 250 Kg apiece.

All pipes and valves are made of PVC.

WATER PRESSURE

Water is fed to the system at about 100 psi and a typical system water pressure is 60 psi.

CURRENT VOLTAGE

The current applied for EDR is 300 volts, DC.

PIPES AND PUMPS

All pipes are conventional plastic. Conventional centrifugal pumps are used.

CAPITAL COST

An EDR plant of this size costs around R3 million including the still building fitted with an overhead crane.

OPERATING COST

Operating costs for Escom units are considered confidential, but for feedwater with higher TDS, the vendors claim that operating costs run about R0.35/m^3. The major factor in operating cost is the cost of capital.

CLEANING AND MAINTENANCE

An EDR stack with 500 cells can be pulled apart for manual cleaning. The top electrode plate weighs 250 Kg and requires a crane to move. A 3t crane is installed in the roof of the Kriel EDR plant.

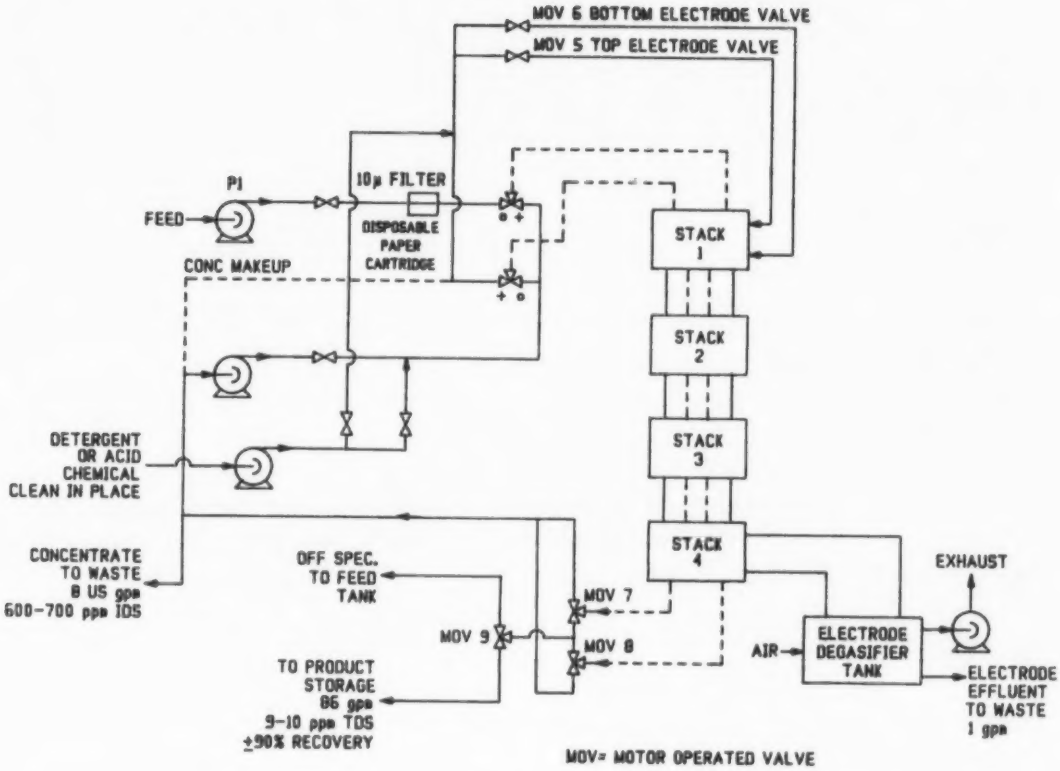
GENERAL APPEARANCE

The EDR plant at Kriel power plant is extremely clean and tidy. The desalination plant was relatively compact compared with what one would expect for a flow of this size.

COMMENT

Although EDR plants are claimed to be suitable for desalination of brackish water - and even seawater according to some accounts, this installation does not represent a true test because the feed water is relatively pure - only 300 ppm TDS. This is not typical of AMD water which is likely to run 3000-5000 ppm TDS.

EDR SYSTEM



MOV= MOTOR OPERATED VALVE

NOTE: THIS DIAGRAM GIVES A GENERAL IDEA OF THE FLOW ARRANGEMENT BUT IT IS INCOMPLETE.

MINE

NORTHFIELD COLLIERY
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NATAL 2930
SOUTH AFRICA

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CONTACTS

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Blinkpan Collieries
Gencor Ltd.
P. O. Blinkpan, Transvaal

Telephone: (0132252) No.7

Mr. Gideon Van Aswegen
Site Restoration Superintendent
Northfield Colliery
P. O. Box 222
Glencoe, Natal 2930

Telephone: (0341) 31137

LOCATION

The now exhausted Northfield Colliery is located in the outskirts of the town of Glencoe, about one hour's drive Southeast of Newcastle, Natal.

CLIMATE

Warm year round with predominantly summer rainfall.

INTRODUCTION

The Northfield Colliery ceased operation in June 1982 after operating continuously since 1917. Final year production was 45,000 tons per month plus 10,000 tons per month of wasterock which was dumped onto a culm pile.

Closure of the mine had to comply with a new environment protection regulation 513-3 of 1982, and the owners, Gencor Ltd. have spent R3.0 million on restoration of the 1000 hectare site including parts of the adjacent Burnside Colliery which were incorporated into the operation. Although restoration focuses on restoring the land as close as possible to its original contour and condition, preservation of water quality is a major factor that was taken into consideration.

REGULATORY AUTORITIES Department of the Environment
Pretoria
Telephone: (012) 268-402

MEASURES ADOPTED

1. The shaft headgear was dismantled and scrapped. The shafts were filled in.

2. Demolition of all buildings, storage bins, etc. not exempted by the Government Mining Engineer and the Department of the Environment.

3. Compaction of the top surface of the waste rock and reject coal dump to extinguish fires and allow rainwater to drain off rather than to penetrate the dump.

4. Construction of berms around the dump to retain drainage water. The berms also prevent surface water from draining into the dump and becoming contaminated. On the downgrade side of the dump the berms are constructed three deep.

5. Berm dumps prevent surface runoff water from entering or leaving the fine coal waste dam impoundment area. All berm dams are designed to hold runoff water from a 100 year rainfall.

6. Each dump and impoundment area is fenced off with 8 ft. fences and signboarded as a danger area.

7. All scrapiron and discarded equipment has been disposed of. (Either sold to a nearby steel mill or buried.)

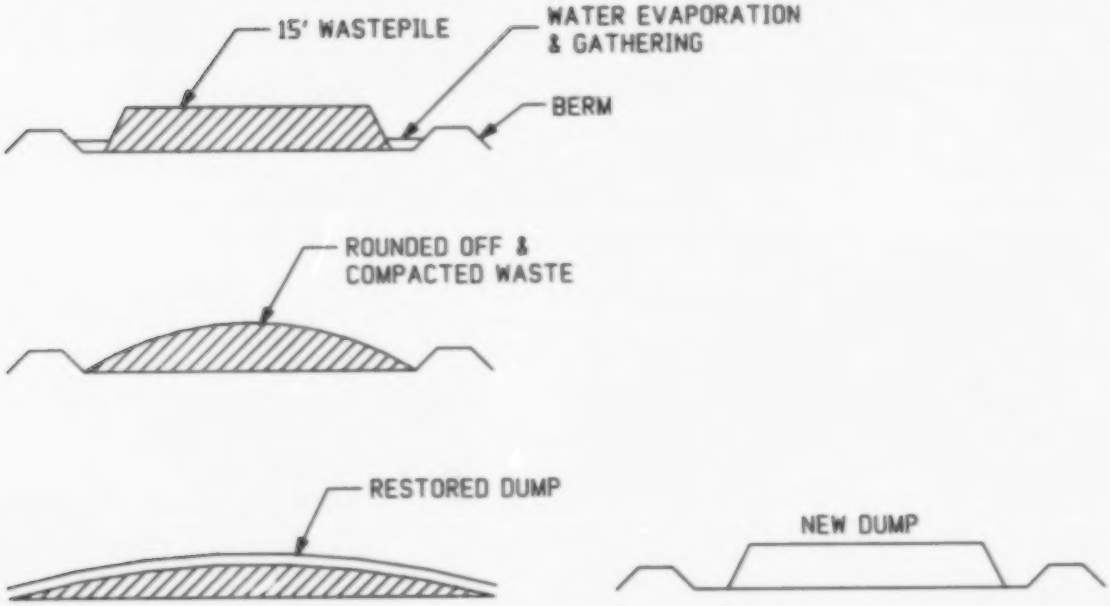
8. Gradients of all disturbed land have been restored as close as possible to the original, and covered with topsoil.

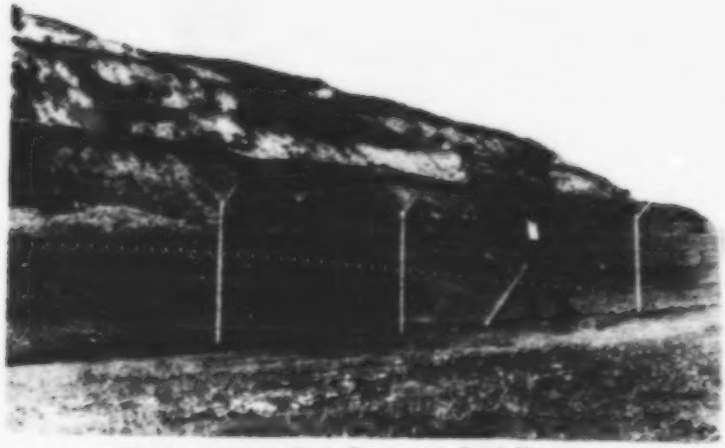
9. Old aggregate pits on the property have been filled in and graded.

10. The berms and all restored areas have been planted with Kikuyu grass.

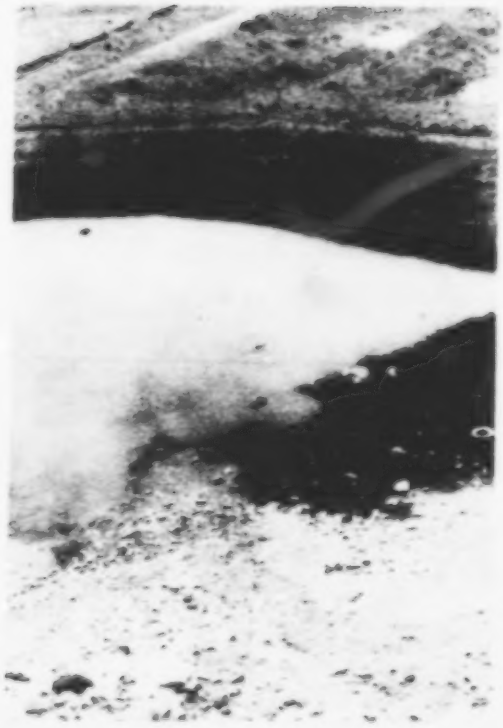
11. The Wasterock and reject coal dump is constructed with a significant slope (in the opposite direction to the slope of the ground. This grade allows water to runoff and drain from the dump surface and avoids ponding of precipitation.

CONCEPT FOR IMPROVED COAL WASTE DUMPS





Kikuyu Grass Can Grow on Coal Waste



Containment & Evaporation of Runoff

Revival of trees and note pumpkin seedling and grazing in foreground after compaction of Waste Dump and installation of berms.

CONCLUSIONS

1. Compaction of the dump surface to limit seepage of water into the dump as well as air to fuel the combustion results in greatly reduced SO_2 emission and hence less acid generation. The compacted dump at Northfield Colliery is evidence of this. Old gum trees that appeared to have been killed are now sprouting new leaves.

2. Kikuyu grass planted as cuttings and sod are growing very well on the berm embankments and surrounding areas. Grass has also been planted on the dump itself. In test areas planted one year ago, the dump is almost covered in grass which appears to grow even without additional topsoil covering the dump material.

   The use of acclimated grass plants from the same acid environment is said to make a big difference to its survival in a relatively harsh environment.

   Pumpkins have been planted on restored waste areas as a test because it is reputed that pumpkins thrive in acid soil.

3. The older evaporation ponds which were much more extensive than the current berm ponds, are now almost completely grass covered, and apparently lifeless trees are coming to life again. By keeping runoff water from draining into the area, the need for evaporation pond area has been cut down significantly.

4. The restoration efforts at the old Northfield minesite have been encouraging, and it is clear that the areas affected by highly acidic water can be restored or at least greatly improved. Acid generation from wasterock and reject coal dumps seems in this case to be controllable. Only the smallest signs of combustion were observed on the dump, which hopefully will be eliminated altogether once grass cover is established over the whole dump.

5. It is not known to what extent the 60 mm (2.3 inches) of rain that fell on the dump within 72 hours preceding the visit contributed to extinguishing the dump fire.

6. No groundwater monitoring program was mentioned or in evidence at the site. Considering the extent of rainfall over the previous three days the level of water in the berm dams was surprisingly low. No quantitative data was available on groundwater quality effects. The dump is located adjacent to a clay deposit mined by COROBRICK and it is possible that the clay deposit extends beneath the waste dump.

7. Boreholes have been drilled into the underground workings. Water although at neutral pH 7 has a high salt content. The municipality of Coligny draws water from the Northfield underground workings when there is adequate fresh water in the dams with which to blend it. Farmers are also said to have tapped water from the Northfield underground workings and it was also stated that although at a neutral pH the water is too high in salt content for most agricultural uses.

8. Based on the operator's experiences in restoration of the Northfield Colliery it was stated that new operations would be planned so that waste dumps would not exceed 15 ft. in height. These would be progressively restored as they became filled. In this way combustion would be controlled, acid runoff would be reduced and ultimate contours of the dump area would blend into the natural topography.

9. Details gathered during the visit on 13 December 1983 were qualitative in nature. It remains to gather quantitative data on the following:

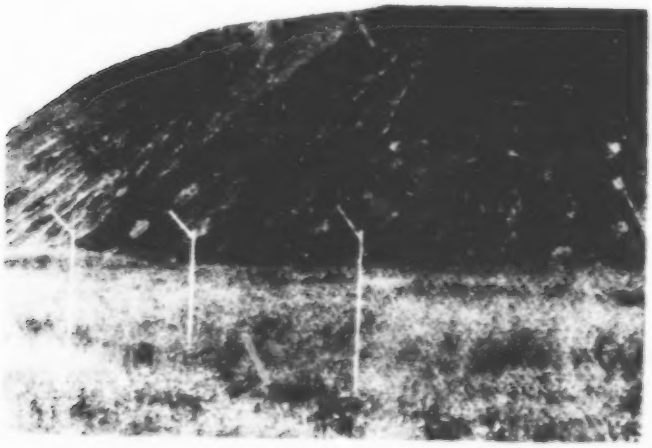
   - Water quality monitoring program (if any)
   - Water quality before/after restoration
   - Plan of affected areas
   - Breakdown of restoration costs
   - Analysis of how a new mine would be planned so as to minimize restoration costs
   - Regulation 513-3 of 1982 regulating mine closure
   - List of regulations affecting water quality at a coal mine
   - Climatic constraints
   - Water quality of underground minewater and discussion
   - Diagram of area showing affected areas
   - List of regulatory authorities and names, addresses and phone numbers of individuals concerned
   - Names of consultants involved (if any)

QUESTIONS

1. Breakdown of expenditures on restoration of the sites at Burnside and Northfield Collieries.

2. Which items and what cost can be assigned to measures that improve ro preserve water quality?

Berm keeps runoff water inside the Waste Area to evaporate. Note natural marsh.



Note Revival of tree after Waste Pile was compacted and fires extinguished.

3. Details of any monitoring program to measure water quality before restoration and after restoration.

4. Government Departments and names of individuals involved or consulted in connection with the restoration plan. Names and addresses, please.

5. Names of independent consulting firms or contractors employed to assist in the environmental aspects of the restoration plans.

6. Where mineshaft openings are sealed and fitted with a valved pipe outlet to bleed minewater:
   1) Who specifically will monitor the need to bleed minewater?
   2) Who will make decisions as to bleeding minewater?
   3) Who will open/close the valves?

7. When is it anticipated that a mine closing certificate will be granted

8. Full name of the Gencor Division that controls Northfield and Burnside Collieries, i.e., Trans Natal ...

9. Size of the dumps. Surface area. Size of the berm dams (surface area and wall height)

10. Measures to remove silt from berm dams as they fill up?

11. Other ongoing maintenance items.